Lectures on the Thermodynamics of Seawater and Ice,

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Motivation for the first lecture

As heat is exchanged between the atmosphere and the ocean, how can we keep track of "heat" in the ocean? Here is a plot of the isobaric specific heat capacity of seawater.

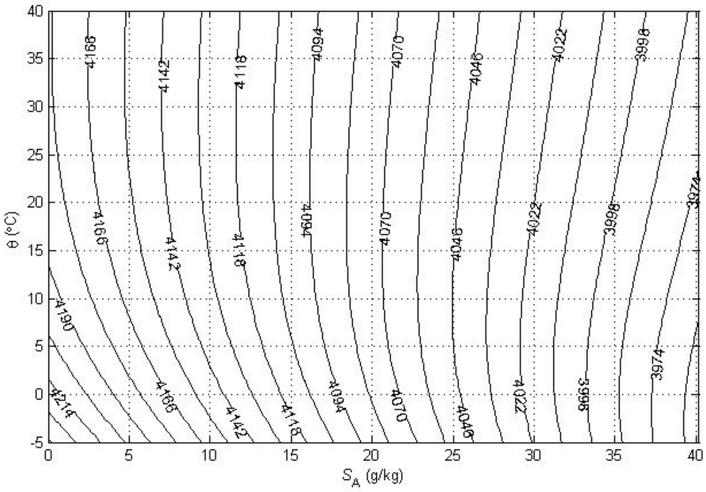


Figure 4. Contours of isobaric specific heat capacity c_p of seawater (in J kg^{-1} K^{-1}), at $p = 0$.

Here is a zoomed-in plot of the isobaric specific heat capacity of seawater.

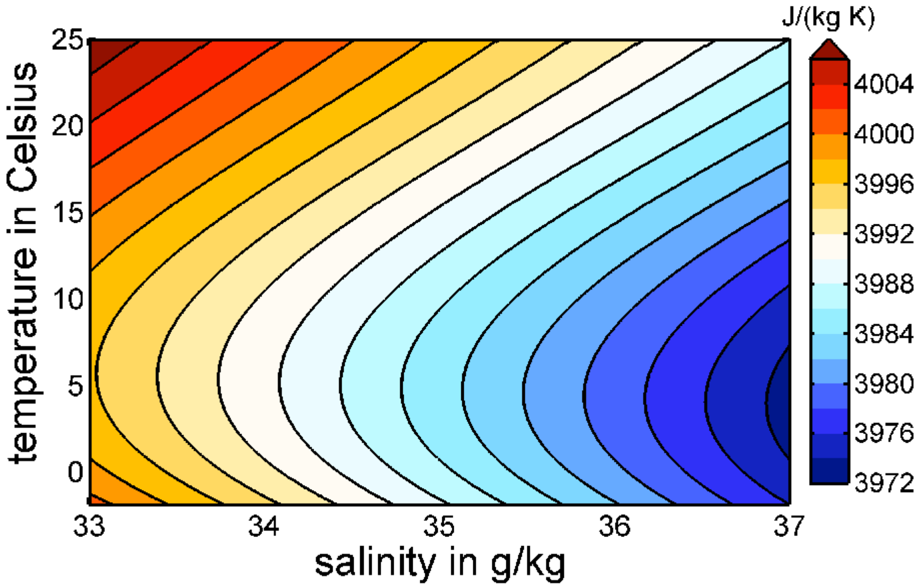


Fig. 1.7 Specific heat of seawater c_p

For the purpose of this introductory lecture, just think of potential temperature θ as simply temperature.

A given air-sea heat flux will affect the potential temperature θ in the ocean at a rate that depends on where you are on this $S_{\mathrm{A}}-\theta$ diagram. That is, the change in temperature at the sea surface due to a Joule of heat being transferred from the atmosphere into a kilogram of seawater, at constant salinity, is equal to the reciprocal of $c_p\left(S_{\mathrm{A}},\theta,0\right)$.

So what variable represents the "heat content per unit mass" of seawater? It clearly is not simply potential temperature θ. Nor is it the product $\theta c_p\left(S_{\mathrm{A}},\theta,0\right)$ (for at least two reasons, (1) because $\theta c_p\left(S_{\mathrm{A}},\theta,0\right) \neq \int c_p\left(S_{\mathrm{A}},\theta,0\right) d\theta$ and (2) because the "*heat content*" of seawater also depends separately on salinity ($\mathrm{d}h_0 = \mathrm{d}h\left(S_{\mathrm{A}},\theta,0\right) = c_p\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}\theta + \tilde{h}_{S_{\mathrm{A}}}\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}S_{\mathrm{A}}$, with the enthalpy h being a credible candidate for "heat content" at this stage).

And even if we were able to answer this question of "what is the "*heat content*" per unit mass" of seawater at $p=0$, what do we do in the sub-surface ocean where changes in pressure and specific volume v cause changes in the internal energy u and enthalpy h of $-P\mathrm{d}v$ and $v\mathrm{d}P$ respectively?

In short, we are asking the question

"what is "*heat*" in the ocean?";

that is, more specifically, we are asking what is the "*heat content per unit mass*" of seawater, applicable throughout the ocean at all depths. We seek a "*heat content per unit mass*" variable whose transport and turbulent mixing can be used to track the transport and the turbulent mixing of the heat that enters the ocean across the air-sea boundary and across the sea floor (the geothermal heat flux). This paragraph neatly summarizes the purpose of the first several lectures of this course.

The route to answering our question, "what is "*heat*" in the ocean?"

In order to answer this question we need to have a thorough understanding of the First Law of Thermodynamics which in turn, can only be derived from the Conservation Equation for Total Energy, which in turn relies on the Fundamental Thermodynamic Relation, which in turn embodies the definition of entropy and the Second Law of Thermodynamics. In the coming lectures we will derive each of these three equations, but for now, here they are.

The Continuity Equation is

$$\boxed{\rho_t + \nabla\cdot\left(\rho\mathbf{u}\right) = 0} \,. \tag{A.21.2}$$

The Fundamental Thermodynamic Relation is

$$\boxed{\mathrm{d}u + \left(p+P_0\right)\mathrm{d}v = \mathrm{d}h - v\,\mathrm{d}P = \left(T_0+t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_\mathrm{A}} \,. \tag{A.7.1}$$

The Conservation Equation for Total Energy is

$$\begin{aligned}\left(\rho\mathcal{E}\right)_t + \nabla\cdot\left(\rho\mathbf{u}\mathcal{E}\right) = \rho\,\mathrm{d}\mathcal{E}/\mathrm{d}t &= -\nabla\cdot\left(\left[p+P_0\right]\mathbf{u}\right) - \nabla\cdot\mathbf{F}^\mathrm{R} - \nabla\cdot\mathbf{F}^\mathrm{Q} \\ &\quad + \nabla\cdot\left(\rho v^\mathrm{visc}\nabla\tfrac{1}{2}\left[\mathbf{u}\cdot\mathbf{u}\right]\right).\end{aligned} \tag{B.15}$$

where the total energy $\mathcal{E}$ per unit mass is defined as the sum of the internal, kinetic and gravitational potential energies, that is,

$$\mathcal{E} = u + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi \,. \tag{B.14}$$

The First Law of Thermodynamics is

$$\boxed{\begin{aligned}\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) = \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t} + \left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) &= \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t} + \mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right) \\ &= -\nabla\cdot\mathbf{F}^\mathrm{R} - \nabla\cdot\mathbf{F}^\mathrm{Q} + \rho\varepsilon\end{aligned}} \,. \tag{B.19}$$

Nomenclature

h is specific enthalpy and u is specific internal energy, related by $h = u + Pv = u + \left(p+P_0\right)v$ ("specific" means "per unit mass of seawater")

v is the specific volume

η is specific entropy

μ is the relative chemical potential of seawater

S_A is the Absolute Salinity of seawater

$\mathbf{F}^\mathrm{R}$ is the radiative flux of heat

$\mathbf{F}^\mathrm{Q}$ is the molecular flux of heat

ε is the rate of dissipation of kinetic energy

Equations numbers are from the TEOS-10 Manual,

> IOC, SCOR and IAPSO, 2010: *The international thermodynamic equation of seawater – 2010: Calculation and use of thermodynamic properties*. Intergovernmental Oceanographic Commission, Manuals and Guides No. 56, UNESCO (English), 196 pp. Available from www.TEOS-10.org

Many of the topics that we cover are discussed in more detail in the TEOS-10 Manual www.teos-10.org/pubs/TEOS-10_Manual.pdf. You should download it to your computer; it is over 200 pages.

A comprehensive list of nomenclature (Thermo_Nomenclature_2017.pdf) is being distributed to the class.

The continuity equation

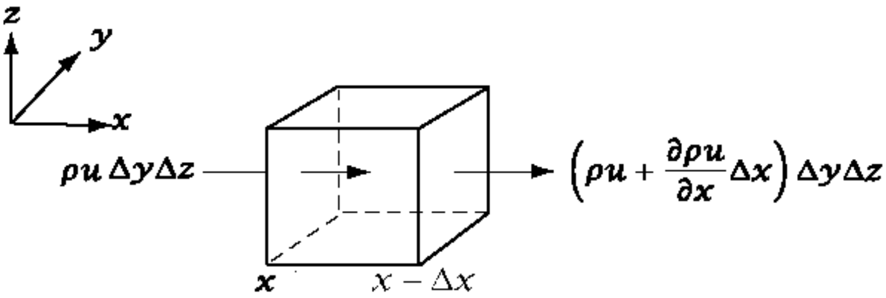


Fig. 1.1 Mass conservation in a cubic Eulerian control volume.

Thus, the accumulation of fluid within the control volume, due to motion in the x-direction only, is

$$\delta y \delta z[(\rho u)_x - (\rho u)_{x+\delta x}] = -\frac{\partial(\rho u)}{\partial x}\delta x \delta y \delta z. \tag{1.25}$$

To this must be added the effects of motion in the y- and z-directions, namely

$$-\left[\frac{\partial(\rho v)}{\partial y} + \frac{\partial(\rho w)}{\partial z}\right]\delta x \delta y \delta z. \tag{1.26}$$

This net accumulation of fluid must be accompanied by a corresponding increase of fluid mass within the control volume. This is

$$\frac{\partial}{\partial t}(\text{Density} \times \text{Volume}) = \delta x \delta y \delta z \frac{\partial \rho}{\partial t}, \tag{1.27}$$

because the volume is constant. Thus, because mass is conserved, (1.25), (1.26) and (1.27) give

$$\delta x \delta y \delta z \left[\frac{\partial \rho}{\partial t} + \frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} + \frac{\partial(\rho w)}{\partial z}\right] = 0. \tag{1.28}$$

Because the control volume is arbitrary the quantity in square brackets must be zero zero and we have the *mass continuity equation:*

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \boldsymbol{v}) = 0. \tag{1.29}$$

For a finite, arbitrary volume that is fixed in space …

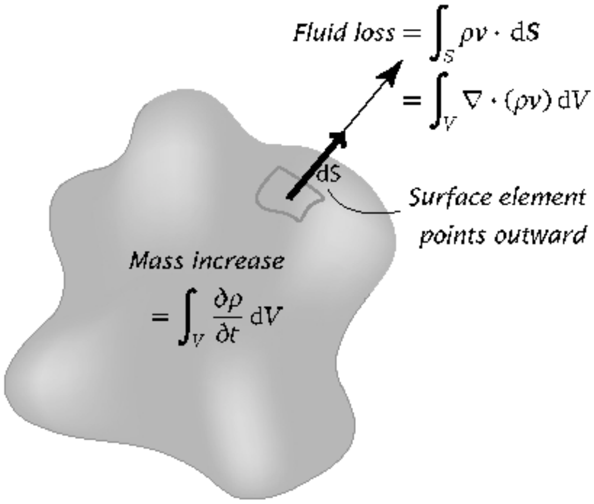


Figure 1.2 Mass conservation in an arbitrary Eulerian control volume V bounded by a surface S. The mass gain, $\int_V (\partial \rho/\partial t)\,\mathrm{d}V$ is equal to the mass flowing into the volume, $-\int_S (\rho \boldsymbol{v}) \cdot \mathrm{d}\boldsymbol{S} = -\int_V \nabla \cdot (\rho \boldsymbol{v})\,\mathrm{d}V$.

and if the arbitrary volume moves and changes shape, the continuity equation becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V \rho\,\mathrm{d}V = \int_S \rho \mathbf{v} \cdot \mathrm{d}\boldsymbol{S} = \int_V \nabla \cdot (\rho \mathbf{v})\,\mathrm{d}V$$

The material derivative

The material derivative $\frac{\mathrm{d}\phi}{\mathrm{d}t}$ is the derivative following the flow.

Let us suppose that a fluid is characterized by a (given) velocity field $\boldsymbol{v}(\boldsymbol{x}, t)$, which determines its velocity throughout. Let us also suppose that it has another property ϕ, and let us seek an expression for the rate of change of ϕ of a fluid element. Since ϕ is changing in time and in space we use the chain rule:

$$\delta\phi = \frac{\partial\phi}{\partial t}\delta t + \frac{\partial\phi}{\partial x}\delta x + \frac{\partial\phi}{\partial y}\delta y + \frac{\partial\phi}{\partial z}\delta z = \frac{\partial\phi}{\partial t}\delta t + \delta\boldsymbol{x}\cdot\nabla\phi. \tag{1.4}$$

This is true in general for any δt, $\delta\boldsymbol{x}$, etc. Thus the total time derivative is

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = \frac{\partial\phi}{\partial t} + \frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}t}\cdot\nabla\phi. \tag{1.5}$$

If this is to be a material derivative we must identify the time derivative in the second term on the right-hand side with the rate of change of position of a fluid element, namely its velocity. Hence, the material derivative of the property ϕ is

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = \frac{\partial\phi}{\partial t} + \boldsymbol{v}\cdot\nabla\phi. \tag{1.6}$$

A brief introduction to Absolute Salinity and Practical Salinity

Practical Salinity S_P has been measured and reported by oceanographers for 37 years (since it was defined in 1978). Practical Salinity is found from knowledge of a seawater sample's *in situ* temperature, pressure and electrical conductivity.

In the past ten years it has become acknowledged that the composition of seawater is not constant throughout the world ocean, and that the spatially variable ratio of the constituents leads to horizontal gradients of density that are too large to ignore (leading to ~1Sv change in the meridional [northward] vertical overturning circulation of the North Atlantic).

This issue is an active area of research, but will not be a central part of this course. We will deal with only one salinity variable, namely Absolute Salinity S_A, as defined by TEOS-10.

For completeness, we will make a few remarks comparing four salinity variables

Practical Salinity, S_P
Reference Salinity, S_R
Absolute Salinity, S_A
Preformed Salinity, S_*

"Standard Seawater" has (reasonably well) known composition, but the Practical Salinity S_P of Standard Seawater is not quite equal to the mass fraction of dissolved material in seawater. Rather, this mass fraction for Standard Seawater is estimated to be the Reference Salinity, S_R, of TEOS-10,

$$S_R = \left(\frac{35.165\,04\ \mathrm{g\,kg^{-1}}}{35} \right) S_P = u_{PS} S_P \ . \qquad (2.4.1)$$

"Standard Seawater" is based on surface water from the North Atlantic, and it contains no nutrients. Deeper in the ocean, and particularly in the deep Southern Ocean and the deep North Pacific, the concentration of nutrients is high (as a result of biogeochemical processes). Nutrients do not conduct electricity very well (particularly silicic acid which is almost non-conductive) and so an estimate of salinity based on a sample's electrical conductivity underestimates the mass fraction of dissolved material and so underestimates the density of seawater.

Given sufficient measurements of nutrients, we can now allow for their presence on the mass fraction (and on the density) of seawater according to

$$\begin{aligned}&\left(S_A - S_R\right)/(\mathrm{g\,kg^{-1}}) = \\ &\qquad \left(55.6\,\Delta\mathrm{TA} + 4.7\,\Delta\mathrm{DIC} + 38.9\,\mathrm{NO_3^-} + 50.7\ \mathrm{Si(OH)_4}\right)\Big/(\mathrm{mol\,kg^{-1}})\ .\end{aligned} \qquad (A.4.10)$$

(TA is Total Alkalinity, DIC is Dissolved Inorganic Carbon, $\mathrm{NO_3^-}$ is nitrate and $\mathrm{Si(OH)_4}$ is silicate, or silicic acid).

We normally do not have these measurements, so TEOS-10 also provides an algorithm to evaluate Absolute Salinity from a spatial look-up table of the Absolute Salinity Anomaly Ratio, R^{δ},

$$S_A = S_R\left[1 + R^{\delta}\left(\mathrm{long, lat}, p\right)\right] . \qquad (A.5.10)$$

The subroutine **gsw_SA_from_SP** converts from Practical Salinity S_P to Absolute Salinity S_A.

The Absolute Salinity S_A is the correct salinity argument to be used to evaluate density and other thermodynamic properties.

The Absolute Salinity Anomaly, $\delta S_{\mathrm{A}} \equiv S_{\mathrm{A}} - S_{\mathrm{R}}$, is the improvement in today's salinity estimates compared to those of the Practical Salinity era (1978 – 2009). This improvement is shown in the following two figures.

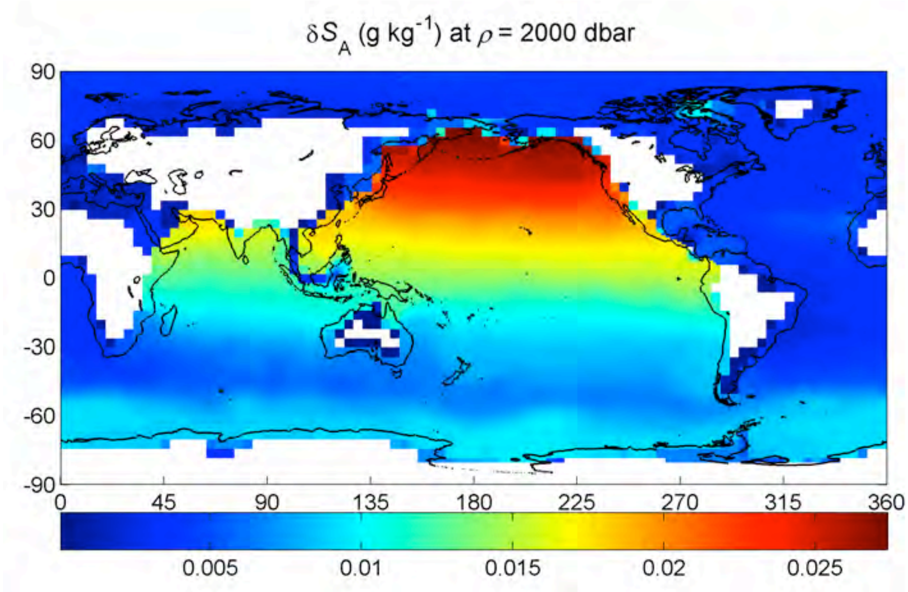


Figure 2 (a). Absolute Salinity Anomaly δS_{A} at p = 2000 dbar.

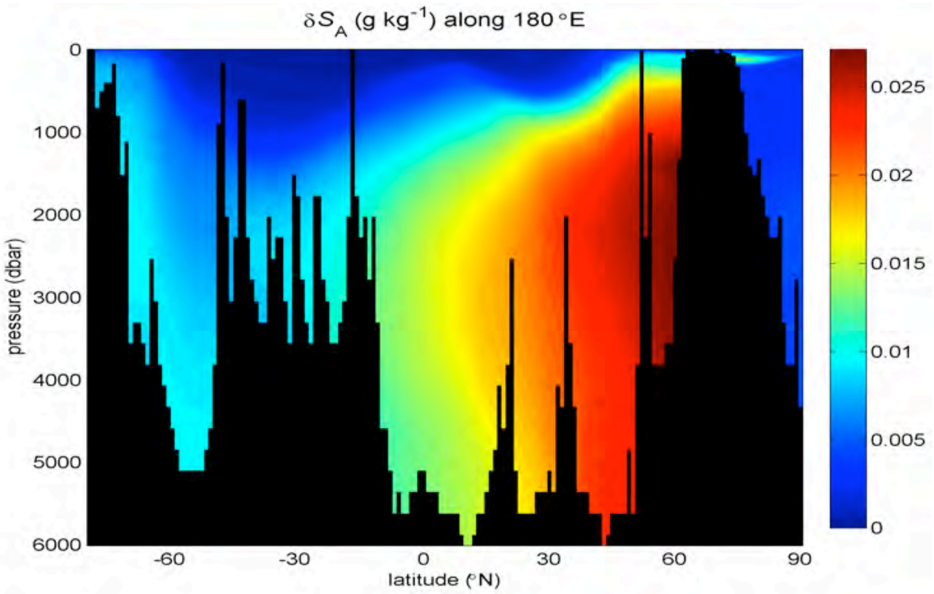


Figure 2 (b). A vertical section of Absolute Salinity Anomaly δS_{A} along 180°E in the Pacific Ocean.

The horizontal gradients of density are responsible for driving the world's deep ocean currents (via the so-called "thermal wind" equation). The neglect of the spatial variation of seawater composition (that is, the use of S_R instead of S_A in the evaluation of density) leads to non-trivial errors in the horizontal density gradient. Globally, half the ocean below 1000 dbar is affected by more than 2% (see **Fig. A.5.1**) while in the North Pacific, half the ocean below 1000 dbar is affected by more than 10%.

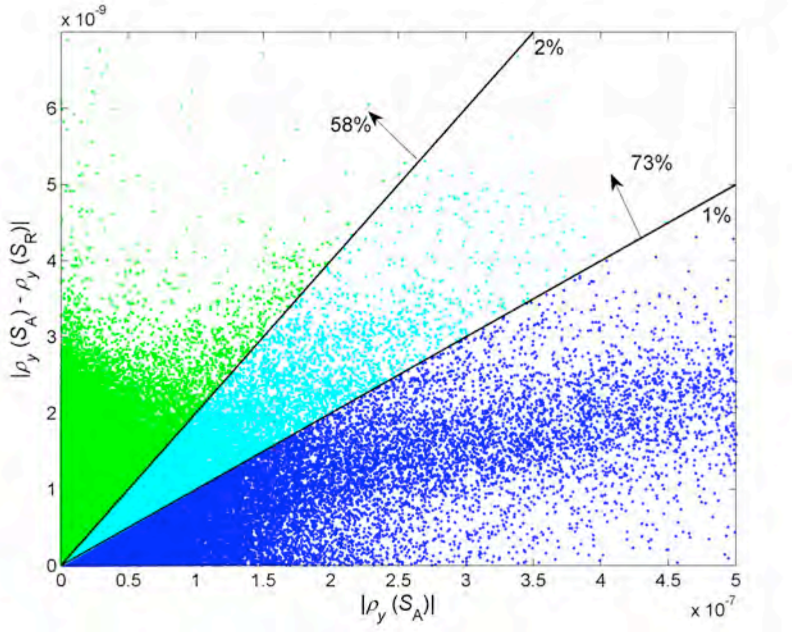


Figure A.5.1. The northward density gradient at constant pressure (the horizontal axis) for data in the global ocean atlas of Gouretski and Koltermann (2004) for $p > 1000\,\text{dbar}$. The vertical axis is the magnitude of the difference between evaluating the density gradient using S_A versus S_R as the salinity argument in the TEOS-10 expression for density.

We now introduce Preformed Salinity S_*. Preformed Salinity S_* is designed to be as close as possible to being a conservative variable. That is, S_* is designed to be insensitive to the *biogeochemical processes* that affect the other types of salinity to varying degrees. S_* is formed by first estimating the contribution of *biogeochemical processes* to $S_{\rm A}$, and then subtracting this contribution from $S_{\rm A}$. Because it is designed to be a conservative oceanographic variable, S_* is the ideal salinity variable for ocean modeling.

As a practical thing, the difference $S_{\rm R} - S_*$ is taken to be $0.35\left(S_{\rm A} - S_{\rm R}\right)$.

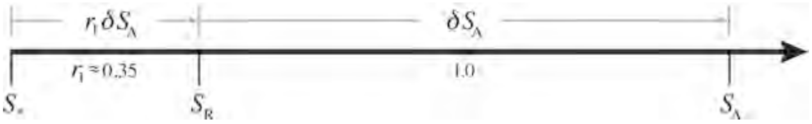


Figure A.4.1. Number line of salinity, illustrating the differences between Preformed Salinity S_*, Reference Salinity $S_{\rm R}$, and Absolute Salinity $S_{\rm A}$ for seawater whose composition differs from that of Standard Seawater.

For seawater of Standard Composition, $S_* = S_{\rm R} = S_{\rm A} = \left(35.165\,04 \text{ g kg}^{-1}/35\right)S_{\rm P}$, but when the seawater sample has undergone some biogeochemical activity, its nutrient levels will be greater than zero, its conductivity will be increased a little and its Absolute Salinity will be increased more. Specifically, if the increase in Absolute Salinity due to the change in chemical composition, $S_{\rm A} - S_*$, is say 1.35 on some scale, then only 0.35/1.35 (~26%) of this increase will be reflected in the sample's electrical conductivity and hence in its Practical Salinity and Reference Salinity.

In this course we will deal exclusively with Absolute Salinity, and we will also simplify things and consider Absolute Salinity to be a Conservative variable. That is, we will assume that

$$\boxed{\left(\rho S_{\rm A}\right)_t + \nabla\cdot\left(\rho\mathbf{u}S_{\rm A}\right) = \rho\frac{{\rm d}S_{\rm A}}{{\rm d}t} = -\nabla\cdot\mathbf{F}^{\rm S}}\,, \qquad \textit{approximate} \quad \text{(A.21.8a)}$$

where $\mathbf{F}^{\rm S}$ is the molecular flux of salt. It is actually the Preformed Salinity S_* that obeys such a conservative evolution equation, namely

$$\left(\rho S_*\right)_t + \nabla\cdot\left(\rho\mathbf{u}S_*\right) = \rho\frac{{\rm d}S_*}{{\rm d}t} = -\nabla\cdot\mathbf{F}^{\rm S}. \qquad \text{(A.21.1)}$$

By making the assumption that Absolute Salinity obeys the conservative equation (A.21.8a) rather than the real form of this equation, namely

$$\left(\rho S_{\rm A}\right)_t + \nabla\cdot\left(\rho\mathbf{u}S_{\rm A}\right) = \rho\frac{{\rm d}S_{\rm A}}{{\rm d}t} = -\nabla\cdot\mathbf{F}^{\rm S} + \rho\,\mathcal{S}^{S_{\rm A}} \qquad \text{(A.21.8)}$$

we are ignoring $\mathcal{S}^{S_{\rm A}}$, the non-conservative source term. This non-conservative source term is due to *biogeochemical processes*, for example, the remineralization of biological material; the turning of particulate matter into dissolved seasalt.

For numerical integrations of an ocean model that exceed about a century, this neglect will be significant, leading to errors in the "thermal wind" 1.35 times as large as those described above in **Fig. A.5.1**. For shorter numerical integrations, the errors will be small. For small time, the important thing is that the expression for density is being called with Absolute Salinity as the salinity argument, not Reference or Practical Salinity. Over the first few decades of integration the errors will be small, and then they will build to be 1.35 times those in **Fig. A.5.1** above.

Who was J. W. Gibbs?

Josiah Willard Gibbs (February 11, 1839 – April 28, 1903) was an American scientist who made important theoretical contributions to physics, chemistry, and mathematics. His work on the applications of thermodynamics was instrumental in transforming physical chemistry into a rigorous deductive science. Together with James Clerk Maxwell and Ludwig Boltzmann, he created statistical mechanics (a term that he coined), explaining the laws of thermodynamics as consequences of the statistical properties of large ensembles of particles. Gibbs also worked on the application of Maxwell's equations to problems in physical optics. As a mathematician, he invented modern vector calculus (independently of the British scientist Oliver Heaviside, who carried out similar work during the same period).

In 1863, Yale awarded Gibbs the first American doctorate in engineering. After a three-year sojourn in Europe, Gibbs spent the rest of his career at Yale, where he was professor of mathematical physics from 1871 until his death. Working in relative isolation, he became the earliest theoretical scientist in the United States to earn an international reputation and was praised by Albert Einstein as "the greatest mind in American history".

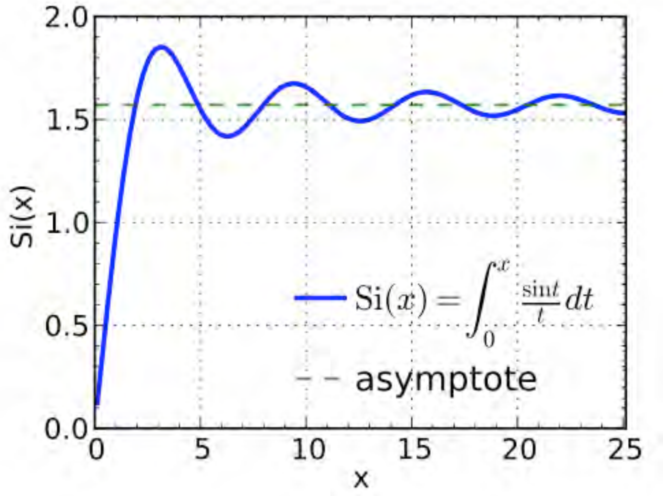
In 1897 he was elected a Member of the National Academy of Sciences in the USA, and as a foreign member of the Royal Society of London, and in 1901 Gibbs received what was then considered the highest honor awarded by the international scientific community, the Copley Medal of the Royal Society of London, "for his contributions to mathematical physics". But Gibbs was so retiring he had the US naval attaché in London collect the medal on his behalf.

Commentators and biographers have remarked on the contrast between Gibbs's quiet, solitary life in turn of the century New England and the great international impact of his ideas. Though his work was almost entirely theoretical, the practical value of Gibbs's contributions became evident with the development of industrial chemistry during the first half of the 20th century. According to Robert A. Millikan, in pure science Gibbs "did for statistical mechanics and for thermodynamics what Laplace did for celestial mechanics and Maxwell did for electrodynamics, namely, made his field a well-nigh finished theoretical structure."

Maxwell was an admirer and collaborator of Gibbs, and Maxwell's early death in 1879, at the age of 48, precluded further collaboration between him and Gibbs. The joke later circulated in New Haven that "only one man lived who could understand Gibbs's papers. That was Maxwell, and now he is dead."

When Dutch physicist J. D. van der Waals received the 1910 Nobel Prize "for his work on the equation of state for gases and liquids" he acknowledged the great influence of Gibbs's work on that subject. Max Planck received the 1918 Nobel Prize for his work on quantum mechanics, particularly his 1900 paper on Planck's law for quantized black-body radiation. That work was based largely on the thermodynamics of Kirchhoff, Boltzmann, and Gibbs. Planck declared that Gibbs's name "not only in America but in the whole world will ever be reckoned among the most renowned theoretical physicists of all times."

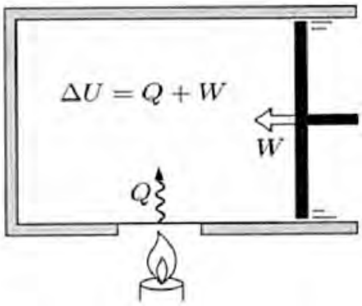
The “Gibbs Phenomenon” is another well-known example of his influence; this being the sine integral showing the overshoot and ringing of a Fourier Series approximation to a step function.



Basic Thermodynamic Concepts: internal energy, enthalpy and PdV work

Consider a fluid in a piston arrangement shown below. The fluid receives an amount of heat Q and mechanical work is done on the fluid at the rate W. The internal energy of the fluid U, changes by the amount $\Delta U = Q + W$.

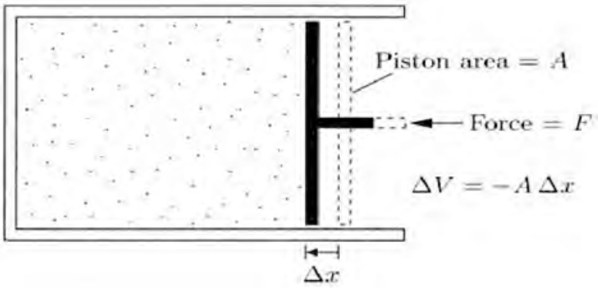
Figure 1.7. The total change in the energy of a system is the sum of the heat added to it and the work done on it.



Internal energy u represents (1) the kinetic energy involved in the vibration of molecules plus (2) the potential energy of chemical bonds and electrostatic charges. For liquids, and especially for water, this second aspect to internal energy is extremely important, while for a perfect gas, only the first part counts. Understanding thermodynamics from the scale of molecular behaviour is the field called "statistical thermodynamics"; we will not touch on this in these lectures.

The most common type of work W done on or by a fluid is the work done by compression or expansion, as in the following figure. This is how a car internal combustion engine extracts useful work from the high pressure gas that results from igniting the fuel-air mixture in an engine cylinder.

Figure 1.8. When the piston moves inward, the volume of the gas changes by ΔV (a negative amount) and the work done on the gas (assuming quasistatic compression) is $-P\Delta V$.



For infinitesimal changes we can write $dU + PdV = \delta Q$. Defining enthalpy H as $H = U + PV$ our attempt at writing down "energy conservation" so far can be written as

$$dH - V\,dP = \delta Q . \qquad (\sim\text{B.1a})$$

To motivate enthalpy H consider how much energy is required to magically create a blob of fluid out of nothing, and place it at its present location at pressure P.

Figure 1.15. To create a rabbit out of nothing and place it on the table, the magician must summon up not only the energy U of the rabbit, but also some additional energy, equal to PV, to push the atmosphere out of the way to make room. The *total* energy required is the **enthalpy**, $H = U + PV$.

Entropy and the Second Law of Thermodynamics

A "closed system", such as the piston illustration on the previous page, is one where there is exchange of heat with the environment, and there is mechanical work done between the system and the environment, but there is no exchange of mass of any species. That is, for seawater, a "closed system" is a seawater parcel with fixed mass of both water and of salt, and having no exchange of water or salt with the surrounding fluid.

We begin by repeating our progress so far with the conservation of energy for a "closed system", but now written in terms of "specific" variables, that is variables that represent the amount of stuff per unit mass of seawater,

$$\mathrm{d}h - v\mathrm{dP} = \delta q \ . \qquad \text{(\~B.1b)}$$

For a "closed system" the Second Law of Thermodynamics states that

1. there is a state variable entropy $\eta = \eta\left(S_{\mathrm{A}}, T, P\right)$ whose infinitesimal changes obey

$$\mathrm{d}\eta = \frac{\delta q}{T}, \qquad \textit{for a closed system} \qquad \text{(2}^{\text{nd}}\text{\_Law)}$$

2. and that irreversible processes (like diffusion and turbulent mixing) always result in the production entropy.

Entropy represents the amount of "disorder" in a system, and things naturally become more disordered in nature.

Note that δq itself is a complicated animal (which I passionately dislike). It is not the divergence of a flux; for example the dissipation of turbulent kinetic energy, ε, is part of δq. I emphasise that this dissipation ε heats the fluid but it is not the divergence of a heat flux. This nasty nature of δq is why it is written as δq rather than $\mathrm{d}q$. δq is not a total differential and q is not a state variable, that is $q \neq q\left(S_{\mathrm{A}}, T, P\right)$.

We can combine Eqns. (~B.1b) and (2nd_Law) to find

$$\mathrm{d}h - v\mathrm{dP} = T\mathrm{d}\eta \qquad \textit{for a closed system} \qquad \text{(Fundamental\_Closed)}$$

This is the Fundamental Thermodynamic Relation for a closed system; it applies when there are no variations of Absolute Salinity (e.g. it applies to a lake). It is a differential relationship between three state variables, specific enthalpy, specific volume and specific entropy.

The Fundamental Thermodynamic Relation (or Gibbs relation)

Now we will generalize this relationship to an "open system" where the system exchanges not only heat and work energy with its environment, but it also exchanges mass. That is, a seawater parcel that is an "open system" exchanges not only "heat" and "work", both also water and salt with its environment.

Consider a situation where we have a seawater parcel exchanging water and salt with its environment at constant temperature and pressure. It is simplest to assume that there is no change in the parcel's total mass. Specifically, envisage two seawater parcels that are in contact with each other, having different Absolute Salinities but the same temperature and pressure. A small part of each parcel is now exchanged with the other parcel, with the amount exchanged in both directions having the same mass.

We now define the "system" as being one of these two seawater parcels. If the system were closed we would have the relation $\mathrm{d}h - v\mathrm{dP} = T\mathrm{d}\eta$ but now the change in the seawater sample's enthalpy and entropy must incorporate the change in the Absolute Salinity $\mathrm{d}S_\mathrm{A}$. By Taylor series expansion of $h\left(S_\mathrm{A},T,P\right)$ and $\eta\left(S_\mathrm{A},T,P\right)$, the changes in enthalpy and entropy are related to those of the corresponding closed system by

$$\mathrm{d}h \;=\; \mathrm{d}h^{\mathrm{closed}} \;+\; \left.\frac{\partial h}{\partial S_\mathrm{A}}\right|_{T,P} \mathrm{d}S_\mathrm{A} \;, \qquad (\mathrm{d}h)$$

$$\mathrm{d}\eta \;=\; \mathrm{d}\eta^{\mathrm{closed}} \;+\; \left.\frac{\partial \eta}{\partial S_\mathrm{A}}\right|_{T,P} \mathrm{d}S_\mathrm{A} \;. \qquad (\mathrm{d}\eta)$$

We know that $\mathrm{d}h^{\mathrm{closed}} - v\mathrm{dP} \;=\; T\mathrm{d}\eta^{\mathrm{closed}}$ and these three equations can be combined to find

$$\mathrm{d}h - v\mathrm{dP} \;=\; T\mathrm{d}\eta \;+\; \left(\left.\frac{\partial h}{\partial S_\mathrm{A}}\right|_{T,P} - T\left.\frac{\partial \eta}{\partial S_\mathrm{A}}\right|_{T,P} \right)\mathrm{d}S_\mathrm{A} \;. \qquad (\mathrm{d}h - T\mathrm{d}\eta)$$

This is the Fundamental Thermodynamic Relation. We can write it in more familiar nomenclature once we have defined the Gibbs function (also called "free enthalpy" and sometimes "free energy") by

$$\boxed{g\left(S_\mathrm{A},T,P\right) = g \equiv h - T\eta \;\equiv\; u + Pv - T\eta} \;. \qquad \text{(definition\_of\_g)}$$

We also use the symbol μ for the *relative chemical potential of seawater* defined as the partial derivative of the Gibbs function with respect to Absolute Salinity,

$$\mu \;=\; \left.\frac{\partial g}{\partial S_\mathrm{A}}\right|_{T,P} \qquad (\text{or } \mu = g_{S_\mathrm{A}}). \qquad \text{(rel chem pot)}$$

This gives the usual form of the Fundamental Thermodynamic Relation (FTR)

$$\boxed{\mathrm{d}u + \left(p + P_0\right)\mathrm{d}v \;=\; \mathrm{d}h - v\mathrm{d}P \;=\; \left(T_0 + t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_\mathrm{A}} \;. \qquad \text{(FTR)}$$

Here we have written the Absolute Pressure P as $p + P_0$ where $P_0 \equiv 101325\ \mathrm{Pa}$ is the pressure of one standard atmosphere and p is the "sea pressure", and we have written the Absolute Temperature $T = T_0 + t$ as the sum of the Celsius zero point $T_0 \equiv 273.15\ \mathrm{K}$ and the temperature t in degrees Celsius.

In Tutorial class you will be asked to prove that (using $g = g\left(S_\mathrm{A},T,P\right)$)

$$\eta \;=\; -\,g_T\,, \qquad v \;=\; g_P \quad \text{and} \quad c_p \;=\; \left.\frac{\partial h}{\partial T}\right|_{S_\mathrm{A},P} \;=\; -\left(T_0 + t\right)g_{TT} \;. \qquad (\eta\,,\,v \text{ and } c_p)$$

The Gibbs function is a thermodynamic potential, from which all thermodynamic properties can be found by simple operations such as differentiation.

The alternative name of "free enthalpy" comes from considering again the amount of energy required to create our seawater parcel out of nothing. The total amount of energy required per unit mass is h but some of this energy, namely $T\eta$, can be extracted from the environment if the parcel is created slowly enough so it is always at the temperature T of the environment.

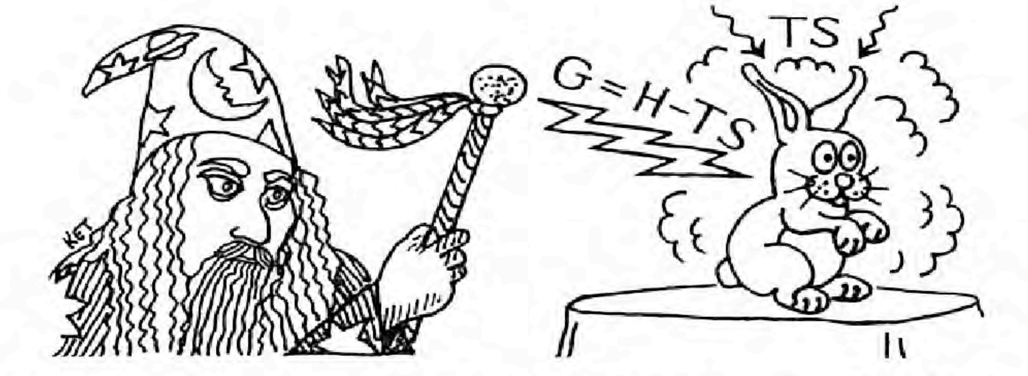


Figure 5.1. To create a rabbit out of nothing and place it on the table, the magician need not summon up the entire enthalpy, $H = U + PV$. Some energy, equal to TS, can flow in spontaneously as heat; the magician must provide only the difference, $G = H - TS$, as work.

Review of the last lecture

We learnt that the Practical Salinity variable, defined in 1980, is essentially a measure of the electrical conductivity seawater, but is blind to spatial variations of the concentrations of nutrients which affect the density and the electrical conductivity of a seawater sample differently to how the major dissolved ions affect density and conductivity.

This has now been addressed, and beginning in 2010 oceanographers have a new variable, Absolute Salinity, S_A, which better represents thermodynamic quantities such as density. This definition of seawater salinity and the Gibbs function of seawater goes by the name of the

International Thermodynamic Equation Of Seawater – 2010,
or TEOS-10, see www.TEOS-10.org.

We derived the Gibbs Relation, or Fundamental Thermodynamic Relation

$$\boxed{\mathrm{d}u + \left(p+P_0\right)\mathrm{d}v \;=\; \mathrm{d}h - v\,\mathrm{d}P \;=\; \left(T_0+t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_\mathrm{A}}\;. \qquad \text{(FTR)}$$

which is a relationship between the total differentials of several state variables, u, v, h, η and μ.

We defined the Gibbs function in terms of enthalpy and entropy by

$$\boxed{g\left(S_\mathrm{A},T,P\right) = g \equiv h - T\eta \;\equiv\; u + Pv - T\eta}\;. \qquad \text{(definition\_of\_g)}$$

All the thermodynamic properties of a fluid can be derived from this one "parent" function, $g\left(S_\mathrm{A},t,p\right)$, by simple mathematical operations such as differentiation. Hence the fundamental importance of the Gibbs function for a substance.

As for understanding the difference between enthalpy h, internal energy u and the Gibbs function g we learnt that enthalpy is a better estimate of the total amount of thermodynamic energy in a fluid parcel, recognizing that the parcel's creation involved pushing its environment out of the way (because it occupies volume v (per unit mass) at ambient Absolute Pressure P). Enthalpy h is useful for understanding processes that occur at constant pressure, while internal energy u is useful for understanding processes that occur at constant volume.

The Gibbs function $g \equiv h - T\eta$ is the part of enthalpy h that is "free" or "available". The part $T\eta$ of h is not available "for sale" on the energy market, because it is not "available" to do any useful work. Hence the Gibbs function is sometimes called "free enthalpy" or "free energy". The adjective "available" makes sense if you are selling the energy of the seawater parcel to someone who wants to use the energy of the parcel to do some useful work in say an energy cycle machine. The adjective "free" makes sense if you consider yourself to be the magician, creating the seawater parcel out of nothing, and getting a free ride from the environment to the extent $T\eta$.

Warning on Nomenclature. For the state variables such as u, v, h, η we use lower case letters when they are per unit mass ("specific" variables), and upper case when they represent the total amount of that quantity in a mass of fluid of mass M. But the use of upper case P and T is different. These upper case letters stand for Absolute Pressure (in $\mathrm{Pa} = \mathrm{N\,m^{-2}}$) and Absolute Temperature (K), while the lower case letters p and t are for $p = P - P_0$ (often in units of dbar) and $t = T - T_0$ (in degrees Celsius).

$P_0 \equiv 101\,325\ \mathrm{Pa}$ (= 10.1325 dbar), and
$T_0 \equiv 273.15\ \mathrm{K}$.

A rough derivation of the First Law of Thermodynamics for a pure substance

For a pure fluid in which there is no dissolved material (such as pure water with zero Absolute Salinity) the derivation of the First Law of Thermodynamics usually starts with our Eqn. (~B.1b), namely $\mathrm{d}h - v\mathrm{dP} = \delta q$, written in terms of material derivatives as (where δq is now "per unit volume" rather than "per unit mass")

$$\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) = \frac{\delta q}{\mathrm{d}t}. \qquad \textit{for pure water} \ \text{(B.1)}$$

Now we have to guess what the nasty, obnoxious, odious, $\delta q/\mathrm{d}t$ term might be. We know that there is such a thing as the molecular flux of heat $\mathbf{F}^{\mathrm{Q}} = -\rho c_p k^T \nabla T$ (where k^T is the molecular diffusivity of temperature) whose (negative) divergence one might imagine should be part of $\delta q/\mathrm{d}t$. We know there is such a thing as the radiative heat flux $\mathbf{F}^{\mathrm{R}}$ whose (negative) divergence should also be part of $\delta q/\mathrm{d}t$. We also know that when the kinetic energy of turbulent motions is dissipated by the molecular viscosity, energy changes from its kinetic form to its "heat" form", and the fluid warms up as a result. So we do the sensible thing and add this term to $\delta q/\mathrm{d}t$. This term is written as $\rho\varepsilon$ where ε is the rate of dissipation of kinetic energy per unit mass of fluid. After this educated guesswork we have the First Law of Thermodynamics *for a pure substance*,

$$\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) = \frac{\delta q}{\mathrm{d}t} = -\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \rho\varepsilon. \qquad \textit{for pure water} \ \text{(B.2)}$$

So far so good; this educated guesswork has allowed us to arrive at a correct result in this simple case for a fluid that is a *pure substance*.

But we have actually assumed that the molecular flux of heat appears on the right-hand side as $\nabla\cdot\left(\rho c_p k^T \nabla T\right)$. We have no right to assume that. We cannot rule out the form $\rho c_p \nabla\cdot\left(k^T \nabla T\right)$ for example, for this term. So, what will turn out to be the key feature of Eqn. (B.2), namely that apart from $\rho\varepsilon$ the other terms on the right-hand side appear as flux divergences, we have actually assumed, not proven. This is not satisfactory and we must do better.

A false start at deriving the First Law of Thermodynamics for seawater

But lets stay with this rough, hand-waving approach for a little bit longer, and see how far we can get with deriving the First Law of Thermodynamics for seawater when there *are* spatial variations of Absolute Salinity. The same traditional discussion of the First Law of Thermodynamics involving the "heating" and the application of compression work (as in Eqn. (~B.1a) above), and now the change of salinity to a fluid parcel shows that the change of enthalpy of the fluid parcel is given by ($\mu - \left[T_0 + t\right]\mu_T$ being $h_{S_{\mathrm{A}}}\big|_{T,P}$)

$$\mathrm{d}H - V\mathrm{d}P = \delta Q + \left(\mu - [T_0 + t]\mu_T\right) M \,\mathrm{d}S_{\mathrm{A}}, \qquad \text{(B.3)}$$

where M is the mass of the fluid parcel. When written in terms of the specific enthalpy h, and δQ per unit volume (δq), this equation becomes (using $\rho \mathrm{d}S_{\mathrm{A}}/\mathrm{d}t = -\nabla\cdot\mathbf{F}^{S}$)

$$\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}p}{\mathrm{d}t}\right) = \frac{\delta q}{\mathrm{d}t} - \left(\mu - \left[T_0 + t\right]\mu_T\right)\nabla\cdot\mathbf{F}^{\mathrm{S}}. \qquad \text{(B.4)}$$

Does this help with the task of constructing an expression for the right-hand side of (B.4) in terms of the dissipation of mechanical energy and the molecular, radiative and boundary fluxes of "heat" and salt? If the "heating" term $\delta q/\mathrm{d}t$ in Eqn. (B.4) were the same as in the pure water case, Eqn. (B.2), then we would have successfully derived the First Law of Thermodynamics in a saline ocean via this route. However, we will now show that $\delta q/\mathrm{d}t$ in Eqn. (B.4) is not the same as that in the pure water case, Eqn. (B.2).

Substituting the expression for $\delta q/\mathrm{d}t$ from (B.2) into the right-hand side of (B.4) we find that the right-hand side is not the same as the First Law of Thermodynamics (B.19) which we derive below (this comparison involves using the correct expression (B.27)) for the molecular flux $\mathbf{F}^{\mathrm{Q}}$). The two versions of the First Law of Thermodynamics are different by

$$\mathbf{F}^{\mathrm{S}}\cdot\nabla\left(\mu-\left[T_0+t\right]\mu_T\right) \;+\; \nabla\cdot\left[\frac{B'\mu_{S_{\mathrm{A}}}}{\rho k^{S}\left[T_0+t\right]}\mathbf{F}^{\mathrm{S}}\right]. \qquad \text{(B.5)}$$

Note that the fact that the right-hand side of Eqn. (B.4) is not the divergence of a flux was already apparent in that equation; this is a damning shortcoming. This inconsistency means that the rather poorly defined "rate of heating" $\delta q/\mathrm{d}t$ must be different in the saline case than in the pure water situation by this amount. We know of no way of justifying this difference, so we conclude that any attempt to derive the First Law of Thermodynamics via this route involving the loosely defined "rate of heating" $\delta q/\mathrm{d}t$ is doomed to failure. This is not to say that Eqn. (B.4) is incorrect. Rather, the point is that it is not useful, since $\delta q/\mathrm{d}t$ cannot be deduced directly by physical reasoning.

In particular, the expression in (B.5) is not the divergence of a flux and so when two parcels are mixed at constant pressure, enthalpy will not be conserved (see later). We were able to correctly guess the form of the right-hand side of the First Law of Thermodynamics in the case of pure substance, but in the presence of salinity gradients, our intuition fails us. Let's stop this guessing game and derive the First Law of Thermodynamics properly.

The proper derivation of the First Law of Thermodynamics for seawater

Since there is no way of deriving the First Law of Thermodynamics that involves the "heating" term $\delta q / \mathrm{d}t$, we follow Landau and Lifshitz (1959) and de Groot and Mazur (1984) and derive the First Law via the following circuitous route. Rather than attempting to guess the form of the molecular forcing terms in this equation directly, we first construct a conservation equation for the total energy, being the sum of the kinetic, gravitational potential and internal energies. It is in this equation that we insert the molecular fluxes of heat and momentum and the radiative and boundary fluxes of heat. We know that the evolution equation for total energy must have the conservative form, and so we insist that the forcing terms in this equation appear as the divergence of fluxes.

Having formed the conservation equation for total energy, the known evolution equations for two of the types of energy, namely the kinetic and gravitational potential energies, are subtracted, leaving a prognostic equation for either internal energy or enthalpy, that is, the First Law of Thermodynamics.

We start by developing the evolution equations for gravitational potential energy and for kinetic energy (via the momentum equation). The sum of these two evolution equations is noted. We then step back a little and consider the simplified situation where there are no molecular fluxes of heat and salt and no effects of viscosity and no radiative or boundary heat fluxes. In this "adiabatic" limit we are able to develop the conservation equation for total energy, being the sum of internal energy, kinetic energy and gravitational potential energy. To this equation we introduce the molecular, radiative and boundary flux divergences. Finally the First Law of Thermodynamics is found by subtracting from this total energy equation the conservation statement for the sum of the kinetic and gravitational potential energies.

We start by writing the Fundamental Thermodynamic Relation (FTR) in terms of material derivatives following the instantaneous motion of a fluid parcel $\mathrm{d}/\mathrm{d}t = \partial/\partial t|_{x,y,z} + \mathbf{u}\cdot\nabla$,

$$\frac{\mathrm{d}u}{\mathrm{d}t} + \left(p + P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t} = \frac{\mathrm{d}h}{\mathrm{d}t} - \frac{1}{\rho}\frac{\mathrm{d}P}{\mathrm{d}t} = \left(T_0 + t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t} + \mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t} \quad . \tag{B.6}$$

Gravitational potential energy

If the gravitational acceleration g is taken to be constant the gravitational potential energy per unit mass with respect to the height $z = 0$ is simply gz. Allowing g to be a function of height means that the gravitational potential energy per unit mass Φ with respect to some fixed height z_0 is defined by

$$\Phi = \int_{z_0}^{z} g(z')\, dz'. \tag{B.7}$$

At a fixed location in space Φ is independent of time while its spatial gradient is given by $\nabla\Phi = g\,\mathbf{k}$ where $\mathbf{k}$ is the unit vector pointing upwards in the vertical direction. The evolution equation for Φ is then readily constructed as

$$\left(\rho\Phi\right)_t + \nabla\cdot\left(\rho\Phi\mathbf{u}\right) = \rho\frac{\mathrm{d}\Phi}{\mathrm{d}t} = \rho g w, \tag{B.8}$$

where w is the vertical component of the three-dimensional velocity, that is $w = \mathbf{u}\cdot\mathbf{k}$. (Clearly in this section g is the gravitational acceleration, not the Gibbs function). Note that this local balance equation for gravitational potential energy is not in the form

$$\left(\rho C\right)_t + \nabla\cdot\left(\rho\mathbf{u}C\right) = \rho\frac{\mathrm{d}C}{\mathrm{d}t} = -\nabla\cdot\mathbf{F}^\mathrm{C}. \tag{A.8.1}$$

that is required of a conservative variable, since the right-hand side of (B.8) is not minus the divergence of a flux.

Momentum evolution equation

The momentum evolution equation is derived in many textbooks including Landau and Lifshitz (1959), Batchelor (1970), Gill (1982) and Griffies (2004). The molecular viscosity appears in the exact momentum evolution equation in the rather complicated expressions appearing in equations (3.3.11) and (3.3.12) of Batchelor (1970). We ignore the term that depends on the product of the kinematic viscosity ν^{visc} and the velocity divergence $\nabla\cdot\mathbf{u}$ (following Gill (1982)), so arriving at

$$\rho\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t} + f\,\mathbf{k}\times\rho\mathbf{u} = -\nabla P - \rho g\mathbf{k} + \nabla\cdot\left(\rho\nu^{\text{visc}}\overgroup{\nabla\mathbf{u}}\right), \tag{B.9}$$

where f is the Coriolis frequency, ν^{visc} is the kinematic viscosity and $\overgroup{\nabla\mathbf{u}}$ is twice the symmetrized velocity shear, $\overgroup{\nabla\mathbf{u}} = \left(\partial u_i/\partial x_j + \partial u_j/\partial x_i\right)$. The centripetal acceleration associated with the coordinate system being on a rotating planet can be taken into account by an addition to the gravitational acceleration in (B.9) (Griffies (2004)).

Kinetic energy evolution equation

The kinetic energy evolution equation is found by taking the scalar product of Eqn. (B.9) with $\mathbf{u}$ giving

$$\begin{aligned} &\left(\rho\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u}\right)_t + \nabla\cdot\left(\rho\mathbf{u}\tfrac{1}{2}[\mathbf{u}\cdot\mathbf{u}]\right) \\ &\qquad = \rho\,\mathrm{d}\left(\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u}\right)/\mathrm{d}t \;=\; -\mathbf{u}\cdot\nabla P - \rho g w + \nabla\cdot\left(\rho\nu^{\text{visc}}\nabla\tfrac{1}{2}[\mathbf{u}\cdot\mathbf{u}]\right) - \rho\varepsilon, \end{aligned} \tag{B.10}$$

where the dissipation of mechanical energy ε is the positive definite quantity

$$\varepsilon \equiv \tfrac{1}{2}\nu^{\text{visc}}\left(\overgroup{\nabla\mathbf{u}}\cdot\overgroup{\nabla\mathbf{u}}\right). \tag{B.11}$$

Evolution equation for the sum of kinetic and gravitational potential energies

The evolution equation for total mechanical energy $\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi$ is found by adding Eqns. (B8) and (B10) giving

$$\begin{aligned} &\left(\rho\left[\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi\right]\right)_t + \nabla\cdot\left(\rho\mathbf{u}\left[\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi\right]\right) \\ &\qquad = \rho\,\mathrm{d}\left(\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi\right)/\mathrm{d}t \;=\; -\mathbf{u}\cdot\nabla P + \nabla\cdot\left(\rho\nu^{\text{visc}}\nabla\tfrac{1}{2}\left[\mathbf{u}\cdot\mathbf{u}\right]\right) - \rho\varepsilon. \end{aligned} \tag{B.12}$$

Notice that the term $\rho g w$ which has the role of exchanging energy between the kinetic and gravitational potential forms has cancelled when these two evolution equations were added.

Conservation equation for total energy $\mathcal{E}$ in the absence of molecular fluxes

In the absence of molecular or other irreversible processes (such as radiation of heat), both the specific entropy η and the Absolute salinity S_{A} of each fluid parcel is constant following the fluid motion so that the right-hand side of the FTR, Eqn. (B.6), is zero and the material derivative of internal energy satisfies $\mathrm{d}u/\mathrm{d}t = -\left(p+P_0\right)\mathrm{d}v/\mathrm{d}t$ so that the internal energy changes only as a result of the work done in compressing the fluid parcel. Realizing that $v = \rho^{-1}$ and using the continuity Eqn. (A.8.1) in the form $\mathrm{d}\rho/\mathrm{d}t + \rho\nabla\cdot\mathbf{u} = 0$, $\mathrm{d}u/\mathrm{d}t$ can be expressed in this situation of no molecular, radiative or boundary fluxes as $\mathrm{d}u/\mathrm{d}t = -\rho^{-1}\left(p+P_0\right)\nabla\cdot\mathbf{u}$. Adding this equation to the inviscid, non-dissipative version of the mechanical energy equation, Eqn. (B.12), gives

$$\left(\rho\mathcal{E}\right)_t + \nabla\cdot\left(\rho\mathbf{u}\mathcal{E}\right) = \rho\,\mathrm{d}\mathcal{E}/\mathrm{d}t = -\nabla\cdot\left(\left[p+P_0\right]\mathbf{u}\right), \quad \textit{no molecular fluxes} \tag{B.13}$$

where the total energy

$$\mathcal{E} = u + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi \tag{B.14}$$

is defined as the sum of the internal, kinetic and gravitational potential energies.

Note that this is the first variable that we have considered so far which has the right-hand side being the divergence of a flux. This was not true of the gravitational potential energy, Eqn. (B.8), it was not true of the kinetic energy equation, (B.10), and it was not true of the sum of the kinetic and gravitational potential energies, Eqn. (B.12). Note that the divergence-as-right-hand-side is not true of either (B.8), (B.10) or (B.12), even for flows without molecular fluxes. That fact that we have now found a variable, $\mathcal{E}$, whose evolution equation (B.13) has a right-hand-side which is the divergence of something in this adiabatic isohaline limit is extremely important. For example, if we substitute enthalpy h for internal energy u in the quantity $\mathcal{E}$, we lose this property.

Conservation equation for total energy in the presence of molecular fluxes

Now, following section 49 Landau and Lifshitz (1959) we need to consider how molecular fluxes of heat and salt and the radiation of heat will alter the simplified conservation equation of total energy (B.13). The molecular viscosity gives rise to a stress in the fluid represented by the tensor $\boldsymbol{\sigma}$, and the interior flux of energy due to this stress tensor is $\mathbf{u}\cdot\boldsymbol{\sigma}$ so that there needs to be the additional term $-\nabla\cdot\left(\mathbf{u}\cdot\boldsymbol{\sigma}\right)$ added to the right-hand side of the total energy conservation equation. Consistent with Eqn. (B.9) above we take the stress tensor to be $\boldsymbol{\sigma} = -\rho v^{\mathrm{visc}}\widehat{\nabla\mathbf{u}}$ so that the extra term is $\nabla\cdot\left(\rho v^{\mathrm{visc}}\nabla\tfrac{1}{2}\left[\mathbf{u}\cdot\mathbf{u}\right]\right)$. Also heat fluxes at the ocean boundaries and by radiation $\mathbf{F}^{\mathrm{R}}$ and molecular diffusion $\mathbf{F}^{\mathrm{Q}}$ necessitate the additional terms $-\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}}$. At this stage we have not specified the form of the molecular diffusive flux of heat $\mathbf{F}^{\mathrm{Q}}$ in terms of gradients of temperature and Absolute Salinity; this is done below in Eqn. (B.24). The total energy conservation equation in the presence of molecular, radiative and boundary fluxes is

$$\begin{aligned}\left(\rho\mathcal{E}\right)_t + \nabla\cdot\left(\rho\mathbf{u}\mathcal{E}\right) = \rho\,\mathrm{d}\mathcal{E}/\mathrm{d}t &= -\nabla\cdot\left(\left[p+P_0\right]\mathbf{u}\right) - \nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} \\ &\quad + \nabla\cdot\left(\rho v^{\mathrm{visc}}\nabla\tfrac{1}{2}\left[\mathbf{u}\cdot\mathbf{u}\right]\right).\end{aligned} \tag{B.15}$$

The right-hand side of the $\mathcal{E}$ conservation equation (B.15) is the divergence of a flux, ensuring that total energy $\mathcal{E}$ is both a "conservative" variable and an "isobaric conservative" variable (see appendix A.8 for the definition of these characteristics).

Two alternative forms of the conservation equation for total energy

Another way of expressing the total energy equation (B.15) is to write it in a quasi-divergence form, with the temporal derivative being of $\rho\mathcal{E} = \rho\left(u + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi\right)$ while the divergence part of the left-hand side is based on a different quantity, namely the Bernoulli function $\mathcal{B} = h + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi$. This form of the total energy equation is

$$\left(\rho\mathcal{E}\right)_t + \nabla\cdot\left(\rho\mathbf{u}\mathcal{B}\right) = -\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \nabla\cdot\left(\rho\nu^{\mathrm{visc}}\nabla\tfrac{1}{2}\left[\mathbf{u}\cdot\mathbf{u}\right]\right). \qquad \text{(B.16)}$$

In an ocean modelling context, it is rather strange to contemplate the energy variable that is advected through the face of a model grid, $\mathcal{B}$, to be different to the energy variable that is changed in the grid cell, $\mathcal{E}$. Hence this form of the total energy equation has not proved popular.

A third way of expressing the total energy equation (B.15) is to write the left-hand side in terms of only the Bernoulli function $\mathcal{B} = h + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi$ so that the prognostic equation for the Bernoulli function is

$$\left(\rho\mathcal{B}\right)_t + \nabla\cdot\left(\rho\mathbf{u}\mathcal{B}\right) = \rho\,\mathrm{d}\mathcal{B}/\mathrm{d}t = P_t - \nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \nabla\cdot\left(\rho\nu^{\mathrm{visc}}\nabla\tfrac{1}{2}\left[\mathbf{u}\cdot\mathbf{u}\right]\right). \qquad \text{(B.17)}$$

When the flow is steady, and in particular, when the pressure field is time invariant at every point in space, this Bernoulli form of the total energy equation has the desirable property that $\mathcal{B}$ is conserved following the fluid motion in the absence of radiative, boundary and molecular fluxes. Subject to this steady-state assumption, the Bernoulli function $\mathcal{B}$ possesses the "potential" property. The negative aspect of this $\mathcal{B}$ evolution equation (B.17) is that in the more general situation where the flow is unsteady, the presence of the P_t term means that the Bernoulli function does not behave as a conservative variable because the right-hand side of (B.17) is not the divergence of a flux. In this general non-steady situation $\mathcal{B}$ is "isobaric conservative" but is not a "conservative" variable nor does it posses the "potential" property.

Noting that the total energy $\mathcal{E}$ is related to the Bernoulli function by $\mathcal{E} = \mathcal{B} - \left(p + P_0\right)/\rho$ and even if we take the whole ocean to be in a steady state so that $\mathcal{B}$ has the "potential" property, it is clear that $\mathcal{E}$ does not have the "potential" property in this situation. That is, if a seawater parcel moves from say 2000 dbar to 0 dbar without exchange of material or heat with its surroundings and with $P_t = 0$ everywhere, then $\mathcal{B}$ remains constant while the parcel's total energy $\mathcal{E}$ changes by the difference in the quantity $-\left(p + P_0\right)/\rho$ between the two locations. Hence we conclude that even in a steady ocean $\mathcal{E}$ does not possess the "potential" property. This means that total energy $\mathcal{E}$ is useless as far as being a marker of fluid flow.

When the viscous production term $\nabla\cdot\left(\rho\nu^{\mathrm{visc}}\nabla\tfrac{1}{2}\left[\mathbf{u}\cdot\mathbf{u}\right]\right)$ in the above equations is integrated over the ocean volume, the contribution from the sea surface is the power input by the wind stress $\boldsymbol{\tau}$, namely the area integral of $\boldsymbol{\tau}\cdot\mathbf{u}^{\mathrm{surf}}$ where $\mathbf{u}^{\mathrm{surf}}$ is the surface velocity of the ocean.

Obtaining the First Law of Thermodynamics by subtraction

The evolution equation (B.12) for the sum of kinetic and gravitational potential energies is now subtracted from the total energy conservation equation (B.15) giving

$$\left(\rho u\right)_t + \nabla\cdot\left(\rho\mathbf{u}u\right) = \rho\,\mathrm{d}u/\mathrm{d}t = -\left(p + P_0\right)\nabla\cdot\mathbf{u} - \nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \rho\varepsilon. \qquad \text{(B.18)}$$

Using the continuity equation in the form $\rho\mathrm{d}v/\mathrm{d}t = \nabla\cdot\mathbf{u}$ and the Fundamental Thermodynamic Relation (B.6), this equation can be written as

$$\boxed{\begin{aligned}\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t}-v\frac{\mathrm{d}P}{\mathrm{d}t}\right) &= \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t}+\left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) = \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t}+\mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right)\\ &= -\nabla\cdot\mathbf{F}^\mathrm{R}-\nabla\cdot\mathbf{F}^\mathrm{Q}+\rho\varepsilon\end{aligned}}\;. \qquad \text{(B.19)}$$

which is the First Law of Thermodynamics.

The corresponding evolution equation for Absolute Salinity is (Eqn. (A.21.8))

$$\rho\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t} = \left(\rho S_\mathrm{A}\right)_t + \nabla\cdot\left(\rho\mathbf{u}S_\mathrm{A}\right) = -\nabla\cdot\mathbf{F}^\mathrm{S}+\rho\,\mathcal{S}^{S_\mathrm{A}}, \qquad \text{(A.21.8)}$$

where $\mathbf{F}^\mathrm{S}$ is the molecular flux of salt and $\rho\,\mathcal{S}^{S_\mathrm{A}}$ is the non-conservative source of Absolute Salinity due to the remineralization of particulate matter which we are going to ignore in this course. Hence, in this course we take the salt evolution equation to be

$$\boxed{\left(\rho S_\mathrm{A}\right)_t+\nabla\cdot\left(\rho\mathbf{u}S_\mathrm{A}\right) = \rho\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t} = -\nabla\cdot\mathbf{F}^\mathrm{S}}\;, \qquad \textit{approximate}\ \text{(A.21.8a)}$$

For many purposes in oceanography the exact dependence of the molecular fluxes of heat and salt on the gradients of Absolute Salinity, temperature and pressure is unimportant, nevertheless, Eqns. (B.23) - (B.27) below list these molecular fluxes in terms of the spatial gradients of these quantities.

At first sight Eqn. (B.19) has little to recommend it; there is a non-conservative source term $\rho\varepsilon$ on the right-hand side and even more worryingly, the left-hand side is not ρ times the material derivative of any quantity as is required of a conservation equation of a conservative variable. It is this aspect of the left-hand side of the First Law of Thermodynamics, namely the presence of the $-\mathrm{d}P/\mathrm{d}t$ term that has scared oceanographers and held up thermodynamic progress for a century.

In summary, the approach used here to develop the First Law of Thermodynamics seems rather convoluted in that the conservation equation for total energy is first formed, and then the evolution equations for kinetic and gravitational potential energies are subtracted. Moreover, the molecular, radiative and boundary fluxes were included into the total energy conservation equation as separate deliberate flux divergences, rather than coming from an underlying basic conservation equation. This approach is adopted for the following reasons. First this approach ensures that the molecular, radiative and boundary fluxes do enter the total energy conservation equation (B.15) as the divergence of fluxes so that the total energy $\mathcal{E} = u+\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u}+\Phi$ is guaranteed to be a conservative variable. This is essential. Second, it is rather unclear how one would otherwise arrive at the molecular fluxes of heat and salt on the right-hand side of the First Law of Thermodynamics since the direct approach which was attempted involved the poorly defined (and obnoxious) "rate of heating" $\delta q/\mathrm{d}t$ and did not lead us to the First Law.

Expressions for the molecular fluxes of heat and salt

The molecular fluxes of salt and heat, $\mathbf{F}^{\mathrm{S}}$ and $\mathbf{F}^{\mathrm{Q}}$, are now written in the general matrix form in terms of the thermodynamic "forces" $\nabla\left(-\mu/T\right)$ and $\nabla\left(1/T\right)$ as

$$\mathbf{F}^{\mathrm{S}} = A\nabla\left(-\mu/T\right) + B\nabla\left(1/T\right), \tag{B.21}$$

$$\mathbf{F}^{\mathrm{Q}} = B\nabla\left(-\mu/T\right) + C\nabla\left(1/T\right), \tag{B.22}$$

where A, B and C are three independent coefficients. The equality of the off-diagonal diffusion coefficients, B, results from the Onsager (1931a,b) reciprocity relation. When these fluxes are substituted into the First Law of Thermodynamics Eqn. (B.19) and this is written as an evolution equation for entropy, the Second Law constraint that the entropy production must be positive requires that $A > 0$ and that $C > B^2/A$.

The part of the salt flux that is proportional to $-\nabla S_{\mathrm{A}}$ is traditionally written as $-\rho k^S \nabla S_{\mathrm{A}}$ implying that $A = \rho k^S T/\mu_{S_{\mathrm{A}}}$. The molecular fluxes of salt and heat, $\mathbf{F}^{\mathrm{S}}$ and $\mathbf{F}^{\mathrm{Q}}$, can now be written in terms of the gradients of Absolute Salinity, temperature and pressure in the convenient forms

$$\mathbf{F}^{\mathrm{S}} = -\rho k^S\left(\nabla S_{\mathrm{A}} + \frac{\mu_P}{\mu_{S_{\mathrm{A}}}}\nabla P\right) - \left(\frac{\rho k^S T}{\mu_{S_{\mathrm{A}}}}\left(\frac{\mu}{T}\right)_T + \frac{B}{T^2}\right)\nabla T\ , \tag{B.23}$$

$$\mathbf{F}^{\mathrm{Q}} = -\frac{1}{T^2}\left(C - \frac{B^2}{A}\right)\nabla T + \frac{B\mu_{S_{\mathrm{A}}}}{\rho k^S T}\mathbf{F}^{\mathrm{S}} = -\rho c_p k^T\,\nabla T + \frac{B\mu_{S_{\mathrm{A}}}}{\rho k^S T}\mathbf{F}^{\mathrm{S}}, \tag{B.24}$$

where the fact that $C > B^2/A$ has been used to write the regular diffusion of heat down the temperature gradient as $-\rho c_p k^T\,\nabla T$ where k^T is the positive molecular diffusivity of temperature. These expressions involve the (strictly positive) molecular diffusivities of temperature and salinity (k^T and k^S) and the single cross-diffusion parameter B. The other parameters in these equations follow directly from the Gibbs function of seawater.

It is common to introduce a "reduced heat flux" by reducing the molecular flux of heat by $\partial h/\partial S_{\mathrm{A}}\big|_{T,p}\,\mathbf{F}^{\mathrm{S}} = \left(\mu - T\mu_T\right)\mathbf{F}^{\mathrm{S}}$, being the flux of enthalpy due to the molecular flux of salt. This prompts the introduction of a revised cross-diffusion coefficient defined by

$$B' \equiv B + \frac{\rho k^S T^3}{\mu_{S_{\mathrm{A}}}}\left(\frac{\mu}{T}\right)_T\ , \tag{B.25}$$

and in terms of this cross-diffusion coefficient Eqns. (B.23) and (B.24) can be written as

$$\mathbf{F}^{\mathrm{S}} = -\rho k^S\left(\nabla S_{\mathrm{A}} + \frac{\mu_P}{\mu_{S_{\mathrm{A}}}}\nabla P\right) - \frac{B'}{T^2}\nabla T\ , \tag{B.26}$$

and

$$\begin{aligned}\mathbf{F}^{\mathrm{Q}} - \left(\mu - T\mu_T\right)\mathbf{F}^{\mathrm{S}} &= -\rho c_p k^T\,\nabla T + \frac{B'\mu_{S_{\mathrm{A}}}}{\rho k^S T}\mathbf{F}^{\mathrm{S}} \\ &= -\rho c_p K^T\,\nabla T - \frac{B'\mu_{S_{\mathrm{A}}}}{T}\left(\nabla S_{\mathrm{A}} + \frac{\mu_P}{\mu_{S_{\mathrm{A}}}}\nabla P\right),\end{aligned} \tag{B.27}$$

where K^T, defined by $\rho c_p K^T = \rho c_p k^T + B'^2/\left(AT^2\right)$, is a revised molecular diffusivity of temperature.

The term in (B.26) that is proportional to the pressure gradient ∇P represents "barodiffusion" as it causes a flux of salt down the gradient of pressure. The last term in (B.26) is a flux of salt due to the gradient of *in situ* temperature and is called the Soret effect, while the last term in the second line of Eqn. (B.27) is called the Dufour effect.

If the ocean were in thermodynamic equilibrium, its temperature would be the same everywhere, as would the chemical potentials of water and of each dissolved species; see Eqns. (B.21) and (B.22). Such a situation with $\mathbf{F}^{\mathrm{Q}} = \mathbf{F}^{\mathrm{S}} = 0$ would have entropy and the concentrations of each species being functions of pressure. Turbulent mixing acts very differently, tending to homogenize the concentration of each species and to make entropy constant, but in the process causing gradients in temperature and in the chemical potentials as functions of pressure. That is, turbulent mixing acts to maintain a non-equilibrium state. This difference between the roles of molecular versus turbulent mixing results from the symmetry breaking role of the gravity field; for example, in a laboratory without gravity, turbulent and molecular mixing would have indistinguishable effects.

Reference states

The Gibbs function $g\left(S_{\mathrm{A}},t,p\right)$ contains four arbitrary constants that cannot be determined by any set of thermodynamic measurements. These arbitrary constants mean that the Gibbs function is unknown and unknowable up to the arbitrary function of temperature and Absolute Salinity (where T_0 is the Celsius zero point, $273.15\ \mathrm{K}$)

$$a_1 + a_2\left(T_0+t\right) + a_3 S_{\mathrm{A}} + a_4\left(T_0+t\right)S_{\mathrm{A}} \ . \qquad (2.6.2)$$

This is equivalent to saying that both enthalpy h and entropy η are unknown and unknowable up to linear functions of Absolute Salinity; enthalpy is unknown up to $a_1 + a_3 S_{\mathrm{A}}$ and entropy is unknown up to $-a_2 - a_4 S_{\mathrm{A}}$.

There are no known or conceivable experiments that could possibly constrain these four arbitrary numbers. By the same token, there can be no conceivable consequences to any arbitrary choice that is made for these four numbers.

Now we can play

So we've spent 25 pages of lecture notes deriving the Fundamental Thermodynamic Relation and the First Law of Thermodynamics. Now it's time to play. Here is a revision of our underlying equations.

The Continuity Equation is

$$\boxed{\rho_t + \nabla\cdot\left(\rho\mathbf{u}\right) = 0}\,. \qquad \text{(A.21.2)}$$

The Fundamental Thermodynamic Relation is

$$\boxed{\mathrm{d}u + \left(p+P_0\right)\mathrm{d}v = \mathrm{d}h - v\,\mathrm{d}P = \left(T_0+t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_\mathrm{A}}\,. \qquad \text{(A.7.1)}$$

The First Law of Thermodynamics is

$$\boxed{\begin{aligned}\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) = \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t} + \left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) &= \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t} + \mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right)\\ &= -\nabla\cdot\mathbf{F}^\mathrm{R} - \nabla\cdot\mathbf{F}^\mathrm{Q} + \rho\varepsilon\end{aligned}}\,. \qquad \text{(B.19)}$$

The conservation equation of Absolute Salinity is

$$\boxed{\left(\rho S_\mathrm{A}\right)_t + \nabla\cdot\left(\rho\mathbf{u}S_\mathrm{A}\right) = \rho\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t} = -\nabla\cdot\mathbf{F}^\mathrm{S}}\,, \qquad \textit{approximate}\ \text{(A.21.8a)}$$

The definition of the Gibbs function

$$\boxed{g\left(S_\mathrm{A},T,P\right) = g \equiv h - T\eta \equiv u + Pv - T\eta}\,. \qquad \text{(definition\_of\_g)}$$

We will concentrate on the parts of these equations that involve enthalpy h (rather than internal energy u), that is, we will concentrate on the red parts of the equations.

The above equations have several variables appearing in more than one equation (especially when you realize that $\rho = v^{-1}$), but the Gibbs function appears in just the last equation, so why bother with it? The answer is that it is the Gibbs function that defines the fluid. That is, we have an internationally defined and accepted algorithm for $g\left(S_\mathrm{A},t,p\right)$, and all the other thermodynamic variables are actually not separate quantities but are actually various derivatives of the Gibbs function.

Enthalpy is "isobaric conservative"

There is an important consequence of the First Law that is really easy to derive, and its too beautiful to delay discussing, so we will do so right away. The First Law of Thermodynamics can be put in divergence form by invoking the continuity equation, giving

$$\left(\rho h\right)_t + \nabla\cdot\left(\rho\mathbf{u}h\right) - \frac{\mathrm{d}P}{\mathrm{d}t} = -\nabla\cdot\mathbf{F}^\mathrm{R} - \nabla\cdot\mathbf{F}^\mathrm{Q} + \rho\varepsilon\,. \qquad \text{(A.13.2)}$$

An important consequence of Eqn. (A.13.2) is that when two finite sized parcels of seawater are mixed at constant pressure and under ideal conditions, the total amount of enthalpy is conserved. To see this, integrate over the volume that encompasses both fluid parcels while assuming there to be no radiative, boundary or molecular fluxes across the boundary of this control volume. This control volume may change with time as the fluid moves (at constant pressure), mixes and contracts. The dissipation of kinetic energy by viscous friction $\rho\varepsilon$ is commonly ignored during such mixing processes but in fact the dissipation term does cause a small increase in the enthalpy of the mixture with respect to that of the two original parcels, and it is easy to include it. Apart from this non-conservative source term, $\rho\varepsilon$, under these assumptions Eqn. (A.13.2) reduces to the statement that the volume integrated amount of ρh is the same for the two initial fluid parcels as for the final mixed parcel, that is, the total amount of enthalpy is unchanged.

This result of non-equilibrium thermodynamics (it is non-equilibrium because of the finite size of the parcels and the finite property differences) has been known since the days of Gibbs in the nineteenth century, and it is of the utmost importance in oceanography. The fact that enthalpy is conserved when fluid parcels mix at constant pressure is the central result upon which all of our understanding of "heat fluxes" and of "heat content" in the ocean now rests.

As important as this result is, it does not follow that enthalpy is the best variable to represent "heat content" in the ocean. Enthalpy is actually a very poor representation of "heat content" in the ocean because it does not posses the "potential" property. It will be seen that potential enthalpy h^0 (referenced to zero sea pressure) is the best thermodynamic variable to represent "heat content" in the ocean.

Review of the past couple of lectures

The left-hand side of the First Law of Thermodynamics is identical to one of the three parts of the Fundamental Thermodynamic Relation,

$$\boxed{\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t}-v\frac{\mathrm{d}P}{\mathrm{d}t}\right) = \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t}+\left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) = \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t}+\mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right)}, \qquad \text{(B.6)}$$

but the right-hand side of the First Law of Thermodynamics contains the physical processes that affect the "heat-like" variables u, h and η that appear on the left-hand side. These physical processes are minus the divergences of the fluxes of heat by radiation and by molecular diffusion plus the dissipation of kinetic energy into "heat".

We learnt that the way to derive the First Law of Thermodynamics is a bit torturous. One must first develop the conservation equation for Total Energy $\mathcal{E} = u+\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u}+\Phi$ and then one subtracts off the evolution equation for $\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u}+\Phi$. What is left is the First Law of Thermodynamics. This is the only way of deriving the First Law of Thermodynamics even for a pure substance (like freshwater) and it is especially obvious that this is the only viable route when the fluid is not a pure substance (e.g. seawater which is pure water plus sea-salt in solution).

We then looked at the form of the molecular fluxes of salt and heat

$$\begin{bmatrix}\mathbf{F}^\mathrm{S}\\ \mathbf{F}^\mathrm{Q}\end{bmatrix} = \begin{bmatrix}A & B\\ B & C\end{bmatrix}\begin{bmatrix}\nabla\left(-\mu/T\right)\\ \nabla\left(1/T\right)\end{bmatrix}, \qquad \text{(B.21, B.22))}$$

and examined the constraints on A, B and C required to ensure that entropy is never destroyed.

We then looked at the First Law of Thermodynamics, namely

$$\boxed{\begin{aligned}\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t}-v\frac{\mathrm{d}P}{\mathrm{d}t}\right) &= \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t}+\left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) = \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t}+\mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right)\\ &= -\nabla\cdot\mathbf{F}^\mathrm{R}-\nabla\cdot\mathbf{F}^\mathrm{Q}+\rho\varepsilon\end{aligned}}. \qquad \text{(B.19)}$$

and were able to show that when turbulent mixing occurs between two fluid parcels, enthalpy is conserved (apart from the heating caused by any dissipation of kinetic energy $\rho\varepsilon$). This is true because for fluid parcels to mix they have to be at the same physical location and therefore at the same pressure. This "isobaric conservative" nature of enthalpy is the most important consequence of the First Law of Thermodynamics for a turbulent fluid such as the atmosphere and the ocean. However enthalpy has another drawback that makes it an undesirable variable; it varies quite strongly with pressure, even for an adiabatic and isohaline change in pressure. We will find that a new variable that is based on enthalpy, namely potential enthalpy, is a much better variable for representing the "heat content" per unit mass of seawater.

"isohaline", "adiabatic" and "isentropic"; reversible and irreversible processes

The adjective "isohaline" means "at constant salinity" and describes a process in which the Absolute Salinity of a fluid parcel is constant because $-\nabla\cdot\mathbf{F}^{\mathrm{S}}$ is zero.

The adjective "adiabatic" is traditionally taken to mean a process during which there is no exchange of heat between the environment and the fluid parcel one is considering. However, with this definition of "adiabatic" it is still possible for the entropy η, of a fluid parcel to change during an isohaline and adiabatic process (see Eqn. (B.19)). This is because the dissipation of mechanical energy ε causes an increase in η.

$$\boxed{\begin{aligned}\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t}-v\frac{\mathrm{d}P}{\mathrm{d}t}\right) &= \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t}+\left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) = \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t}+\mu\frac{\mathrm{d}S_{\mathrm{A}}}{\mathrm{d}t}\right) \\ &= -\nabla\cdot\mathbf{F}^{\mathrm{R}}-\nabla\cdot\mathbf{F}^{\mathrm{Q}}+\rho\varepsilon\end{aligned}}\,. \qquad \text{(B.19)}$$

While the dissipation of mechanical energy is a small term whose influence is routinely neglected in the First Law of Thermodynamics in oceanography, it seems advisable to modify the meaning of the word "adiabatic" in oceanography so that our use of the word more accurately reflects the properties we normally associate with an adiabatic process. Accordingly the word "adiabatic" in oceanography is taken to describe a process occurring without exchange of heat and also without the internal dissipation of mechanical energy. With this definition of "adiabatic", a process that is both isohaline and adiabatic *does* imply that the entropy η is constant, that is, it is an "isentropic" process.

With this definition of "adiabatic", an "adiabatic and isohaline" process, is identical to an "isentropic and isohaline" process. Often such a process is simply described as being simply "isentropic". However, it is possible to have an isentropic process in which there are changes in both temperature and in Absolute Salinity in just the right proportion to achieve no change in entropy. Hence one needs to say "adiabatic and isohaline" or "isentropic and isohaline"; two constancies are required, not one.

A reversible thermodynamic process must entail no change in entropy or salinity during the process, and no dissipation of mechanical energy. That is, a reversible thermodynamic process must have $\mathbf{F}^{\mathrm{S}}=\mathbf{F}^{\mathrm{R}}=\mathbf{F}^{\mathrm{Q}}=\varepsilon=0$. A slow change in the pressure of a fluid parcel may occur during a reversible process while $\mathbf{F}^{\mathrm{S}}=\mathbf{F}^{\mathrm{R}}=\mathbf{F}^{\mathrm{Q}}=\varepsilon=0$. If any of $\mathbf{F}^{\mathrm{S}}$, $\mathbf{F}^{\mathrm{R}}$, $\mathbf{F}^{\mathrm{Q}}$ or ε are non-zero, the processes is irreversible. The most common reversible processes is an adiabatic and isohaline change of pressure such as occurs during the vertical heaving motion of an internal gravity wave. During such motion both the entropy and the Absolute Salinity of the parcel are constant. Molecular diffusion of heat and salt are examples of irreversible processes, as are turbulent mixing processes.

potential temperature of seawater

Potential temperature θ is the temperature that a fluid parcel would have if its pressure were changed to a fixed reference pressure p_{r} in an isentropic and isohaline (and hence, reversible) manner. For a fluid parcel $\left(S_{\mathrm{A}},t,p\right)$ at pressure p the following thought experiment is conducted. You wrap the fluid parcel in an insulating plastic bag and then you slowly move it to a different location where the pressure is p_{r}. The parcel experiences the changing pressure during this movement. When the parcel arrives at p_{r} you put a thermometer into the parcel and measure its *in situ* temperature at p_{r}. This temperature is called the parcel's potential temperature.

Potential temperature referred to reference pressure p_{r} is often written as the pressure integral of the adiabatic lapse rate (Fofonoff (1962), (1985))

$$\theta = \theta\left(S_{\mathrm{A}},t,p,p_{\mathrm{r}}\right) = t + \int_{P}^{P_{\mathrm{r}}} \Gamma\left(S_{\mathrm{A}},\theta\left[S_{\mathrm{A}},t,p,p'\right],p'\right) dP' \,, \qquad (3.1.1)$$

where $\Gamma = \partial t/\partial P\big|_{S_{\mathrm{A}},\eta}$ is the rate at which *in situ* temperature changes with pressure at fixed entropy and salinity.

The algorithm that is used in the TEOS-10 code to evaluate potential temperature θ equates the specific entropies of two seawater parcels, one before and the other after the isentropic and isohaline pressure change. In this way, θ is evaluated using a Newton-Raphson type iterative solution technique to solve the following equation for θ

$$\eta\left(S_{\mathrm{A}},\theta,p_{\mathrm{r}}\right) = \eta\left(S_{\mathrm{A}},t,p\right), \qquad \text{or} \qquad -\,g_{T}\left(S_{\mathrm{A}},\theta,p_{\mathrm{r}}\right) = -\,g_{T}\left(S_{\mathrm{A}},t,p\right). \qquad (3.1.2)$$

This relation is formally equivalent to Eqn. (3.1.1).

In equating the specific entropies of the seawater parcel at the two different pressures in Eqn. (3.1.2) we are exploiting the fact that in the thought experiment the slow change in pressure is done isentropically.

Consider now two seawater parcels with the same Absolute Salinities but at different *in situ* temperatures and different pressures. If these two seawater parcels have the same value of specific entropy then the two seawater parcels must also have the same value of potential temperature θ at p_{r} (see Eqn. (3.1.2) where the right-hand side is the same for the two parcels).

potential enthalpy

Potential enthalpy h^0 is the enthalpy that a fluid parcel would have if its pressure were changed to a fixed reference pressure p_r in an isentropic and isohaline manner. Because heat fluxes into and out of the ocean occur mostly near the sea surface, the reference pressure for potential enthalpy is almost always taken to be p_r = 0 dbar (that is, at zero sea pressure). The thought process involved with potential enthalpy is the same as for potential temperature, namely the parcel is enclosed in an insulating plastic bag and its pressure is slowly change to p_r. At this new pressure the parcel's enthalpy is calculated, and this is called potential enthalpy.

Now considering specific enthalpy to be a function of entropy (rather than of temperature t), that is, taking $h = \overset{\frown}{h}\left(S_\mathrm{A},\eta,p\right)$, the Fundamental Thermodynamic Relation (FTR, Eqn. (A.7.1)) becomes

$$\overset{\frown}{h}_\eta\,\mathrm{d}\eta + \overset{\frown}{h}_{S_\mathrm{A}}\mathrm{d}S_\mathrm{A} + \overset{\frown}{h}_P\,\mathrm{d}P - v\,\mathrm{d}P \;=\; \left(T_0+t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_\mathrm{A}\,. \qquad \text{(A.11.4)}$$

For an isentropic and isohaline process during which $\mathrm{d}\eta = \mathrm{d}S_\mathrm{A} = 0$, this equation reduces to $\overset{\frown}{h}_P \equiv \partial\overset{\frown}{h}/\partial P\big|_{S_\mathrm{A},\eta} = v$ which allows us to simplify Eqn. (A.11.4) to

$$\overset{\frown}{h}_\eta\,\mathrm{d}\eta + \overset{\frown}{h}_{S_\mathrm{A}}\mathrm{d}S_\mathrm{A} \;=\; \left(T_0+t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_\mathrm{A} \qquad \text{while} \qquad \partial\overset{\frown}{h}/\partial P\big|_{S_\mathrm{A},\eta} = v, \qquad \text{(A.11.4)}$$

Also, from the previous section we know that if S_A and η are constant, then so is potential temperature θ. Hence we also know that

$$\partial h/\partial P\big|_{S_\mathrm{A},\theta} = v\ . \qquad \text{(A.11.6)}$$

Since we also know that $g_P = v$ we can note that

$$\partial h/\partial P\big|_{S_\mathrm{A},\theta} \;=\; v \;=\; \partial g/\partial P\big|_{S_\mathrm{A},T}\,. \qquad \left(v = g_P = \tilde{h}_P = \overset{\frown}{h}_P = \hat{h}_P\right)$$

Potential enthalpy h^0 can be expressed as the pressure integral of specific volume as

$$\begin{aligned} h^0\left(S_\mathrm{A},t,p\right) = h\left(S_\mathrm{A},\theta,0\right) = \tilde{h}^0\left(S_\mathrm{A},\theta\right) \;&=\; h\left(S_\mathrm{A},t,p\right) - \int_{P_0}^{P} v\left(S_\mathrm{A},\theta\left(S_\mathrm{A},t,p,p'\right),p'\right) dP' \\ &=\; h\left(S_\mathrm{A},t,p\right) - \int_{P_0}^{P} \overset{\frown}{v}\left(S_\mathrm{A},\eta,p'\right) dP' \\ &=\; h\left(S_\mathrm{A},t,p\right) - \int_{P_0}^{P} \tilde{v}\left(S_\mathrm{A},\theta,p'\right) dP' \\ &=\; h\left(S_\mathrm{A},t,p\right) - \int_{P_0}^{P} \hat{v}\left(S_\mathrm{A},\Theta,p'\right) dP', \end{aligned} \qquad \text{(3.2.1)}$$

and we emphasize that the pressure integrals here must be done with respect to pressure expressed in Pa rather than dbar. In this equation we have introduced the over-tilde, over-hat etc. which we will use to indicate the functional dependence of a variable; see the list of Nomenclature that has been distributed. Note that in the first line of the above equation, specific volume v is a function of $\left(S_\mathrm{A},t,p\right)$ while $\theta\left(S_\mathrm{A},t,p,p'\right)$ (see Eqn. (3.1.1)) is the potential temperature of parcel $\left(S_\mathrm{A},t,p\right)$ with respect to the reference pressure p'.

In terms of the Gibbs function, potential enthalpy h^0 is evaluated as

$$h^0\left(S_\mathrm{A},t,p\right) \;= h\left(S_\mathrm{A},\theta,0\right) = \;g\left(S_\mathrm{A},\theta,0\right) - \left(T_0+\theta\right)g_T\left(S_\mathrm{A},\theta,0\right). \qquad \text{(3.2.2)}$$

Conservative Temperature

Conservative Temperature Θ is defined to be proportional to potential enthalpy,

$$\Theta\left(S_{\mathrm{A}},t,p\right) = \tilde{\Theta}\left(S_{\mathrm{A}},\theta\right) = h^{0}\left(S_{\mathrm{A}},t,p\right)\big/c_p^0 = \tilde{h}^{0}\left(S_{\mathrm{A}},\theta\right)\big/c_p^0 \qquad (3.3.1)$$

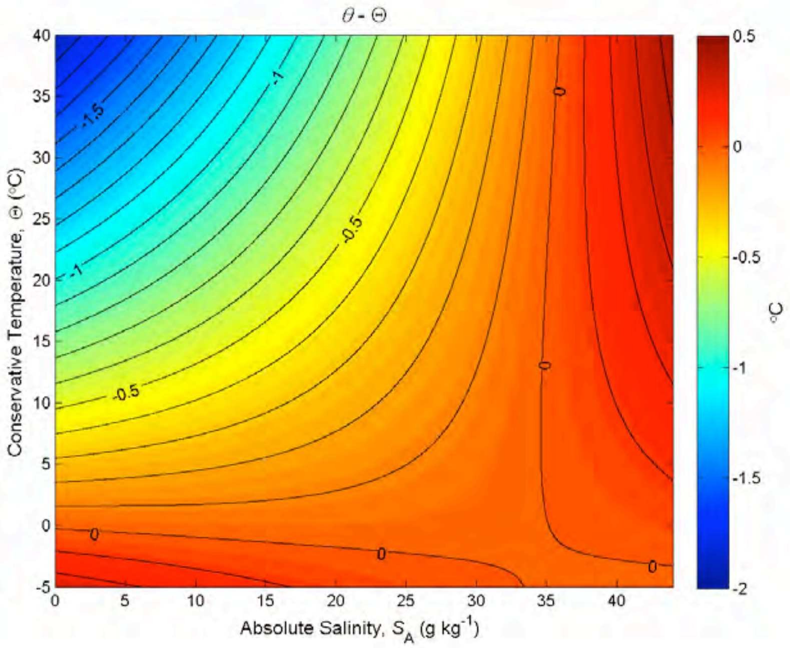
where the value that is chosen for c_p^0 is motivated in terms of potential enthalpy evaluated at an Absolute Salinity of $S_{\mathrm{SO}} = 35u_{\mathrm{PS}} = 35.165\,04\ \mathrm{g\,kg^{-1}}$ and at $\theta = 25\ °\mathrm{C}$ by

$$\frac{\left[h\left(S_{\mathrm{SO}},\, 25°\mathrm{C},\, 0\right) - h\left(S_{\mathrm{SO}},\, 0°\mathrm{C},\, 0\right)\right]}{(25\ \mathrm{K})} \approx 3991.867\,957\,119\,63\ \ \mathrm{J\,kg^{-1}\,K^{-1}}, \qquad (3.3.2)$$

noting that $h\left(S_{\mathrm{SO}},\, 0\ °\mathrm{C},\, 0\,\mathrm{dbar}\right)$ is zero according to the way the Gibbs function is defined. We adopt the exact definition for c_p^0 to be the 15-digit value in (3.3.2), so that

$$c_p^0 \equiv 3991.867\,957\,119\,63\ \ \mathrm{J\,kg^{-1}\,K^{-1}}. \qquad (3.3.3)$$

The value of c_p^0 in Eqn. (3.3.3) is very close to the average value of the specific heat capacity c_p at the sea surface of today's global ocean. This value of c_p^0 also causes the average value of $\theta - \Theta$ at the sea surface to be very close to zero. Since c_p^0 is simply a constant of proportionality between potential enthalpy and Conservative Temperature, it is totally arbitrary.



The difference between potential temperature and Conservative Temperature can be as large as $\theta - \Theta = -1.4°\mathrm{C}$ but is more typically no more than $\pm\,0.1°\mathrm{C}$. To put a temperature difference of $0.1°\mathrm{C}$ in context, this is the typical difference between *in situ* and potential temperatures for a pressure difference of 1000 dbar, and it is approximately 40 times as large as the typical differences between t_{90} and t_{68} in the ocean.

potential temperature of a perfect gas

An ideal gas obeys

$$Pv = RT \qquad \text{(Perfect\_Gas\_A)}$$

where R is the universal gas constant $R \approx 287 \text{ J kg}^{-1} \text{ K}^{-1}$. For an adiabatic change in pressure (this also being an isentropic processes) the Fundamental Thermodynamic Relation tells us that $\mathrm{d}h = v\mathrm{d}P$. For an ideal gas, specific enthalpy h is equal to $c_p^{\text{gas}} T$ where $c_p^{\text{gas}} = \tfrac{7}{2} R \approx 1004.5 \text{ J kg}^{-1} \text{ K}^{-1}$ for a diatomic gas. Hence for a perfect gas we have

$$c_p^{\text{gas}} \mathrm{dT} = \tfrac{7}{2} R \mathrm{dT} = \frac{RT}{P} \mathrm{d}P \qquad \text{or} \qquad \mathrm{d}(\ln T) = \tfrac{2}{7} \mathrm{d}(\ln P) . \qquad \text{(Perfect\_Gas\_B)}$$

Performing the adiabatic change in pressure from P to P_0 gives

$$\int_P^{P_0} \mathrm{d}(\ln T)' = \tfrac{2}{7} \int_P^{P_0} \mathrm{d}(\ln P)' \qquad \text{or} \qquad \frac{T_0 + \theta}{T_0 + t} = \left(\frac{P_0}{P} \right)^{\frac{2}{7}} \qquad \text{(Perfect\_Gas\_C)}$$

specific entropy of a perfect gas

Now consider a more general situation where the parcel of perfect gas does exchange heat with its surroundings, then the Fundamental Thermodynamic Relation

$$\mathrm{d}h - v\,\mathrm{d}P = \left(T_0 + t\right) \mathrm{d}\eta \qquad \text{(A.7.1)}$$

shows that

$$\begin{aligned} d\eta &= c_p^{\text{gas}} \frac{\mathrm{dT}}{T_0 + t} - R \frac{\mathrm{d}P}{P} = c_p^{\text{gas}} \mathrm{d}(\ln\left[T_0 + t\right]) - \tfrac{2}{7} c_p^{\text{gas}} \mathrm{d}(\ln P) \\ &= c_p^{\text{gas}} \mathrm{d}(\ln\left[T_0 + \theta\right]). \end{aligned} \qquad \text{(Perfect\_Gas\_D)}$$

Hence for a perfect gas, specific entropy is simply proportional to the natural logarithm of potential temperature (absolute potential temperature),

$$\begin{aligned} \eta &= c_p^{\text{gas}} \ln\left[T_0 + \theta\right] + \text{constant} \\ &= c_p^{\text{gas}} \ln\left[1 + \theta / T_0\right], \end{aligned} \qquad \text{(Perfect\_Gas\_E)}$$

where the constant is defined so that entropy is zero at a Celsius temperature of $0\,^\circ\text{C}$ (see Eqn. (J.6) and (J.7) of IOC *et al.* (2010)).

The enthalpy of a perfect gas (e.g. dry air) is also defined to be zero at a Celsius temperature of $0\,^\circ\text{C}$, so the potential enthalpy of a perfect gas is $h^0 = c_p^{\text{gas}} \theta$ and if a "conservative temperature of a perfect gas" were to be defined, then it would be equal to potential temperature θ.

An approximate specific entropy of seawater

One wonders how accurate a correspondingly simple logarithm expression would be for the entropy of seawater, defined by either $c_p^0 \ln\left[T_0 + \theta\right] + \text{constant}$ or $c_p^0 \ln\left[T_0 + \Theta\right] + \text{constant}$. The constants can be chosen so that it makes the estimate of entropy zero if $\theta = 0\,^\circ\text{C}$ or $\Theta = 0\,^\circ\text{C}$ in the two cases respectively since entropy is defined to be zero for Standard Seawater ($S_\text{A} = S_\text{SO}$) at these temperatures. Hence we try the two approximations

$$c_p^0 \ln\left[1 + \theta / T_0\right], \qquad \text{(approx\_entropy\_pt)}$$

and

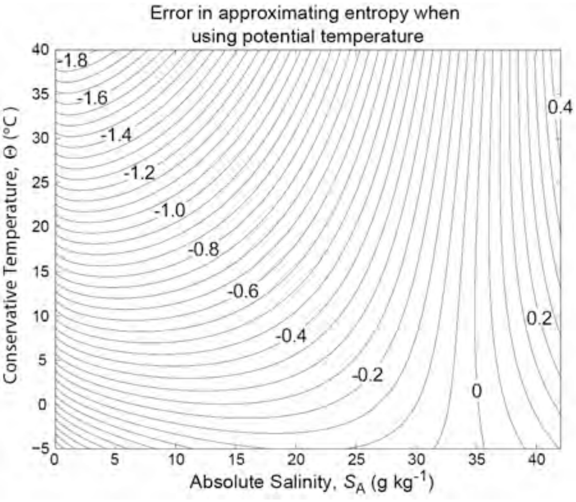
$$c_p^0 \ln\left[1 + \Theta / T_0\right]. \qquad \text{(approx\_entropy\_CT)}$$

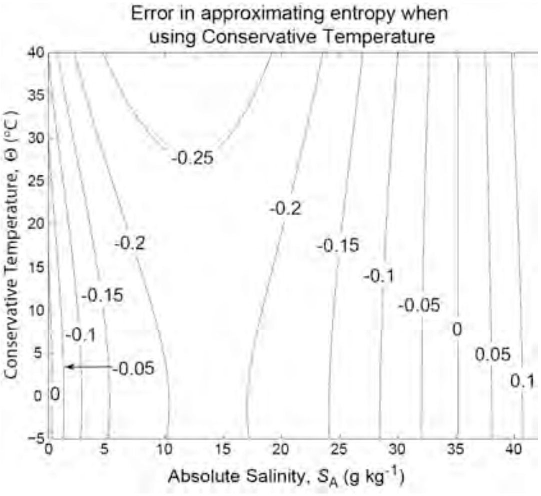
The figures below show the difference between these approximate expressions and the specific entropy of seawater, and each plot has been divided by

$$13.983265450613318 \text{ J kg}^{-1}\text{K}^{-2} = \frac{\hat{\eta}\left(35.16504 \text{ g kg}^{-1}, 25\,^\circ\text{C}\right)}{25\text{K}}, \qquad \text{(scaling\_factor)}$$

(i.e. essentially $14 \text{ J kg}^{-1}\text{K}^{-2}$) in order to express the error in the approximation in temperature units.

It is seen that the expression involving Conservative Temperature, $c_p^0 \ln\left[1+\Theta/T_0\right]$, is a better approximation to entropy than is the one involving potential temperature, $c_p^0 \ln\left[1+\theta/T_0\right]$. (Note that for seawater, c_p^0 is approximately four times as large as the specific heat capacity of air, c_p^{gas}).





Can we understand the relative performance of these two approximate expressions? Starting from the Fundamental Thermodynamic Relationship

$$\mathrm{d}h - v\,\mathrm{d}P \;=\; \left(T_0 + t\right)\mathrm{d}\eta \;+\; \mu\,\mathrm{d}S_{\mathrm{A}}\,, \qquad \text{(A.7.1)}$$

we consider this differential relationship at the fixed pressure of $p = 0$ dbar where the *in situ* temperature is equal to the potential temperature θ, so the FTR becomes

$$c_p^0\mathrm{d}\Theta \;=\; \left(T_0+\theta\right)\mathrm{d}\eta \;+\; \mu\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}S_{\mathrm{A}}\,, \qquad \text{(d\_entropy\_1)}$$

or

$$\mathrm{d}\eta \;=\; \frac{c_p^0}{\left(T_0+\theta\right)}\mathrm{d}\Theta \;-\; \frac{\mu\left(S_{\mathrm{A}},\theta,0\right)}{\left(T_0+\theta\right)}\mathrm{d}S_{\mathrm{A}}\,, \qquad \text{(d\_entropy\_2)}$$

or

$$\boxed{\mathrm{d}\eta \;=\; \frac{\left(T_0+\Theta\right)}{\left(T_0+\theta\right)}c_p^0\,\mathrm{d}(\ln\left[T_0+\Theta\right]) \;-\; \frac{\mu\left(S_{\mathrm{A}},\theta,0\right)}{\left(T_0+\theta\right)}\mathrm{d}S_{\mathrm{A}}}\,. \qquad \text{(d\_entropy\_3)}$$

This is the relevant differential expression for entropy in terms of Θ.

Now to develop the corresponding expression in terms of θ we go back to the FTR, Eqn. (A.7.1), evaluated at $p = 0$ dbar in the form

$$c_p\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}\theta \;+\; h_{S_{\mathrm{A}}}\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}S_{\mathrm{A}} \;=\; \left(T_0+\theta\right)\mathrm{d}\eta \;+\; \mu\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}S_{\mathrm{A}}\,. \qquad \text{(d\_entropy\_4)}$$

Since $h = g - Tg_T$ it follows that $h_{S_{\mathrm{A}}} = g_{S_{\mathrm{A}}} - Tg_{S_{\mathrm{A}}T} = \mu - T\mu_T$ so we can rewrite this last equation as

$$\boxed{\mathrm{d}\eta \;=\; c_p\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}(\ln\left[T_0+\theta\right]) \;-\; \mu_T\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}S_{\mathrm{A}}}\,. \qquad \text{(d\_entropy\_5)}$$

Our approximate straw-men expressions for entropy, namely $c_p^0 \ln\left[1+\theta/T_0\right]$ and $c_p^0 \ln\left[1+\Theta/T_0\right]$, amount to ignoring the dependence of entropy on Absolute Salinity in the above boxed equations, as well as

(i) in the case of θ, approximating $c_p\left(S_{\mathrm{A}},\theta,0\right)$ as c_p^0, and

(ii) in the case of Θ, approximating $\left(T_0+\Theta\right)/\left(T_0+\theta\right)$ by unity.

The specific heat capacity $c_p\left(S_{\mathrm{A}},\theta,0\right)$ varies by 5.5% in the ocean whereas the ratio $\left(T_0+\Theta\right)/\left(T_0+\theta\right)$ varies by no more than 0.67%, and this goes some way towards explaining why the approximate expression $\eta \approx c_p^0 \ln\left[1+\Theta/T_0\right]$ outperforms $c_p^0 \ln\left[1+\theta/T_0\right]$ by a factor of about 15.

The “conservative” property

A thermodynamic variable C is said to be “conservative” if its evolution equation (that is, its prognostic equation) has the form

$$(\rho C)_t + \nabla\cdot(\rho \mathbf{u} C) \;=\; \rho \frac{\mathrm{d}C}{\mathrm{d}t} \;=\; -\nabla\cdot\mathbf{F}^{\mathrm{C}}. \qquad \text{(A.8.1)}$$

For such a “conservative” property, in the absence of fluxes $\mathbf{F}^{\mathrm{C}}$ at the boundary of a control volume, the total amount of C-stuff is constant inside the control volume. In the special case when the material derivative of a property is zero (that is, the middle part and the right-hand side of Eqn. (A.8.1) are zero) the property is said to be “materially conserved”.

The only three quantities that can be regarded as 100% conservative in the ocean are (1) mass [equivalent to taking $C=1$ and $\mathbf{F}^{\mathrm{C}}=\mathbf{0}$ in Eqn. (A.8.1), giving the continuity equation, which is the equation representing the conservation of mass], (2) total energy $\mathcal{E}=u+\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u}+\Phi$ (see Eqn. (B.15)), and (3) Preformed Salinity S_*. Conservative Temperature Θ (or equivalently, potential enthalpy h^0) is not completely conservative, but we will find that the error in assuming it to be conservative is negligible. Because we are ignoring the non-conservative source term of Absolute Salinity in this course, we may also take Absolute Salinity to be conservative (as we have done in going from Eqn. (B.20) to Eqn. (B.20a) above).

Other variables such as potential temperature θ, enthalpy h, internal energy u, entropy η, density ρ, potential density ρ^{Θ}, specific volume v, potential specific volume, v^{Θ}, and the Bernoulli function $\mathcal{B}=h+\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u}+\Phi$ (see Eqn. (B.17)) are not conservative variables.

The “isobaric conservative” property

A different form of “conservation” attribute, namely “isobaric conservation” occurs when the total amount of the quantity is conserved when two fluid parcels are mixed at constant pressure without external input of heat or matter. This “isobaric conservative” property is a very valuable attribute for an oceanographic variable. Any “conservative” variable is also “isobaric conservative”, thus the conservative variables listed above, namely mass, total energy $\mathcal{E}$ and Preformed Salinity S_* are exactly “isobaric conservative” variables, while Absolute Salinity S_{A} is almost (but not exactly) “isobaric conservative”.

In addition, the Bernoulli function $\mathcal{B}$ and specific enthalpy h are also almost exactly “isobaric conservative”. The issue with the Bernoulli function in this regard is the presence of the unsteady term P_t, while the issue with enthalpy not being totally 100% “isobaric conservative” is the presence of the dissipation of mechanical energy $\rho\varepsilon$. We will find that this is also the largest of several terms that cause Conservative Temperature and specific potential enthalpy h^0 to not be 100% “conservative” or “isobaric conservative”. Note that while h is almost exactly “isobaric conservative”, it is not a “conservative” variable.

Some variables that are not “isobaric conservative” include potential temperature θ, internal energy u, entropy η, density ρ, potential density ρ^{Θ}, specific volume v, and potential specific volume v^{Θ}.

The “potential” property

Any thermodynamic property of seawater that remains constant when a parcel of seawater is moved from one pressure to another adiabatically, without exchange of mass and without interior conversion between its turbulent kinetic and internal energies, is said to possess the “potential” property, or in other words, to be a “potential” variable. Prime examples of “potential” variables are entropy η, potential temperature θ and potential density ρ^{Θ}. Recall that the constancy of entropy η can be seen from the First Law of Thermodynamics in Eqn. (B.19);

$$\boxed{\begin{aligned}\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t}-v\frac{\mathrm{d}P}{\mathrm{d}t}\right) \;=\; \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t}+\left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) \;&=\; \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t}+\mu\frac{\mathrm{d}S_{\mathrm{A}}}{\mathrm{d}t}\right)\\ &=\; -\nabla\cdot\mathbf{F}^{\mathrm{R}}-\nabla\cdot\mathbf{F}^{\mathrm{Q}}+\rho\varepsilon\end{aligned}}\;. \qquad (B.19)$$

since, with the right-hand side of Eqn. (B.19) being zero, and with no change in Absolute Salinity, it follows that entropy is also constant. Any thermodynamic property that is a function of only Absolute Salinity and entropy also remains unchanged by this procedure and is said to possess the “potential” property.

Recall that in oceanography we now define the word “adiabatic” to describe a process occurring without exchange of heat and also without the internal dissipation of kinetic energy. With this definition of “adiabatic”, a process that is both isohaline and adiabatic *does* imply that the entropy η, potential temperature θ and Conservative Temperature Θ are all constant.

Thermodynamic properties that posses the “potential” attribute include potential temperature θ, potential enthalpy h^0, Conservative Temperature Θ, potential density ρ^{Θ} and potential specific volume v^{Θ} (no matter what fixed reference pressure is chosen). Some thermodynamic properties that do not posses the potential property are temperature t, enthalpy h, internal energy u, specific volume v, density ρ, specific volume v, specific volume anomaly δ, total energy $\mathcal{E}$ and the Bernoulli function $\mathcal{B}$. From Eqn. (B.17) we notice that in the absence of molecular fluxes the Bernoulli function $\mathcal{B}$ is constant following the fluid flow only if the pressure field is steady; in general this is not the case. The non-potential nature of $\mathcal{E}$ is explained in the discussion following Eqn. (B.17) on page 22 of these lecture notes.

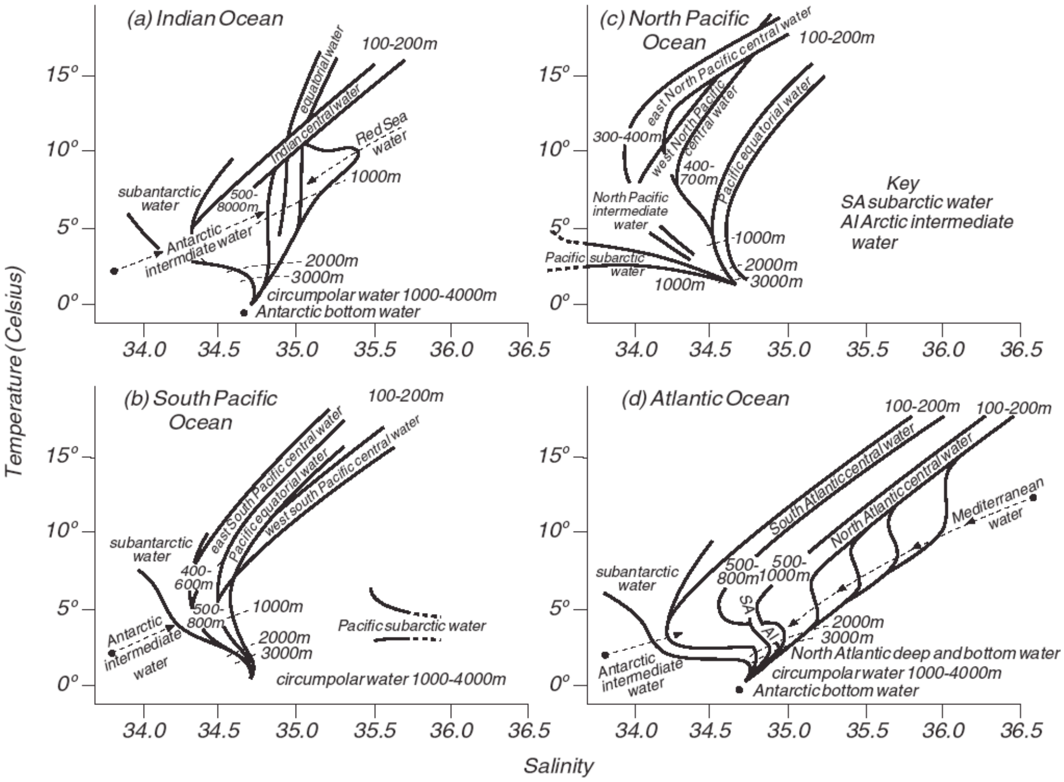


Figure 13.11 T-S plots of water in the various ocean basins. After Tolmazin (1985: 138).

Oceanographers analyze "water-masses" on this $S_{\mathrm{A}}-\Theta$ diagram. The salinity and temperature variables on these axes should ideally be both "potential" and "conservative" properties so that turbulent mixing processes can be accurately visualized on such a diagram.

A "water mass" is defined to be a line (not necessarily a straight line) on this $S_{\mathrm{A}}-\Theta$ diagram.

The figure below is of near-surface water from the global ocean. It is a bit of a mess, with some regions being plotted on top of others, but some are distinct.

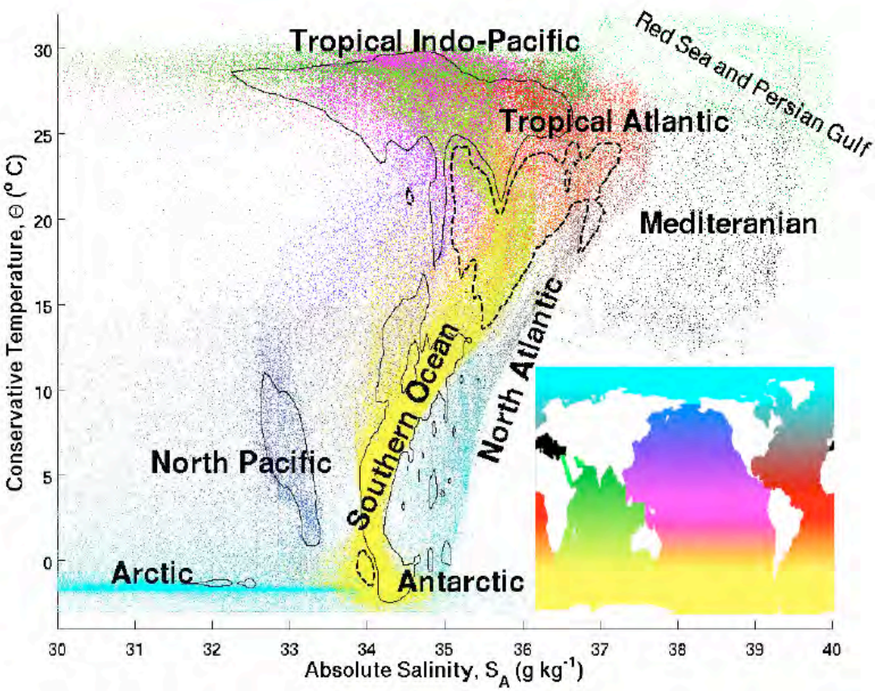


Table A.9.1 The "potential", "conservative", "isobaric conservative" and the functional nature, of various oceanographic variables

Variable	"potential"?	"conservative"?	"isobaric conservative"?	function of (S_A, t, p)?
S_*	✓	✓	✓	✗
S_A	✓	✗[1]	✗[1]	✓
t	✗	✗	✗	✓
θ	✓	✗	✗	✓
η	✓	✗	✗	✓
h	✗	✗	✓[2]	✓
Θ, h^0	✓	✓[3]	✓[3]	✓
u	✗	✗	✗	✓
$\mathcal{B}$	✗	✗	✓[4]	✗
$\mathcal{E}$	✗	✓[4]	✓[4]	✗
ρ, v	✗	✗	✗	✓
ρ^Θ	✓	✗	✗	✓
δ	✗	✗	✗	✓
γ^n	✗	✗	✗	✗

[1] The remineralization of organic matter changes S_A.

[2] Taking ε and the effects of remineralization to be negligible.

[3] Taking ε and other terms of similar size to be negligible (see the discussion following Eqn. (A.21.13)).

[4] Taking the effects of remineralization to be negligible.

In Table A.9.1 various oceanographic variables are categorized according to whether they posses the "potential" property, whether they are "conservative" variables, whether they are "isobaric conservative", and whether they are functions of only (S_A, t, p). Note that Θ is the only variable that achieve four "ticks" in this table, while Preformed Salinity S_* has ticks in the first three columns, but not in the last column since it is a function not only of (S_A, t, p) (since it also depends on the composition of seawater). Hence Θ is the most "ideal" thermodynamic variable. If it were not for the non-conservation of Absolute Salinity, it too would be an "ideal" thermodynamic variable, but in this sense, Preformed Salinity is superior to Absolute Salinity. Conservative Temperature Θ and Preformed Salinity S_* are the only two variables in this table to be both "potential" and "conservative". The last three rows of Table A.9.1 are for potential density, ρ^Θ, specific volume anomaly, δ, and Neutral Density γ^n. We will discuss these variables later in the course.

In this course we are assuming that Absolute Salinity is 100% conservative (hence the yellow highlighting in the table above). This is not strictly true. The important thing is that we use Absolute Salinity and not Practical or Reference Salinity in an ocean model and as the salinity argument to the expression for density. The non-conservative source term of Absolute Salinity is small on a timescale of less than a century.

Proof that $\theta = \theta(S_\mathrm{A},\eta)$ and $\Theta = \Theta(S_\mathrm{A},\theta)$

Consider changes occurring at the sea surface, (specifically at $p = 0$ dbar) where the temperature is the same as the potential temperature referenced to 0 dbar and the increment of pressure dp is zero. Regarding specific enthalpy h and chemical potential μ to be functions of entropy η (in place of temperature t), that is, considering the functional form of h and μ to be $h = \hat{h}(S_\mathrm{A},\eta,p)$ and $\mu = \hat{\mu}(S_\mathrm{A},\eta,p)$, it follows from the Fundamental Thermodynamic Relation (Eqn. (A.7.1)) that

$$\hat{h}_\eta\left(S_\mathrm{A},\eta,0\right)\mathrm{d}\eta + \hat{h}_{S_\mathrm{A}}\left(S_\mathrm{A},\eta,0\right)\mathrm{d}S_\mathrm{A} = \left(T_0+\theta\right)\mathrm{d}\eta + \hat{\mu}\left(S_\mathrm{A},\eta,0\right)\mathrm{d}S_\mathrm{A}\,, \qquad \text{(A.10.1)}$$

which shows that specific entropy η is simply a function of Absolute Salinity S_A and potential temperature θ, that is $\eta = \tilde{\eta}(S_\mathrm{A},\theta)$, with no separate dependence on pressure. It follows that $\theta = \theta(S_\mathrm{A},\eta)$.

Similarly, from the definition of potential enthalpy and Conservative Temperature in Eqns. (3.2.1) and (3.3.1), at $p = 0$ dbar it can be seen that the Fundamental Thermodynamic Relation (A.7.1) implies

$$\mathrm{d}h^0 = c_p^0\,\mathrm{d}\Theta = \left(T_0+\theta\right)\mathrm{d}\eta + \tilde{\mu}\left(S_\mathrm{A},\theta,0\right)\mathrm{d}S_\mathrm{A}\,. \qquad \text{(A.10.2)}$$

This shows that Conservative Temperature is also simply a function of Absolute Salinity and potential temperature, $\Theta = \tilde{\Theta}(S_\mathrm{A},\theta)$, with no separate dependence on pressure. It then follows that Θ may also be expressed as a function of only S_A and η. It follows that Θ has the "potential" property.

So we see that the four variables S_A, θ, η and Θ are all "potential" variables, they are all properties of a seawater parcel, they are all independent of pressure (for adiabatic and isohaline pressure changes), and they are related to each other in the sense that if you know any two of them, you know the other two. Absolute Salinity S_A has a clear meaning and is different in character to the other three variables θ, η and Θ which are very "temperature-like" variables.

Various isobaric derivatives of specific enthalpy

We will not derive the following derivatives here, but here they are.

$$\partial\hat{h}/\partial\eta\big|_{S_\mathrm{A},p} = \left(T_0+t\right) \qquad \text{(A.11.5a)}$$

$$\partial\hat{h}/\partial S_\mathrm{A}\big|_{\eta,p} = \mu. \qquad \text{(A.11.5b)}$$

$$\boxed{\tilde{h}_\theta\big|_{S_\mathrm{A},p} = c_p\left(S_\mathrm{A},\theta,0\right)\frac{\left(T_0+t\right)}{\left(T_0+\theta\right)} = -\left(T_0+t\right)g_{TT}\left(S_\mathrm{A},\theta,0\right).} \qquad \text{(A.11.9)}$$

$$\boxed{\begin{aligned}\tilde{h}_{S_\mathrm{A}}\big|_{\theta,p} &= \mu\left(S_\mathrm{A},t,p\right) - \left(T_0+t\right)\mu_T\left(S_\mathrm{A},\theta,0\right)\\ &= g_{S_\mathrm{A}}\left(S_\mathrm{A},t,p\right) - \left(T_0+t\right)g_{TS_\mathrm{A}}\left(S_\mathrm{A},\theta,0\right).\end{aligned}} \qquad \text{(A.11.11)}$$

$$\boxed{\hat{h}_\Theta\big|_{S_\mathrm{A},p} = \frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}\,c_p^0\,.} \qquad \text{(A.11.15)}$$

$$\boxed{\begin{aligned}\hat{h}_{S_\mathrm{A}}\big|_{\Theta,p} &= \mu\left(S_\mathrm{A},t,p\right) - \frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}\mu\left(S_\mathrm{A},\theta,0\right)\\ &= g_{S_\mathrm{A}}\left(S_\mathrm{A},t,p\right) - \frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}g_{S_\mathrm{A}}\left(S_\mathrm{A},\theta,0\right).\end{aligned}} \qquad \text{(A.11.18)}$$

Differential relationships between η, θ, Θ and S_{A}

Taking specific enthalpy to be a function of potential temperature (rather than of temperature t), that is, taking $h = \tilde{h}(S_{\mathrm{A}},\theta,p)$, the fundamental thermodynamic relation (A.7.1) becomes

$$\tilde{h}_{\theta}\,\mathrm{d}\theta + \tilde{h}_{S_{\mathrm{A}}}\mathrm{d}S_{\mathrm{A}} \;=\; \left(T_0+t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_{\mathrm{A}} \qquad \text{while} \qquad \partial\tilde{h}/\partial P\big|_{S_{\mathrm{A}},\theta} = v. \qquad \text{(A.11.6)}$$

Similarly, considering specific enthalpy to be a function of Conservative Temperature (rather than of temperature t), that is, taking $h = \hat{h}(S_{\mathrm{A}},\Theta,p)$, the fundamental thermodynamic relation (A.7.1) becomes

$$\hat{h}_{\Theta}\,\mathrm{d}\Theta + \hat{h}_{S_{\mathrm{A}}}\mathrm{d}S_{\mathrm{A}} \;=\; \left(T_0+t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_{\mathrm{A}} \qquad \text{while} \qquad \partial\hat{h}/\partial P\big|_{S_{\mathrm{A}},\Theta} = v. \qquad \text{(A.11.12)}$$

Using these forms of the Fundamental Thermodynamic Relation, together with the four boxed equations for the partial derivative of enthalpy (A.11.9), (A.11.11), (A.11.15) and (A.11.18), we find

$$\begin{aligned}\left(T_0+t\right)\mathrm{d}\eta+\mu\left(p\right)\mathrm{d}S_{\mathrm{A}} \;&=\; \frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}\,c_p\left(0\right)\mathrm{d}\theta \;+\; \left[\mu\left(p\right)-\left(T_0+t\right)\mu_T\left(0\right)\right]\mathrm{d}S_{\mathrm{A}} \\ &=\; \frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}\,c_p^0\,\mathrm{d}\Theta \;+\; \left[\mu\left(p\right)-\frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}\mu\left(0\right)\right]\mathrm{d}S_{\mathrm{A}}\,.\end{aligned} \qquad \text{(A.12.1)}$$

The quantity $\mu\left(p\right)\mathrm{d}S_{\mathrm{A}}$ is now subtracted from each of these three expressions and the whole equation is then multiplied by $\left(T_0+\theta\right)/\left(T_0+t\right)$ obtaining

$$\left(T_0+\theta\right)\mathrm{d}\eta \;=\; c_p\left(0\right)\mathrm{d}\theta - \left(T_0+\theta\right)\mu_T\left(0\right)\mathrm{d}S_{\mathrm{A}} \;=\; c_p^0\,\mathrm{d}\Theta - \mu\left(0\right)\mathrm{d}S_{\mathrm{A}}\,. \qquad \text{(A.12.2)}$$

From this follows all the following partial derivatives between η, θ, Θ and S_{A},

$$\Theta_{\theta}\big|_{S_{\mathrm{A}}} = c_p\left(S_{\mathrm{A}},\theta,0\right)/c_p^0, \qquad \Theta_{S_{\mathrm{A}}}\big|_{\theta} = \left[\mu\left(S_{\mathrm{A}},\theta,0\right)-\left(T_0+\theta\right)\mu_T\left(S_{\mathrm{A}},\theta,0\right)\right]/c_p^0, \qquad \text{(A.12.3)}$$

$$\Theta_{\eta}\big|_{S_{\mathrm{A}}} = \left(T_0+\theta\right)/c_p^0, \qquad \Theta_{S_{\mathrm{A}}}\big|_{\eta} = \mu\left(S_{\mathrm{A}},\theta,0\right)/c_p^0, \qquad \text{(A.12.4)}$$

$$\theta_{\eta}\big|_{S_{\mathrm{A}}} = \left(T_0+\theta\right)/c_p\left(S_{\mathrm{A}},\theta,0\right), \qquad \theta_{S_{\mathrm{A}}}\big|_{\eta} = \left(T_0+\theta\right)\mu_T\left(S_{\mathrm{A}},\theta,0\right)/c_p\left(S_{\mathrm{A}},\theta,0\right), \qquad \text{(A.12.5)}$$

$$\theta_{\Theta}\big|_{S_{\mathrm{A}}} = c_p^0/c_p\left(S_{\mathrm{A}},\theta,0\right), \qquad \theta_{S_{\mathrm{A}}}\big|_{\Theta} = -\left[\mu\left(S_{\mathrm{A}},\theta,0\right)-\left(T_0+\theta\right)\mu_T\left(S_{\mathrm{A}},\theta,0\right)\right]/c_p\left(S_{\mathrm{A}},\theta,0\right), \qquad \text{(A.12.6)}$$

$$\eta_{\theta}\big|_{S_{\mathrm{A}}} = c_p\left(S_{\mathrm{A}},\theta,0\right)/\left(T_0+\theta\right), \qquad \eta_{S_{\mathrm{A}}}\big|_{\theta} = -\mu_T\left(S_{\mathrm{A}},\theta,0\right), \qquad \text{(A.12.7)}$$

$$\eta_{\Theta}\big|_{S_{\mathrm{A}}} = c_p^0/\left(T_0+\theta\right), \qquad \eta_{S_{\mathrm{A}}}\big|_{\Theta} = -\mu\left(S_{\mathrm{A}},\theta,0\right)/\left(T_0+\theta\right). \qquad \text{(A.12.8)}$$

The First Law of Thermodynamics in terms of θ, η and Θ

Here we repeat the First Law of Thermodynamics

$$\boxed{\begin{aligned}\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t}-v\frac{\mathrm{d}P}{\mathrm{d}t}\right) &= \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t}+\left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) = \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t}+\mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right)\\ &= -\nabla\cdot\mathbf{F}^\mathrm{R}-\nabla\cdot\mathbf{F}^\mathrm{Q}+\rho\varepsilon\end{aligned}}\ . \qquad \text{(B.19)}$$

We wish to interpret this statement as a conservation statement for a "potential" variable, since this is how ocean models treat their heat-like variable, which to date has been potential temperature θ. None of enthalpy h, internal energy u or specific volume v are "potential" variables. Rather, these variables change simply due to a change in pressure even in the absence of heat or salt fluxes. The "heat-like" variables that are "potential" variables are entropy η, potential temperature θ, and Conservative Temperature Θ.

The First Law of Thermodynamics, Eqn. (B.19), can be written as an evolution equation for entropy as

$$\rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t}+\mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right)=-\nabla\cdot\mathbf{F}^\mathrm{R}-\nabla\cdot\mathbf{F}^\mathrm{Q}+\rho\varepsilon\ . \qquad \text{(A.13.3)}$$

The First Law of Thermodynamics can also be written in terms of potential temperature θ (with respect to reference pressure $p_\mathrm{r}=0$) by taking $h=\tilde{h}\left(S_\mathrm{A},\theta,p\right)$ and using Eqns. (A.11.9) and (A.11.11) as

$$\rho\left(\frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}c_p\left(0\right)\frac{\mathrm{d}\theta}{\mathrm{d}t}+\left[\mu\left(p\right)-\left(T_0+t\right)\mu_T\left(0\right)\right]\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right)=-\nabla\cdot\mathbf{F}^\mathrm{R}-\nabla\cdot\mathbf{F}^\mathrm{Q}+\rho\varepsilon\,, \qquad \text{(A.13.4)}$$

while in terms of Conservative Temperature Θ, the First Law of Thermodynamics is (using $h=\hat{h}\left(S_\mathrm{A},\Theta,p\right)$ and Eqns. (A.11.15) and (A.11.18))

$$\rho\left(\frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}c_p^0\frac{\mathrm{d}\Theta}{\mathrm{d}t}+\left[\mu\left(p\right)-\frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}\mu\left(0\right)\right]\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right)=-\nabla\cdot\mathbf{F}^\mathrm{R}-\nabla\cdot\mathbf{F}^\mathrm{Q}+\rho\varepsilon\ . \qquad \text{(A.13.5)}$$

A quick ranking of these three variables, η, θ and Θ, from the viewpoint of the amount of their non-conservation, can be gleaned by examining the range of the red terms (at fixed pressure) that multiply the material derivatives on the left-hand sides of the above Eqns. (A.13.3), (A.13.4) and (A.13.5).

Why are we able to settle for examining the variation of these red terms only at constant pressure? The ocean circulation may be viewed as a series of adiabatic and isohaline movements of seawater parcels interrupted by a series of isolated turbulent mixing events. During any of the adiabatic and isohaline transport stages every "potential" property is constant, so each of the above variables, entropy, potential temperature and Conservative Temperature are 100% ideal during these adiabatic and isohaline advection stages. The turbulent mixing events occur at fixed pressure so the non-conservative production of say entropy depends on the extent to which the coefficients $\left(T_0+t\right)$ and μ in Eqn. (A.13.3) vary at fixed pressure.

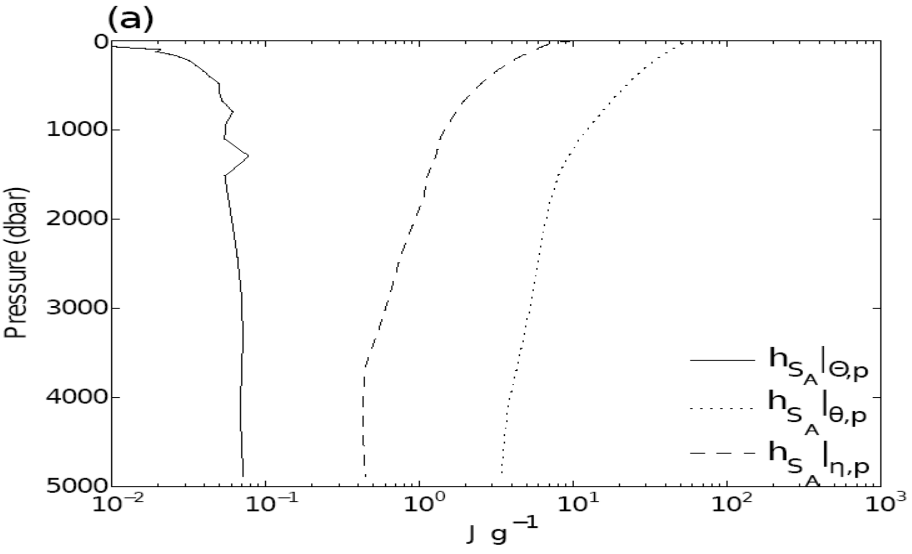
Similarly the non-conservative production of potential temperature depends on the extent to which the coefficients $c_p\left(0\right)\left(T_0+t\right)/\left(T_0+\theta\right)$ and $\left[\mu\left(p\right)-\left(T_0+t\right)\mu_T\left(0\right)\right]$ in Eqn. (A.13.4) vary at fixed pressure, while the non-conservative production of Conservative Temperature depends on the extent to which the coefficients $\left(T_0+t\right)/\left(T_0+\theta\right)$ and $\left[\mu\left(p\right)-\mu\left(0\right)\left(T_0+t\right)/\left(T_0+\theta\right)\right]$ in Eqn. (A.13.5) vary at fixed pressure.

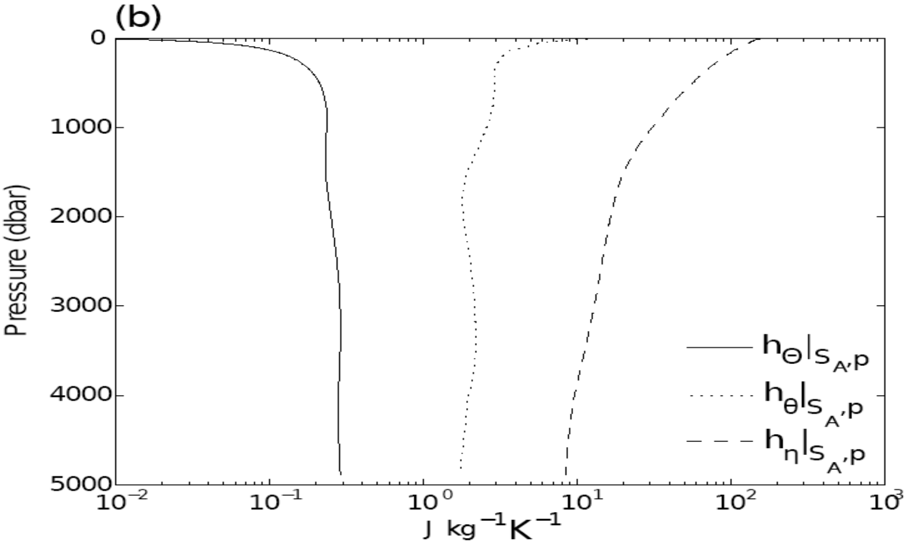
According to this way of looking at these equations we note that the material derivative of entropy appears in Eqn. (A.13.3) multiplied by the absolute temperature $\left(T_0+t\right)$ which varies by about 15% at the sea surface ($\left(273.15+40\right)/273.15 \approx 1.146$), the term that multiplies $\mathrm{d}\theta/\mathrm{d}t$ in (A.13.4) is dominated by the variations in the isobaric specific heat $c_p\left(S_\mathrm{A},t,p_\mathrm{r}\right)$ which is mainly a function of S_A and which varies by 5.5% at the sea surface (see **Figure 4** on page 1), while the material derivative of Conservative Temperature $\mathrm{d}\Theta/\mathrm{d}t$ in Eqn. (A.13.5) is multiplied by the product of a constant "heat capacity" c_p^0 and the factor $\left(T_0+t\right)/\left(T_0+\theta\right)$ which varies very little in the ocean, especially when one realizes that it is only the variation of this ratio at each pressure level that is of concern. This factor is unity at the sea surface and is also very close to unity in the deep ocean.

More quantitatively, the r.m.s. variation of these six terms is shown in the following figure (from Graham, F. S. and T. J. McDougall, 2013: Quantifying the non-conservative production of Conservative Temperature, potential temperature and entropy. *Journal of Physical Oceanography*, **43**, 838-862.). The variations of temperature in the ocean are about five times as large as the variations of Absolute Salinity (in g/kg) so if the horizontal axis of Fig (a) is divided by a factor of 5, the figures can be compared numerically.

This figure shows that both the red terms in the potential temperature version of the First Law contribute to non-conservation about equally (we will find out why shortly). The non-constancy of the terms that multiply $\mathrm{d}S_\mathrm{A}/\mathrm{d}t$ in both the entropy and Conservative Temperature cases are very small compared to the variation of the terms multiplying $\mathrm{d}\eta/\mathrm{d}t$ and $\mathrm{d}\Theta/\mathrm{d}t$ respectively.

So the ranking of the variables can be seen simply by looking at Fig (b), especially if we mentally move the dotted line (the line for θ) to the right by a factor of two.


(a)
Pressure (dbar)
0
1000
2000
3000
4000
5000
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
J g^{-1}
$h_{S_A}|_{\Theta,p}$
$h_{S_A}|_{\theta,p}$
$h_{S_A}|_{\eta,p}$


(b)
Pressure (dbar)
0
1000
2000
3000
4000
5000
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}
10^{3}
J kg^{-1}K^{-1}
$h_{\Theta}|_{S_A,p}$
$h_{\theta}|_{S_A,p}$
$h_{\eta}|_{S_A,p}$

Review of the last lecture

We discussed potential temperature, both for a real liquid (like seawater) and for a perfect gas, where things are considerably simpler.

We then extended the "potential" concept to enthalpy, defining potential enthalpy, and writing down the relationship between enthalpy and potential enthalpy as a pressure integral of specific volume.

The "conservative" and "isobaric conservative" properties were defined, and many oceanographic variables were categorized according to whether they are "potential" variables, "conservative" variables, "isobaric conservative" variables, and according to whether they are thermodynamic variables (that is, variables that are a function of Absolute Salinity, temperature and pressure).

We proved that once you know the Absolute Salinity of a seawater parcel as well as one of entropy, potential temperature or Conservative Temperature, then you know the other two of these "temperature-like" variables.

We used the various partial derivatives of enthalpy to rewrite the First Law of Thermodynamics

$$\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) \;=\; -\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \rho\varepsilon \;, \qquad \text{(B.19)}$$

as

$$\rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t} + \mu\frac{\mathrm{d}S_{\mathrm{A}}}{\mathrm{d}t}\right) \;=\; -\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \rho\varepsilon \;, \qquad \text{(A.13.3)}$$

$$\rho\left(\frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}c_p\left(0\right)\frac{\mathrm{d}\theta}{\mathrm{d}t} + \left[\mu\left(p\right) - \left(T_0+t\right)\mu_T\left(0\right)\right]\frac{\mathrm{d}S_{\mathrm{A}}}{\mathrm{d}t}\right) \;=\; -\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \rho\varepsilon \,, \qquad \text{(A.13.4)}$$

$$\rho\left(\frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}c_p^0\frac{\mathrm{d}\Theta}{\mathrm{d}t} + \left[\mu\left(p\right) - \frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}\mu\left(0\right)\right]\frac{\mathrm{d}S_{\mathrm{A}}}{\mathrm{d}t}\right) \;=\; -\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \rho\varepsilon \,. \qquad \text{(A.13.5)}$$

We then estimated a rough ranking of entropy, potential temperature and Conservative Temperature, in terms of how "conservative" these variables are. We did this by simply seeing how much the partial derivative of enthalpy with respect to these variables varied at fixed pressure in the ocean.

Non-conservative production of entropy

Here the non-conservative nature of entropy will be quantified by considering the mixing of a pair of seawater parcels at fixed pressure. The mixing is taken to be complete so that the end state is a seawater parcel that is homogeneous in Absolute Salinity and entropy. That is, we will be considering mixing to completion by a turbulent mixing process.

Consider the mixing of two fluid parcels (parcels 1 and 2) that have initially different temperatures and salinities. The mixing process occurs at pressure p. Because the mixing is assumed to happen to completion, it follows that in the final state Absolute Salinity, entropy and all the other properties are uniform. Assuming that the mixing happens with a vanishingly small amount of dissipation of kinetic energy, the ε term can be dropped from the First Law of Thermodynamics, (A.13.1), this equation becoming

$$\left(\rho h\right)_t + \nabla\cdot\left(\rho\mathbf{u}h\right) = -\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}}. \qquad \textit{at constant pressure} \quad \text{(A.16.1)}$$

Note that this equation has the "conservative" form and so h is conserved during mixing at constant pressure, that is, h is "isobaric conservative". In the case we are considering of mixing the two seawater parcels, the system is closed and there are no radiative, boundary or molecular heat fluxes coming through the outside boundary so the integral over space and time of the right-hand side of Eqn. (A.16.1) is zero. The surface integral of $\left(\rho\mathbf{u}h\right)$ through the boundary is also zero because there is no flow through the boundary. Hence it is apparent that the volume integral of ρh is the same at the final state as it is at the initial state, that is, enthalpy is conserved. Hence during the mixing process the mass, salt content and enthalpy are conserved, that is

$$m_1 + m_2 = m, \tag{A.16.2}$$

$$m_1 S_{\mathrm{A}1} + m_2 S_{\mathrm{A}2} = m S_{\mathrm{A}}, \tag{A.16.3}$$

$$m_1 h_1 + m_2 h_2 = m h, \tag{A.16.4}$$

while the non-conservative nature of entropy means that it obeys the equation,

$$m_1\eta_1 + m_2\eta_2 + m\delta\eta = m\eta. \tag{A.16.5}$$

Here S_{A}, h and η are the values of Absolute Salinity, enthalpy and entropy of the final mixed fluid and $\delta\eta$ is the production of entropy, that is, the amount by which entropy is not conserved during the mixing process. Entropy η is now regarded as the functional form $\eta = \breve{\eta}\left(S_{\mathrm{A}}, h, p\right)$ and is expanded in a Taylor series of S_{A} and h about the values of S_{A} and h of the mixed fluid, retaining terms to second order in $\left[S_{\mathrm{A}2} - S_{\mathrm{A}1}\right] = \Delta S_{\mathrm{A}}$ and in $\left[h_2 - h_1\right] = \Delta h$. Then η_1 and η_2 are evaluated and (A.16.4) and (A.16.5) used to find

$$\delta\eta = -\tfrac{1}{2}\frac{m_1 m_2}{m^2}\left\{\breve{\eta}_{hh}\left(\Delta h\right)^2 + 2\breve{\eta}_{hS_{\mathrm{A}}}\,\Delta h\,\Delta S_{\mathrm{A}} + \breve{\eta}_{S_{\mathrm{A}}S_{\mathrm{A}}}\left(\Delta S_{\mathrm{A}}\right)^2\right\}. \tag{A.16.6}$$

Shortly the production of entropy, Eqn. (A.16.6), will be quantified, but for now we ask what constraints the Second Law of Thermodynamics might place on the form of the Gibbs function $g\left(S_{\mathrm{A}}, t, p\right)$ of seawater. The Second Law of Thermodynamics tells us that the entropy excess $\delta\eta$ must not be negative for all possible combinations of the differences in enthalpy and salinity between the two fluid parcels. From (A.16.6) this requirement implies the following three inequalities,

$$\breve{\eta}_{hh} < 0, \qquad \breve{\eta}_{S_{\mathrm{A}}S_{\mathrm{A}}} < 0, \tag{A.16.8}$$

$$\left(\breve{\eta}_{hS_{\mathrm{A}}}\right)^2 < \breve{\eta}_{hh}\,\breve{\eta}_{S_{\mathrm{A}}S_{\mathrm{A}}}, \tag{A.16.9}$$

where the last requirement reflects the need for the discriminant of the quadratic in (A.16.6) to be negative. Since entropy is already a first order derivative of the Gibbs function, these constraints would seem to be three different constraints on various third order derivatives of the Gibbs function. In fact, we will see that they amount to only two rather well-known constraints on second order derivatives of the Gibbs function.

From the fundamental thermodynamic relation (A.7.1) we find that (where T is the absolute temperature, $T = T_0 + t$)

$$\breve{\eta}_h = \left.\frac{\partial \eta}{\partial h}\right|_{S_\mathrm{A},p} = \frac{1}{T} \qquad \text{(A.16.10)}$$

$$\breve{\eta}_{S_\mathrm{A}} = \left.\frac{\partial \eta}{\partial S_\mathrm{A}}\right|_{h,p} = -\frac{\mu}{T}\,, \qquad \text{(A.16.11)}$$

and from these relations the following expressions for the second order derivatives of $\breve{\eta}$ can be found,

$$\breve{\eta}_{hh} = \left.\frac{\partial^2 \eta}{\partial h^2}\right|_{S_\mathrm{A},p} = \left.\frac{\partial\left(1/T\right)}{\partial h}\right|_{S_\mathrm{A},p} = -\frac{1}{c_p T^2}\,, \qquad \text{(A.16.12)}$$

$$\breve{\eta}_{S_\mathrm{A}h} = \left.\frac{\partial^2 \eta}{\partial h \partial S_\mathrm{A}}\right|_{p} = \left.\frac{\partial\left(-\mu/T\right)}{\partial h}\right|_{S_\mathrm{A},p} = -\frac{1}{c_p}\left(\frac{\mu}{T}\right)_T\,, \qquad \text{(A.16.13)}$$

$$\begin{aligned}\breve{\eta}_{S_\mathrm{A}S_\mathrm{A}} = \left.\frac{\partial^2 \eta}{\partial S_\mathrm{A}^2}\right|_{h,p} &= \left.\frac{\partial\left(-\mu/T\right)}{\partial S_\mathrm{A}}\right|_{T,p} - \left.\frac{\partial\left(-\mu/T\right)}{\partial h}\right|_{S_\mathrm{A},p}\left.\frac{\partial h}{\partial S_\mathrm{A}}\right|_{T,p} \\ &= -\frac{\mu_{S_\mathrm{A}}}{T} - \frac{T^2}{c_p}\left[\left(\frac{\mu}{T}\right)_T\right]^2 .\end{aligned} \qquad \text{(A.16.14)}$$

The last equation comes from regarding $\breve{\eta}_{S_\mathrm{A}}$ as $\breve{\eta}_{S_\mathrm{A}} = \breve{\eta}_{S_\mathrm{A}}\left(S_\mathrm{A}, h\left[S_\mathrm{A}, t, p\right], p\right)$.

The constraint (A.16.8) that $\breve{\eta}_{hh} < 0$ simply requires (from (A.16.12)) that the isobaric heat capacity c_p is positive, or that $g_{TT} < 0$. Physically this constraint simply means that when you apply heat to a fluid parcel it warms up, rather than cools down.

The constraint (A.16.8) that $\breve{\eta}_{S_\mathrm{A}S_\mathrm{A}} < 0$, requires (from (A.16.14)) that

$$g_{S_\mathrm{A}S_\mathrm{A}} > -\frac{T^3}{c_p}\left[\left(\frac{\mu}{T}\right)_T\right]^2, \qquad \text{(A.16.15)}$$

that is, the second derivative of the Gibbs function with respect to Absolute Salinity $g_{S_\mathrm{A}S_\mathrm{A}}$ must exceed some negative number. The constraint (A.16.9) that $(\breve{\eta}_{hS_\mathrm{A}})^2 < \breve{\eta}_{hh}\breve{\eta}_{S_\mathrm{A}S_\mathrm{A}}$ requires that (substituting from (A.16.12), (A.16.13) and (A.16.14))

$$\frac{g_{S_\mathrm{A}S_\mathrm{A}}}{T^3 c_p} > 0\,, \qquad \text{(A.16.16)}$$

and since the isobaric heat capacity must be positive, this requirement is that $g_{S_\mathrm{A}S_\mathrm{A}} > 0$, and so is more demanding than (A.16.15).

We conclude that while there are the three requirements (A.16.8) to (A.16.9) on the functional form of entropy $\eta = \breve{\eta}\left(S_\mathrm{A}, h, p\right)$ in order to satisfy the constraint of the Second Law of Thermodynamics that entropy be produced when water parcels mix, these three constraints are satisfied by the following two constraints on the form of the Gibbs function $g\left(S_\mathrm{A}, t, p\right)$,

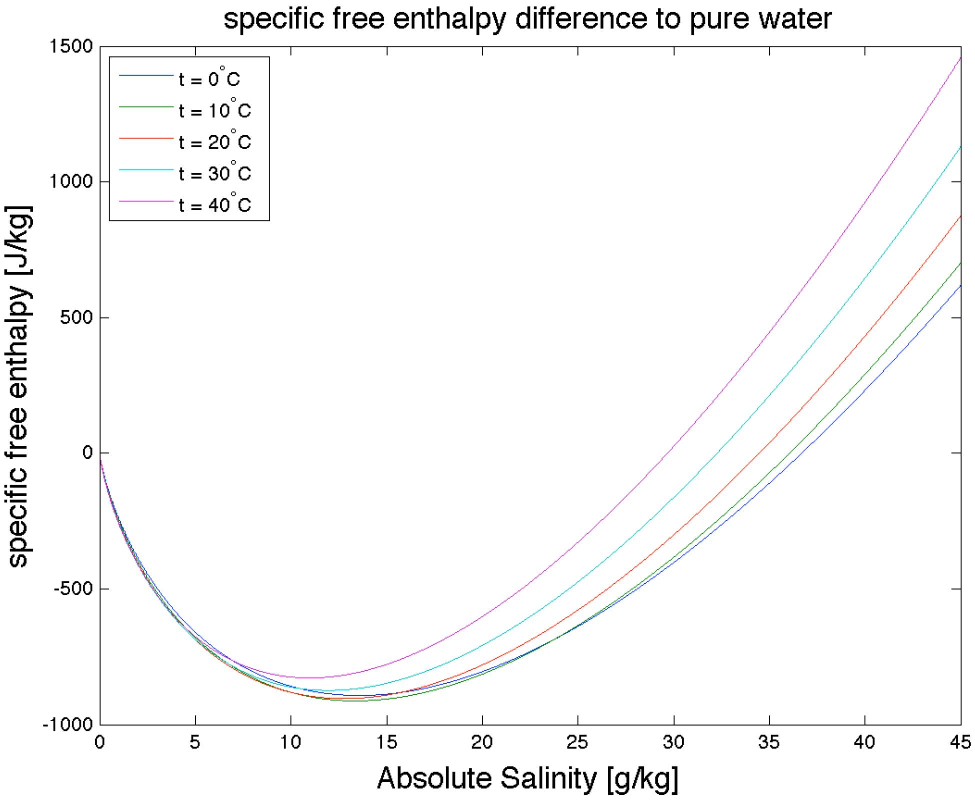
$$g_{TT} < 0 \qquad \text{(A.16.17)}$$

and

$$g_{S_\mathrm{A}S_\mathrm{A}} > 0. \qquad \text{(A.16.18)}$$

The Second Law of Thermodynamics does not impose any additional requirement on the cross derivatives $g_{S_{\mathrm{A}}T}$ nor on any third order derivatives of the Gibbs function! (In any case, recall that $g_{S_{\mathrm{A}}T}$ is completely arbitrary and unknowable.)

The constraint $g_{S_{\mathrm{A}}S_{\mathrm{A}}} > 0$ can be understood by considering the molecular diffusion of salt, which, in an isothermal ocean, is known to be directed down the gradient of chemical potential $\mu(S_{\mathrm{A}},t,p)/T$ (see Eqn. (B.21)). That is, the leading term in the molecular flux of salt is proportional to $-\nabla\mu$. Expanding $-\nabla\mu$ in terms of gradients of Absolute Salinity, of temperature, and of pressure, one finds that the first term is $-\mu_{S_{\mathrm{A}}}\nabla S_{\mathrm{A}}$ and in order to avoid an unstable explosion of salt one must have $\mu_{S_{\mathrm{A}}} = g_{S_{\mathrm{A}}S_{\mathrm{A}}} > 0$. Hence the constraint (A.16.18) amounts to the requirement that the molecular diffusivity of salt is positive. The following figure shows that, indeed, $g_{S_{\mathrm{A}}S_{\mathrm{A}}} = \mu_{S_{\mathrm{A}}} > 0$.



The two constraints (A.16.17) and (A.16.18) on the Gibbs function are well known in the thermodynamics literature. Landau and Lifshitz (1959) derive them on the basis of the contribution of molecular fluxes of heat and salt to the production of entropy (their equations 58.9 and 58.13). It is pleasing to obtain the same constraints on the seawater Gibbs function from the above Non-Equilibrium Thermodynamics approach of mixing fluid parcels since this approach involves turbulent mixing which is the type of mixing that dominates in the ocean; molecular diffusion has the complementary role of dissipating tracer variance.

When the mixing process occurs at $p = 0$, the expression (A.16.6) for the production of entropy can be expressed in terms of Conservative Temperature Θ (since Θ is simply proportional to h at $p = 0$) as follows (now entropy is taken to be the functional form $\eta = \hat{\eta}(S_{\mathrm{A}},\Theta)$)

$$\delta\eta = -\tfrac{1}{2}\frac{m_1 m_2}{m^2}\left\{\hat{\eta}_{\Theta\Theta}(\Delta\Theta)^2 + 2\hat{\eta}_{\Theta S_{\mathrm{A}}}\Delta\Theta\Delta S_{\mathrm{A}} + \hat{\eta}_{S_{\mathrm{A}}S_{\mathrm{A}}}(\Delta S_{\mathrm{A}})^2\right\}. \qquad \text{(A.16.22)}$$

The maximum production occurs when parcels of equal mass are mixed so that $\tfrac{1}{2}m_1 m_2 m^{-2} = \tfrac{1}{8}$ and we adopt this value in what follows.

To illustrate the magnitude of this non-conservation of entropy we first scale entropy by a dimensional constant so that the resulting variable ("entropic temperature") has the value $25\,°\mathrm{C}$ at $\left(S_{\mathrm{A}},\Theta\right)=\left(S_{\mathrm{SO}},25\,°\mathrm{C}\right)$ and then Θ is subtracted. The result is contoured in $S_{\mathrm{A}}-\Theta$ space in Figure A.16.1.

The fact that the variable in Figure A.16.1 is not zero over the whole $S_{\mathrm{A}}-\Theta$ plane is because entropy is not a conservative variable. The non-conservative production of entropy can be read off this figure by selecting two seawater samples and mixing along the straight line between these parcels and then reading off the production (in $°\mathrm{C}$) of entropy from the figure. Taking the most extreme situation with one parcel at $\left(S_{\mathrm{A}},\Theta\right)=\left(0\ \mathrm{g\,kg}^{-1},0\ °\mathrm{C}\right)$ and the other at the warmest and saltiest corner of the figure, the production of η on mixing parcels of equal mass is approximately $0.9\,°\mathrm{C}$.

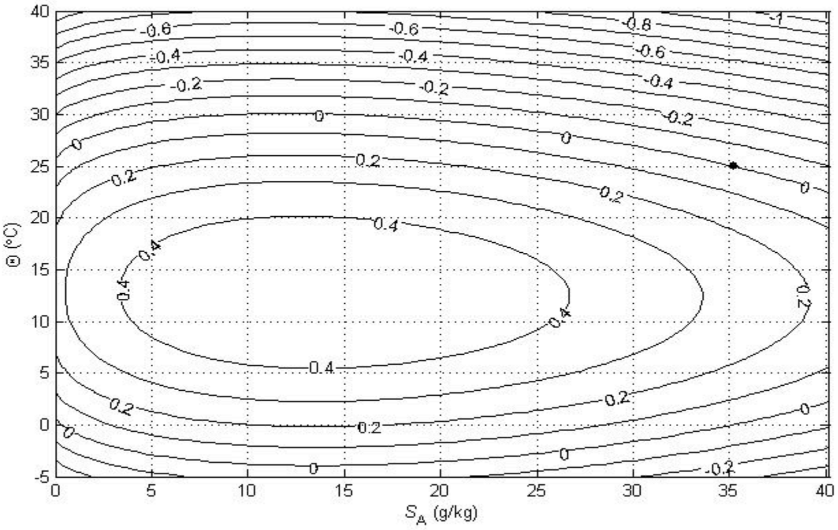


Figure A.16.1. Contours (in $°\mathrm{C}$) of a variable which illustrates the non-conservative production of entropy η in the ocean.

Since entropy can be expressed independently of pressure as a function of only Absolute Salinity and Conservative Temperature $\eta=\hat{\eta}\left(S_{\mathrm{A}},\Theta\right)$, and since at any pressure in the ocean both S_{A} and Θ may quite accurately be considered conservative variables, it is clear that the non-conservative production given by (A.16.22) and illustrated in Figure A.16.1 is very nearly equivalent to the slightly more accurate expression (A.16.6) which applies at any pressure. The only discrepancy between the production of entropy calculated from (A.16.22) and that from (A.16.6) is due to the very small non-conservative production of Θ at pressures other than zero (as well as the fact that both expressions contain only the second order terms in an infinite Taylor series). We have already seen that the non-conservation of entropy is much larger than the non-conservation of Conservative Temperature (by a factor of 1000 as it turns out).

Non-conservative production of potential temperature

When fluid parcels undergo irreversible and complete mixing at constant pressure, the thermodynamic quantities that are conserved during the mixing process are mass, Absolute Salinity and enthalpy. As in the case of entropy, we again consider two parcels being mixed without external input of heat or mass and the three equations that represent the conservation of these quantities are again Eqns. (A.16.2) – (A.16.4). The production of potential temperature during the mixing process is given by

$$m_1\,\theta_1 + m_2\,\theta_2 + m\,\delta\theta \;=\; m\,\theta. \qquad \text{(A.17.1)}$$

Enthalpy in the functional form $h = \tilde{h}(S_{\rm A}, \theta, p)$ is expanded in a Taylor series of $S_{\rm A}$ and θ about the values $S_{\rm A}$ and θ of the mixed fluid, retaining terms to second order in $[S_{\rm A2} - S_{\rm A1}] = \Delta S_{\rm A}$ and in $[\theta_2 - \theta_1] = \Delta\theta$. Then h_1 and h_2 are evaluated and Eqns. (A.16.4) and (A.17.1) used to find

$$\delta\theta \;=\; \tfrac{1}{2}\frac{m_1\,m_2}{m^2}\left\{ \frac{\tilde{h}_{\theta\theta}}{\tilde{h}_\theta}\left(\Delta\theta\right)^2 + 2\frac{\tilde{h}_{\theta S_{\rm A}}}{\tilde{h}_\theta}\Delta\theta\,\Delta S_{\rm A} + \frac{\tilde{h}_{S_{\rm A}S_{\rm A}}}{\tilde{h}_\theta}\left(\Delta S_{\rm A}\right)^2 \right\}. \qquad \text{(A.17.2)}$$

The maximum production occurs when parcels of equal mass are mixed so that $\tfrac{1}{2} m_1\, m_2\, m^{-2} = \tfrac{1}{8}$. The "heat capacity" $\tilde{h}_\theta$ is not a strong function of θ but is a stronger function of $S_{\rm A}$ so the first term in the curly brackets in Eqn. (A.17.2) is generally small compared with the second term. Also, the third term in Eqn. (A.17.2) which causes the so-called "dilution heating", is usually small compared with the second term. A typical value of $\tilde{h}_{\theta S_{\rm A}}$ is approximately -5.4 $\rm J\ kg^{-1}\ K^{-1} (g\ kg^{-1})^{-1}$ (see the dependence of isobaric heat capacity on $S_{\rm A}$ in **Figure 4** on page 1) so that an approximate expression for the production of potential temperature $\delta\theta$ is

$$\frac{\delta\theta}{\Delta\theta} \;\approx\; \tfrac{1}{4}\tilde{h}_{\theta S_{\rm A}}\Delta S_{\rm A}\big/\tilde{h}_\theta \;\approx\; -3.4x10^{-4}\left(\Delta S_{\rm A}/[\mathrm{g\ kg^{-1}}]\right). \qquad \text{(A.17.3)}$$

The same form of the non-conservative production terms in Eqn. (A.17.2) also appears in the following turbulent evolution equation for potential temperature, in both the epineutral and vertical diffusion terms (Graham and McDougall, 2013). (See later for an explanation of the symbols that appear in this thickness-weighted averaged equation.)

$$\begin{aligned} \frac{\mathrm{d}\hat{\theta}}{\mathrm{d}t} \;=\; \left.\frac{\partial\hat{\theta}}{\partial t}\right|_n + \hat{\mathbf{v}}\cdot\nabla_n\hat{\theta} + \tilde{e}\frac{\partial\hat{\theta}}{\partial z} \;&=\; \tilde{\gamma}_z\nabla_n\cdot\left(\tilde{\gamma}_z^{-1}K\nabla_n\hat{\theta}\right) + \left(D\hat{\theta}_z\right)_z + \varepsilon\big/\tilde{h}_\theta \\ &+\; K\left(\frac{\tilde{h}_{\theta\theta}}{\tilde{h}_\theta}\nabla_n\hat{\theta}\cdot\nabla_n\hat{\theta} + 2\frac{\tilde{h}_{\theta S_{\rm A}}}{\tilde{h}_\theta}\nabla_n\hat{\theta}\cdot\nabla_n\hat{S}_{\rm A} + \frac{\tilde{h}_{S_{\rm A}S_{\rm A}}}{\tilde{h}_\theta}\nabla_n\hat{S}_{\rm A}\cdot\nabla_n\hat{S}_{\rm A}\right) \qquad \text{(A.17.4)} \\ &+\; D\left(\frac{\tilde{h}_{\theta\theta}}{\tilde{h}_\theta}\hat{\theta}_z^2 + 2\frac{\tilde{h}_{\theta S_{\rm A}}}{\tilde{h}_\theta}\hat{\theta}_z\hat{S}_{{\rm A}_z} + \frac{\tilde{h}_{S_{\rm A}S_{\rm A}}}{\tilde{h}_\theta}\left(\hat{S}_{{\rm A}_z}\right)^2\right). \end{aligned}$$

Since potential temperature $\theta = \hat{\theta}(S_{\rm A}, \Theta)$ can be expressed independently of pressure as a function of only Absolute Salinity and Conservative Temperature, and since during turbulent mixing both $S_{\rm A}$ and Θ may be considered approximately conservative variables (see section A.18 below), it is clear that the non-conservative production given by (A.17.2) can be approximated by the corresponding production of potential temperature that would occur if the mixing had occurred at $p = 0$, namely

$$\delta\theta \;\approx\; \tfrac{1}{2}\frac{m_1\,m_2}{m^2}\left\{ \frac{\tilde{\Theta}_{\theta\theta}}{\tilde{\Theta}_\theta}\left(\Delta\theta\right)^2 + 2\frac{\tilde{\Theta}_{\theta S_{\rm A}}}{\tilde{\Theta}_\theta}\Delta\theta\,\Delta S_{\rm A} + \frac{\tilde{\Theta}_{S_{\rm A}S_{\rm A}}}{\tilde{\Theta}_\theta}\left(\Delta S_{\rm A}\right)^2 \right\}, \qquad \text{(A.17.5)}$$

where the exact proportionality between potential enthalpy and Conservative Temperature $h^0 \equiv c_p^0 \Theta$ has been exploited. The maximum production occurs when parcels of equal mass are mixed so that $\tfrac{1}{2} m_1 m_2 m^{-2} = \tfrac{1}{8}$ and we adopt this value in what follows.

Equations (A.17.2) or (A.17.5) may be used to evaluate the non-conservative production of potential temperature due to mixing a pair of fluid parcels across a front at which there are known differences in salinity and temperature. The temperature difference $\theta - \Theta$ is contoured in **Figure A.17.1** and can be used to illustrate Eqn. (A.17.5). $\delta\theta$ can be read off this figure by selecting two seawater samples and mixing along the straight line between these parcels (along which both Absolute Salinity and Conservative Temperature are conserved) and then calculating the production (in °C) of θ from the contoured values of $\theta - \Theta$. Taking the most extreme situation with one parcel at $\left(S_{\mathrm{A}}, \Theta\right) = \left(0 \text{ g kg}^{-1}, 0\ {}^\circ\mathrm{C}\right)$ and the other at the warmest and saltiest corner of **Figure A.17.1**, the non-conservative production of θ on mixing parcels of equal mass is approximately -0.55 °C. This is to be compared with the corresponding maximum production of entropy, as discussed above in connection with Figure A.16.1, of approximately 0.9 °C.

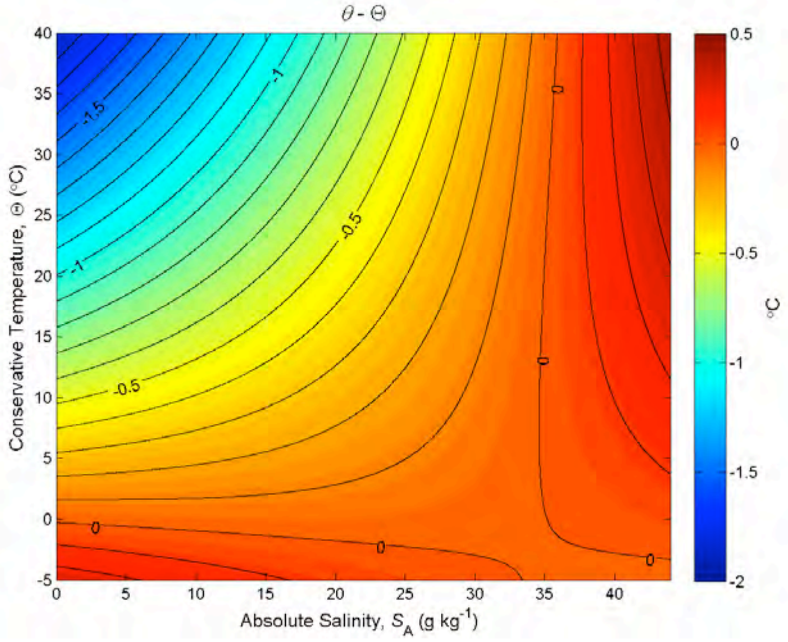


Figure A.17.1. Contours (in °C) of the difference between potential temperature and Conservative Temperature $\theta - \Theta$. This plot illustrates the non-conservative production of potential temperature θ in the ocean.

How NOT to quantify the error involved in using potential temperature

If **Figure A.17.1** were to be used to quantify the errors in oceanographic practice incurred by assuming that θ is a conservative variable, one might select property contrasts that were typical of a prominent oceanic front and decide that because $\delta\theta$ is small at this one front, that the issue can be ignored. But the observed properties in the ocean result from a large and indeterminate number of such prior mixing events and the non-conservative production of θ accumulates during each of these mixing events, often in a sign-definite fashion. How can we possibly estimate the error that is made by treating potential temperature as a conservative variable during all of these unknowably many past individual mixing events?

How to quantify the error involved in using potential temperature

This seemingly difficult issue is partially resolved by considering what is actually done in ocean models today. These models carry a temperature conservation equation that does not have non-conservative source terms, so that the model's temperature variable is best interpreted as being Θ. If an ocean model is written with potential temperature θ as the prognostic temperature variable rather than Conservative Temperature Θ, and is run with the same constant value of the isobaric specific heat capacity c_p^0, the neglect of the non-conservative source terms that should appear in the prognostic equation for θ means that such an ocean model incurs errors in the model output. These errors will depend on the nature of the surface boundary condition; for flux boundary conditions the errors are as shown in **Figure A.17.1**, because in this case the model's temperature variable is actually Conservative Temperature Θ but has been interpreted and initialized incorrectly as potential temperature θ.

The contoured values of temperature difference in **Figure A.17.1** encapsulate the accumulated non-conservative production that has occurred during all the many mixing processes that have lead to the ocean's present state. The maximum such error for η is approximately -1.0 °C (from Figure A.16.1) while for θ the maximum error is approximately -1.8 °C (from Figure A.17.1). From the curvature of the isolines on Figure A.17.1 it is clear that the non-conservative production of θ takes both positive and negative signs.

Here is an enlarged view of $\theta - \Theta$ on the $S_\text{A} - \Theta$ diagram, and also of the error involved with using another previous suggestion for the "heat content" of seawater, $\theta\, c_p\left(S_\text{A}, \theta, p\right) / c_p^0$.

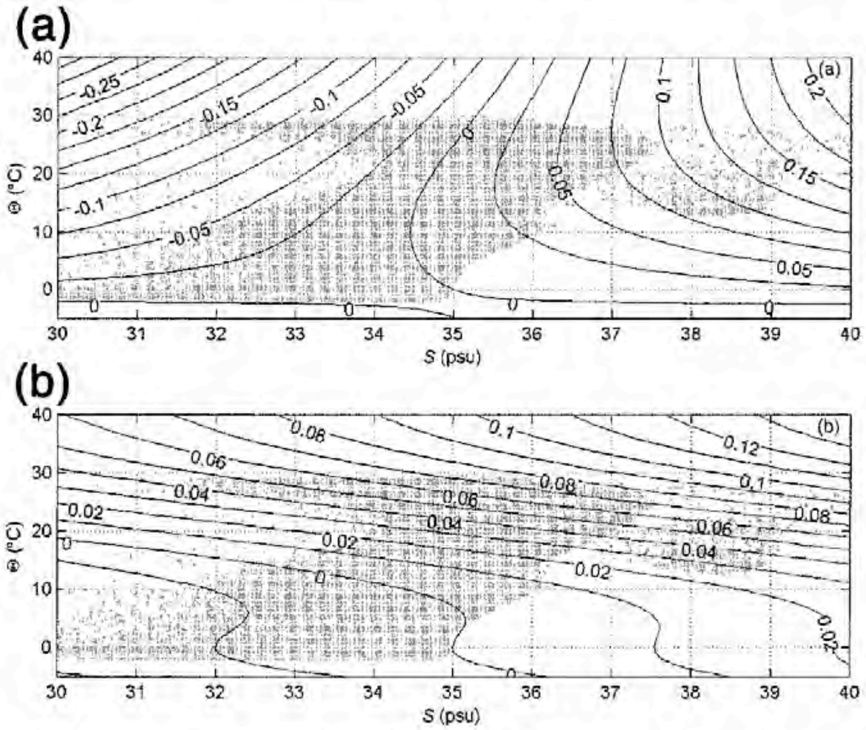


FIG. 3. Contours of (a) $\theta - \Theta$ and of (b) $C_p(S, \theta, 0)\theta/C_p^0 - \Theta$ in a smaller range of salinity than in Figs. 1 and 4. Panel (a) illustrates the error in regarding $C_p^0\theta$ as heat content; panel (b) illustrates the error in regarding $C_p(S, \theta, 0)\theta$ as heat content, in both cases measured in temperature units. The background cloud of points illustrate where there is data from somewhere in the World Ocean.

One percent of the data at the sea surface of the world ocean have values of $\theta - \Theta$ that lie outside a range that is 0.25 °C wide (see **Figure A.13.1**), implying that this is the magnitude of the error incurred by ocean models when they treat θ as a conservative quantity. To put a temperature difference of 0.25 °C in context, this is the typical difference between *in situ* and potential temperatures for a pressure difference of 2500 dbar, and it is approximately 100 times as large as the typical differences between t_{90} and t_{68} in the ocean.

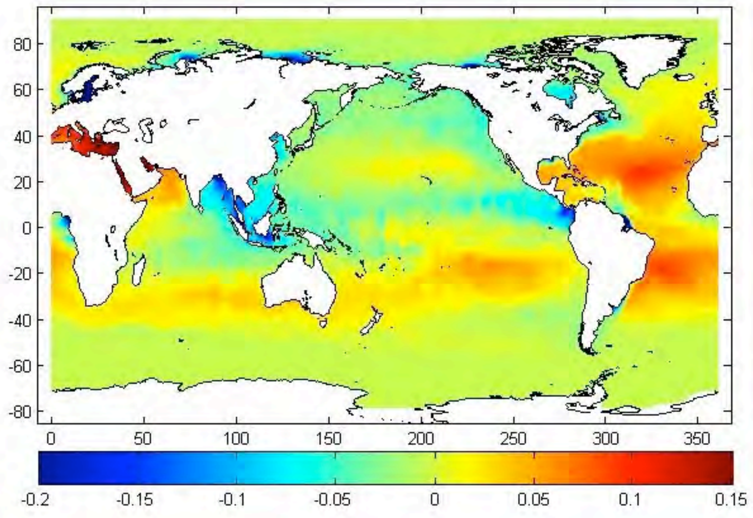
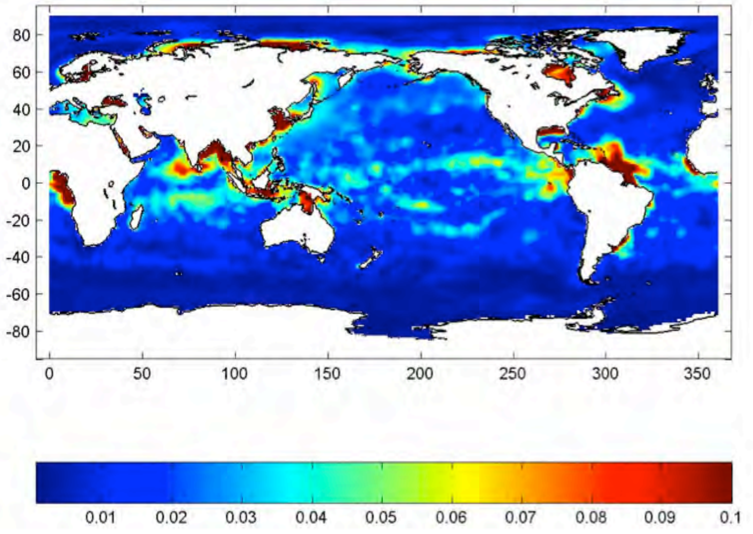


Figure A.13.1. The difference $\theta - \Theta$ (in °C) between potential temperature θ and Conservative Temperature Θ at the sea surface of the annually-averaged atlas of Gouretski and Koltermann (2004).



The maximum value of the seasonal variation in $|\theta - \Theta|$ (in °C) at the sea surface throughout the annual cycle of the hydrographic atlas of Gouretski and Koltermann (2004).

Review of the recent lectures

We examined the process of turbulent mixing and showed that in order for the Second Law of Thermodynamics to be obeyed (and entropy to be always produced), there are only two constraints on the form of the Gibbs function, namely

$$g_{TT} < 0 \qquad \text{(A.16.17)}$$

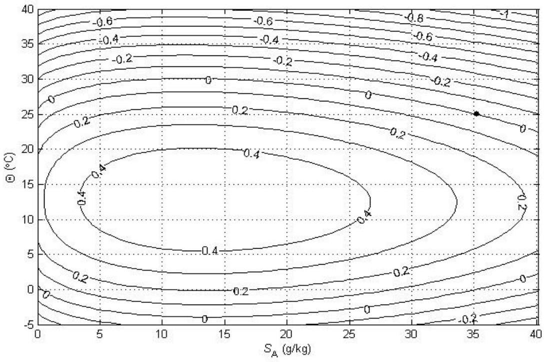
and

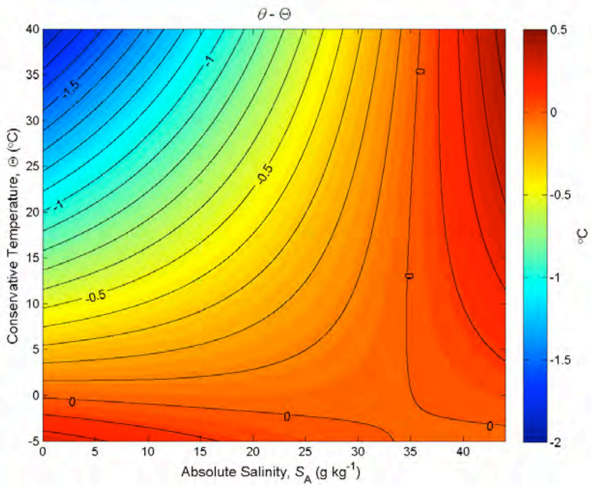
$$g_{S_A S_A} > 0. \qquad \text{(A.16.18)}$$

These constraints mean that (i) the fluid must increase its temperature when it is heated, and (ii) the solute should not spontaneously "unmix". These constraints on the Gibbs function are well known from considerations of molecular fluxes. It is encouraging that they emerge also from the turbulent mixing process, which happens quite independently of the form of the molecular fluxes.

We considered the turbulent mixing of pairs of seawater parcels that had finite amplitude differences of Absolute Salinity and of temperature. By employing a Taylor series analysis, we were able to get an expression for the non-conservative production of entropy and of potential temperature when the parcels are mixed to uniformity.

We were able to illustrate the non-conservative production of entropy and of potential temperature, when mixing occurs between pairs of fluid parcels, on the following carefully-constructed diagrams.





We then showed that these diagrams are the measure of the error involved with assuming that entropy or potential temperature is conserved in the ocean. Because of the unknowably many mixing events in the life-history of a seawater parcel, these diagrams illustrate the sum of these non-conservative sources in the past, over many different mixing events over the past 1000 years.

Non-conservative production of specific volume

Specific volume is expressed as a function of Absolute Salinity S_A, specific enthalpy h and pressure as $v = \breve{v}\left(S_\mathrm{A}, h, p\right)$ and the same mixing process between two fluid parcels is considered as in the previous appendices. Mass, salt and enthalpy are conserved during the turbulent mixing process (Eqns. (A.16.2) - (A.16.4)) while the non-conservative nature of specific volume means that it obeys the equation,

$$m_1 v_1 + m_2 v_2 + m\,\delta v = m v . \tag{A.19.1}$$

Specific volume is expanded in a Taylor series of S_A and h about the values of S_A and h of the mixed fluid at pressure p, retaining terms to second order in $\left[S_{\mathrm{A}2} - S_{\mathrm{A}1}\right] = \Delta S_\mathrm{A}$ and in $\left[h_2 - h_1\right] = \Delta h$. Then v_1 and v_2 are evaluated and (A.19.1) is used to find

$$\begin{aligned} \delta v &= -\tfrac{1}{2}\frac{m_1 m_2}{m^2}\left\{ \breve{v}_{hh}\left(\Delta h\right)^2 + 2\breve{v}_{hS_\mathrm{A}}\,\Delta h\,\Delta S_\mathrm{A} + \breve{v}_{S_\mathrm{A}S_\mathrm{A}}\left(\Delta S_\mathrm{A}\right)^2 \right\} \\ &\approx -\tfrac{1}{2}\frac{m_1 m_2}{m^2}\left\{ \hat{v}_{\Theta\Theta}\left(\Delta\Theta\right)^2 + 2\hat{v}_{\Theta S_\mathrm{A}}\,\Delta\Theta\,\Delta S_\mathrm{A} + \hat{v}_{S_\mathrm{A}S_\mathrm{A}}\left(\Delta S_\mathrm{A}\right)^2 \right\}. \end{aligned} \tag{A.19.2}$$

The non-conservative destruction of specific volume of Eqn. (A.19.2) is illustrated in **Figure A.19.1** for mixing at $p = 0$ dbar. The quantity contoured on this figure is formed as follows. First the linear function of S_A is found that is equal to specific volume at $\left(S_\mathrm{A} = 0,\ \Theta = 0\ ^\circ\mathrm{C}\right)$ and at $\left(S_\mathrm{A} = 35.165\,04\,\mathrm{g\,kg^{-1}},\ \Theta = 0\ ^\circ\mathrm{C}\right)$. This linear function of S_A is subtracted from v and the result is scaled to equal exactly 25 °C at $\left(S_\mathrm{A} = 35.165\,04\,\mathrm{g\,kg^{-1}},\ \Theta = 25\ ^\circ\mathrm{C}\right)$. The variable that is contoured in Figure A.19.1 is the difference between this scaled linear combination of v and S_A, and Conservative Temperature. This figure allows the non-conservative nature of specific volume to be understood in temperature units. The mixing of extreme fluid parcels on Figure A.19.1 causes the same decrease in specific volume as a cooling of approximately 10 °C, which is approximately 4000 times larger than the corresponding non-conservative production of Θ at 600dbar (from Figure A.18.1).

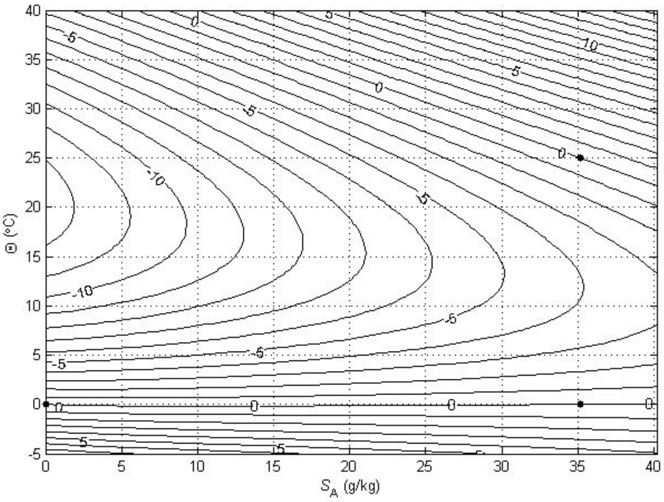


Figure A.19.1. Contours (in °C) of a variable that is used to illustrate the non-conservative production of specific volume at $p = 0$ dbar. The three points that are forced to be zero are shown with black dots.

From Eqn. (A.19.2) it follows that specific volume is always destroyed by turbulent mixing processes if $\breve{v}_{hh} > 0$, $\breve{v}_{S_\mathrm{A}S_\mathrm{A}} > 0$ and $(\breve{v}_{hS_\mathrm{A}})^2 < \breve{v}_{S_\mathrm{A}S_\mathrm{A}}\breve{v}_{hh}$, and Graham and McDougall (2013) have shown that these conditions are satisfied over the full TEOS-10 ranges of salinity, temperature and pressure by both the full TEOS-10 Gibbs function $g\left(S_\mathrm{A}, t, p\right)$ and by the polynomial expression for specific volume $\hat{v}\left(S_{\mathrm{A}},\Theta,p\right)$ of the Gibbs SeaWater (GSW) Oceanographic Toolbox. Note that in contrast to the case of specific volume, the non-conservation of density is not sign-definite. That is, while turbulent mixing always destroys specific volume, it does not always produce density $\rho = v^{-1}$.

Specific volume is the more appropriate variable to consider in this regard because it is volume per unit mass, and mass (which is on the denominator of specific volume $v = V/M$) is a conservative quantity whereas volume is not. So if one considers the non-conservative nature of density, $\rho = v^{-1} = M/V$, then one is actually enquiring about the non-conservation of the reciprocal of a non-conservative quantity, namely the reciprocal of volume V (since mass M is a conservative quantity). This explains how (but not why) specific volume is always destroyed by a turbulent mixing process while density is not always produced non-conservatively by the same turbulent mixing process. I do not know if this is a property that is specific to seawater (and pure water) or if there is a fundamental thermodynamic reason why this should be the case for all fluids; to date I have been unable to find a thermodynamic principle that would ensure that it would be the case for all fluids [I should look for a counterexample fluid]. Specific volume (rather than density) is the variable that naturally appears in the FTR as $P\mathrm{d}v$ and $v\mathrm{d}P$, and for good reason, since like the other variables that appear in the FTR such as internal energy, enthalpy, entropy and Absolute Salinity, specific volume is a "per unit mass" variable, not a "per unit volume" variable.

The fact that turbulent mixing at constant pressure always destroys specific volume v also implies that internal energy u is always produced by this turbulent mixing at constant pressure. To see this we start with the First Law of Thermodynamics, Eqn. (B.19),

$$\boxed{\begin{aligned} \rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) \;=\; \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t} + \left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) \;&=\; \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t} + \mu\frac{\mathrm{d}S_{\mathrm{A}}}{\mathrm{d}t}\right) \\ &=\; -\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \rho\varepsilon\,, \end{aligned}} \qquad \text{(B.19)}$$

and cast it in divergence form so that the First Law of Thermodynamics becomes

$$\begin{aligned} \left(\rho h\right)_t + \nabla\cdot\left(\rho\mathbf{u}h\right) - \frac{\mathrm{d}P}{\mathrm{d}t} \;&=\; \left(\rho u\right)_t + \nabla\cdot\left(\rho\mathbf{u}u\right) + \frac{\left(p+P_0\right)}{v}\frac{\mathrm{d}v}{\mathrm{d}t}\;. \\ &=\; -\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \rho\varepsilon\,. \end{aligned} \qquad \text{(B.19a)}$$

The turbulent mixing at constant pressure conserves enthalpy and each of the parts of this equation is zero for a control volume that encircles the mixing region. Since specific volume is always destroyed by turbulent mixing, that is $\mathrm{d}v < 0$, the second part of Eqn. (B.19a) implies that internal energy, u, is always produced by turbulent mixing at constant pressure. Moreover, the amount of production of internal energy is proportional to the absolute pressure $\left(p + P_0\right)$!

Non-conservative production of Conservative Temperature

When fluid parcels undergo irreversible and complete mixing at constant pressure, the thermodynamic quantities that are conserved are mass, Absolute Salinity and enthalpy. As above we consider two parcels being mixed without external input of heat or mass, and the three equations that represent the conservation of these quantities are Eqns. (A.16.2) – (A.16.4). Potential enthalpy h^0 and Conservative Temperature Θ are not exactly conserved during the mixing process and the production of Θ is given by

$$m_1\,\Theta_1 + m_2\,\Theta_2 + m\,\delta\Theta \;=\; m\Theta. \qquad \text{(A.18.1)}$$

Enthalpy in the functional form $h = \hat{h}\left(S_\mathrm{A},\Theta,p\right)$ is expanded in a Taylor series of S_A and Θ about the values S_A and Θ of the mixed fluid, retaining terms to second order in $\left[S_{\mathrm{A}2} - S_{\mathrm{A}1}\right] = \Delta S_\mathrm{A}$ and in $\left[\Theta_2 - \Theta_1\right] = \Delta\Theta$. Then h_1 and h_2 are evaluated and Eqns. (A.16.4) and (A.18.1) are used to find

$$\delta\Theta \;=\; \tfrac{1}{2}\frac{m_1\,m_2}{m^2}\left\{\frac{\hat{h}_{\Theta\Theta}}{\hat{h}_\Theta}\left(\Delta\Theta\right)^2 + 2\frac{\hat{h}_{\Theta S_\mathrm{A}}}{\hat{h}_\Theta}\,\Delta\Theta\Delta S_\mathrm{A} \;+\; \frac{\hat{h}_{S_\mathrm{A}S_\mathrm{A}}}{\hat{h}_\Theta}\left(\Delta S_\mathrm{A}\right)^2\right\}. \qquad \text{(A.18.2)}$$

Graham and McDougall (2013) have shown that the same form of the non-conservative production terms in Eqn. (A.18.2) also appears in the following turbulent evolution equation for Conservative Temperature, in both the epineutral and vertical diffusion terms (see appendix A.21 for an explanation of the symbols that appear in this thickness-weighted averaged equation),

$$\begin{aligned}\frac{\mathrm{d}\hat{\Theta}}{\mathrm{d}t} \;=\; \left.\frac{\partial\hat{\Theta}}{\partial t}\right|_n \;+\; \hat{\mathbf{v}}\cdot\nabla_n\hat{\Theta} \;+\; \tilde{e}\frac{\partial\hat{\Theta}}{\partial z} \;&=\; \tilde{\gamma}_z\nabla_n\cdot\left(\tilde{\gamma}_z^{-1}K\nabla_n\hat{\Theta}\right) + \left(D\hat{\Theta}_z\right)_z + \varepsilon/\hat{h}_\Theta \\ &\quad+\; K\left(\frac{\hat{h}_{\Theta\Theta}}{\hat{h}_\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n\hat{\Theta} + 2\frac{\hat{h}_{\Theta S_\mathrm{A}}}{\hat{h}_\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n\hat{S}_\mathrm{A} \;+\; \frac{\hat{h}_{S_\mathrm{A}S_\mathrm{A}}}{\hat{h}_\Theta}\nabla_n\hat{S}_\mathrm{A}\cdot\nabla_n\hat{S}_\mathrm{A}\right) \qquad \text{(A.18.3)} \\ &\quad+\; D\left(\frac{\hat{h}_{\Theta\Theta}}{\hat{h}_\Theta}\hat{\Theta}_z^2 + 2\frac{\hat{h}_{\Theta S_\mathrm{A}}}{\hat{h}_\Theta}\hat{\Theta}_z\hat{S}_{\mathrm{A}_z} \;+\; \frac{\hat{h}_{S_\mathrm{A}S_\mathrm{A}}}{\hat{h}_\Theta}\left(\hat{S}_{\mathrm{A}_z}\right)^2\right).\end{aligned}$$

The reasoning behind the derivation of this equation is as follows. A single turbulent mixing event is considered, with the mixing event occurring at the pressure p^m. A new potential enthalpy variable h^m is constructed with the reference pressure of the potential enthalpy being p^m. During the turbulent mixing event at p^m both enthalpy h and the potential enthalpy variable h^m are conserved. Moreover, since h^m is a "potential" variable, it is unchanged as seawater parcels are advected vertically to arrive at the pressure p^m where they are subject to turbulent mixing. Hence, for the purpose of analyzing the turbulent mixing process at pressure p^m, h^m behaves as both a "potential" variable and a conservative variable. This ensures that the epineutral turbulent flux of h^m and the small-sale isotropic diffusion h^m can be treated in the same way as the corresponding turbulent fluxes of an ordinary conservative variable such as Preformed Salinity (we outline this averaging procedure on pages 96 – 99 of these lectures below).

This enables the appropriate averaging of the instantaneous conservation equation of h^m to be performed and the final step to arrive at Eqn. (A.18.3) above is to relate the gradients of h^m to the corresponding gradients of Absolute Salinity and Conservative Temperature using the functional relationship $h^m = \hat{h}\left(S_\mathrm{A},\Theta,p^m\right)$. This reasoning and the derivation of Eqn. (A.18.3) can be found in sections 3(b) and 3(c) of Graham and McDougall (2103).

In order to evaluate the partial derivatives in Eqns. (A.18.2) and (A.18.3), first write enthalpy in terms of potential enthalpy ($c_p^0\,\Theta$) using Eqn. (3.2.1), as

$$h = \hat{h}\left(S_{\mathrm{A}},\Theta,p\right) = c_p^0\,\Theta + \int_{P_0}^{P} \hat{v}\left(S_{\mathrm{A}},\Theta,p'\right) dP'. \qquad \text{(A.18.4)}$$

Below we will use the relevant thermal expansion coefficient α^{Θ} and saline contraction coefficient β^{Θ}, defined with respect to Absolute Salinity and Conservative Temperature by

$$\alpha^{\Theta} = -\frac{1}{\rho}\frac{\partial\rho}{\partial\Theta}\bigg|_{S_{\mathrm{A}},p} \qquad \text{and} \qquad \beta^{\Theta} = \frac{1}{\rho}\frac{\partial\rho}{\partial S_{\mathrm{A}}}\bigg|_{\Theta,p}. \qquad \text{(2.18.3), (2.19.3)}$$

Eqn. (A.18.4) is now differentiated with respect to Θ giving

$$h_{\Theta}\big|_{S_{\mathrm{A}},p} = \hat{h}_{\Theta} = c_p^0 + \int_{P_0}^{P} \hat{v}_{\Theta}\left(S_{\mathrm{A}},\Theta,p'\right) dP' = c_p^0 + \int_{P_0}^{P} \alpha^{\Theta}/\rho \; dP'. \qquad \text{(A.18.5)}$$

The right-hand side of Eqn. (A.18.5) scales as $c_p^0 + \rho^{-1}\left(P-P_0\right)\alpha^{\Theta}$, which is more than c_p^0 by only about $0.0015c_p^0$ for $\left(P-P_0\right)$ as large as 4×10^7 Pa (4,000 dbar). Hence, to a very good approximation, $\hat{h}_{\Theta}$ in Eqns. (A.18.2) and (A.18.3) may be taken to be simply c_p^0.

As an exercise, use Eqn. (A.18.4) to show that an adiabatic and isohaline pressure change of 10^7 Pa (1,000 dbar) causes a change in enthalpy h as large as does an isobaric change in temperature of about $2.5\,{}^{\circ}\mathrm{C}$. This is because enthalpy h does not possess the "potential" property.

Why is the approximation $\hat{h}_{\Theta} \approx c_p^0$ so accurate when the difference between enthalpy, h, and potential enthalpy, h^0, as given by Eqns. (3.2.1) and (A.18.4), scales as $\rho^{-1}\left(P-P_0\right)$ which is as large as typical values of potential enthalpy?

The reason is that the integral in Eqns. (3.2.1) or (A.18.4) is dominated by the integral of the mean value of ρ^{-1}, so causing a significant offset between h and h^0 as a function of pressure but not affecting the partial derivative $\hat{h}_{\Theta}$ which is taken at fixed pressure. Even the dependence of specific volume on pressure alone does not affect $\hat{h}_{\Theta}$. It is only the dependence of specific volume on Θ *at fixed pressure* that affects $\hat{h}_{\Theta}$.

Recall from Eqn. (A.11.15), namely

$$\boxed{\hat{h}_{\Theta}\big|_{S_{\mathrm{A}},p} = \frac{\left(T_0+t\right)}{\left(T_0+\theta\right)}\,c_p^0.} \qquad \text{(A.11.15)}$$

and combining this with (A.18.5) we see that

$$\frac{\left(t-\theta\right)}{\left(T_0+\theta\right)}\,c_p^0 = \int_{P_0}^{P} \alpha^{\Theta}/\rho \; dP' = \int_{P_0}^{P} \hat{v}_{\Theta}\left(S_{\mathrm{A}},\Theta,p'\right) dP' \qquad \text{(A.18.5a)}$$

which is an interesting relationship between a temperature difference on the left-hand side (which is related directly to the functional dependence of entropy on *in situ* temperature and pressure) and a pressure integral of essentially the thermal expansion coefficient on the right-hand side. We actually go between *in situ* and potential temperatures by solving the identity $\eta\left(S_{\mathrm{A}},\theta,p_{\mathrm{r}}\right) = \eta\left(S_{\mathrm{A}},t,p\right)$, but Eqn. (A.18.5a) shows that we could instead calculate the difference between the *in situ* and potential temperatures from knowledge only of $\hat{v}\left(S_{\mathrm{A}},\Theta,p\right)$.

The second order derivatives of $\hat{h}$ are needed in Eqns. (A.18.2) and (A.18.3), and these can be estimated by differentiating Eqn. (A.18.4) or (A.18.5), so that, for example,

$$\hat{h}_{\Theta\Theta} = \int_{P_0}^{P} \hat{v}_{\Theta\Theta} \; dP' = \int_{P_0}^{P} \left(\alpha^{\Theta}/\rho\right)_{\Theta} \; dP', \qquad \text{(A.18.6)}$$

so that we may write Eqn. (A.18.2) approximately as (assuming $m_1 = m_2$)

$$\delta\Theta \approx \frac{\left(P-P_0\right)}{8c_p^0}\left\{\hat{v}_{\Theta\Theta}\left(\Delta\Theta\right)^2 + 2\,\hat{v}_{S_{\mathrm{A}}\Theta}\,\Delta\Theta\,\Delta S_{\mathrm{A}} + \hat{v}_{S_{\mathrm{A}}S_{\mathrm{A}}}\left(\Delta S_{\mathrm{A}}\right)^2\right\}. \qquad \text{(A.18.7)}$$

This equation is approximate because the variation of $\hat{v}_{\Theta\Theta}$, $\hat{v}_{\Theta S_{\mathrm{A}}}$ and $\hat{v}_{S_{\mathrm{A}}S_{\mathrm{A}}}$ with pressure has been ignored. The dominant term in Eqn. (A.18.7) is usually the term in $\hat{v}_{\Theta\Theta}$ and from Eqn. (A.19.2) above we see that $\delta\Theta$ is approximately proportional to the non-conservative destruction of specific volume at fixed pressure δv caused by the "cabbeling" non-linearities in the equation of state (McDougall, 1987b), so that

$$\delta\Theta \;\approx\; \frac{\left(P-P_0\right)}{8c_p^0}\,\hat{v}_{\Theta\Theta}\left(\Delta\Theta\right)^2 \;\approx\; -\,\frac{\left(P-P_0\right)}{c_p^0}\,\delta v. \qquad \text{(A.18.8)}$$

The production of Θ causes an increase in Conservative Temperature and a consequent decrease in density of $-\rho\alpha^{\Theta}\delta\Theta$. The ratio of this change in density (using Eqn. (A.18.7)) to that caused by cabbeling (from Eqn. (A.19.2) and using $\delta\rho \approx -\rho^2\,\delta v$) is $-\left(P-P_0\right)\alpha^{\Theta}\big/\rho c_p^0$ which is about 0.0015 for a value of $\left(P-P_0\right)$ of 40 MPa. Hence it is clear that "cabbeling" has a much larger effect on density than does the non-conservation of Θ. Nevertheless, it is interesting to note from Eqn. (A.18.7) that the non-conservative production of Θ is approximately proportional to the product of sea pressure and the strength of cabbeling, δv.

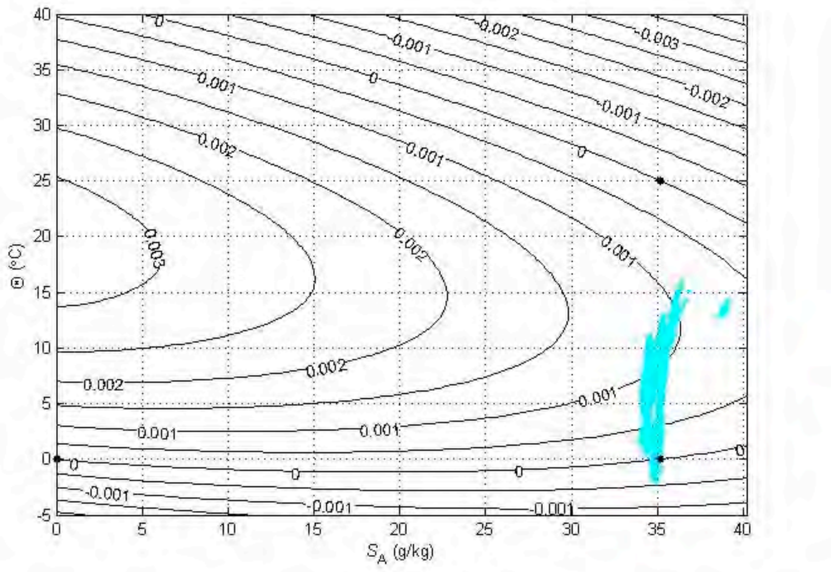


Figure A.18.1. Contours (in °C) of a variable that is used to illustrate the non-conservative production of Conservative Temperature Θ at $p = 600$ dbar. The cloud of points show where most of the oceanic data reside at $p = 600$ dbar. The three points that are forced to be zero are shown with black dots.

At the sea surface Conservative Temperature Θ is totally conserved ($\delta\Theta = 0$). The expression for the non-conservative production of Conservative Temperature, $\delta\Theta$, increases almost linearly with pressure (see Eqn. (A.18.7)) but at large pressures the range of temperature and salinity in the ocean decreases, and from the above equations it is clear that the magnitude of $\delta\Theta$ is proportional to the square of the temperature and salinity contrasts. McDougall (2003) concluded that the production $\delta\Theta$ between extreme seawater parcels at each pressure is largest at 600 dbar. The magnitude of the non-conservative production of Conservative Temperature, $\delta\Theta$, is illustrated in **Figure A.18.1** for data at this pressure.

The quantity contoured on this figure is the difference between Θ and the following totally conservative quantity at $p = 600$ dbar. This conservative quantity was constructed by taking the conservative property enthalpy h at this pressure and adding the linear function of S_{A} which makes the result equal to zero at $\left(S_{\mathrm{A}}=0,\ \Theta=0°\mathrm{C}\right)$ and at $\left(S_{\mathrm{A}}=35.165\,04\,\mathrm{g\,kg^{-1}},\ \Theta=0\ °\mathrm{C}\right)$. This quantity is then scaled so that it becomes exactly 25 °C at $\left(S_\mathrm{A} = 35.165\,04\,\mathrm{g\,kg^{-1}},\ \Theta = 25\ °\mathrm{C}\right)$. In this manner the quantity that is contoured in Figure A.18.1 has units of °C and represents the amount by which Conservative Temperature Θ is not a totally conservative variable at a pressure of 600 dbar. The maximum amount of production by mixing seawater parcels at the boundaries of Figure A.18.1 is about 4×10^{-3} °C although the range of values encountered in the real ocean at this pressure is actually quite small, as indicated in Figure A.18.1.

From the curvature of the isolines on Figure A.18.1 it is clear that the non-conservative production of Conservative Temperature at $p = 600$ dbar is positive, so that an ocean model that ignores this production of Conservative Temperature will slightly underestimate Θ. From Eqn. (A.18.2) one sees the non-conservative production of Conservative Temperature is always positive if $\hat{h}_{\Theta\Theta} > 0$, $\hat{h}_{S_\mathrm{A}S_\mathrm{A}} > 0$ and $(\hat{h}_{\Theta S_\mathrm{A}})^2 < \hat{h}_{\Theta\Theta}\,\hat{h}_{S_\mathrm{A}S_\mathrm{A}}$, and Graham and McDougall (2013) have shown that these requirements are met everywhere in the full TEOS-10 ranges of salinity, temperature and pressure for both the full TEOS-10 Gibbs function $g\left(S_\mathrm{A},t,p\right)$ and by the polynomial expression for specific enthalpy $\hat{h}\left(S_\mathrm{A},\Theta,p\right)$ of the Gibbs SeaWater (GSW) Oceanographic Toolbox.

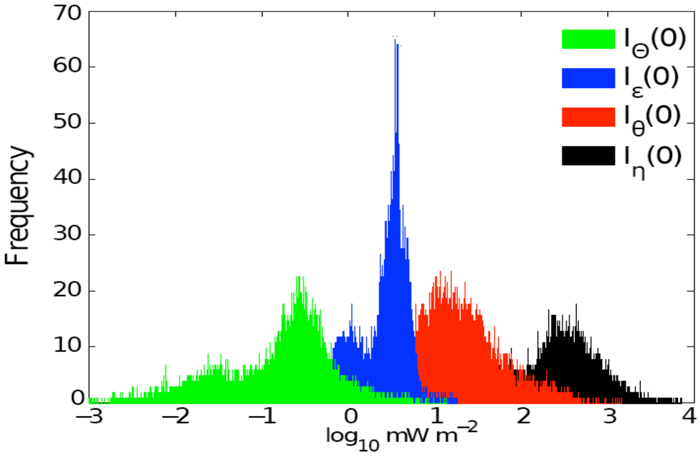
Depth-integrated measures of the non-conservation of θ, η and Θ

Graham and McDougall (2013) have derived the evolution equations for potential temperature, Conservative Temperature and specific entropy in a turbulent ocean, with the one for Conservative Temperature being

$$
\begin{aligned}
\frac{\mathrm{d}\hat{\Theta}}{\mathrm{d}t} = \left.\frac{\partial\hat{\Theta}}{\partial t}\right|_n + \hat{\mathbf{v}}\cdot\nabla_n\hat{\Theta} + \tilde{e}\frac{\partial\hat{\Theta}}{\partial z} &= \gamma_z\nabla_n\cdot\left(\gamma_z^{-1}K\nabla_n\hat{\Theta}\right) + \left(D\hat{\Theta}_z\right)_z + \varepsilon/\hat{h}_\Theta \\
&+ K\left(\frac{\hat{h}_{\Theta\Theta}}{\hat{h}_\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n\hat{\Theta} + 2\frac{\hat{h}_{\Theta S_\mathrm{A}}}{\hat{h}_\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n\hat{S}_\mathrm{A} + \frac{\hat{h}_{S_\mathrm{A}S_\mathrm{A}}}{\hat{h}_\Theta}\nabla_n\hat{S}_\mathrm{A}\cdot\nabla_n\hat{S}_\mathrm{A}\right) \qquad \text{(A.18.3)} \\
&+ D\left(\frac{\hat{h}_{\Theta\Theta}}{\hat{h}_\Theta}\hat{\Theta}_z^2 + 2\frac{\hat{h}_{\Theta S_\mathrm{A}}}{\hat{h}_\Theta}\hat{\Theta}_z\hat{S}_{\mathrm{A}_z} + \frac{\hat{h}_{S_\mathrm{A}S_\mathrm{A}}}{\hat{h}_\Theta}\left(\hat{S}_{\mathrm{A}_z}\right)^2\right).
\end{aligned}
$$

The red terms on the second and third lines of this equation are the non-conservative production terms and they can be evaluated in an ocean model.

One way of quantifying the magnitude of these red terms in Eqn. (A.18.3) is to vertically integrate these terms and to express this vertical integral as a vertical heat flux. That is, consider a vertical ocean water column that is the full depth of the ocean and is one square meter in area. In terms of its effect on the depth-integrated heat budget, the vertical integral of the red source terms is equivalent to an extra air-sea or geothermal heat flux. This equivalent surface flux is shown as a histogram for the whole world ocean in the figure below.



The 95 percentile largest values of these four error measures is shown below.

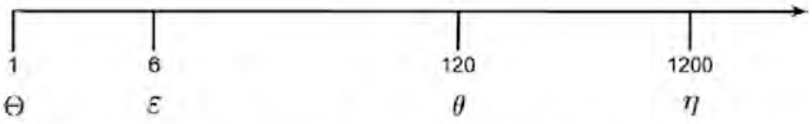


FIG. 10. The 95% error occurrences of the depth-integrated nonconservative source terms for ε, θ , and η to that of Θ (10^{-3} W m^{-2}) on a logarithmic scale.

This demonstrates that the non-conservative source terms of potential temperature are two orders of magnitude larger than those for Conservative Temperature, and that the dissipation of kinetic energy is almost an order of magnitude larger than the non-conservative source terms in the evolution equation for Conservative Temperature.

To put this in perspective, the mean geothermal heat flux is ~86.4 mW m^{-2}, and the extra surface heat flux that the planet is receiving now from global warming is ~1.5 W m^{-2}.

Keeping track of "heat" in the ocean; advection and diffusion of heat

We have seen that the First Law of Thermodynamics is practically equivalent to the conservation equation for Conservative Temperature Θ. We have emphasized that this means that the advection of "heat" is very accurately given as the advection of $c_p^0 \Theta$. In this way $c_p^0 \Theta$ can be regarded as the "heat content" per unit mass of seawater. The error involved with making this association is approximately 1% of the error in assuming that either $c_p^0 \theta$ or $c_p\left(S_{\mathrm{A}}, \theta, 0\,\mathrm{dbar}\right)\theta$ is the "heat content" per unit mass of seawater.

A flux of heat across the sea surface at a sea pressure of 0 dbar is identical to the flux of potential enthalpy which is exactly equal to c_p^0 times the flux of Conservative Temperature Θ. By contrast, the same heat flux across the sea surface changes potential temperature θ in inverse proportion to $c_p\left(S_{\mathrm{A}}, \theta, 0\right)$ which varies by 5% at the sea surface, depending mainly on salinity.

The First Law of Thermodynamics can be approximated as

$$\rho c_p^0 \frac{\mathrm{d}\Theta}{\mathrm{d}t} = c_p^0 \left(\rho\Theta\right)_t + c_p^0 \nabla\cdot\left(\rho\Theta\mathbf{u}\right) \approx -\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \rho\varepsilon , \qquad (3.23.1)$$

with an error in Θ that is approximately one percent of the error incurred by treating either $c_p^0 \theta$ or $c_p\left(S_{\mathrm{A}}, \theta, 0\right)\theta$ as the "heat content" of seawater, and approximately 10% of the error in ignoring the dissipation rate of turbulent kinetic energy term $\rho\varepsilon$ in this equation. Equation (3.23.1) is exact at 0 dbar.

Because the left-hand side of the First Law of Thermodynamics, Eqn. (3.23.1), can be written as density times the material derivative of $c_p^0 \Theta$ it follows that Θ can be treated as a conservative variable in the ocean and that $c_p^0 \Theta$ is transported by advection and mixed by turbulent epineutral and dianeutral diffusion as though it is the "heat content" of seawater. For example, the advective meridional flux of "heat" is the area integral of $\rho v h^0 = \rho v c_p^0 \Theta$ (here v is the northward velocity).

Some have argued that because enthalpy is unknown up to a linear function of salinity, it is only possible to talk of a flux of "heat" through an ocean section if the fluxes of mass and salt through the ocean section are both zero. This opinion seems to be widely held, but it is incorrect. The fact that $c_p^0 \Theta$ is unknowable up to a linear function of S_{A} does not affect the usefulness of h^0 or $c_p^0 \Theta$ as measures of "heat content":- the difference between the meridional (i.e. northward) fluxes of $c_p^0 \Theta$ across two latitudes is equal to the area-integrated air-sea and geothermal heat fluxes between these latitudes (after allowing for any unsteady accumulation of $c_p^0 \Theta$ in the volume), irrespective of whether there are non-zero fluxes of mass or salt across the sections. This powerful result follows directly from the fact that $c_p^0 \Theta$ is taken to be a conservative variable, obeying the simple conservation statement Eqn. (3.23.1) (modulo the dissipation of kinetic energy, $\rho\varepsilon$). No one would doubt the sensibleness of calculating the meridional flux of a general passive tracer that obeyed such a conservation evolution equation, and the same applies to the flux of potential enthalpy.

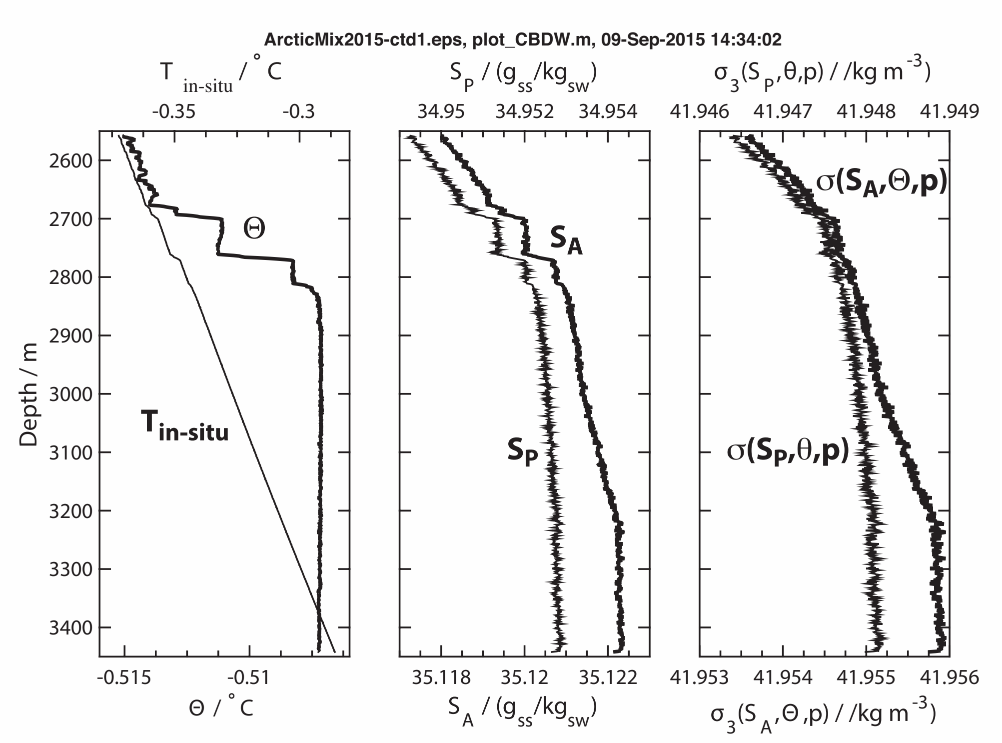
The intuitive explanation of why Conservative Temperature makes sense

These lectures have largely demonstrated the benefits of potential enthalpy and Conservative Temperature from the viewpoint of conservation equations, but the benefits can also be deduced by the following parcel-based argument.

1. First, the air-sea heat flux needs to be recognized as a flux of potential enthalpy which is exactly c_p^0 times the flux of Conservative Temperature.
2. Second, the non-conservative production of Conservative Temperature at non-zero pressure is calculated from the mixture of two seawater parcels (as in the non-equilibrium, Taylor series analysis of Eqn. (A.18.2)) and shown to be much less than that for potential temperature.
3. Third, note that the ocean circulation can be regarded as a series of adiabatic and isohaline movements during which Θ is absolutely unchanged (because of its "potential" nature) followed by a series of turbulent mixing events during which Θ is almost totally conserved.

Hence it is clear that Θ is the quantity that is advected and diffused in an almost conservative fashion and whose surface flux is exactly proportional to the air-sea heat flux.

The correct explanation of the adiabatic lapse rate Γ



The adiabatic lapse rate Γ is the change in *in situ* temperature t with pressure when entropy η and Absolute Salinity S_A are held constant. This vertical gradient of *in situ* temperature is commonly observed in the ocean in well-mixed layers, for example, the surface mixed layer, the benthic (bottom) mixed layer and occasionally at mid depth (e.g. in Meddies).

From the Fundamental Thermodynamic Relation Eqn. (A.7.1)

$$\boxed{\mathrm{d}u + \left(p+P_0\right)\mathrm{d}v \;=\; \mathrm{d}h - v\,\mathrm{d}P \;=\; \left(T_0+t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_\mathrm{A}} \,. \qquad \text{(A.7.1)}$$

we find that

$$\left.\frac{\partial h}{\partial \eta}\right|_{S_\mathrm{A},p} = \hat{h}_\eta = \left(T_0+t\right) \quad \text{and} \quad \left.\frac{\partial h}{\partial P}\right|_{S_\mathrm{A},\eta} = \hat{h}_P = v\,, \qquad \text{(Laspse\_1a,b)}$$

where we consider enthalpy in the functional form $h=\hat{h}\left(S_\mathrm{A},\eta,p\right)$. Now differentiate Eqn. (Lapse_1a) with respect to pressure, to find that

$$\begin{aligned}\Gamma &= \left.\frac{\partial t}{\partial P}\right|_{S_\mathrm{A},\eta} = \left.\frac{\partial t}{\partial P}\right|_{S_\mathrm{A},\Theta} = \left.\frac{\partial^2 h}{\partial\eta\,\partial P}\right|_{S_\mathrm{A}} = \hat{h}_{\eta P} = \left.\frac{\partial v}{\partial \eta}\right|_{S_\mathrm{A},p} = \left.\frac{v_T}{\eta_T}\right|_{S_\mathrm{A},p} = \left.\frac{v_\theta}{\eta_\theta}\right|_{S_\mathrm{A},p} = \left.\frac{v_\Theta}{\eta_\Theta}\right|_{S_\mathrm{A},p}\\ &= -\frac{g_{TP}}{g_{TT}} = -\frac{\eta_P}{\eta_T} = \frac{\left(T_0+t\right)\alpha^t}{\rho\, c_p\left(S_\mathrm{A},t,p\right)}\\ &= \frac{\tilde{v}_\theta}{\tilde{\eta}_\theta} = \frac{\left(T_0+\theta\right)\alpha^\theta}{\rho\, c_p\left(S_\mathrm{A},\theta,0\right)}\\ &= \frac{\hat{v}_\Theta}{\hat{\eta}_\Theta} = \frac{\left(T_0+\theta\right)}{c_p^0}\,\hat{v}_\Theta = \frac{\left(T_0+\theta\right)}{c_p^0}\,\hat{h}_{P\Theta} = \frac{\left(T_0+\theta\right)\alpha^\Theta}{\rho\, c_p^0}\,.\end{aligned} \qquad (2.22.1)$$

The reference pressure of the potential temperature θ that appears in the last two lines of Eqn. (2.22.1) is $p_\mathrm{r}=0$ dbar. Here the thermal expansion coefficients are

$$\begin{aligned}
\alpha^{t} &= -\frac{1}{\rho}\frac{\partial\rho}{\partial T}\Big|_{S_{\mathrm{A}},p} = \frac{1}{v}\frac{\partial v}{\partial T}\Big|_{S_{\mathrm{A}},p} = \frac{g_{TP}}{g_{P}} \\
\alpha^{\theta} &= -\frac{1}{\rho}\frac{\partial\rho}{\partial \theta}\Big|_{S_{\mathrm{A}},p} = \frac{1}{v}\frac{\partial v}{\partial \theta}\Big|_{S_{\mathrm{A}},p} = \frac{g_{TP}}{g_{P}}\frac{g_{TT}\left(S_{\mathrm{A}},\theta,0\right)}{g_{TT}} \\
\alpha^{\Theta} &= -\frac{1}{\rho}\frac{\partial\rho}{\partial \Theta}\Big|_{S_{\mathrm{A}},p} = \frac{1}{v}\frac{\partial v}{\partial \Theta}\Big|_{S_{\mathrm{A}},p} = -\frac{g_{TP}}{g_{P}}\frac{c_{p}^{0}}{\left(T_{0}+\theta\right)g_{TT}} \; .
\end{aligned} \tag{thermal\_expansion}$$

The adiabatic (and isohaline) lapse rate Γ is commonly (and incorrectly) explained as being proportional to the $\left(p+P_0\right)\mathrm{d}v$ work done on a fluid parcel as its volume changes in response to a change of pressure. According to this explanation the adiabatic lapse rate Γ would increase linearly with (i) pressure and (ii) the fluid's compressibility, but neither of these dependencies occur.

This incorrect explanation starts with the Fundamental Thermodynamic Relation in the form

$$\mathrm{d}u + \left(p+P_0\right)\mathrm{d}v \;=\; \left(T_0+t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_{\mathrm{A}}\,, \tag{A.7.1}$$

and for an isentropic and isohaline change in pressure the right-hand side is zero. An increase in pressure in this isentropic and isohaline situation means that the change in specific volume v is given in terms of the isentropic and isohaline compressibility $\kappa = -v^{-1}v_P\big|_{S_{\mathrm{A}},\eta}$ as $\mathrm{d}v \;=\; -v\kappa\,\mathrm{dP}$ and the change in internal energy is

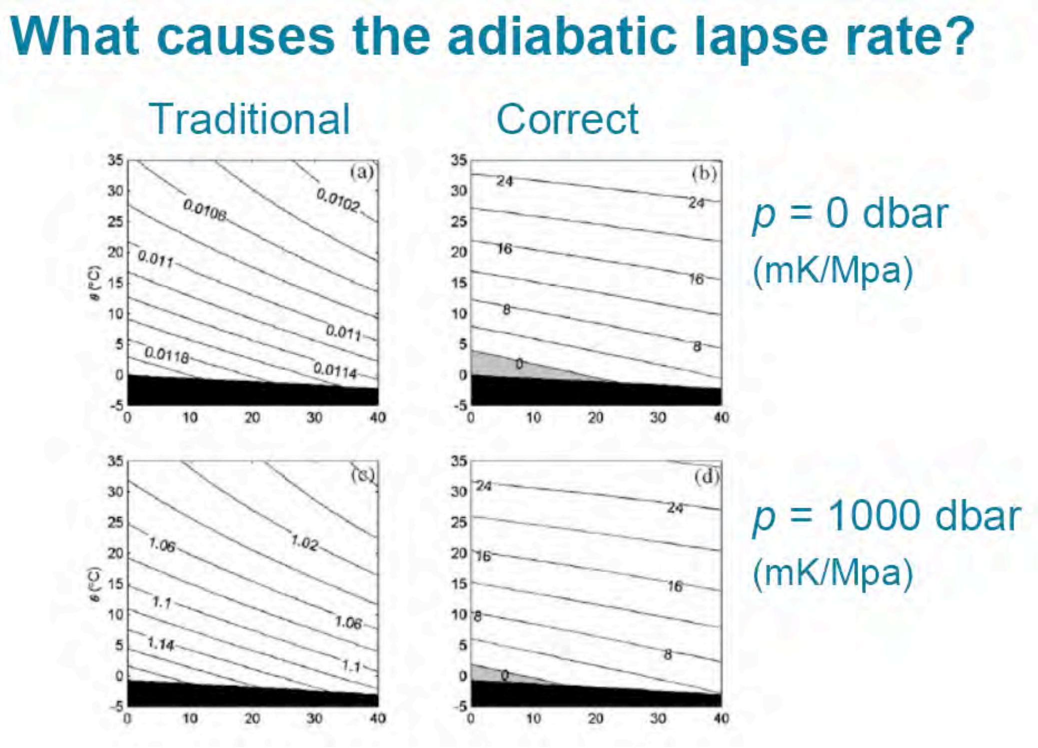
$$\mathrm{d}u \;=\; \left(p+P_0\right)v\kappa\,\mathrm{d}P \;=\; v\kappa\,\mathrm{d}\left(\tfrac{1}{2}\left[p+P_0\right]^2\right). \tag{Lapse\_1}$$

So far this is correct; an isentropic and isohaline increase in pressure does indeed increase the parcel's internal energy u by exactly this amount.

Then the traditional (and incorrect) explanation says that this increase in internal energy u results in a corresponding increase in *in situ* temperature, by dividing $\mathrm{d}u$ by an appropriate specific heat capacity. This step is incorrect because the dependence of internal energy on pressure has been ignored. That is, regarding $u = u\left(S_{\mathrm{A}},t,p\right)$, the total derivative of internal energy is

$$\mathrm{d}u \;=\; u_{S_{\mathrm{A}}}\,\mathrm{d}S_{\mathrm{A}} + u_T\,\mathrm{dT} + u_P\,\mathrm{d}P\;, \tag{Lapse\_2}$$

and the traditional explanation of the adiabatic lapse rate assumes that the last term here is zero. While this is true of a perfect gas, it is very "untrue" of a liquid like water and seawater. For a liquid this term can be two or three orders of magnitude larger than $\mathrm{d}u \;=\; \left(p+P_0\right)v\kappa\,\mathrm{d}P$, so the dominant balance in Eqn. (Lapse_2) for a liquid is $0 \;\approx\; u_T\,\mathrm{dT} + u_P\,\mathrm{d}P$.



What causes the adiabatic lapse rate?

Traditional

Correct

p = 0 dbar
(mK/Mpa)

p = 1000 dbar
(mK/Mpa)

The adiabatic lapse rate is (a) proportional to the thermal expansion coefficient and (b) is independent of the fluid's compressibility. Indeed, the adiabatic lapse rate changes sign at the temperature of maximum density (where α^t, α^θ and α^Θ all change sign) whereas the compressibility is always positive. This change in sign of the adiabatic lapse rate Γ occurs even though the work done by compression, $\left(p+P_0\right)\mathrm{d}v$, is always positive (for a increase in pressure).

Hence, in cold lakes where the thermal expansion coefficient is negative, the adiabatic lapse rate is negative, so that as the pressure is increased adiabatically, the *in situ* temperature actually decreases! The adiabatic lapse rate Γ represents that change in temperature that is required to keep the entropy (and also θ and Θ) of a seawater parcel constant when its pressure is changed in an adiabatic and isohaline manner.

The traditional explanation has found its way into our textbooks because it works perfectly for a perfect gas; the missing term that we identified just happens to be zero for a perfect gas, but it is the dominant term for a liquid.

Remember, the adiabatic lapse rate has nothing whatsoever to do with the $\left(p+P_0\right)\mathrm{d}v$ work done in changing the internal energy of a fluid parcel. This explanation is wrong even for a perfect gas (where you get the right answer for the wrong reason); for a liquid it is wrong by orders of magnitude.

The adiabatic lapse rate and the potential temperature of ice Ih

Ice Ih is the form of ice with hexagonal packing of the water molecules. This is the form of ice that is found in the range of temperatures and pressures found on planet earth.

The adiabatic lapse rate is equal to the change of *in situ* temperature experienced when pressure is changed while keeping entropy (and salinity) constant. This definition applies separately to both ice and seawater (where one needs to keep not only entropy but also Absolute Salinity constant during the pressure change). In terms of the Gibbs functions of seawater and of ice Ih the adiabatic lapse rates of seawater Γ and of ice Γ^{Ih} are expressed respectively as

$$\Gamma = \left.\frac{\partial t}{\partial P}\right|_{S_{\text{A}},\eta} = \left.\frac{\partial t}{\partial P}\right|_{S_{\text{A}},\Theta} = \left.\frac{\partial t}{\partial P}\right|_{S_{\text{A}},\theta} = -\frac{g_{TP}}{g_{TT}} = \frac{\left(T_0 + t\right)\alpha^{t}}{\rho\, c_p}, \qquad \text{(Ice\_1)}$$

and

$$\Gamma^{\text{Ih}} = \left.\frac{\partial t}{\partial P}\right|_{\eta} = \left.\frac{\partial t}{\partial P}\right|_{\theta^{\text{Ih}}} = -\frac{g_{TP}^{\text{Ih}}}{g_{TT}^{\text{Ih}}} = \frac{\left(T_0 + t^{\text{Ih}}\right)\alpha^{t\text{Ih}}}{\rho^{\text{Ih}}\, c_p^{\text{Ih}}}, \qquad \text{(Ice\_2)}$$

where α^{t} and $\alpha^{t\text{Ih}}$ are the thermal expansion coefficients of seawater and ice Ih respectively with respect to *in situ* temperature.

The adiabatic lapse rates of seawater and of ice are numerically substantially different from each other. The thermal expansion coefficient of ice does not change sign as does that of seawater when it is cooler than the temperature of maximum density, and the specific heat capacity of ice c_p^{Ih} is only approximately 52% that of seawater c_p.

Figure Ice_1(a) below shows the ratio $\Gamma/\Gamma^{\text{Ih}}$ of the adiabatic lapse rates of seawater and ice at the freezing temperature, as a function of the Absolute Salinity of seawater and pressure. For salinities typical of the open ocean, the ratio $\Gamma/\Gamma^{\text{Ih}}$ is about 0.1 indicating that the *in situ* temperature of ice varies ten times as strongly with pressure when both seawater and ice Ih are subjected to the same isentropic pressure variations. This must be taken into account when considering the vertical motion of frazil ice and the vertical motion of seawater and frazil ice mixtures.

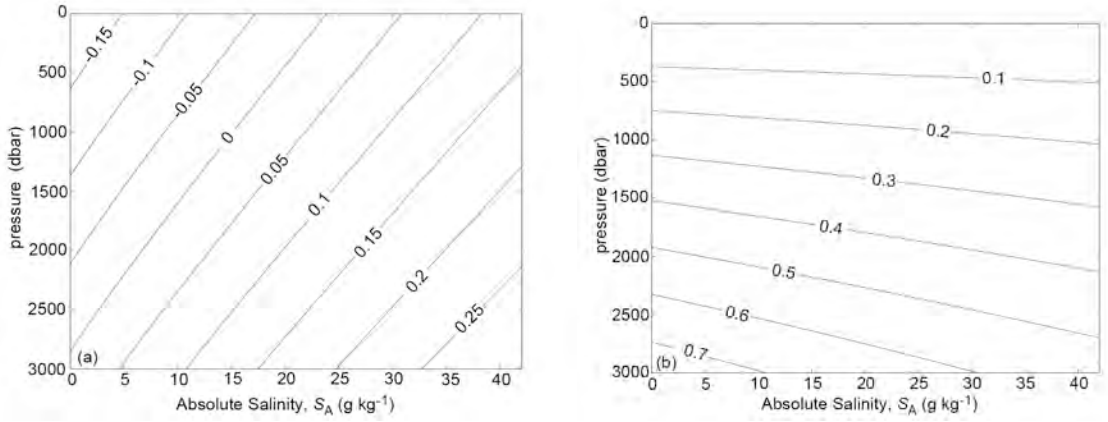


Figure Ice_1. (a) The ratio of the adiabatic lapse rates of seawater and of ice Ih, $\Gamma/\Gamma^{\text{Ih}}$, at the freezing temperature. (b) The difference (in °C) between the potential temperatures of seawater θ and of ice θ^{Ih} for parcels of seawater and ice whose *in situ* temperature is the *in situ* freezing temperature.

The freezing temperature of ice in contact with seawater

The freezing of seawater occurs at the temperature t_{freezing} at which the chemical potential of water in seawater μ^{W} equals the chemical potential of ice μ^{Ih}. Hence the freezing temperature t_{freezing} is found by solving the implicit equation

$$\mu^{\text{W}}\left(S_{\text{A}}, t_{\text{freezing}}, p\right) = \mu^{\text{Ih}}\left(t_{\text{freezing}}, p\right), \qquad \text{(Ice\_3)}$$

or equivalently, in terms of the two Gibbs functions,

$$g\left(S_{\text{A}}, t_{\text{freezing}}, p\right) - S_{\text{A}}\, g_{S_{\text{A}}}\left(S_{\text{A}}, t_{\text{freezing}}, p\right) = g^{\text{Ih}}\left(t_{\text{freezing}}, p\right). \qquad \text{(Ice\_4)}$$

The freezing *in situ* temperatures derived from Eqn. (Ice_4) were converted to the Conservative Temperature at which air-free seawater freezes and are shown in Figure Ice_2(a) as a function of pressure and Absolute Salinity. You can see that whether a water molecule prefers to remain in seawater or prefers to join the solid matrix of water molecules called "ice" depends on the salinity of the seawater and on pressure.

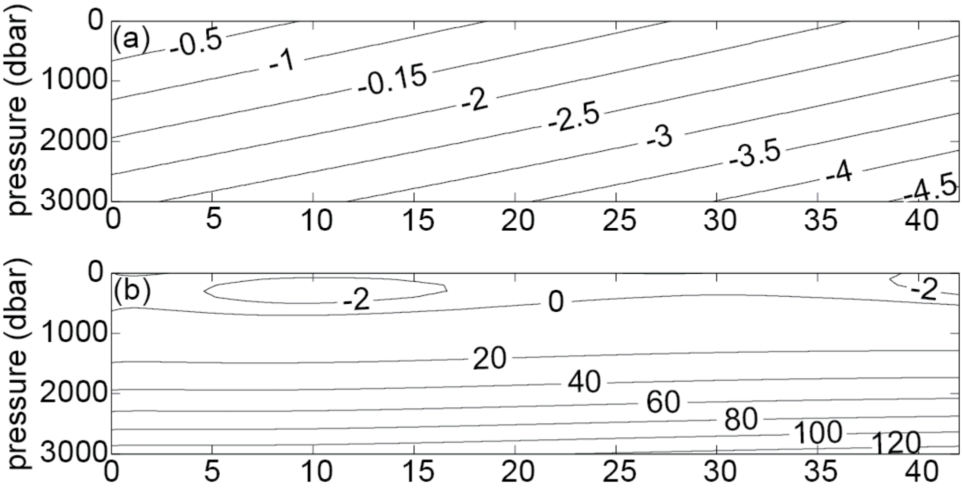


Figure Ice_2. (a) The Conservative Temperature (in °C) at which air-free seawater freezes as a function of pressure and Absolute Salinity. (b) The difference between the freezing Conservative Temperature derived from EOS-80 and that of TEOS-10, with the contours being in mK.

The figure below is another way of plotting the freezing temperature of seawater.

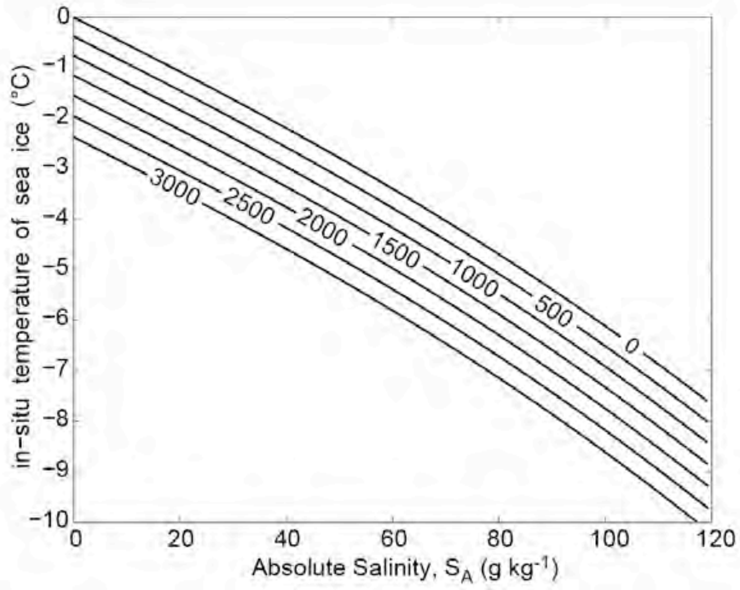


Figure Ice_3. The *in-situ* freezing temperature (in °C) of air-free seawater as a function of pressure (in dbar) and Absolute Salinity, determined from the equilibrium freezing condition Eqn. (Ice_4). In the context of sea ice, the *in situ* temperature is the temperature of both the pure ice Ih phase t^{Ih} and of the trapped pockets of brine.

When discussing the thermodynamic equilibrium between seawater and ice in the oceanographic context there are two common situations. One is called "sea ice" where there are trapped pockets of seawater inside a matrix of ice crystals. This trapped seawater is commonly called "brine" as its salinity can be very large when the temperature is cold.

The other situation is where there are small ice crystals (frazil) are suspended in a much larger volume of seawater so that the mass fraction of ice is small.

In both situations the ice and the seawater exist in thermodynamic equilibrium, so that their *in situ* temperatures are the same. However, as we have seen, the potential temperatures of the ice and seawater phases are different (unless the sea pressure is zero).

Melting of ice into seawater

The First Law of Thermodynamics says that when a process occurs at constant pressure, and without any external input of energy with the environment, then total enthalpy is conserved.

So the conservation equations for mass, salt and enthalpy during an adiabatic melting event at constant pressure are

$$m_{\mathrm{SW}}^{\mathrm{f}} = m_{\mathrm{SW}}^{\mathrm{i}} + m_{\mathrm{Ih}}\,, \tag{Ice\_5}$$

$$m_{\mathrm{SW}}^{\mathrm{f}} S_{\mathrm{A}}^{\mathrm{f}} = m_{\mathrm{SW}}^{\mathrm{i}} S_{\mathrm{A}}^{\mathrm{i}}\,, \tag{Ice\_6}$$

$$m_{\mathrm{SW}}^{\mathrm{f}} h^{\mathrm{f}} = m_{\mathrm{SW}}^{\mathrm{i}} h^{\mathrm{i}} + m_{\mathrm{Ih}} h^{\mathrm{Ih}}\,. \tag{Ice\_7}$$

The superscripts i and f stand for the "initial" and "final" values, that is, the values before and after the melting event, while the subscripts SW and Ih stand for "seawater" and "ice Ih". The mass of ice m_{Ih} is assumed to melt completely, so in the final state there is no ice as all; it is all seawater.

The mass, salinity and enthalpy conservation equations (Ice_5) – (Ice_7) can be combined to give the following expressions for the differences in the Absolute Salinity and the specific enthalpy of the seawater phase due to the melting of the ice,

$$\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right) = -\frac{m_{\mathrm{Ih}}}{m_{\mathrm{SW}}^{\mathrm{f}}} S_{\mathrm{A}}^{\mathrm{i}} = -\,w^{\mathrm{Ih}} S_{\mathrm{A}}^{\mathrm{i}}\,, \tag{Ice\_8}$$

$$\left(h^{\mathrm{f}} - h^{\mathrm{i}}\right) = -\,w^{\mathrm{Ih}}\left(h^{\mathrm{i}} - h^{\mathrm{Ih}}\right) = \frac{\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right)}{S_{\mathrm{A}}^{\mathrm{i}}}\left(h^{\mathrm{i}} - h^{\mathrm{Ih}}\right), \tag{Ice\_9}$$

where we have defined the mass fraction of ice Ih w^{Ih} as $m_{\mathrm{Ih}} / m_{\mathrm{SW}}^{\mathrm{f}}$. The initial and final values of the specific enthalpy of seawater are given by $h^{\mathrm{i}} = h\left(S_{\mathrm{A}}^{\mathrm{i}}, t^{\mathrm{i}}, p\right) = \hat{h}\left(S_{\mathrm{A}}^{\mathrm{i}}, \Theta^{\mathrm{i}}, p\right)$ and $h^{\mathrm{f}} = h\left(S_{\mathrm{A}}^{\mathrm{f}}, t^{\mathrm{f}}, p\right) = \hat{h}\left(S_{\mathrm{A}}^{\mathrm{f}}, \Theta^{\mathrm{f}}, p\right)$. These equations are illustrated in the following diagram

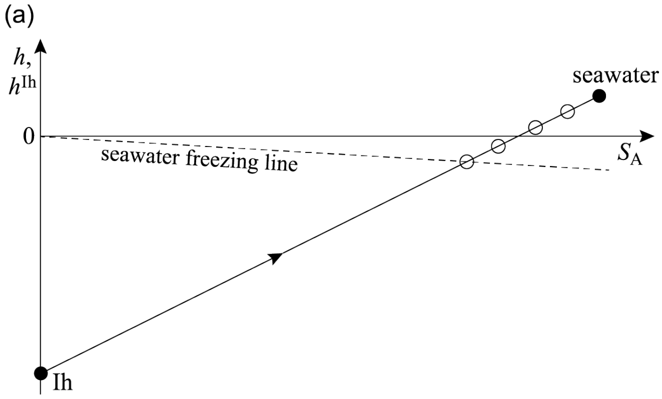


Figure Ice_4(a). This Absolute Salinity – enthalpy diagram illustrates Eqns. (Ice_8) and (Ice_9) which embody the conservation of Absolute Salinity and enthalpy when ice Ih melts into seawater at fixed pressure. The initial values of the Absolute Salinity and enthalpy of seawater and of ice Ih are shown by the two solid dots, and the final values of Absolute Salinity and enthalpy of the seawater after the ice has melted are shown by the four open circles (for four different values of the ice mass fraction w^{Ih}). These final values lie on the straight line on this diagram that connects the initial values (the solid dots).

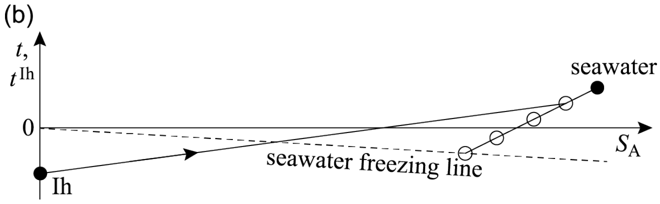


Figure Ice_4(b). The same initial and final data are shown on the Absolute Salinity – *in situ* temperature diagram. Note that the final points (the open circles) do not lie on the straight line connecting the initial points (the solid dots) on this diagram.

The final values of Absolute Salinity, $S_{\mathrm{A}}^{\mathrm{f}}$, and enthalpy, h^{f}, given by Eqns. (8) and (9) are illustrated in Fig. Ice_4(a) for four different values of the ice mass fraction w^{Ih} (the four open circles). These final values, $\left(S_{\mathrm{A}}^{\mathrm{f}}, h^{\mathrm{f}}\right)$, lie on the straight line on the Absolute Salinity - enthalpy diagram connecting $\left(S_{\mathrm{A}}^{\mathrm{i}}, h^{\mathrm{i}}\right)$ and $\left(0, h^{\mathrm{Ih}}\right)$. The fact that the same data does not fall on a straight line on the Absolute Salinity – *in situ* temperature diagram in Fig. Icw_4(b) nicely illustrates that temperature is not conserved when melting occurs.

The linearized expression for the $S_{\mathrm{A}} - \Theta$ ratio when melting occurs

Here we linearize equations (Ice_8) and (Ice_9) to find the expressions (Ice_16) – (Ice_18) for the ratio of the changes in salinity and temperature when a vanishingly small mass fraction of ice melts into seawater at a given pressure.

The enthalpy difference $h^{\mathrm{f}} - h^{\mathrm{i}}$ in Eqn. (Ice_9) is expanded as a Taylor series in the differences in Absolute Salinity and temperature, and the first order terms in these differences are retained, leading to

$$\left(t^{\mathrm{f}} - t^{\mathrm{i}}\right)c_p + \left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right)h_{S_{\mathrm{A}}} \approx \frac{\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right)}{S_{\mathrm{A}}^{\mathrm{i}}}\left(h^{\mathrm{i}} - h^{\mathrm{Ih}}\right) = -\,w^{\mathrm{Ih}}\left(h^{\mathrm{i}} - h^{\mathrm{Ih}}\right), \qquad \text{(Ice\_10)}$$

where c_p is the specific heat capacity of seawater, $c_p = \partial h/\partial T\big|_{S_{\mathrm{A}},p}$, and $h_{S_{\mathrm{A}}} = \partial h/\partial S_{\mathrm{A}}\big|_{T,p}$ is the derivative of the seawater specific enthalpy with respect to Absolute Salinity at constant *in situ* temperature and constant pressure.

By regarding specific enthalpy to be a function of Conservative Temperature in the functional form $\hat{h}\left(S_{\mathrm{A}},\Theta,p\right)$ the Taylor series expansion of Eqn. (Ice_9) yields

$$\left(\Theta^{\mathrm{f}} - \Theta^{\mathrm{i}}\right)\hat{h}_{\Theta} + \left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right)\hat{h}_{S_{\mathrm{A}}} \approx \frac{\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right)}{S_{\mathrm{A}}^{\mathrm{i}}}\left(h^{\mathrm{i}} - h^{\mathrm{Ih}}\right) = -\,w^{\mathrm{Ih}}\left(h^{\mathrm{i}} - h^{\mathrm{Ih}}\right), \qquad \text{(Ice\_11)}$$

where $\hat{h}_{\Theta} = \partial h/\partial\Theta\big|_{S_{\mathrm{A}},p}$ is the partial derivative of the seawater specific enthalpy with respect to Conservative Temperature Θ at fixed Absolute Salinity, and $\hat{h}_{S_{\mathrm{A}}} = \partial h/\partial S_{\mathrm{A}}\big|_{\Theta,\,p}$ is the partial derivative of the seawater specific enthalpy with respect to Absolute Salinity at fixed Conservative Temperature Θ. These equations can be rewritten as

$$\delta T\,c_p \equiv \left(t^{\mathrm{f}} - t^{\mathrm{i}}\right)c_p \approx \frac{\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right)}{S_{\mathrm{A}}^{\mathrm{i}}}\left(h - h^{\mathrm{Ih}} - S_{\mathrm{A}}h_{S_{\mathrm{A}}}\right) = -\,w^{\mathrm{Ih}}\left(h - h^{\mathrm{Ih}} - S_{\mathrm{A}}h_{S_{\mathrm{A}}}\right). \qquad \text{(Ice\_12)}$$

$$\delta\Theta\,\hat{h}_{\Theta} \;\equiv\; \left(\Theta^{\mathrm{f}} - \Theta^{\mathrm{i}}\right)\hat{h}_{\Theta} \;\approx\; \frac{\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right)}{S_{\mathrm{A}}^{\mathrm{i}}}\left(h - h^{\mathrm{Ih}} - S_{\mathrm{A}}\hat{h}_{S_{\mathrm{A}}}\right) \;=\; -\,w^{\mathrm{Ih}}\left(h - h^{\mathrm{Ih}} - S_{\mathrm{A}}\hat{h}_{S_{\mathrm{A}}}\right). \qquad \text{(Ice\_13)}$$

The bracket on the right-hand side of Eqn. (Ice_12), $h - h^{\mathrm{Ih}} - S_{\mathrm{A}} h_{S_{\mathrm{A}}}$, if evaluated at the freezing temperature $t_{\mathrm{freezing}}\left(S_{\mathrm{A}}, p\right)$, is the latent heat of melting (that is, the isobaric melting enthalpy) of ice into seawater. Note that at $p = 0$ dbar $\hat{h}_{S_{\mathrm{A}}}$ is zero while $h_{S_{\mathrm{A}}}$ is nonzero.

The derivation of the isobaric melting enthalpy in Feistel *et al*. (2010) and IOC *et al*. (2010) considered the seawater and ice to be in thermodynamic equilibrium during a slow processes in which heat was supplied to melt the ice while maintaining a state of thermodynamic equilibrium during which the temperature of the combined system changed only because the freezing temperature is a function of the seawater salinity. During this reversible process the enthalpy of the combined system increased due to the heat externally applied. The latent heat of melting is defined to be (from Eqn. (3.34.6) of IOC *et al*. (2010))

$$L_{p}^{\mathrm{SI}}\left(S_{\mathrm{A}}, p\right) \;=\; h\left(S_{\mathrm{A}}, t_{\mathrm{freezing}}, p\right) - h^{\mathrm{Ih}}\left(t_{\mathrm{freezing}}, p\right) - S_{\mathrm{A}} h_{S_{\mathrm{A}}}\left(S_{\mathrm{A}}, t_{\mathrm{freezing}}, p\right). \qquad \text{(Ice\_14)}$$

In contrast, the present derivation (that is, Eqns. (Ice_12) and (Ice_13)) applies to the common situation when the seawater is warmer than the ice which is melting into it, so that the two phases *are not in thermodynamic equilibrium* with each other during the *irreversible* melting process. That is, the seawater temperature may be larger than its freezing temperature and the ice temperature may or may not be less than its freezing temperature. The guiding thermodynamic principle is that there is no change in the enthalpy of the combined seawater and ice system during the irreversible melting process, since this process occurs adiabatically at constant pressure.

When freezing (as opposed to melting) is considered, the Second Law of Thermodynamics implies that spontaneous freezing cannot occur except when the seawater is at the freezing temperature, and there must be some incremental external change (for example a decrease in pressure in the case of frazil formation, or a loss of heat from the system) in order to induce the freezing.

Taking the limit of melting a small amount of ice into a seawater parcel so that the changes in the seawater temperature and salinity are small, we find from Eqn. (Ice_12) that the ratio of the changes in *in situ* temperature and Absolute Salinity are given by (using Eqn. (Ice_8) for the salinity increment)

$$\begin{aligned} S_{\mathrm{A}} \left.\frac{\delta t}{\delta S_{\mathrm{A}}}\right|_{\text{melting at constant p}} &= \frac{h - h^{\mathrm{Ih}} - S_{\mathrm{A}}\, h_{S_{\mathrm{A}}}}{c_p} \\ &= \frac{h\left(S_{\mathrm{A}}, t, p\right) - h^{\mathrm{Ih}}\left(t^{\mathrm{Ih}}, p\right) - S_{\mathrm{A}}\, h_{S_{\mathrm{A}}}\left(S_{\mathrm{A}}, t, p\right)}{c_p\left(S_{\mathrm{A}}, t, p\right)} \end{aligned} . \qquad \text{(Ice\_15)}$$

while the corresponding ratio of the changes in Conservative Temperature and Absolute Salinity are (from Eqn. (Ice_13))

$$\begin{aligned} S_{\mathrm{A}} \left.\frac{\delta\Theta}{\delta S_{\mathrm{A}}}\right|_{\text{melting at constant p}} &= \frac{h - h^{\mathrm{Ih}} - S_{\mathrm{A}}\, \hat{h}_{S_{\mathrm{A}}}}{\hat{h}_{\Theta}} \\ &= \frac{\hat{h}\left(S_{\mathrm{A}}, \Theta, p\right) - h^{\mathrm{Ih}}\left(t^{\mathrm{Ih}}, p\right) - S_{\mathrm{A}}\, \hat{h}_{S_{\mathrm{A}}}\left(S_{\mathrm{A}}, \Theta, p\right)}{\hat{h}_{\Theta}\left(S_{\mathrm{A}}, \Theta, p\right)}, \end{aligned} \qquad \textbf{(Ice\_16)}$$

where the second lines of these equations have been included to be very clear about how these quantities are evaluated. At $p = 0\ \text{dbar}$ these equations become

$$\begin{aligned} S_{\text{A}} \frac{\delta\theta}{\delta S_{\text{A}}}\bigg|_{\text{melting at } p=0} &= \frac{h_0 - h_0^{\text{Ih}} - S_{\text{A}}\, h_{S_{\text{A}}}\big(S_{\text{A}},\theta,0\big)}{c_p\big(S_{\text{A}},\theta,0\big)} \\ &= \frac{h\big(S_{\text{A}},\theta,0\big) - h^{\text{Ih}}\big(\theta^{\text{Ih}},0\big) - S_{\text{A}}\, h_{S_{\text{A}}}\big(S_{\text{A}},\theta,0\big)}{c_p\big(S_{\text{A}},\theta,0\big)}, \end{aligned} \qquad \text{(Ice\_17)}$$

and

$$S_{\text{A}} \frac{\delta\Theta}{\delta S_{\text{A}}}\bigg|_{\text{melting at } p\,=\,0} = \frac{h_0 - h_0^{\text{Ih}}}{c_p^0} = \Theta - \frac{h^{\text{Ih}}\big(\theta^{\text{Ih}},0\big)}{c_p^0}, \qquad \text{(Ice\_18)}$$

where the potential temperatures of seawater θ and of ice θ^{Ih} are both referenced to $p = 0\ \text{dbar}$. Note that the potential enthalpy of seawater referenced to $p = 0\ \text{dbar}$, $h_0 = h\big(S_{\text{A}},\theta,0\big) = \hat{h}\big(S_{\text{A}},\Theta,0\big)$ is simply c_p^0 times Conservative Temperature Θ where c_p^0 is the constant "specific heat" $c_p^0 \equiv 3991.867\,957\,119\,63\ \text{J kg}^{-1}\,\text{K}^{-1}$.

The use of Conservative Temperature rather than potential temperature means that the slope of the melting process on the $S_{\text{A}} - \Theta$ diagram, $\delta\Theta/\delta S_{\text{A}}$, involves a simpler expression, especially when the melting occurs at the sea surface at $p = 0\ \text{dbar}$, Eqn. (Ice_18), where (i) $\hat{h}_{S_{\text{A}}}\big(S_{\text{A}},\Theta,0\big)$ is zero, and (ii), the relevant "specific heat capacity" of seawater, $\hat{h}_{\Theta} = c_p^0\,\big(T_0 + t\big)/\big(T_0 + \theta\big)$, reduces to the constant c_p^0, so that the specific enthalpy of seawater is simply c_p^0 multiplied by the Conservative Temperature Θ. Note that the numerator of the middle expression of Eqn. (Ice_18) is simply the difference between the potential enthalpies of seawater and of ice.

Note that the right-hand side of Eqn. (Ice_18) is independent of the Absolute Salinity of the seawater into which the ice melts.

We first illustrate these equations for the ratio of the changes of Conservative Temperature to those of Absolute Salinity by considering the melting to occur very close to thermodynamic equilibrium conditions. If both the seawater and the ice were exactly at the freezing temperature at the given values of Absolute Salinity and pressure, then no melting or freezing would occur. In Fig. Ice_5 we consider the limit as the temperatures of both the seawater and the ice approach the freezing temperature. The ratio $\delta\Theta/\delta S_{\text{A}}\big|_{\text{equilibrium}}$ from Eqn. (Ice_16) is shown in Fig. Ice_5(a) with the seawater enthalpy evaluated at the freezing Conservative Temperature and with the ice enthalpy evaluated at the *in situ* freezing temperature, at each value of pressure and Absolute Salinity. This ratio is proportional to the reciprocal of Absolute Salinity, so it is more informative to simply multiply $\delta\Theta/\delta S_{\text{A}}\big|_{\text{equilibrium}}$ by Absolute Salinity S_{A} and this is shown in Fig. Ice_5(b). It is seen that the melting of a given mass of ice into seawater near equilibrium conditions requires between approximately 81 and 83 times as much heat as would be required to raise the temperature of the same mass of seawater by $1\,^{\circ}\text{C}$.

The corresponding result for the ratio of the changes of *in situ* temperature and Absolute Salinity near equilibrium conditions $S_{\text{A}}\,\delta t/\delta S_{\text{A}}\big|_{\text{equilibrium}} = L_p^{\text{SI}}\big(S_{\text{A}},p\big)/c_p\big(S_{\text{A}},t_{\text{freezing}},p\big)$ can be calculated from Eqn. (Ice_15), and the difference between $S_{\text{A}}\,\delta t/\delta S_{\text{A}}\big|_{\text{equilibrium}}$ and $S_{\text{A}}\,\delta\Theta/\delta S_{\text{A}}\big|_{\text{equilibrium}}$ is shown in Fig. Ice_5(c). The largest contributor to this difference between Eqns.

(Ice_15) and (Ice_16) is due to the dependence of the specific heat capacity $c_p\left(S_{\mathrm{A}}, t_{\text{freezing}}, p\right)$ on (i) Absolute Salinity, involving a 6.8% variation over this full range of salinity, and (ii) on pressure, involving a change of 2.2% between $0\ \mathrm{dbar}$ to $3000\ \mathrm{dbar}$.

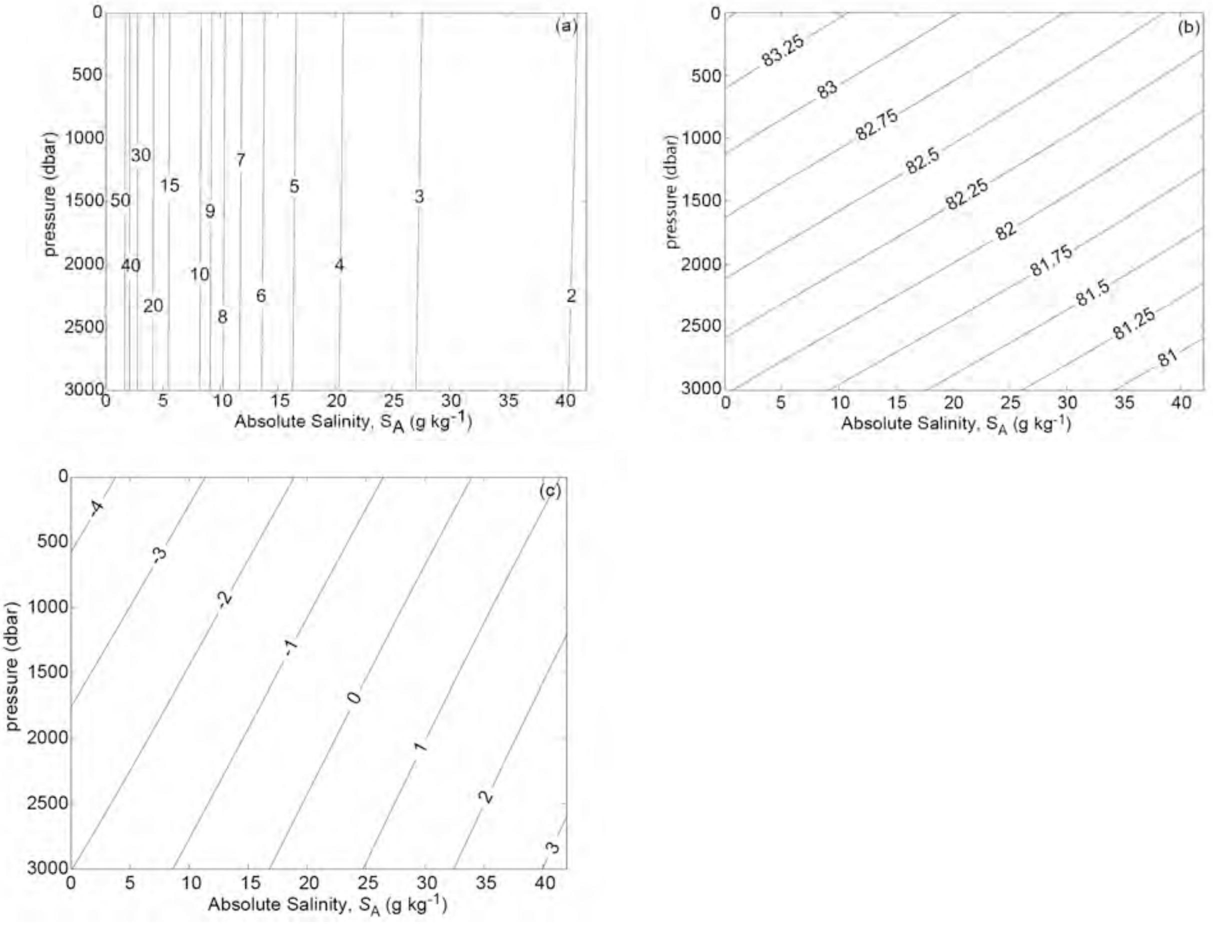
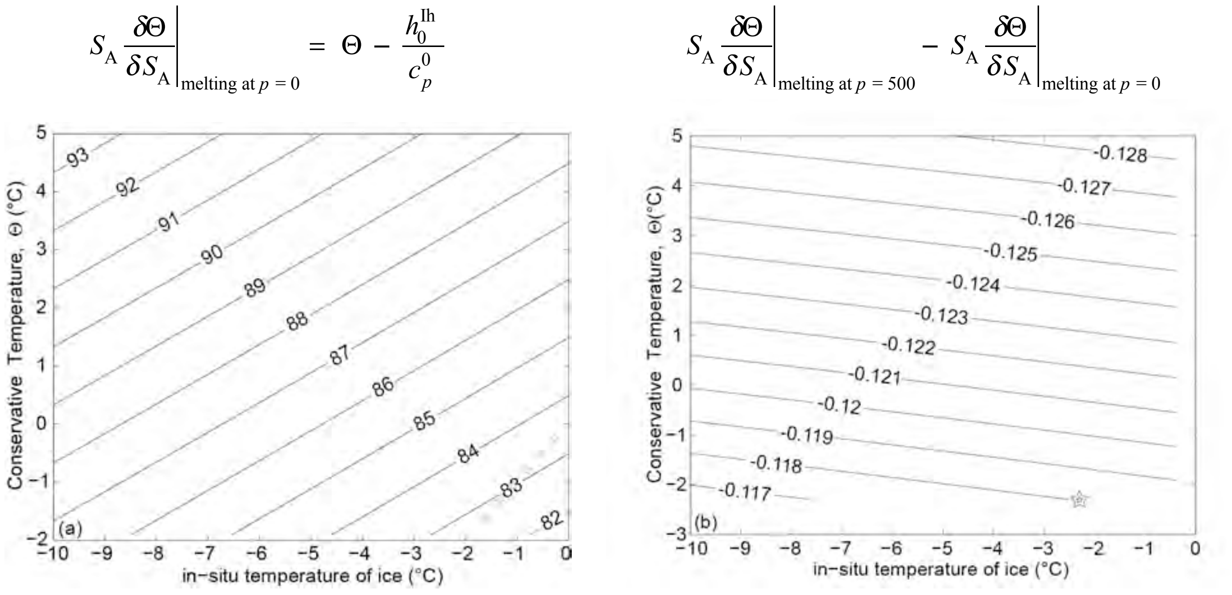


Figure Ice_5. (a) The ratio of the change of Conservative Temperature to that of Absolute Salinity when the melting occurs *very near thermodynamic equilibrium* conditions, $\delta\Theta/\delta S_{\mathrm{A}}\big|_{\text{equilibrium}}$, from Eqn. (Ice_16) with the seawater enthalpy evaluated at the freezing Conservative Temperature and with the ice enthalpy evaluated at the *in situ* freezing temperature, at each value of pressure and Absolute Salinity. The values contoured have units of $\mathrm{K}\left(\mathrm{g\ kg}^{-1}\right)^{-1}$.

(b) This panel is simply Absolute Salinity S_{A} times the values of panel (a), that is, it is the right-hand side of Eqn. (Ice_16), evaluated at equilibrium conditions.

(c) The right-hand side of Eqn. (Ice_15) minus the right-hand side of Eqn. (Ice_16), both evaluated at equilibrium conditions, illustrating the difference between using *in situ* temperature versus Conservative Temperature. The quantities contoured in panels (b) and (c) have units of temperature, K.

Equation (Ice_16) for $S_{\mathrm{A}}\,\delta\Theta/\delta S_{\mathrm{A}}\big|_{\text{melting at constant p}}$ is now illustrated when the seawater and the ice Ih phases are not at the same temperature and *they are not in thermodynamic equilibrium* at the freezing temperature. We begin by considering melting of ice Ih at the sea surface, specifically at $p = 0\ \mathrm{dbar}$, when Eqn. (Ice_16) reduces to Eqn. (Ice_18), and this equation is illustrated in Fig. Ice_6(a) which applies at all values of Absolute Salinity. The contoured values of Fig. Ice_6(a), $\left(h_0 - h_0^{\mathrm{Ih}}\right)/c_p^0 = \Theta - \tilde{h}^{\mathrm{Ih}}\left(\theta^{\mathrm{Ih}}\right)/c_p^0$, increase as 1.0 times changes in Θ and decrease approximately as $c_p^{\mathrm{Ih}} / c_p^0 \approx 0.52$ times changes in the temperature of the ice.



$$S_{\mathrm{A}} \frac{\delta\Theta}{\delta S_{\mathrm{A}}}\bigg|_{\text{melting at } p\,=\,0} = \Theta - \frac{h_0^{\mathrm{Ih}}}{c_p^0}$$

$$S_{\mathrm{A}} \frac{\delta\Theta}{\delta S_{\mathrm{A}}}\bigg|_{\text{melting at } p\,=\,500} - S_{\mathrm{A}} \frac{\delta\Theta}{\delta S_{\mathrm{A}}}\bigg|_{\text{melting at } p\,=\,0}$$

Figure Ice_6. (a) Contours of Eqn. (Ice_18), $S_{\mathrm{A}}\,\delta\Theta/\delta S_{\mathrm{A}}\big|_{\text{melting at } p\,=\,0} = \left(h_0 - h_0^{\mathrm{Ih}}\right)/c_p^0 = \Theta - \tilde{h}^{\mathrm{Ih}}\left(\theta^{\mathrm{Ih}}\right)/c_p^0$, for the melting of ice Ih into seawater at $p = 0\,\mathrm{dbar}$. The six stars are at the freezing temperatures (t and Θ) for Absolute Salinity values starting at $5\,\mathrm{g\,kg^{-1}}$ with increments of $5\,\mathrm{g\,kg^{-1}}$ up to $30\,\mathrm{g\,kg^{-1}}$. (b) Difference between contours of Eqn. (16) at $p = 500\,\mathrm{dbar}$, $S_{\mathrm{A}}\,\delta\Theta/\delta S_{\mathrm{A}}\big|_{\text{melting at } p\,=\,500}$, and the corresponding ratio of panel (a) (where the pressure was $0\,\mathrm{dbar}$) at $S_{\mathrm{A}}^{\mathrm{i}} = S_{\mathrm{SO}} = 35.16504\ \mathrm{g\ kg^{-1}}$. The double-starred point is at the freezing temperatures (t and Θ) at $p = 500\,\mathrm{dbar}$ and $S_{\mathrm{A}}^{\mathrm{i}} = S_{\mathrm{SO}} = 35.16504\ \mathrm{g\ kg^{-1}}$.

Taking the potential enthalpy of ice Ih to be a conservative variable

By comparing panels (a) and (b) of Fig. Ice_6 we are able to deduce a very important approximation that will prove invaluable to coupled ocean/ice modelling. Panel (b) shows the error in assuming that it is the potential enthalpy of ice that is conserved when ice melts into seawater, rather than taking the enthalpy of ice to be conserved, which is the correct thing to do. At a pressure of 500 dbar the assumption that the sum of the *potential* enthalpies of ice and seawater are conserved leads to an error of 0.15% in the change in Conservative Temperature of the seawater as a result of melting. Most of this error is due to the assumption regarding ice, not seawater, since the error involved with assuming that the Conservative Temperature of seawater is totally conservative reaches a maximum of 0.15% only at a much larger pressure of 4000 dbar (Graham and McDougall, 2013).

The ratio of Eqns. (Ice_16) to (Ice_18) is

$$\frac{\left.\dfrac{\delta\Theta}{\delta S_{\mathrm{A}}}\right|_{\text{melting at constant p}}}{\left.\dfrac{\delta\Theta}{\delta S_{\mathrm{A}}}\right|_{\text{melting at } p\,=\,0}} = \frac{\left(T_0+\theta\right)}{\left(T_0+t\right)}\left[\frac{h - h^{\mathrm{Ih}} - S_{\mathrm{A}}\,\hat{h}_{S_{\mathrm{A}}}}{h_0 - h_0^{\mathrm{Ih}}}\right] \qquad \text{(Ice\_19)}$$

$$= 1 + \frac{\left(\theta - t\right)}{\left(T_0+t\right)} + \frac{\left(T_0+\theta\right)}{\left(T_0+t\right)}\frac{\left[\left(h-h_0\right)-\left(h^{\mathrm{Ih}}-h_0^{\mathrm{Ih}}\right)-S_{\mathrm{A}}\,\hat{h}_{S_{\mathrm{A}}}\right]}{\left(h_0 - h_0^{\mathrm{Ih}}\right)},$$

and the combination of enthalpy differences in the numerator of the last term can be expressed as

$$\left[h - h_0 - \left(h^{\mathrm{Ih}} - h_0^{\mathrm{Ih}}\right) - S_{\mathrm{A}}\,\hat{h}_{S_{\mathrm{A}}}\right] =$$

$$\int_{P_0}^{P}\left[\hat{v}\left(S_{\mathrm{A}},\Theta,p'\right) - \tilde{v}^{\mathrm{Ih}}\left(\theta^{\mathrm{Ih}},p'\right)\right]dP' - S_{\mathrm{A}}\int_{P_0}^{P}\hat{v}_{S_{\mathrm{A}}}\left(S_{\mathrm{A}},\Theta,p'\right)dP'. \qquad \text{(Ice\_20)}$$

The last term here is small, showing that the dominant contribution is simply the pressure integral of the difference in the specific volumes of seawater and of ice.

In Eqn. (Ice_19) the second term on the right-hand side, $\left(\theta - t\right)/\left(T_0+t\right)$, is small compared with the third, so that the non-unity nature of Eqn. (Ice_19) can be understood as being due to this third term, evaluated with the aid of Eqn. (Ice_20), and this evaluation agrees with the plot of Fig. Ice_6(b).

We will take advantage of the smallness of panel (b) versus panel (a) of Fig. Ice_6, or equivalently, the fact that Eqn. (Ice_19) is quite close to unity, to treat the potential enthalpy of ice as conserved during not only advection but also during melting and freezing events. This will greatly reduce the complexity of coupled ocean/ice numerical models. This approximation brings the same simplicity to ice as the introduction of Conservative Temperature has brought to physical oceanography, in that the only variables that now need to be considered when discussing "heat" budgets of seawater and of ice are the potential enthalpies of seawater and of ice.

An illustration from the Amery Ice Shelf

Figure Ice_7 shows oceanographic data obtained under the Amery Ice Shelf that illustrates the ratio of the changes in Absolute Salinity and Conservative Temperature, as given by Eqn. (Ice_16), when melting of ice occurs. The vertical profile named AM06 begins under the ice at a pressure of 546 dbar and the uppermost 175 of the vertical profile is shown. The data in the uppermost 50-100 dbar is closely aligned with the ratio given by Eqn. (Ice_16) (as shown by the dashed line) evaluated at this pressure and with the ice temperature being the freezing temperature at this salinity and pressure. Two freezing lines are shown in Fig. Ice_7(b), for pressures of 0 dbar and 578 dbar.

Any observations cooler than the freezing temperature appropriate to 0 dbar is evidence of the influence of melting of ice or of heat lost by conduction through the ice. AM06 is located on the eastern side of the ice shelf in an area that is melting, as can be inferred by the presence of ocean water at AM06 that is well above the *in situ* freezing temperature at the base of the ice shelf. This water is thought to be flowing in a primarily southwards direction from the open ocean as it enters the under-ice cavity. The other CTD profile was taken from borehole AM05, located on the western side of the ice shelf in an area that is refreezing (as is drawn in panel (a)) and represents flow that has likely come from deeper in the sub-ice-shelf cavity, than at AM06 (Post *et al*., 2013) and hence has been in contact with the ice for longer. The upper 50m or so of this cast is at the freezing temperature of seawater at this pressure. For both casts the data near the upper part of the water column has the ratio of the changes of S_A and Θ in close agreement to the ratio given by Eqn. (Ice_16), the ratio predicted from melting ice into seawater (dashed lines). The ice temperature that is needed to calculate this $S_\mathrm{A} - \Theta$ ratio for each location has been taken to be the *in situ* freezing temperature of ice in contact with the seawater at the pressure at the base of the ice shelf. Moreover, on this figure the uppermost 100m of data of the AM05 data is approximately related to that of the AM06 data through the $S_\mathrm{A} - \Theta$ ratio of Eqn. (Ice_16). This would be consistent with the notion that the same fluid is proceeding from AM06 to AM05 without being exposed to significant heat loss Q to the ice (see panel (a)). The vertical profiles shown in panel (b) are the average of several vertical profiles taken over the course of two days, and the two locations were drilled within two weeks of each other.

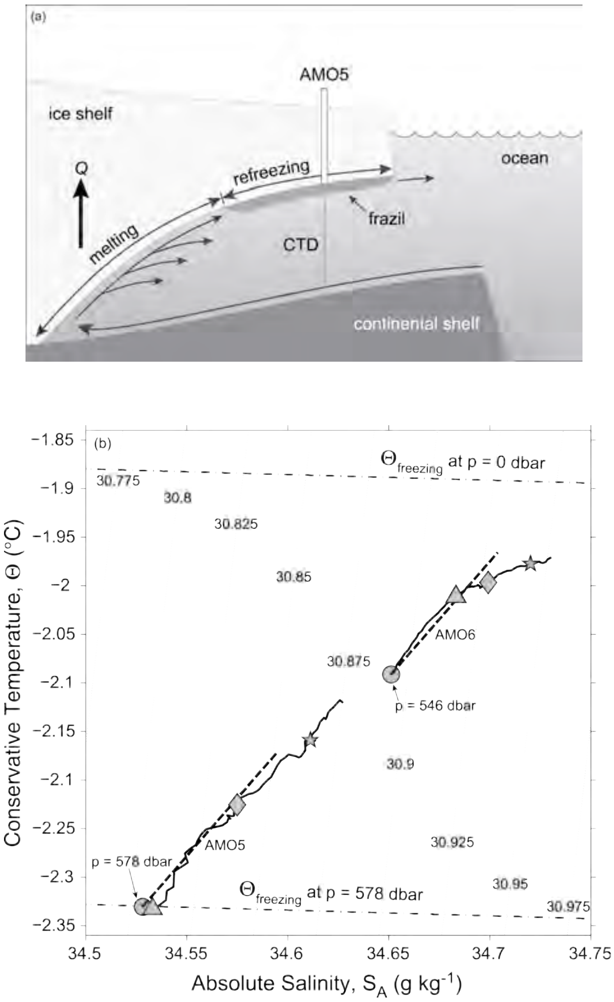


Figure Ice_7. (a) Sketch of the flow under an ice shelf. An inflow of relatively warm water from the open ocean provides heat to melt the ice shelf. Buoyant freshwater that is released during the melting process rises along the underside of the ice shelf and can become locally supercooled at a shallower depth, leading to the formation of frazil and basal accretion of marine ice.

(b) The top 175m of two CTD profiles taken below the Amery Ice Shelf in East Antarctica at a melt site and at a refreeze site are shown. The warmer and saltier of the two casts is AM06 (see Fig 1 of Galton-Fenzi *et al.* (2012)) starting at a pressure of 546 dbar. The large round dot is ocean data very near the ice at 546 dbar, the triangle is 50 dbar deeper, the diamond 100 dbar deeper and the star is 150 dbar below the bottom of the ice shelf at this location, indicated by the circle. The other vertical cast, AM05, is typical of re-freezing locations. The uppermost 50 dbar of this cast is all at the freezing temperature at this pressure.

Melting of sea ice into seawater

Sea ice contains a certain mass fraction of brine trapped inside the ice matrix. Sea ice is produced when the surface of the ocean is cooled rapidly by very cool air. The ice crystals then form so fast that some of the seawater is trapped in small "pockets" inside the matrix of ice crystals.

We can quantify the melting of sea ice into seawater by conserving the same three quantities, namely (i) mass, (ii) salt, and (iii) enthalpy, leading to

(see McDougall, T. J., P. M. Barker, R. Feistel and B. K. Galton-Fenzi, 2014: Melting of ice and sea ice into seawater, and frazil ice formation. *Journal of Physical Oceanography*, **44**, 1751-1775. for details)

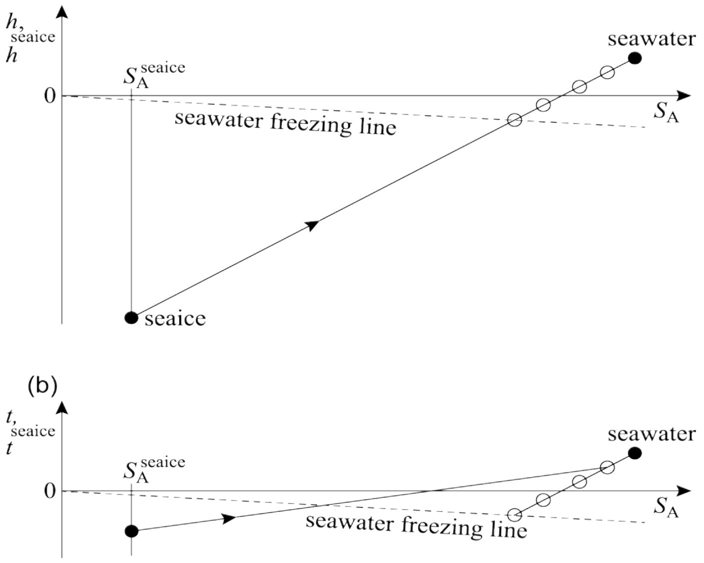
$$\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right) = -\frac{m_{\mathrm{seaice}}}{m_{\mathrm{SW}}^{\mathrm{f}}}\left(S_{\mathrm{A}}^{\mathrm{i}} - S_{\mathrm{A}}^{\mathrm{seaice}}\right) = -w^{\mathrm{seaice}}\left(S_{\mathrm{A}}^{\mathrm{i}} - S_{\mathrm{A}}^{\mathrm{seaice}}\right)$$

$$\begin{aligned}\left(h^{\mathrm{f}} - h^{\mathrm{i}}\right) &= -w^{\mathrm{seaice}}\left(h^{\mathrm{i}} - h^{\mathrm{Ih}}\right) + w^{\mathrm{seaice}}\frac{m_{\mathrm{brine}}}{m_{\mathrm{seaice}}}\left(h^{\mathrm{brine}} - h^{\mathrm{Ih}}\right)\\ &= -w^{\mathrm{seaice}}\left(h^{\mathrm{i}} - h^{\mathrm{seaice}}\right).\end{aligned}$$

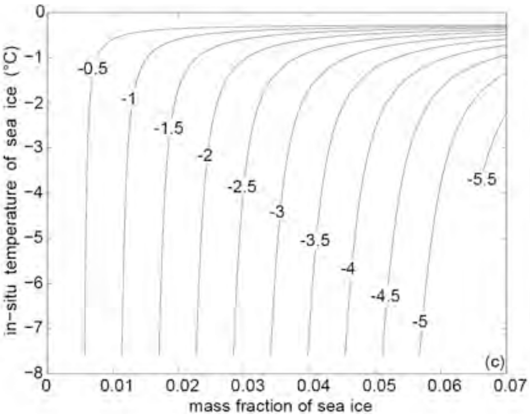
where the specific enthalpy of the composite material "seaice" is defined as the mass-weighted sum of the specific enthalpies of the two phases,

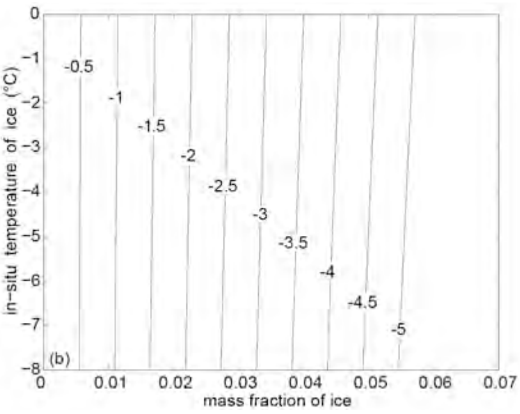
$$h^{\mathrm{seaice}} = \left(m_{\mathrm{Ih}}/m_{\mathrm{seaice}}\right)h^{\mathrm{Ih}} + \left(m_{\mathrm{brine}}/m_{\mathrm{seaice}}\right)h^{\mathrm{brine}},$$

and the Absolute Salinity – enthalpy mixing diagram looks like



For sea ice melting into seawater at $p = 0$ dbar with initial properties $S_{\mathrm{A}}^{\mathrm{i}} = S_{\mathrm{SO}} = 35.16504\ \mathrm{g\ kg}^{-1}$, $\Theta^{\mathrm{i}} = 4°\mathrm{C}$, and with the sea ice salinity taken to be $S_{\mathrm{A}}^{\mathrm{seaice}} = 5\ \mathrm{g kg}^{-1}$, the change in Conservative Temperature is shown in the left-hand figure below. The right-hand figure shows the corresponding plot when $S_{\mathrm{A}}^{\mathrm{seaice}} = 0\ \mathrm{g kg}^{-1}$.





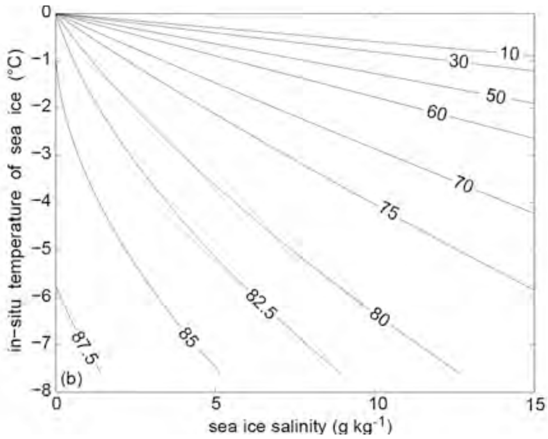
What is the ratio of the changes in Conservative Temperature and Absolute Salinity of seawater when a vanishingly small mass of sea ice melts into it? To find this ratio we again linearize the above expressions for a vanishingly small mass fraction of sea ice that melts, giving

$$\left(S_{\mathrm{A}} - S_{\mathrm{A}}^{\mathrm{seaice}}\right)\frac{\delta\Theta}{\delta S_{\mathrm{A}}}\bigg|_{\text{melting at constant p}} =$$

$$\frac{\left(1 - \dfrac{S_{\mathrm{A}}^{\mathrm{seaice}}}{S_{\mathrm{A}}^{\mathrm{brine}}}\right)\left(h - h^{\mathrm{Ih}} - S_{\mathrm{A}}\hat{h}_{S_{\mathrm{A}}}\right) + \dfrac{S_{\mathrm{A}}^{\mathrm{seaice}}}{S_{\mathrm{A}}^{\mathrm{brine}}}\left(h - h^{\mathrm{brine}} - \left[S_{\mathrm{A}} - S_{\mathrm{A}}^{\mathrm{brine}}\right]\hat{h}_{S_{\mathrm{A}}}\right)}{\hat{h}_{\Theta}}$$

and this is illustrated below at $p = 0$ dbar and at $S_{\mathrm{A}}^{\mathrm{i}} = S_{\mathrm{SO}} = 35.16504\ \mathrm{g\ kg}^{-1}$ and $\Theta^{\mathrm{i}} = 1°\mathrm{C}$.

$$\left(S_{\mathrm{A}} - S_{\mathrm{A}}^{\mathrm{seaice}}\right)\frac{\delta\Theta}{\delta S_{\mathrm{A}}}\bigg|_{\text{melting at } p\,=\,0}$$



Frazil ice formation

When seawater at the freezing temperature undergoes upwards vertical motion so that its pressure decreases, frazil forms, primarily due to the increase in the freezing temperature as a result of the reduction in pressure. When this mixture of seawater and frazil continues to rise to lower pressures (assisted by the buoyancy provided by the presence of the ice), the frazil crystals will experience a larger change in *in situ* temperature than does the seawater, simply because the adiabatic lapse rate of ice is much larger (ten times as large) than that of seawater (as we have found above).

We will here consider this situation under the assumption that the frazil and the seawater moves together, so ignoring the tendency of the frazil to rise faster than the seawater, driven by the buoyancy of the individual ice crystals. We further assume that the uplift rate is sufficiently small that the *in situ* temperature of the ice and the seawater are the same at each pressure, this temperature being the freezing temperature. Under these conditions no entropy is produced during the freezing process, i.e., this freezing process is reversible and can be reversed by increasing the pressure, leading to the related reversible ice melt.

We will study the thermodynamics of this process of adiabatic uplift of a seawater-ice mixture via a thought process composed of two separate steps (Fig. Ice_13). First we imagine the mixture of pre-existing ice and seawater to undergo a reduction in pressure *but without any exchange* of heat, water or salt between the two phases. That is, during this first part of the process the mass of ice and the mass of seawater remain constant, and the change in the enthalpy of the ice and the change in the enthalpy of the seawater are only due to the pressure change. During this adiabatic process an (infinitesimal) contrast in *in situ* temperature will develop between the ice phase and the seawater phase because the adiabatic lapse rate of ice is much larger (by about an order of magnitude) than that of seawater.

During the second part of our thought experiment the ice and seawater phases will be allowed to equilibrate their temperatures and further frazil ice will form so that the temperature of both the ice and seawater phases and the final Absolute Salinity of the seawater phase will be consistent with the freezing temperature at this pressure. This part of our thought experiment occurs at constant pressure and so, from the First Law of Thermodynamics, we know that enthalpy is conserved.

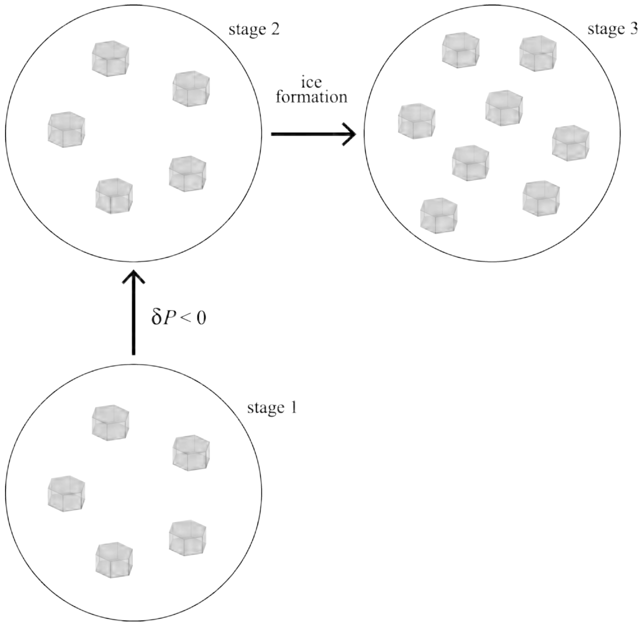


Figure 13. Sketch showing the two-step thought process involved with quantifying the formation of frazil ice Ih by the adiabatic uplift of a seawater parcel which may contain pre-existing frazil ice. The step from stage 1 to stage 2 is undertaken without any exchange of heat or mass between the seawater and ice Ih phases. While the *in situ* temperatures of the seawater and ice phases are assumed to be identical at stage 1, at stage 2 they are unequal because the adiabatic lapse rate of ice Ih is much larger than that of seawater. The step from stage 2 to stage 3 is undertaken at constant pressure. In this step further ice forms (as shown by the increase in number of the frazil ice crystals) and at the end of this step, the seawater and ice phases have the same *in situ* temperature, namely the freezing temperature appropriate to (i) that pressure and (ii) the final value of seawater salinity.

Let the mass fraction of ice be w^{Ih}; the mass fraction of seawater in the ice-seawater mixture is then $\left(1 - w^{\mathrm{Ih}}\right)$. The total enthalpy per unit mass of the ice-seawater mixture at stage 1 of Fig. 13 is the weighted sum of the specific enthalpies of the two phases, namely

$$\left(1 - w_1^{\mathrm{Ih}}\right)\hat{h}\left(S_{\mathrm{A}1},\Theta_1,p_1\right) \;+\; w_1^{\mathrm{Ih}}\tilde{h}^{\mathrm{Ih}}\left(\theta_1^{\mathrm{Ih}},p_1\right), \qquad \text{(Ice\_34)}$$

where we have chosen to write the specific enthalpy of ice in the functional form $\tilde{h}^{\mathrm{Ih}}\left(\theta^{\mathrm{Ih}},p\right)$ where the temperature variable is the potential temperature of ice θ^{Ih} with reference pressure 0 dbar (θ^{Ih} is not to be confused with the potential temperature of seawater θ, since these two potential temperatures are not equal).

In going from stage 1 to stage 2, both the seawater and ice phases undergo an adiabatic change of pressure δP which changes their specific enthalpies by $v\,\delta P$ and $v^{\mathrm{Ih}}\,\delta P$ respectively (here v and v^{Ih} are the specific volumes). Hence at stage 2 the total enthalpy per unit mass of the ice-seawater mixture is (noting that $w_2^{\mathrm{Ih}} = w_1^{\mathrm{Ih}}$ and that at leading order in the perturbation quantities, it is immaterial whether v and v^{Ih} are evaluated at the properties of stage 1 or those of stage 2)

$$\left(1 - w_1^{\rm Ih}\right)\left[\hat{h}\left(S_{\rm A1},\Theta_1,p_1\right) + v\,\delta P\right] \;+\; w_1^{\rm Ih}\left[\tilde{h}^{\rm Ih}\left(\theta_1^{\rm Ih},p_1\right) + v^{\rm Ih}\,\delta P\right]. \qquad \text{(Ice\_35)}$$

In going from stage 2 to stage 3, the total enthalpy of the mixture is conserved. Hence we equate the total enthalpies at these two stages, giving

$$\begin{aligned}\left(1 - w_1^{\rm Ih}\right)\left[\hat{h}\left(S_{\rm A1},\Theta_1,p_1\right) + v\,\delta P\right] \;+\; w_1^{\rm Ih}\left[\tilde{h}^{\rm Ih}\left(\theta_1^{\rm Ih},p_1\right) + v^{\rm Ih}\,\delta P\right] \;=& \\ \left(1 - w_3^{\rm Ih}\right)\hat{h}\left(S_{\rm A3},\Theta_3,p_3\right) \;+\; w_3^{\rm Ih}\tilde{h}^{\rm Ih}\left(\theta_3^{\rm Ih},p_3\right).&\end{aligned} \qquad \text{(Ice\_36)}$$

For an externally-imposed change in pressure this equation may be regarded as giving the amount of new ice formed $w_3^{\rm Ih} - w_1^{\rm Ih}$ due to the adiabatic uplifting of the ice-seawater mixture. The other important constraint that we know is that the ice-seawater mixture is at the freezing temperature at both stages 1 and 3. This turns out to enough information to solve the problem.

The enthalpies $\hat{h}\left(S_{\rm A3},\Theta_3,p_3\right)$ and $\tilde{h}^{\rm Ih}\left(\theta_3^{\rm Ih},p_3\right)$ on the right-hand side of Eq. (Ice_36) are now expanded in a Taylor series about the values at stage 1, keeping the leading order terms. The pressure derivatives of these enthalpies, being the specific volumes of seawater and of ice, give terms that cancel with the corresponding terms on the left-hand side of the equation to leading order. The remaining leading-order terms are

$$\left(h - h^{\rm Ih}\right)\delta w^{\rm Ih} \;-\; \left(1 - w^{\rm Ih}\right)\left(\hat{h}_{S_{\rm A}}\,\delta S_{\rm A} + \hat{h}_{\Theta}\,\delta\Theta\right) \;-\; w^{\rm Ih}\tilde{h}^{\rm Ih}_{\theta^{\rm Ih}}\,\delta\theta^{\rm Ih} \;=\; 0 \qquad \text{(Ice\_37)}$$

where $\delta w^{\rm Ih} = w_3^{\rm Ih} - w_1^{\rm Ih}$. Since the salt always resides in the seawater phase, the product $\left(1 - w^{\rm Ih}\right)S_{\rm A}$ is constant so that

$$S_{\rm A}\,\delta w^{\rm Ih} \;=\; \left(1 - w^{\rm Ih}\right)\delta S_{\rm A}\,, \qquad \text{(Ice\_38)}$$

which reduces Eqn. (Ice_37) to

$$\boxed{\left(h - h^{\rm Ih} - S_{\rm A}\hat{h}_{S_{\rm A}}\right)\delta S_{\rm A} \;-\; S_{\rm A}\hat{h}_{\Theta}\,\delta\Theta \;-\; S_{\rm A}\frac{w^{\rm Ih}}{\left(1 - w^{\rm Ih}\right)}\tilde{h}^{\rm Ih}_{\theta^{\rm Ih}}\,\delta\theta^{\rm Ih} \;=\; 0}. \qquad \text{(Ice\_39)}$$

One of our key results for frazil ice is already apparent from this equation, namely that as the mass fraction of frazil ice $w^{\rm Ih}$ tends to zero, Eqn. (Ice_39) tends to our existing result Eqn. (Ice_16) for the ratio $\delta\Theta/\delta S_{\rm A}$ for the melting of ice Ih into seawater, repeated here,

$$\begin{aligned} \left. S_{\rm A}\frac{\delta\Theta}{\delta S_{\rm A}}\right|_{\text{melting at constant p}} &= \frac{h - h^{\rm Ih} - S_{\rm A}\hat{h}_{S_{\rm A}}}{\hat{h}_{\Theta}} \\ &= \frac{\hat{h}\left(S_{\rm A},\Theta,p\right) - h^{\rm Ih}\left(t^{\rm Ih},p\right) - S_{\rm A}\hat{h}_{S_{\rm A}}\left(S_{\rm A},\Theta,p\right)}{\hat{h}_{\Theta}\left(S_{\rm A},\Theta,p\right)}. \end{aligned} \qquad \textbf{(Ice\_16)}$$

However, there is an important difference as well, namely that the present frazil ice relation Eqn. (Ice_39) for the ratio $\delta\Theta/\delta S_{\rm A}$ is actually simpler (or more restrictive) than Eqn. (Ice_16) because the temperatures of both the ice and seawater components are constrained to be at the freezing temperature; the ice temperature cannot be lower that the freezing temperature nor can the Conservative Temperature of the seawater exceed its freezing temperature. Hence in the limit as the mass fraction of frazil ice $w^{\rm Ih}$ tends to zero, as the pressure of a seawater-frazil mixture is changed, the ratio $\delta\Theta/\delta S_{\rm A}$ is illustrated by the *equilibrium* situation of our existing Figures Ice_5(a) and (b). We will return to this; for now this paragraph is just a heads up on the comparison between what we have derived already (Eqn. (Ice_16)) and where we are headed with the equations for frazil.

Returning to the more general situation in which w^{Ih} is not vanishingly small, we need to evaluate $\tilde{h}^{\mathrm{Ih}}_{\theta^{\mathrm{Ih}}}\,\delta\theta^{\mathrm{Ih}}$ in terms of differentials of Absolute Salinity and pressure. The partial differential $\tilde{h}^{\mathrm{Ih}}_{\theta^{\mathrm{Ih}}}$ can be written as

$$\tilde{h}^{\mathrm{Ih}}_{\theta^{\mathrm{Ih}}} \;\equiv\; \left.\frac{\partial h^{\mathrm{Ih}}}{\partial \theta^{\mathrm{Ih}}}\right|_{p} \;=\; \left.\frac{\partial h^{\mathrm{Ih}}}{\partial t^{\mathrm{Ih}}}\right|_{p} \left.\frac{\partial t^{\mathrm{Ih}}}{\partial \theta^{\mathrm{Ih}}}\right|_{p} \;=\; c_p^{\mathrm{Ih}} \left.\frac{\partial t^{\mathrm{Ih}}}{\partial \theta^{\mathrm{Ih}}}\right|_{p} . \qquad \text{(Ice\_40)}$$

The *in situ* temperature of ice Ih can be expressed as a function of the potential temperature of ice Ih and pressure as $t^{\mathrm{Ih}} = t^{\mathrm{Ih}}\left(\theta^{\mathrm{Ih}}, p\right)$ so that the total differential of the *in situ* temperature of ice is

$$dt^{\mathrm{Ih}} \;=\; \left.\frac{\partial t^{\mathrm{Ih}}}{\partial \theta^{\mathrm{Ih}}}\right|_{p} d\theta^{\mathrm{Ih}} \;+\; \Gamma^{\mathrm{Ih}} dP\,. \qquad \text{(Ice\_41)}$$

This equation applies to any material differentials $dt^{\mathrm{Ih}}, d\theta^{\mathrm{Ih}}$ and dP, and in particular will apply to the differences between these properties at stage 1 and stage 3 of our thought process. Hence we can write

$$\delta t^{\mathrm{Ih}} \;=\; \left.\frac{\partial t^{\mathrm{Ih}}}{\partial \theta^{\mathrm{Ih}}}\right|_{p} \delta\theta^{\mathrm{Ih}} \;+\; \Gamma^{\mathrm{Ih}} \delta P\,. \qquad \text{(Ice\_42)}$$

But the ice at both stages 1 and 3 is at the freezing temperature $t_{\mathrm{freezing}} = t_{\mathrm{freezing}}\left(S_{\mathrm{A}}, p\right)$ so that δt^{Ih} can also be expressed as

$$\delta t^{\mathrm{Ih}} \;=\; \left.\frac{\partial t_{\mathrm{freezing}}}{\partial S_{\mathrm{A}}}\right|_{p} \delta S_{\mathrm{A}} \;+\; \left.\frac{\partial t_{\mathrm{freezing}}}{\partial P}\right|_{S_{\mathrm{A}}} \delta P\,, \qquad \text{(Ice\_43)}$$

and the partial derivatives here are known functions of the Gibbs functions of ice Ih and seawater.

Combining Eqns. (Ice_42) and (Ice_43) and using the result in Eqn. (Ice_40) gives our desired result for $\tilde{h}^{\mathrm{Ih}}_{\theta^{\mathrm{Ih}}}\,\delta\theta^{\mathrm{Ih}}$, namely

$$\tilde{h}^{\mathrm{Ih}}_{\theta^{\mathrm{Ih}}}\,\delta\theta^{\mathrm{Ih}} \;=\; c_p^{\mathrm{Ih}} \left[\left.\frac{\partial t_{\mathrm{freezing}}}{\partial S_{\mathrm{A}}}\right|_{p} \delta S_{\mathrm{A}} \;+\; \left(\left.\frac{\partial t_{\mathrm{freezing}}}{\partial P}\right|_{S_{\mathrm{A}}} \;-\; \Gamma^{\mathrm{Ih}} \right) \delta P \right]. \qquad \text{(Ice\_44)}$$

Substituting this equation into Eq. (39) gives a relationship between only $\delta S_{\mathrm{A}}, \delta\Theta$, and δP, namely

$$\begin{aligned} &\left(h - h^{\mathrm{Ih}} - S_{\mathrm{A}} \hat{h}_{S_{\mathrm{A}}} \;-\; S_{\mathrm{A}} \frac{w^{\mathrm{Ih}}}{\left(1 - w^{\mathrm{Ih}}\right)} c_p^{\mathrm{Ih}} \left.\frac{\partial t_{\mathrm{freezing}}}{\partial S_{\mathrm{A}}}\right|_{p} \right) \delta S_{\mathrm{A}} \;-\; S_{\mathrm{A}} \hat{h}_{\Theta}\, \delta\Theta \\ &\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{(Ice\_45)} \\ &\qquad -\; S_{\mathrm{A}} \frac{w^{\mathrm{Ih}}}{\left(1 - w^{\mathrm{Ih}}\right)} c_p^{\mathrm{Ih}} \left(\left.\frac{\partial t_{\mathrm{freezing}}}{\partial P}\right|_{S_{\mathrm{A}}} \;-\; \Gamma^{\mathrm{Ih}} \right) \delta P \;=\; 0. \end{aligned}$$

Another relationship between $\delta S_{\mathrm{A}}, \delta\Theta$, and δP can be found from the knowledge that in both stages 1 and 3 the seawater is at the freezing Conservative Temperature, and since $\Theta_{\mathrm{freezing}}$ is a function of only S_{A} and P, the differences $\delta S_{\mathrm{A}}, \delta\Theta$, and δP are related by

$$\delta\Theta \;=\; \left.\frac{\partial \Theta_{\mathrm{freezing}}}{\partial S_{\mathrm{A}}}\right|_{p} \delta S_{\mathrm{A}} \;+\; \left.\frac{\partial \Theta_{\mathrm{freezing}}}{\partial P}\right|_{S_{\mathrm{A}}} \delta P\,, \qquad \text{(Ice\_46)}$$

and expressions for these partial derivatives are known in terms of the Gibbs functions of seawater and of ice (we do not derive them here).

Eqns. (Ice_45) and (Ice_46) are two equations in δS_{A}, $\delta\Theta$, and δP from which we can find our desired relations for the ratios of changes in our seawater-frazil ice mixture due to adiabatic uplift, namely $\delta\Theta / \delta S_{\mathrm{A}}$, $\delta\Theta / \delta P$ and

$\delta S_{\rm A}/\delta P$. By eliminating the pressure difference from these two equations we find that

$$\boxed{S_{\rm A}\left.\frac{\delta\Theta}{\delta S_{\rm A}}\right|_{\rm frazil} = \frac{\left(h - h^{\rm Ih} - S_{\rm A}\hat{h}_{S_{\rm A}} - S_{\rm A}\frac{w^{\rm Ih}}{\left(1-w^{\rm Ih}\right)}c_p^{\rm Ih}\left[\left.\frac{\partial t_{\rm freezing}}{\partial S_{\rm A}}\right|_p - \frac{\left(\left.\frac{\partial t_{\rm freezing}}{\partial P}\right|_{S_{\rm A}} - \Gamma^{\rm Ih}\right)}{\left.\frac{\partial\Theta_{\rm freezing}}{\partial P}\right|_{S_{\rm A}}}\left.\frac{\partial\Theta_{\rm freezing}}{\partial S_{\rm A}}\right|_p\right]\right)}{\left(\hat{h}_\Theta + \frac{w^{\rm Ih}}{\left(1-w^{\rm Ih}\right)}c_p^{\rm Ih}\frac{\left(\left.\frac{\partial t_{\rm freezing}}{\partial P}\right|_{S_{\rm A}} - \Gamma^{\rm Ih}\right)}{\left.\frac{\partial\Theta_{\rm freezing}}{\partial P}\right|_{S_{\rm A}}}\right)}} \,. \qquad \text{(Ice\_47)}$$

The leading terms in both the numerator and denominator, namely $h - h^{\rm Ih} - S_{\rm A}\hat{h}_{S_{\rm A}}$ and $\hat{h}_\Theta$ are the same as in Eqn. (Ice_16) which applies to the melting of ice Ih into seawater at fixed pressure, the only difference being that in the present case ***both the ice and the seawater are at the freezing temperature***.

So, as the mass fraction of ice tends to zero, Eqn. (Ice_47) tends to Eqn. (Ice_16), so that at $w^{\rm Ih} = 0$ Eqn. (Ice_47) can be illustrated by Fig. Ice_5(a), which is repeated below.

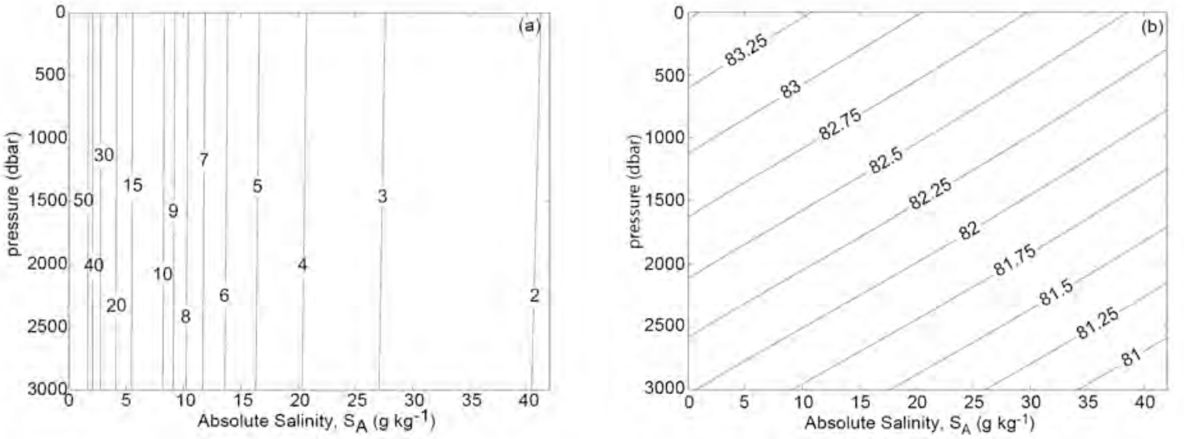


Figure Ice_5. (repeat of this figure) (a) The ratio of the change of Conservative Temperature to that of Absolute Salinity when the melting occurs *very near thermodynamic equilibrium* conditions, $\delta\Theta/\delta S_{\rm A}\big|_{\rm equilibrium}$, from Eqn. (Ice_16) with the seawater enthalpy evaluated at the freezing Conservative Temperature and with the ice enthalpy evaluated at the *in situ* freezing temperature, at each value of pressure and Absolute Salinity. The values contoured have units of $\mathrm{K}\left(\mathrm{g\ kg^{-1}}\right)^{-1}$.
(b) This panel is simply Absolute Salinity $S_{\rm A}$ times the values of panel (a), that is, it is the right-hand side of Eqn. (Ice_16), evaluated at equilibrium conditions.

For non-zero ice mass fraction Eqn. (Ice_47) is plotted in Fig. Ice_14(a) at $S_{\rm A} = S_{\rm SO} = 35.16504\ \mathrm{g\ kg^{-1}}$ (actually what is plotted is $\delta\Theta/\delta S_{\rm A}\big|_{\rm frazil}$). The dependence on the mass fraction of sea ice can be illustrated with the case $w^{\rm Ih} = 0.1$ when $\delta\Theta/\delta S_{\rm A}\big|_{\rm frazil}$ is different to the value at $w^{\rm Ih} = 0$ by about 7.4%. Most of this sensitivity to $w^{\rm Ih}$ comes from the denominator in Eqn. (Ice_47). Eqn. (Ice_47) is again illustrated in Fig. Ice_15(a) where we show contours of $S_{\rm A}\,\delta\Theta/\delta S_{\rm A}\big|_{\rm frazil}$ at the fixed salinity $S_{\rm A} = S_{\rm SO} = 35.16504\ \mathrm{g\ kg^{-1}}$. That is, Fig.

Ice_15(a) is simply $35.16504\ \mathrm{g\ kg}^{-1}$ times Fig. Ice_14(a), so that the quantity contoured in Fig. Ice_15(a) is in temperature units.

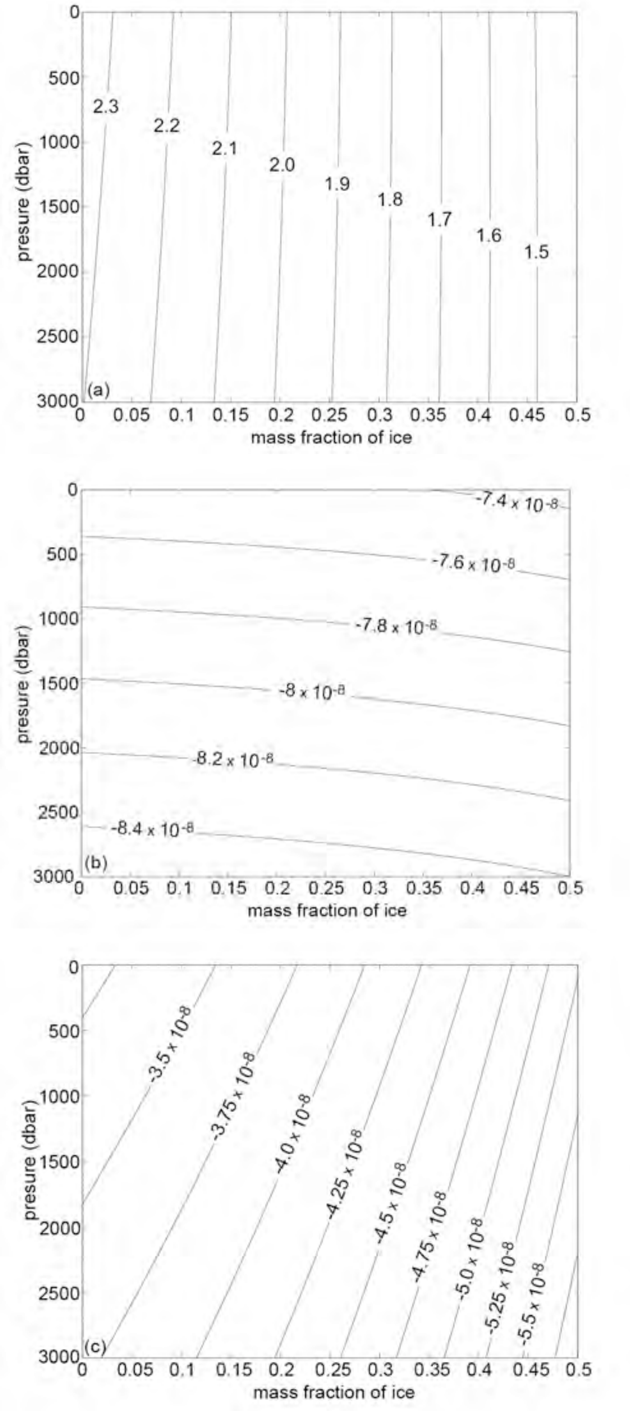


Figure Ice_14. (a) Plot of $\delta\Theta/\delta S_{\mathrm{A}}\big|_{\mathrm{frazil}}$ from Eqn. (Ice_47) as a function of the ice mass fraction w^{Ih} and pressure. (b) Plot of $\delta\Theta/\delta P\big|_{\mathrm{frazil}}$ from Eqn. (Ice_48) as a function of the ice mass fraction w^{Ih} and pressure. (c) Plot of $\delta S_{\mathrm{A}}/\delta P\big|_{\mathrm{frazil}}$ from Eqn. (Ice_49) as a function of the ice mass fraction w^{Ih} and pressure. All three panels have the seawater salinity $S_{\mathrm{A}} = S_{\mathrm{SO}} = 35.16504\ \mathrm{g\ kg}^{-1}$. Panel (a) has units of $\mathrm{K}\left(\mathrm{g\ kg}^{-1}\right)^{-1}$, panel (b) is in $\mathrm{K}\left(\mathrm{Pa}\right)^{-1}$, while panel (c) is in $\left(\mathrm{g\ kg}^{-1}\right)\left(\mathrm{Pa}\right)^{-1}$. The values contoured in this figure were evaluated from the GSW algorithm **gsw_frazil_ratios_adiabatic** of the GSW Oceanographic Toolbox (www.TEOS-10.org).

Similarly, by eliminating δS_{A} from Eqns. (Ice_45) and (Ice_46) we find

$$\left.\frac{\delta\Theta}{\delta P}\right|_{\mathrm{frazil}} = \left.\frac{\partial\Theta_{\mathrm{freezing}}}{\partial P}\right|_{S_{\mathrm{A}}} \frac{\left(h - h^{\mathrm{Ih}} - S_{\mathrm{A}}\hat{h}_{S_{\mathrm{A}}} - S_{\mathrm{A}}\dfrac{w^{\mathrm{Ih}}}{\left(1-w^{\mathrm{Ih}}\right)}c_p^{\mathrm{Ih}}\left[\left.\dfrac{\partial t_{\mathrm{freezing}}}{\partial S_{\mathrm{A}}}\right|_p - \dfrac{\left(\left.\dfrac{\partial t_{\mathrm{freezing}}}{\partial P}\right|_{S_{\mathrm{A}}} - \Gamma^{\mathrm{Ih}} \right)}{\left.\dfrac{\partial\Theta_{\mathrm{freezing}}}{\partial P}\right|_{S_{\mathrm{A}}}} \left.\dfrac{\partial\Theta_{\mathrm{freezing}}}{\partial S_{\mathrm{A}}}\right|_p \right] \right)}{\left(h - h^{\mathrm{Ih}} - S_{\mathrm{A}}\hat{h}_{S_{\mathrm{A}}} - S_{\mathrm{A}}\hat{h}_{\Theta}\left.\dfrac{\partial\Theta_{\mathrm{freezing}}}{\partial S_{\mathrm{A}}}\right|_p - S_{\mathrm{A}}\dfrac{w^{\mathrm{Ih}}}{\left(1-w^{\mathrm{Ih}}\right)}c_p^{\mathrm{Ih}}\left.\dfrac{\partial t_{\mathrm{freezing}}}{\partial S_{\mathrm{A}}}\right|_p \right)}, \quad \text{(Ice\_48)}$$

and when $\delta\Theta$ is eliminated from these same two equations we find

$$\frac{1}{S_{\mathrm{A}}}\left.\frac{\delta S_{\mathrm{A}}}{\delta P}\right|_{\mathrm{frazil}} = \left.\frac{\partial\Theta_{\mathrm{freezing}}}{\partial P}\right|_{S_{\mathrm{A}}} \frac{\left(\hat{h}_{\Theta} + \dfrac{w^{\mathrm{Ih}}}{\left(1-w^{\mathrm{Ih}}\right)}c_p^{\mathrm{Ih}} \dfrac{\left(\left.\dfrac{\partial t_{\mathrm{freezing}}}{\partial P}\right|_{S_{\mathrm{A}}} - \Gamma^{\mathrm{Ih}} \right)}{\left.\dfrac{\partial\Theta_{\mathrm{freezing}}}{\partial P}\right|_{S_{\mathrm{A}}}} \right)}{\left(h - h^{\mathrm{Ih}} - S_{\mathrm{A}}\hat{h}_{S_{\mathrm{A}}} - S_{\mathrm{A}}\hat{h}_{\Theta}\left.\dfrac{\partial\Theta_{\mathrm{freezing}}}{\partial S_{\mathrm{A}}}\right|_p - S_{\mathrm{A}}\dfrac{w^{\mathrm{Ih}}}{\left(1-w^{\mathrm{Ih}}\right)}c_p^{\mathrm{Ih}}\left.\dfrac{\partial t_{\mathrm{freezing}}}{\partial S_{\mathrm{A}}}\right|_p \right)}. \quad \text{(Ice\_49)}$$

The variation of Conservative Temperature with pressure under frazil ice conditions, $\delta\Theta/\delta P|_{\mathrm{frazil}}$, from Eqn. (Ice_48) is plotted in Fig. Ice_14(b) at $S_{\mathrm{A}} = S_{\mathrm{SO}} = 35.16504 \text{ g kg}^{-1}$. It is seen that $\delta\Theta/\delta P|_{\mathrm{frazil}}$ is quite insensitive to the frazil ice mass fraction w^{Ih}. This is confirmed in Fig. Ice_15(c) where we show the difference between $\delta\Theta/\delta P|_{\mathrm{frazil}}$ and the corresponding derivative of $\Theta_{\mathrm{freezing}}$ with pressure *at constant Absolute Salinity*, $\partial\Theta_{\mathrm{freezing}}/\partial P|_{S_{\mathrm{A}}}$.

The variation of Absolute Salinity with pressure under frazil ice conditions, $\delta S_{\mathrm{A}}/\delta P|_{\mathrm{frazil}}$, from Eqn. (Ice_49) is plotted in Figure Ice_14(c) at $S_{\mathrm{A}} = S_{\mathrm{SO}} = 35.16504 \text{ g kg}^{-1}$. This figure follows, of course, as simply the ratio of the figures of panels (a) and (b).

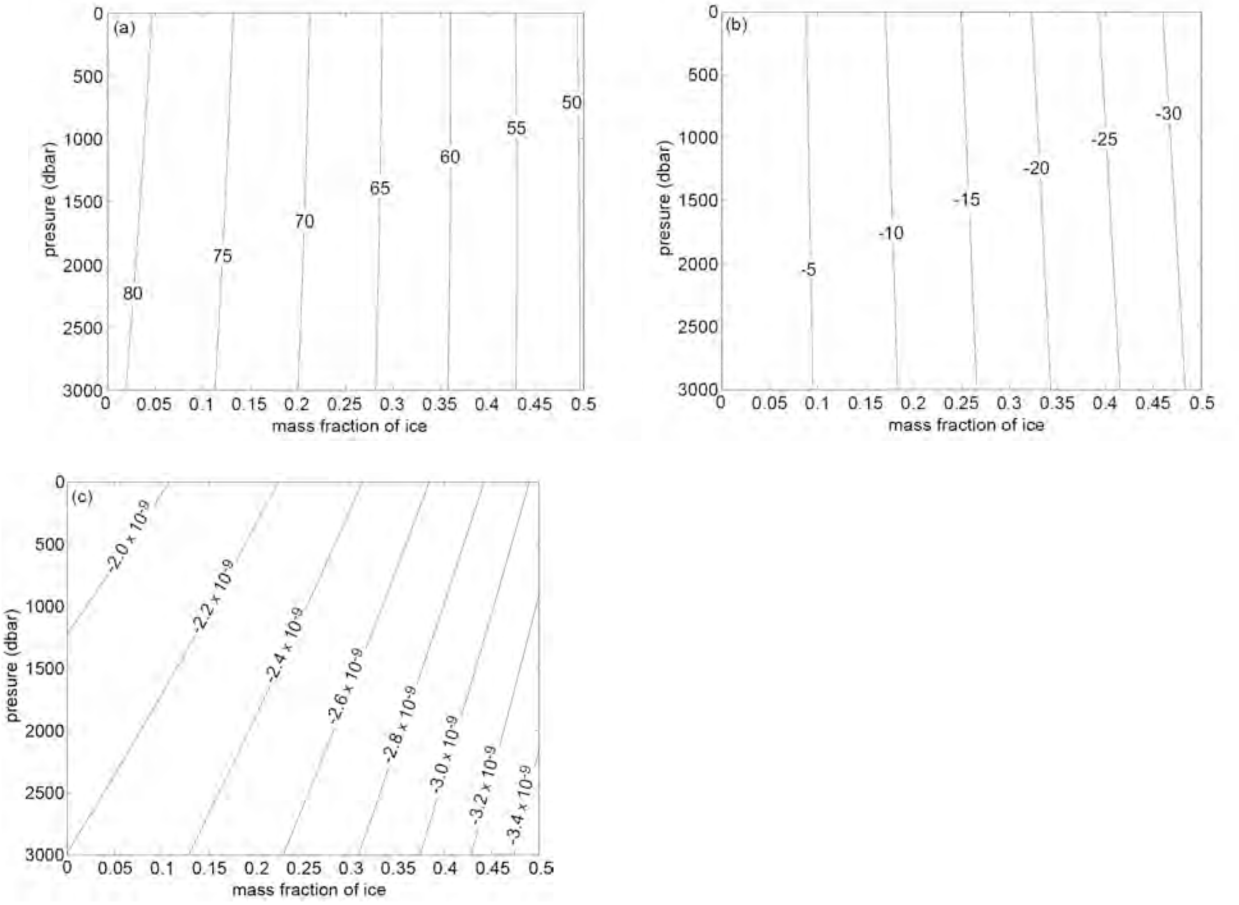


Figure Ice_15. (a) Plot of $S_{\text{A}}\,\delta\Theta/\delta S_{\text{A}}\big|_{\text{frazil}}$ from Eqn. (Ice_47) as a function of the ice mass fraction w^{Ih} and pressure, for $S_{\text{A}} = S_{\text{SO}} = 35.16504\text{ g kg}^{-1}$. This is simply $35.16504\text{ g kg}^{-1}$ times Figure Ice_14(a).

(b) Contour plot of panel (a) with the values of $S_{\text{A}}\,\delta\Theta/\delta S_{\text{A}}\big|_{\text{frazil}}$ evaluated at ice mass fraction $w^{\text{Ih}} = 0$ subtracted at each pressure.

(c) The difference between $\delta\Theta/\delta P\big|_{\text{frazil}}$ and the corresponding derivative of Θ_{freezing} with pressure *at constant Absolute Salinity*, $\partial\Theta_{\text{freezing}}/\partial P\big|_{S_{\text{A}}}$ (obtained from **gsw_CT_freezing_first_derivatives**). The contoured values of panel (c) are in $\text{K}\left(\text{Pa}\right)^{-1}$ and the seawater salinity was taken to be $S_{\text{A}} = S_{\text{SO}} = 35.16504\text{ g kg}^{-1}$. Notice that the numbers contoured here are only a few percent of those of $\delta\Theta/\delta P\big|_{\text{frazil}}$ shown in Fig. Ice_14(b).

The dependence of $S_{\text{A}}\,\delta\Theta/\delta S_{\text{A}}\big|_{\text{frazil}}$ on the mass fraction of ice is illustrated in Fig. Ice_15(b) which shows the difference relative to the case when $w^{\text{Ih}} = 0$.

When no frazil is present in seawater, its Conservative Temperature is unaffected by adiabatic and isohaline changes in pressure, but its *in situ* temperature changes with pressure according to the adiabatic lapse rate Γ which is usually positive. When frazil is present in seawater, an increase in pressure results in changes in Conservative Temperature as contoured in Fig. Ice_14(b). This dependence of the temperature (both Conservative Temperature and *in situ* temperature) of the frazil-seawater mixture to changes in pressure is rather large and negative compared with the (usually positive) adiabatic lapse rate of seawater which is typically less than one twentieth of the values shown in Fig. Ice_14(b) for $\delta\Theta/\delta P\big|_{\text{frazil}}$, and is usually of the opposite sign. Another way of stating this is that the adiabatic lapse rate of the frazil-seawater mixture is large and negative when frazil is present, compared with the small and positive adiabatic lapse rate of seawater in the absence of frazil.

Note that the rate at which the freezing Conservative Temperature changes with Absolute Salinity *at fixed pressure*, $\partial\Theta_{\text{freezing}}/\partial S_{\text{A}}\big|_{p}$, is quite different (even different signs) to the corresponding change involving frazil ice as the pressure varies, $\delta\Theta/\delta S_{\text{A}}\big|_{\text{frazil}}$. A typical value of $\partial\Theta_{\text{freezing}}/\partial S_{\text{A}}\big|_{p}$ is $-0.0583\,\text{K}\,\text{g}^{-1}\,\text{kg}$ while a typical value of $\delta\Theta/\delta S_{\text{A}}\big|_{\text{frazil}}$ is $2.3\,\text{K}\,\text{g}^{-1}\,\text{kg}$. By contrast, we have seen that the variation of Conservative Temperature with pressure for frazil ice, $\delta\Theta/\delta P\big|_{\text{frazil}}$, is only a few percent different to the corresponding change at constant Absolute Salinity, $\partial\Theta_{\text{freezing}}/\partial P\big|_{S_{\text{A}}}$.

All of the material above in these lectures concerning ice, sea ice, and frazil ice can be found in the paper

> McDougall, T. J., P. M. Barker, R. Feistel and B. K. Galton-Fenzi, 2014: Melting of ice and sea ice into seawater, and frazil ice formation. *Journal of Physical Oceanography*, **44**, 1751-1775.

The properties of ice and its equilibrium properties with seawater can be evaluated using the GSW Oceanographic Toolbox, available from www.TEOS-10.org.

The interaction between ice and seawater in ocean models

In a model, the mixture of seawater and frazil ice must be advected and diffused, and the frazil crystals must be allowed to migrate vertically (Stokes drift), but two questions arise.

1 What variables should the model carry to conserve salt and "heat"?

2 How should thermodynamic equilibrium be re-established after the advection, diffusion and frazil-Stokes-drift part of each time step?

Bulk Absolute Salinity and Bulk potential enthalpy

We have shown that conserving the potential enthalpy of ice Ih is sufficiently accurate (rather than having to conserve the enthalpy of ice Ih during melting/freezing and then worry about how the enthalpy of ice Ih varies with pressure).

This greatly simplifies our task because the First Law of Thermodynamics can be simplified to be the conservation of the potential enthalpy of the seawater-ice mixture.

Along with the ice mass fraction, w^{Ih}, the conserved model variables during the advection and diffusion part of the time step should then be the "Bulk Absolute Salinity" $S_{\mathrm{A}}^{\mathrm{B}}$ and the "Bulk potential enthalpy", $\hbar^{\mathrm{B}}$,

$$S_{\mathrm{A}}^{\mathrm{B}} \equiv \left(1-w^{\mathrm{Ih}}\right) S_{\mathrm{A}} \qquad \text{and} \qquad \hbar^{\mathrm{B}} \equiv \left(1-w^{\mathrm{Ih}}\right) c_p^0 \Theta + w^{\mathrm{Ih}} \hbar^{\mathrm{Ih}} .$$

After the advection, diffusion and frazil-Stokes-drift part of the time step, we have values of $S_{\mathrm{A1}}^{\mathrm{B}}$ and $\hbar_1^{\mathrm{B}}$, for the model box, but these values will not be in thermodynamic equilibrium with each other.

How do we re-establish thermodynamic equilibrium in the second half of the time step?

The thermodynamic equilibrium condition between seawater and frazil ice

During the equilibration process, there is no exchange of mass, salt or heat with neighbouring boxes, so the Bulk Absolute Salinity and the Bulk potential enthalpy are conserved, so that when thermodynamic equilibrium is reached at the end of the full time step we must have

$$\left(1-w^{\mathrm{Ih}}\right) S_{\mathrm{A}} = S_{\mathrm{A1}}^{\mathrm{B}} \qquad \text{and} \qquad \left(1-w^{\mathrm{Ih}}\right) c_p^0 \Theta + w^{\mathrm{Ih}} \hbar^{\mathrm{Ih}} = \hbar_1^{\mathrm{B}},$$

and in addition, the values of all these thermodynamic variables mutually adjust so that they satisfy the **freezing condition** at the end of the full time step.

Hence we seek the zero of the function of the ice mass fraction w^{Ih}

$$0 = f\left(w^{\mathrm{Ih}}\right) = \hbar_1^{\mathrm{B}} - \left(1-w^{\mathrm{Ih}}\right) c_p^0 \Theta_{\mathrm{freezing}}\left(S_{\mathrm{A}}, p\right) - w^{\mathrm{Ih}} \hbar_{\mathrm{freezing}}^{\mathrm{Ih}}\left(S_{\mathrm{A}}, p\right).$$

where S_{A} is related to w^{Ih} by $S_{\mathrm{A}} = S_{\mathrm{A1}}^{\mathrm{B}} \big/ \left(1-w^{\mathrm{Ih}}\right)$. Note that $f\left(w^{\mathrm{Ih}}\right)$ is indeed a function of only the ice mass fraction w^{Ih}.

To solve $f\left(w^{\mathrm{Ih}}\right) = 0$ we use an improved version of Newton's Method which converges at the rate $1+\sqrt{2}$ and is described in McDougall T. J. and S. J. Wotherspoon, 2014: A simple modification of Newton's method to achieve convergence of order $1+\sqrt{2}$. *Applied Mathematics Letters*, **29**, 20-25. http://dx.doi.org/10.1016/j.aml.2013.10.008 .

The derivative $f'\left(w^{\mathrm{Ih}}\right)$ is given by

$$f'\left(w^{\mathrm{Ih}}\right) \;=\; c_p^0 \Theta_{\mathrm{freezing}}\left(S_{\mathrm{A}},p\right) \;-\; \hbar^{\mathrm{Ih}}_{\mathrm{freezing}}\left(S_{\mathrm{A}},p\right) \;-\; S_{\mathrm{A}}\, c_p^0 \left.\frac{\partial \Theta_{\mathrm{freezing}}}{\partial S_{\mathrm{A}}}\right|_p$$

$$-\; \frac{S_{\mathrm{A}}\, w^{\mathrm{Ih}}}{\left(1-w^{\mathrm{Ih}}\right)} \left.\frac{\partial \hbar^{\mathrm{Ih}}_{\mathrm{freezing}}}{\partial S_{\mathrm{A}}}\right|_p .$$

An efficient way of determining when there is no frazil ice component

If, at the end of the first part of the time step $\hbar_1^{\mathrm{B}}$ is sufficiently "warm", there will be no frazil ice. In this case the solution is

$$w^{\mathrm{Ih}} \;=\; 0\,, \qquad S_{\mathrm{A}} \;=\; S_{\mathrm{A}1}^{\mathrm{B}} \qquad \text{and} \qquad \Theta \;=\; \hbar_1^{\mathrm{B}} \big/ c_p^0 .$$

What is an efficient way of detecting when $\hbar_1^{\mathrm{B}}$ is "too warm" for frazil ice to be present? Based on the definition of the equilibrium condition (repeated from above),

$$0 \;=\; f\left(w^{\mathrm{Ih}}\right) \;=\; \hbar_1^{\mathrm{B}} - \left(1-w^{\mathrm{Ih}}\right) c_p^0 \Theta_{\mathrm{freezing}}\left(S_{\mathrm{A}},p\right) \;-\; w^{\mathrm{Ih}}\, \hbar^{\mathrm{Ih}}_{\mathrm{freezing}}\left(S_{\mathrm{A}},p\right),$$

we evaluate this function when the ice mass fraction is zero, that is,

$$f\left(w^{\mathrm{Ih}}=0\right) \;=\; \hbar_1^{\mathrm{B}} - c_p^0 \Theta_{\mathrm{freezing}}\left(S_{\mathrm{A}1}^{\mathrm{B}},p\right),$$

and if this is positive then the answer is simply seawater (and no frazil ice), so that we can set, $w^{\mathrm{Ih}} = 0$, $S_{\mathrm{A}} = S_{\mathrm{A}1}^{\mathrm{B}}$ and $\Theta = \hbar_1^{\mathrm{B}} \big/ c_p^0$. The computer time involved with making this decision is simply the time it takes to evaluate the freezing Conservative Temperature $\Theta_{\mathrm{freezing}}\left(S_{\mathrm{A}1},p\right)$.

The computer code needed to restore the seawater/ice properties at the end of the first half of the time step $\left(S_{\mathrm{A}1}^{\mathrm{B}}, \hbar_1^{\mathrm{B}}, p\right)$ to thermodynamic equilibrium is contained in the computationally efficient code

gsw_frazil_properties_potential_poly(SA_bulk, h_pot_bulk, p)

which has outputs of $\left(S_{\mathrm{A}}, \Theta, w^{\mathrm{Ih}}\right)$.

Buoyancy frequency N

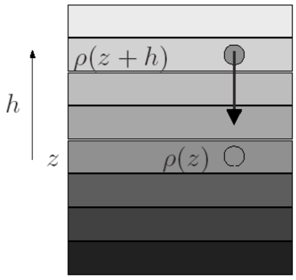


Figure 11-1 When an incompressible fluid parcel of density $\rho(z)$ is vertically displaced from level z to level $z+h$ in a stratified environment, a buoyancy force appears because of the density difference $\rho(z)-\rho(z+h)$ between the particle and the ambient fluid.

First consider the incompressible situation as illustrated in the figure. The figure shows that when a parcel is displaced upwards from its resting position in a stably stratified fluid, it experiences a downwards buoyant force because it is denser than the fluid of the environment that surrounds it at its new location. This force is indicated by the downwards-directed arrow in the figure.

When the fluid is compressible there is a vertical gradient of *in situ* density ρ, given by

$$\left.\frac{\partial\rho}{\partial P}\right|_{S_{\mathrm{A}},\Theta} P_z \;=\; \rho\kappa P_z \,, \qquad \text{(vertical isentropic density gradient)}$$

even when a fluid layer is completely well mixed so that Absolute Salinity, entropy and Conservative Temperature are all independent of height. In this compressible well-mixed case, the fluid parcel illustrated above would decrease its *in situ* density in moving upwards by the distance h, but at its new location, its density would be the same as that of the fluid around it at this height. So in order to quantify the vertical stability, that is, in order to quantify the vertical buoyant force that the parcel experiences at its new location, we need to take into account this vertical gradient of *in situ* density ρ due to the fluid's isentropic (and isohaline) compressibility κ.

The square of the buoyancy frequency (sometimes called the Brunt-Väisälä frequency), N^2, is given in terms of the vertical gradients of density and pressure, or in terms of the vertical gradients of Conservative Temperature and Absolute Salinity by (the g on the left-hand side is the gravitational acceleration, and x, y and z are the spatial Cartesian coordinates)

$$\begin{aligned} g^{-1}N^2 \;&=\; -\rho^{-1}\rho_z + \kappa P_z \;=\; -\rho^{-1}\left(\rho_z - P_z/c^2\right) \\ &=\; \alpha^{\Theta}\,\Theta_z\big|_{x,y} - \beta^{\Theta}\,\partial S_{\mathrm{A}}/\partial z\big|_{x,y}. \end{aligned} \qquad (3.10.1)$$

The buoyancy frequency N has units of radians per second, and since a radian is unitless, N has dimensions of s^{-1}. The buoyancy frequency N is the highest frequency of internal gravity waves in a density-stratified fluid like the ocean or atmosphere. The corresponding shortest period of internal gravity waves is $2\pi/N$ which varies from about 20 minutes in the upper ocean to a few hours in the deep ocean. (This is to be compared with $2\pi/f \ge 12$ hours where $f = 2\Omega\sin\phi = 1.458\,423\,00 x 10^{-4} \sin\phi \ \mathrm{s}^{-1}$, is the Coriolis parameter where ϕ is latitude and Ω is the rotation rate of the earth [in radians per second]).

For two seawater parcels separated by a small distance Δz in the vertical, an equally accurate method of calculating the buoyancy frequency is to bring both seawater parcels adiabatically and without exchange of matter to the average pressure and to calculate the difference in density of the two parcels after this change in pressure. In this way the potential densities, defined with reference pressure being the mean pressure of the two fluid parcels, are being compared at the same pressure. This common procedure calculates the buoyancy frequency N according to

$$N^2 = g\left(\alpha^\Theta \Theta_z - \beta^\Theta S_{\mathrm{A}_z}\right) \approx -\frac{g}{\rho}\frac{\Delta\rho^\Theta}{\Delta z}\,, \tag{3.10.2a}$$

or

$$N^2 = g^2\rho\left(\beta^\Theta S_{\mathrm{A}_P} - \alpha^\Theta \Theta_P\right) \approx \frac{g^2\,\Delta\rho^\Theta}{\Delta P}\,, \tag{3.10.2b}$$

where $\Delta\rho^\Theta$ is the difference between the potential densities of the two seawater parcels with the reference pressure being the average of the two original pressures of the seawater parcels. Eqn. (3.10.2b) has made use of the hydrostatic relation $P_z = -g\rho$, and ΔP is the difference in the pressures of the two parcels, in Pa .

This difference in potential density, $\Delta\rho^\Theta$, between two seawater parcels can be evaluated more easily when density is expressed in the form $\rho = \hat{\rho}\left(S_\mathrm{A}, \Theta, p\right)$ than when it is expressed in the form $\rho = \rho\left(S_\mathrm{A}, t, p\right)$; witness

$$\begin{aligned}\Delta\rho^\Theta &= \hat{\rho}\left(S_\mathrm{A}^\mathrm{deep}, \Theta^\mathrm{deep}, \bar{p}\right) - \hat{\rho}\left(S_\mathrm{A}^\mathrm{shallow}, \Theta^\mathrm{shallow}, \bar{p}\right)\\ &= \rho\left(S_\mathrm{A}^\mathrm{deep}, \theta\left(S_\mathrm{A}^\mathrm{deep}, t^\mathrm{deep}, p^\mathrm{deep}, \bar{p}\right), \bar{p}\right) - \rho\left(S_\mathrm{A}^\mathrm{shallow}, \theta\left(S_\mathrm{A}^\mathrm{shallow}, t^\mathrm{shallow}, p^\mathrm{shallow}, \bar{p}\right), \bar{p}\right)\end{aligned}$$

where $\bar{p} = \tfrac{1}{2}\left(p^\mathrm{deep} + p^\mathrm{shallow}\right)$. Compared with the first line of the above equation, the second line requires more calculations, and the expression is unnecessarily convoluted.

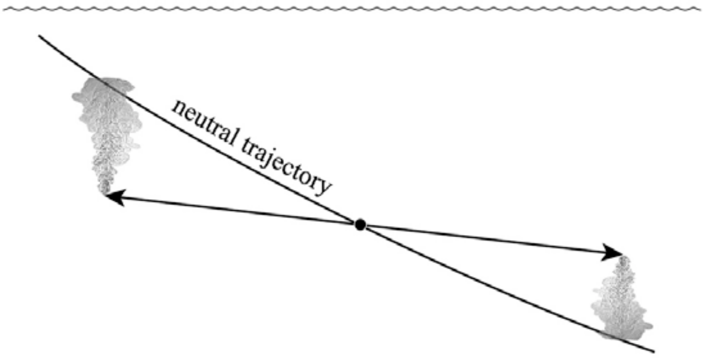
The "Stability Ratio" R_ρ of a vertical water column is defined as

$$R_\rho = \frac{\alpha^\Theta \Theta_z}{\beta^\Theta \left(S_\mathrm{A}\right)_z}\,. \tag{3.15.1}$$

R_ρ is the ratio of the vertical contribution from Conservative Temperature to that from Absolute Salinity to the static stability N^2 of the water column.

The neutral tangent plane

The "neutral tangent plane" is that plane in physical space in which the local parcel of seawater can be moved an infinitesimal distance without being subject to a vertical buoyant restoring force; it is the plane of neutral- or zero- buoyancy.



Take the seawater parcel at the central point and enclose it in an insulating plastic bag, then move it to a new location a small distance away. Its density will change by $\delta\rho = \rho\kappa\delta P$. At the same location the seawater environment has a density difference of $\delta\rho = \rho\left(\kappa\delta P + \beta^\Theta\delta S_\mathrm{A} - \alpha^\Theta\delta\Theta\right)$. If the seawater parcel is happy to sit still at its new location, it must not be feeling a vertical buoyant (Archimedean) force, and this requires that its density is equal to that of the environment at its new location. That is, we must have

$$\rho\kappa\delta P = \rho\left(\kappa\delta P + \beta^\Theta\delta S_\mathrm{A} - \alpha^\Theta\delta\Theta\right). \tag{Neutral\_1}$$

Hence, along a neutral trajectory the variations of S_A and Θ of the ocean obey

$$\beta^{\Theta}\delta S_{\mathrm{A}} = \alpha^{\Theta}\delta\Theta \ . \qquad \text{(Neutral\_2)}$$

Incidentally, this thought experiment involving the adiabatic and isohaline displacement of fluid parcels is typical of our thinking about turbulent fluxes. We imagine the adiabatic and isohaline movement of fluid parcels, and then we let these parcels mix molecularly with their surroundings. Central to this way of thinking about turbulent fluxes are the following two desirable properties of the tracer that is being mixed.

(1) it must be a "potential" property, for otherwise its value will change during the adiabatic and isohaline displacement so it is difficult to define a flux of the quantity, and

(2) it should preferably be a "conservative" fluid property so that when it does mix intimately (that is, molecularly) with its surrounding, we can be sure that no funny business is going on; no magic, undesirable production or destruction of the property.

Expressing this definition of a neutral tangent plane $\beta^{\Theta}\delta S_{\mathrm{A}} = \alpha^{\Theta}\delta\Theta$ in terms of the two-dimensional gradient of properties in the neutral tangent plane, we have that

$$-\rho^{-1}\nabla_n\rho + \kappa\nabla_n P \ = -\rho^{-1}\left(\nabla_n\rho - \nabla_n P/c^2\right) \ = \ \alpha^{\Theta}\nabla_n\Theta - \beta^{\Theta}\nabla_n S_{\mathrm{A}} \ = \ \mathbf{0}, \qquad (3.11.2)$$

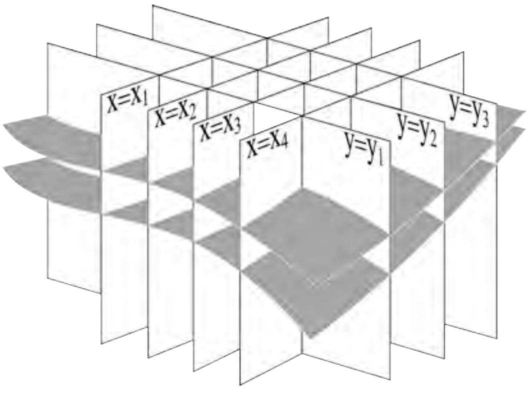
where, by way of reminder the relevant thermal expansion coefficient α^{Θ} and saline contraction coefficient β^{Θ} are defined by

$$\alpha^{\Theta} \ = -\frac{1}{\rho}\frac{\partial\rho}{\partial\Theta}\bigg|_{S_{\mathrm{A}},p} \qquad \text{and} \qquad \beta^{\Theta} \ = \frac{1}{\rho}\frac{\partial\rho}{\partial S_{\mathrm{A}}}\bigg|_{\Theta,p} \ . \qquad (2.18.3), (2.19.3)$$

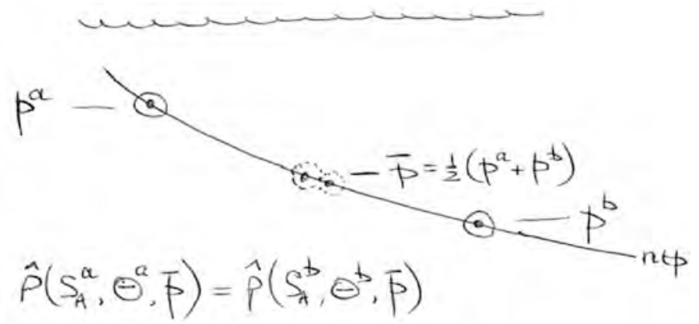
Here ∇_n is an example of a projected non-orthogonal gradient

$$\nabla_r\tau \equiv \frac{\partial\tau}{\partial x}\bigg|_r \mathbf{i} + \frac{\partial\tau}{\partial y}\bigg|_r \mathbf{j} + 0\mathbf{k}, \qquad (3.11.3)$$

that is widely used in oceanic and atmospheric theory and modelling. Horizontal distances are measured between the vertical planes of constant latitude x and longitude y while the values of the property τ are evaluated on the r surface (e. g. an isopycnal surface, or in the case of ∇_n, a neutral tangent plane). Note that $\nabla_r\tau$ has no vertical component; it is not directed along the r surface, but rather it points in exactly the horizontal direction.



A very accurate finite amplitude version of achieving $\beta^{\Theta}\delta S_{\rm A} = \alpha^{\Theta}\delta\Theta$ is to equate the potential densities of the two fluid parcels, each referenced to the average pressure $\bar{p} = 0.5\left(p^{\rm a} + p^{\rm b}\right)$. In this way, when two parcels, parcels a and b, are on a neutral tangent plane then $\hat{\rho}\left(S_{\rm A}^{\rm a},\Theta^{\rm a},\bar{p}\right) = \hat{\rho}\left(S_{\rm A}^{\rm b},\Theta^{\rm b},\bar{p}\right)$; see the figure below which involves the thought process of moving both parcels to pressure $\bar{p}$.



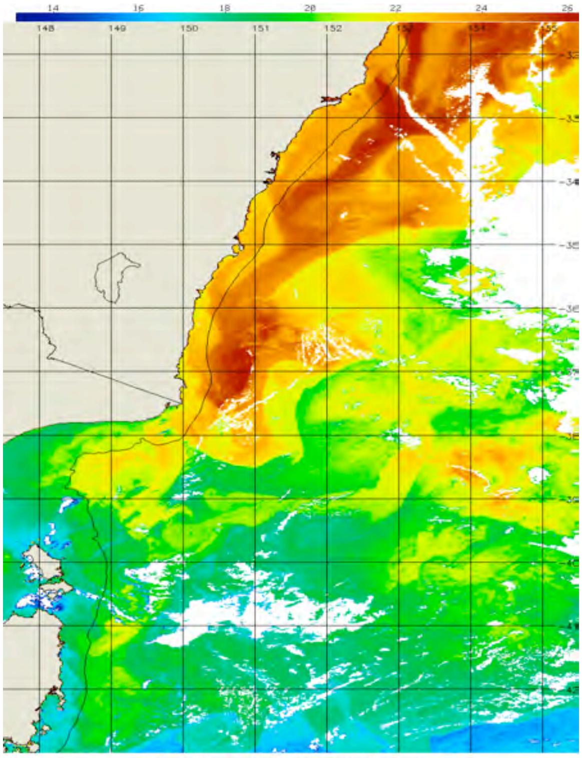
The (three dimensional) normal vector to the neutral tangent plane $\mathbf{n}$ is given by

$$\begin{aligned} g^{-1} N^2 \mathbf{n} &= -\rho^{-1}\nabla\rho + \kappa\nabla P = -\rho^{-1}\left(\nabla\rho - \nabla P / c^2\right) \\ &= \alpha^{\Theta}\nabla\Theta - \beta^{\Theta}\nabla S_{\rm A}. \end{aligned} \tag{3.11.1}$$

As defined, $\mathbf{n}$ is not quite a unit normal vector, rather its vertical component is exactly $\mathbf{k}$, that is, its vertical component is unity ($\mathbf{k}\cdot\mathbf{n} = 1$).

Why do we think that the strong lateral mixing of mesoscale eddies is epineutral?

"mesoscale" in the ocean means the energy-containing scale, which in the ocean is about 20km - 100km. The ocean is full of energetic eddies at the mesoscale. Dynamically, this 100km mesoscale in the ocean corresponds to the ~1,000 km scale of the weather systems in the atmosphere that we see on weather maps.



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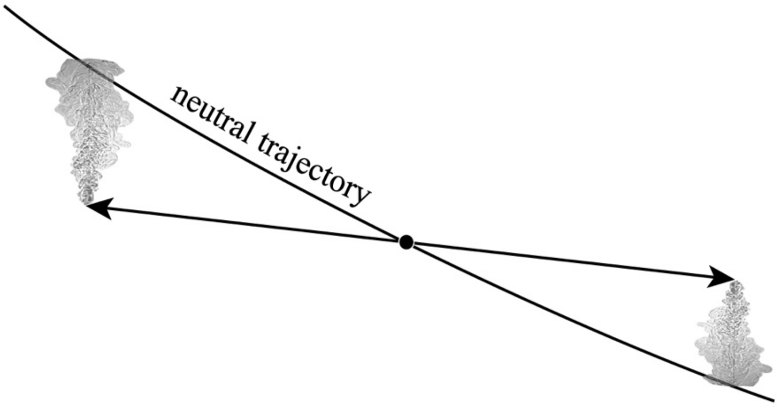
"epineutral" means "along a neutral tangent plane",
[or loosely, "along a neutral density surface", or more loosely, "along an isopycnal" or "along a density surface"]

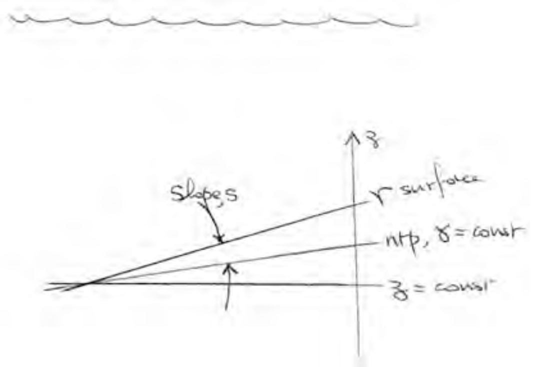
The smallness of the dissipation of mechanical energy ε in the ocean interior provides the strongest evidence that the lateral mixing of mesoscale eddies occurs along the neutral tangent plane. If the lateral diffusivity $K \approx 10^3\,\mathrm{m^2\,s^{-1}}$ of mesoscale dispersion and subsequent molecular diffusion were to occur along a surface that differed in slope from the neutral tangent plane by an angle whose tangent was s, then the individual fluid parcels would be transported above and below the neutral tangent plane and would need to subsequently sink or rise in order to attain a vertical position of neutral buoyancy.



This vertical motion would either (i) involve no small-scale turbulent mixing, in which case the combined process is equivalent to epineutral mixing, or (ii), the sinking and rising parcels would mix and entrain in a plume-like fashion with the ocean environment, so suffering irreversible diffusion (as illustrated in the figure). If this second case were to occur, the dissipation of mechanical energy associated with the diapycnal mixing would be observed. But in fact the dissipation of mechanical energy in the main thermocline is consistent with a diapycnal diffusivity of only $10^{-5}\,\mathrm{m^2\,s^{-1}}$. This small value of the diapycnal (vertical) diffusivity has been confirmed by purposely released tracer experiments.

Fictitious dianeutral diffusion

When lateral diffusion, with diffusivity K is taken to occur along a surface r other than a neutral tangent plane, some dianeutral diffusion occurs.



We will now show that this dianeutral diffusion is the same as is achieved by a vertical diffusivity of $s^2 K$ where s^2 is the square of the vector slope $\nabla_r z - \nabla_n z$ between the r surface and the neutral tangent plane. We call $s^2 K$ the "fictitious" vertical diffusivity of density.

We consider a density variable called Neutral Density γ that we take to be constant along the neutral tangent plane (ntp). The lateral flux of Neutral Density along the r surface is

$$-K\nabla_r\gamma = -K\gamma_z\left(\nabla_r z - \nabla_n z\right)\ , \qquad \text{(Fictitious\_1)}$$

and the component of this lateral flux across the neutral tangent plane is

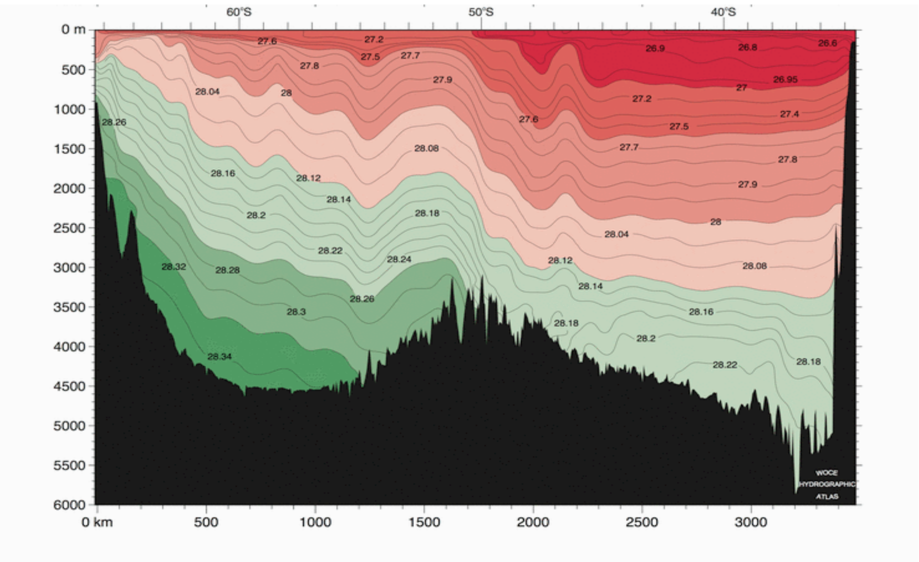
$$-K\nabla_r\gamma\cdot\left(\nabla_r z - \nabla_n z\right) = -K\gamma_z\left(\nabla_r z - \nabla_n z\right)^2\ . \qquad \text{(Fictitious\_2)}$$

Dividing by minus the vertical gradient of Neutral Density, $-\gamma_z$, shows that this flux is the same as that caused by the positive fictitious vertical diffusivity of density $\left(\nabla_r z - \nabla_n z\right)^2 K\ = s^2 K$.

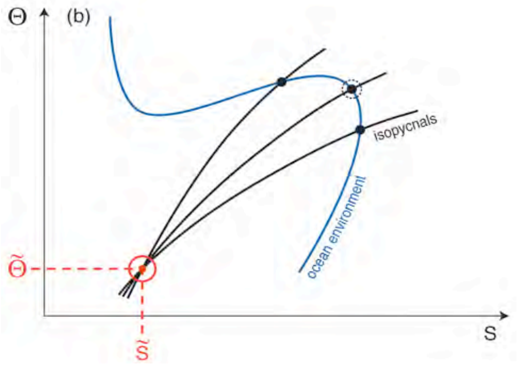
Hence if all of this observed diapycnal diffusivity (based on the observed dissipation of turbulent kinetic energy ε) were due to mesoscale eddies mixing along a direction different to neutral tangent planes, the (tangent of the) angle between this mesoscale mixing direction and the neutral tangent plane, s, would satisfy $10^{-5}\,\mathrm{m^2\,s^{-1}} = s^2 K$. Using $K \approx 10^3\,\mathrm{m^2\,s^{-1}}$ gives the maximum value of s to be 10^{-4}. Since we believe that bona fide interior diapycnal mixing processes (such as breaking internal gravity waves) are responsible for the bulk of the observed diapycnal diffusivity, we conclude that the angular difference s between the direction of mesoscale eddy mixing and the neutral tangent plane must be substantially less than 10^{-4}; say $2x10^{-5}$ for argument's sake. This means that over a horizontal distance of one degree of latitude, which is 110km, we have to be able to evaluate Neutral Density surfaces accurate to within 2m in the vertical!

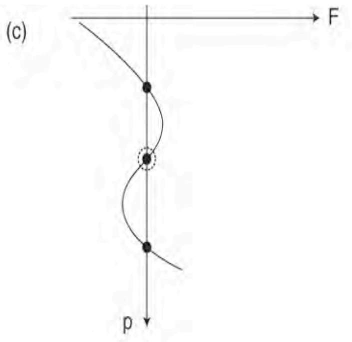
Neutral Surfaces on an ocean section

Consider starting from a "bottle $\left(\tilde{S}_{\mathrm{A}}, \tilde{\Theta}, \tilde{p}\right)$ that is on a particular neutral surface and one wants to find the location on a neighbouring CTD cast that is neutrally related to this "bottle". The "adiabatic leveling method" of Bray and Fofonoff (1981), applied to this neutral calculation, says that two seawater parcels are neutrally related when $F\left(p\right) = \rho\left(S_{\mathrm{A}},\Theta,\bar{p}\right) - \rho\left(\tilde{S}_{\mathrm{A}},\tilde{\Theta},\bar{p}\right) = 0$, where $\bar{p} = 0.5\left(p + \tilde{p}\right)$.



This works fine unless there is more than one solution to $F\left(p\right) = 0$, which only occurs when the cast is very weakly stratified (i.e. low N^2).





This feature of multiple solutions occurs sometimes for potential density surfaces as well. Apart from this feature, calculating neutral directions on a single ocean section is a well-defined problem; neutral helicity does not raise its ugly head. There is still the issue of attaching a Neutral Density label to each surface that is formed in this manner on an ocean section.

What is planetary potential vorticity?

The vertical gradient of Neutral Density is not proportional to N^2

By analogy with fN^2, the Neutral Surface Potential Vorticity ($NSPV$) is defined as $-g\gamma^{-1}$ times $\hat{q} = f\tilde{\gamma}_z$, and the ratio of $NSPV$ to fN^2 can be shown to be

$$\begin{aligned}\frac{NSPV}{fN^2} = b &= \exp\left\{-\int_{\rm ans}\rho g^2 N^{-2}\left(\alpha_P^\Theta \nabla_p \Theta - \beta_P^\Theta \nabla_p S_{\rm A}\right)\cdot d\boldsymbol{l}\right\} \\ &= \exp\left\{\int_{\rm ans}\rho g^2 N^{-2}\nabla_p \kappa \cdot d\boldsymbol{l}\right\}.\end{aligned} \qquad (3.20.15)$$

The integral here is taken along an approximately neutral surface (such as a Neutral Density surface) from a location where $NSPV$ is equal to fN^2. Notice that this is basically proportional to the Thermobaric coefficient $T_{\rm b}^\Theta = \alpha_P^\Theta - \left(\alpha^\Theta/\beta^\Theta\right)\beta_P^\Theta$.

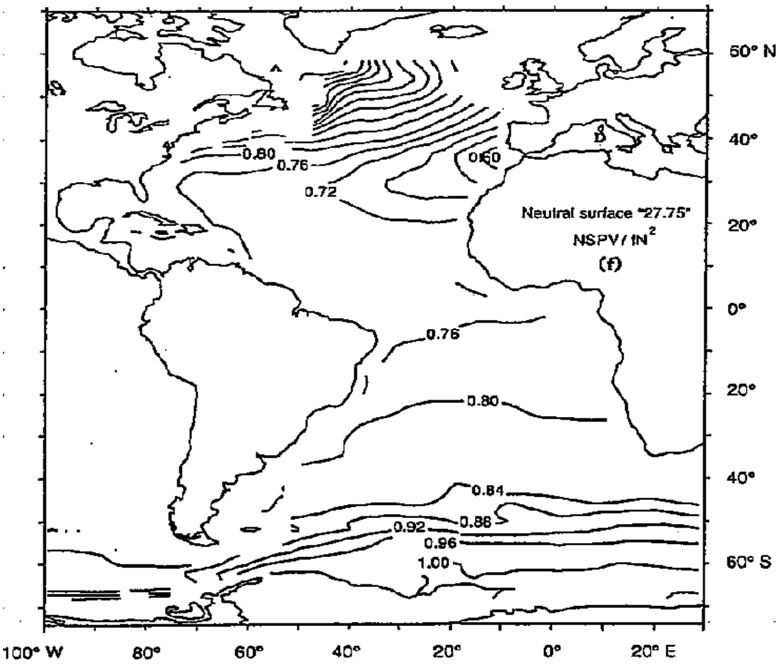


Figure. Map of NSPV versus fN². Plot of the ratio of NSPV to fN^2 on a Neutral Density surface in the Atlantic.

The deficiencies of fN^2 as a form of planetary potential vorticity have not been widely appreciated. Even in a lake, the use of fN^2 as planetary potential vorticity is inaccurate since the right-hand side of (3.20.14) is then

$$-\rho g^2 N^{-2}\alpha_P^\Theta \nabla_p \Theta = \rho g^2 N^{-2}\alpha_P^\Theta \Theta_z \nabla_\Theta P / P_z = -\frac{\alpha_P^\Theta}{\alpha^\Theta}\nabla_\Theta P, \qquad (3.20.16)$$

where the geometrical relationship $\nabla_p \Theta = -\Theta_z \nabla_\Theta P / P_z$ has been used along with the hydrostatic equation. The mere fact that the Conservative Temperature surfaces in the lake have a slope (i. e. $\nabla_\Theta P \neq \mathbf{0}$) means that the spatial variation of contours of fN^2 on a Θ surface will not be the same as for the contours of $NSPV$ on a Θ surface in a lake.

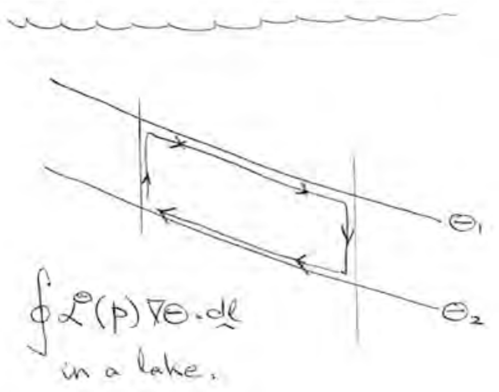


Figure. NSPV versus fN² in a lake. Because the thermal expansion coefficient is a function of pressure, the vertical integral of N^2 on the two vertical parts of the closed loop are not equal, even in a lake.

In the situation where there is no gradient of Conservative Temperature along a Neutral Density surface ($\nabla_\gamma\Theta = \mathbf{0}$) the contours of $NSPV$ along the Neutral Density surface coincide with those of isopycnal-potential-vorticity (IPV), the potential vorticity defined with respect to the vertical gradient of potential density by $IPV = -fg\rho^{-1}\rho_z^{\Theta}$. IPV is related to fN^2 by (McDougall (1988)),

$$\frac{IPV}{fN^2} \equiv \frac{-g\rho^{-1}\rho_z^{\Theta}}{N^2} = \frac{\beta^{\Theta}(p_{\rm r})\left[R_\rho/r-1\right]}{\beta^{\Theta}(p)\left[R_\rho-1\right]}, \qquad (3.20.17)$$

where

$$r = \frac{\alpha^{\Theta}(S_{\rm A},\Theta,p)/\beta^{\Theta}(S_{\rm A},\Theta,p)}{\alpha^{\Theta}(S_{\rm A},\Theta,p_{\rm r})/\beta^{\Theta}(S_{\rm A},\Theta,p_{\rm r})}. \qquad (3.17.2)$$

Hence the ratio of $NSPV$ to IPV, evaluated on an approximately neutral surface, is

$$\frac{NSPV}{IPV} = \frac{\beta^{\Theta}(p)}{\beta^{\Theta}(p_{\rm r})}\frac{\left[R_\rho-1\right]}{\left[R_\rho/r-1\right]}\exp\left\{\int_{\rm ans} g^2 N^{-2}\nabla_P(\rho\kappa)\cdot d\boldsymbol{l}\right\}. \qquad (3.20.18)$$

The sketch below indicates why $NSPV$ is different to IPV; it is the highly differentiated nature of potential vorticity that causes the isolines of IPV and $NSPV$ to not coincide even at the reference pressure $p_{\rm r}$ of the potential density variable. $NSPV$, fN^2 and IPV have the units $\rm s^{-3}$.

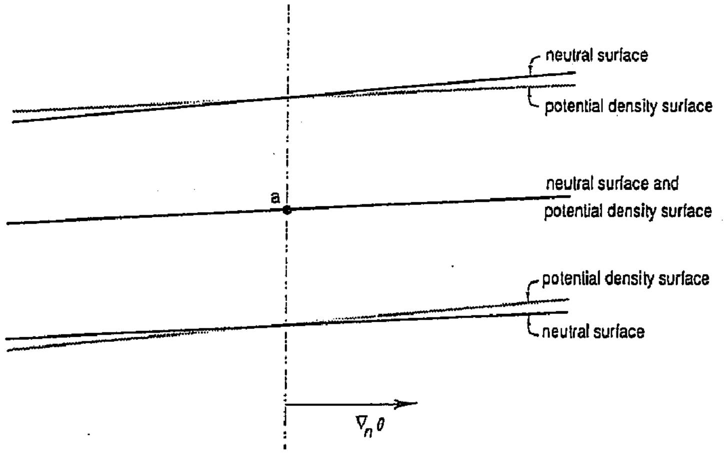
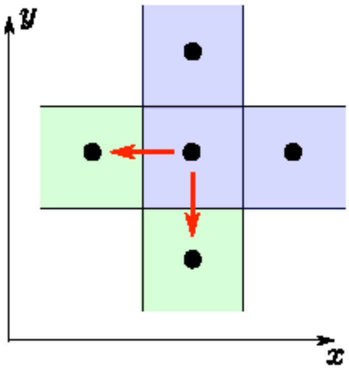


Fig. 14. A vertical cross section through three neutral surfaces and three potential density surfaces. The reference pressure of the potential density is the pressure of the central point, a. The neutral surface and potential density surface that pass though this point are parallel. The slopes of the other pairs of surfaces are different.

Forming a single approximately neutral surface (2-dimesnional problem)



We seek an approximately neutral surface in which the neutral tangent plane equation $\alpha^{\Theta}\nabla_n\Theta - \beta^{\Theta}\nabla_n S_{\mathrm{A}} = \mathbf{0}$ is almost satisfied everywhere on the surface. Because of Neutral Helicity, it will not be possible to satisfy this relationship everywhere on the surface.

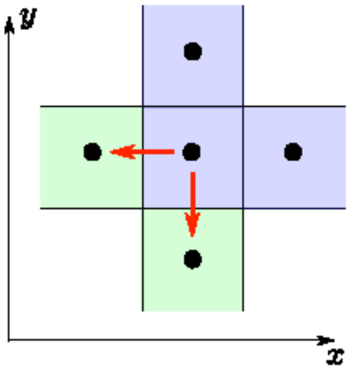
In the ω-surface software we start with an initial surface and iterate to find a more neutral surface, usually requiring about 3 iterations if we start from a potential density surface. In the ans (approximately neutral surface) we calculate $\alpha^{\Theta}\nabla_{ans}\Theta - \beta^{\Theta}\nabla_{ans} S_{\mathrm{A}}$ and a scalar potential Φ is found by least squares such that

$$\nabla_{ans}\Phi \approx \alpha^{\Theta}\nabla_{ans}\Theta - \beta^{\Theta}\nabla_{ans} S_{\mathrm{A}} .$$

This scalar field Φ is interpreted as the natural logarithm of the error in locally referenced potential density of that point on the ans. This gives us the basis for finding a better surface by moving a little bit higher or lower in the water column, finding the point on each cast whose difference in log density is Φ. These heights then define a surface that is the next iteration in the procedure. In the absence of Neutral Helicity, this procedure converges so that the final surface is neutral to machine precision. In the real ocean, the presence of Neutral Helicity means that the final converged surface is not quite neutral.

Labeling a 3-dimensional data set with Neutral Density

Analogous to the 2-dimensional picture,



we can write equations in 3 dimensions that express the spatial differences of Neutral Density in order that the local surface of constant Neutral Density coincides with the neutral tangent plane. We have code that works for this problem, but are still fine-tuning it (fine tuning the weights).

How the Neutral Density code of 1997 works

Many approximately neutral surfaces were formed in a global hydrographic atlas, using the best ideas we had in the mid 1990's. These surfaces were then labeled in the mid equatorial Pacific so that there Neutral Density via a vertical integral of N^2 so that

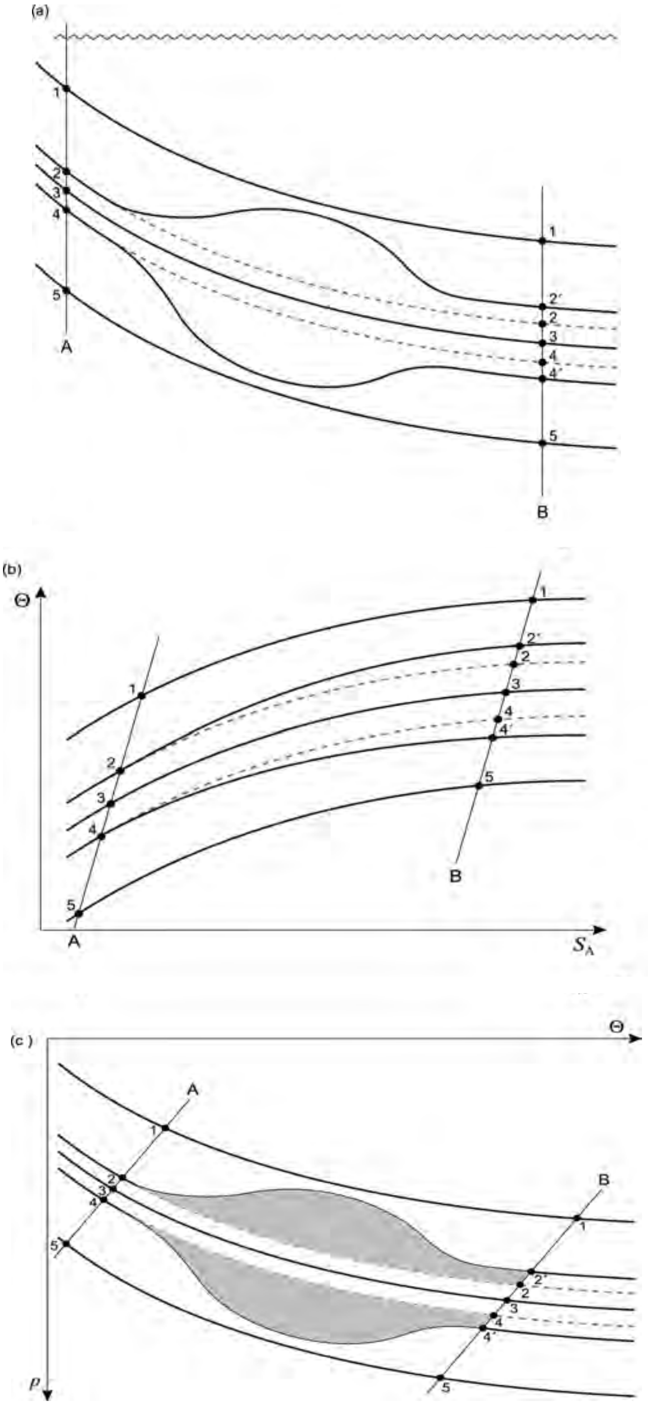
$$N^2 = -\frac{g}{\gamma}\frac{\mathrm{d}\gamma}{\mathrm{d}z}$$

That is, we set $b = NSPV\big/\left(fN^2\right)$ to be unity down this one vertical cast. Clearly then $b = NSPV\big/\left(fN^2\right)$ varied throughout the rest of the ocean.

When a "bottle" $\left(\tilde{S}_{\mathrm{A}}, \tilde{\Theta}, \tilde{p}\right)$ is labeled with Neutral Density using this 1997 γ^n code, the bottle's location in latitude and longitude is used to find the surrounding four labeled casts. The bottle $\left(\tilde{S}_{\mathrm{A}}, \tilde{\Theta}, \tilde{p}\right)$ is then presented to each of these four casts in turn, finding the depth at which $F\left(p\right) = \rho\left(S_{\mathrm{A}},\Theta,\bar{p}\right) - \rho\left(\tilde{S}_{\mathrm{A}},\tilde{\Theta},\bar{p}\right)$ is zero. At this depth, the value of the pre-labeled value of γ^n is obtained. The final value of Neutral Density is a suitable average of these four values of γ^n.

An undesirable feature of Neutral Density

An adiabatic heaving of a water column can alter the Neutral Density label that a seawater parcel receives, even when this parcel is a long way away (in physical space) from the heaving motion.



Advective and diffusive "heat" fluxes of Θ and θ

The turbulent flux of a "potential" property can be thought of as the exchange of parcels of equal mass but contrasting values of the "potential" property, and the turbulent flux can be parameterized as being down the gradient of the "potential" property. The conservative form of Eqn. (A.21.15) implies that the turbulent flux of heat should be directed down the mean gradient of Conservative Temperature rather than down the mean gradient of potential temperature. Here we quantify the ratio of the mean gradients of potential temperature and Conservative Temperature along the neutral tangent plane; along a surface of constant "density" if you like.

The epineutral gradients of θ, Θ and S_A are related by (using $\theta = \hat{\theta}(S_\mathrm{A},\Theta)$)

$$\nabla_n\theta \ = \ \hat{\theta}_\Theta \nabla_n\Theta \ + \ \hat{\theta}_{S_\mathrm{A}} \nabla_n S_\mathrm{A} \,, \qquad \text{(A.14.3)}$$

and using the neutral relationship $\nabla_n S_\mathrm{A} = \left(\alpha^\Theta/\beta^\Theta\right)\nabla_n\Theta$ we find

$$\nabla_n\theta = \left(\hat{\theta}_\Theta + \left[\alpha^\Theta/\beta^\Theta\right]\hat{\theta}_{S_\mathrm{A}}\right)\nabla_n\Theta \ , \qquad \text{(A.14.4)}$$

or

$$\frac{\left|\nabla_n\theta\right|}{\left|\nabla_n\Theta\right|} \ = \ \hat{\theta}_\Theta + \left[\alpha^\Theta/\beta^\Theta\right]\hat{\theta}_{S_\mathrm{A}} \,. \qquad \text{(A.14.5)}$$

The ratio, Eqn. (A.14.5), of the epineutral gradients of θ and Θ is shown in Figure A.14.1 at $p = 0$, indicating that the epineutral gradient of potential temperature is sometimes more that 1% different to that of Conservative Temperature. This ratio $\left|\nabla_n\theta\right|/\left|\nabla_n\Theta\right|$ is only a weak function of pressure.

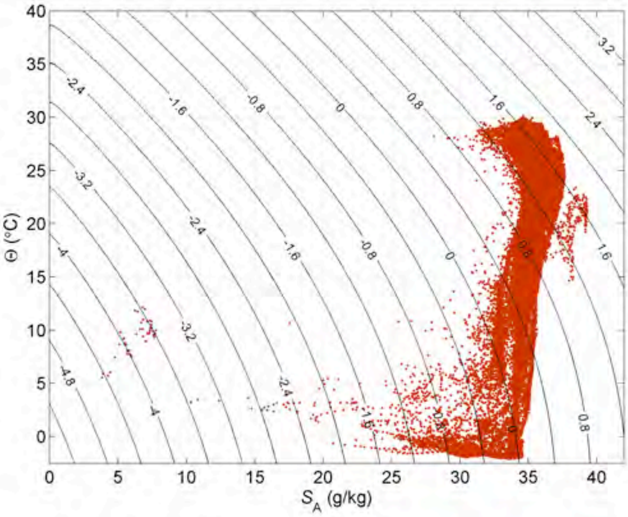


Figure A.14.1. Contours of $\left(\left|\nabla_n\theta\right|/\left|\nabla_n\Theta\right| \ - \ 1\right) \times 100\%$ at $p = 0$, showing the percentage difference between the epineutral gradients of θ and Θ. The red dots are from the ocean atlas of Gouretski and Koltermann (2004) at $p = 0$.

Averaging the Conservation Equations

We will illustrate the averaging issues using Preformed Salinity S_* which is designed to be a conservative variable which obeys the following instantaneous conservation equation

$$\left(\rho S_*\right)_t + \nabla\cdot\left(\rho \mathbf{u} S_*\right) \;=\; \rho\frac{\mathrm{d}S_*}{\mathrm{d}t} \;=\; -\nabla\cdot\mathbf{F}^{\mathrm{S}}. \qquad \text{(A.21.1)}$$

The molecular flux of salt $\mathbf{F}^{\mathrm{S}}$, is given by Eqn. (B.26) on page ~22 of these lecture notes. However, in an ocean that is dominated by turbulent mixing processes, it is completely unimportant what form the molecular fluxes take, so long as they appear in the conservation equation as the divergence of a flux.

For completeness, we repeat the continuity equation

$$\rho_t + \nabla\cdot\left(\rho\mathbf{u}\right) \;=\; 0. \qquad \text{(A.21.2)}$$

Temporally averaging this equation in Cartesian coordinates (i. e. at fixed x, y, z) gives

$$\bar{\rho}_t + \nabla\cdot\left(\overline{\rho\mathbf{u}}\right) \;=\; 0, \qquad \text{(A.21.3)}$$

which we choose to write in the following form, after division by a constant density ρ_0 (usually taken to be 1035 kg m^{-3})

$$\left(\bar{\rho}/\rho_0\right)_t + \nabla\cdot\tilde{\bar{\mathbf{u}}} \;=\; 0 \quad \text{where} \quad \tilde{\bar{\mathbf{u}}} \;\equiv\; \overline{\rho\mathbf{u}}/\rho_0 . \qquad \text{(A.21.4)}$$

This velocity $\tilde{\bar{\mathbf{u}}}$ is actually proportional to the average mass flux of seawater per unit area.

The conservation equation for Preformed Salinity (A.21.1) is now averaged in the corresponding manner obtaining

$$\left(\tfrac{\bar{\rho}}{\rho_0}\overline{S_*}^{\rho}\right)_t + \nabla\cdot\left(\overline{S_*}^{\rho}\,\tilde{\bar{\mathbf{u}}}\right) \;=\; \tfrac{\bar{\rho}}{\rho_0}\frac{\partial \overline{S_*}^{\rho}}{\partial t} \;+\; \tilde{\bar{\mathbf{u}}}\cdot\nabla\overline{S_*}^{\rho} \;=\; -\tfrac{1}{\rho_0}\nabla\cdot\overline{\mathbf{F}^{\mathrm{S}}} - \tfrac{1}{\rho_0}\nabla\cdot\left(\overline{\rho S_*''\mathbf{u}''}\right) . \qquad \text{(A.21.5)}$$

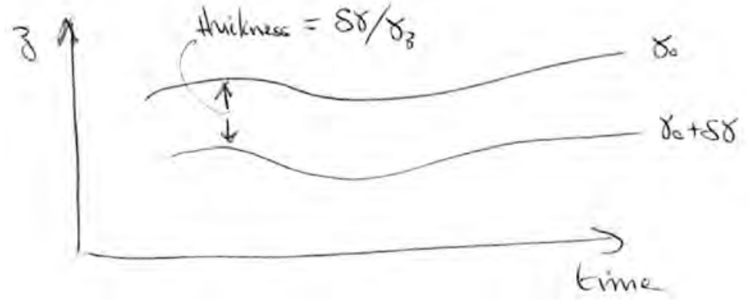
Here the Preformed Salinity has been density-weighted averaged, that is, $\overline{S_*}^{\rho} \equiv \overline{\rho S_*}/\bar{\rho}$, and the double primed quantities are deviations of the instantaneous quantity from its density-weighted average value. Since the turbulent fluxes are many orders of magnitude larger than molecular fluxes in the ocean, the molecular flux of salt is henceforth ignored.

The averaging process involved in Eqn. (A.21.5) has not invoked the traditional Boussinesq approximation (where density variations are ignored except in the gravitational force term). The above averaging process is best viewed as an average over many small-scale mixing processes over several hours, but not over mesoscale time and space scales. The two-stage averaging processes, without invoking the Boussinesq approximation, over first small-scale mixing processes (several meters) followed by averaging over the mesoscale (of order 100 km) has been performed by Greatbatch and McDougall (2003), yielding the prognostic equation for Preformed Salinity

$$\begin{aligned} h^{-1}\left(\tfrac{\tilde{\rho}}{\rho_0}h\hat{S}_*\right)_t\Big|_n + h^{-1}\nabla_n\cdot\left(\tfrac{\tilde{\rho}}{\rho_0}h\hat{\mathbf{v}}\hat{S}_*\right) + \left(\tfrac{\tilde{\rho}}{\rho_0}\tilde{e}\,\hat{S}_*\right)_z \;&=\; \tfrac{\tilde{\rho}}{\rho_0}\frac{\partial\hat{S}_*}{\partial t}\Big|_n \;+\; \tfrac{\tilde{\rho}}{\rho_0}\hat{\mathbf{v}}\cdot\nabla_n\hat{S}_* + \tfrac{\tilde{\rho}}{\rho_0}\tilde{e}\frac{\partial\hat{S}_*}{\partial z} \\ &=\; \tilde{\gamma}_z\nabla_n\cdot\left(\tilde{\gamma}_z^{-1}K\nabla_n\hat{S}_*\right) + \left(D\frac{\partial\hat{S}_*}{\partial z}\right)_z . \end{aligned} \qquad \text{(A.21.6)}$$

Here the over-caret means that the variable (e.g. $\hat{S}_*$) has been averaged in a thickness-and-density-weighted manner between a pair of "neutral surfaces" a small distance apart in the vertical, $\hat{\mathbf{v}}$ is the thickness-and-density-weighted horizontal velocity, e is the dianeutral velocity (the vertical velocity that penetrates through the neutral tangent plane) and $\tilde{e}$ is the temporal average of e on the "neutral surface" (that is, $\tilde{e}$ is not thickness-weighted). The turbulent fluxes are parameterized by the epineutral diffusivity K and the dianeutral (or vertical) diffusivity D. $\tilde{\gamma}_z$ is the vertical gradient of a suitable compressibility-corrected density such as Neutral Density or locally-referenced potential density, and the averaging involved in forming $\tilde{\gamma}_z$ is done to preserve the average thickness between closely-spaced neutral tangent planes; that is, the averaging is performed on $\tilde{\gamma}_z^{-1}$.

The issues of averaging involved in Eqns. (A.21.5) and (A.21.6) are subtle, and are not central to our purpose in this thermodynamics course. Hence we proceed with the more standard Boussinesq approach, but retain the over-carets to remind ourselves of the thickness-weighted nature of the variables.



It is important to recognize that our intuition about ocean mixing is based on the idea of weak turbulent mixing in the vertical direction (sometimes called "dianeutral" mixing, or "diapycnal mixing") and strong mixing along the density surfaces (epineutral mixing). The vertical diffusivity D is typically a few by $10^{-5}\,\mathrm{m^2\,s^{-1}}$ while the epineutral diffusivity is typically $K \approx 10^2\,\mathrm{m^2\,s^{-1}} - 10^3\,\mathrm{m^2\,s^{-1}}$. So the turbulent diffusivity along the neutral tangent plane is typically ~10,000,000 times greater than in the vertical direction. Actually, the so-called "vertical" or "dianeutral" diffusivity D acts isotropically in space (that is, it acts uniformly in all three spatial directions).

We now follow common practice and invoke the Boussinesq approximation of ignoring variations of density except in the gravitational acceleration term. In this common case, we begin with the instantaneous continuity equation ($\nabla\cdot\mathbf{u}=0$) and the instantaneous conservation equation for Preformed Salinity, written in density coordinates (where we have ignored the very small molecular flux of salt),

$$\left(\frac{1}{\gamma_z}\bigg|_\gamma\right)_t + \nabla_\gamma\cdot\left(\frac{\mathbf{v}}{\gamma_z}\right) + \big(e\big)_\gamma = 0\,, \qquad (3.20.6)$$

and

$$\left(\frac{S_*}{\gamma_z}\bigg|_\gamma\right)_t + \nabla_\gamma\cdot\left(\frac{\mathbf{v}\,S_*}{\gamma_z}\right) + \big(eS_*\big)_\gamma = 0\,. \qquad \text{(instantaneous)}$$

The averaging of these equation over time between a pair of closely-spaced Neutral Density γ surfaces leads to the thickness-weighted continuty equation,

$$\left(\frac{1}{\tilde{\gamma}_z}\bigg|_n\right)_t + \nabla_n\cdot\left(\frac{\hat{\mathbf{v}}}{\tilde{\gamma}_z}\right) + \frac{\tilde{e}_z}{\tilde{\gamma}_z} = 0\,, \qquad (3.20.6)$$

where the thickness-weighted horizontal velocity $\hat{\mathbf{v}}$ is given by

$$\hat{\mathbf{v}} \equiv \tilde{\gamma}_z\overline{\big(\mathbf{v}/\gamma_z\big)\Big|_\gamma}\,, \qquad \text{(thickness\_weighted\_horiz\_velocity)}$$

where $1/\gamma_z$ is proportional to the vertical distance, the "thickness", between two closely-spaced Neutral Density surfaces (the thickness is $\delta\gamma/\gamma_z$).

The thickness-weighted averaged version of the salinity conservation equation is

$$\left(\frac{\hat{S}_*}{\tilde{\gamma}_z}\bigg|_n\right)_t \;+\; \nabla_n\cdot\left(\frac{\hat{S}_*\,\hat{\mathbf{v}}}{\tilde{\gamma}_z}\right) \;+\; \frac{\left(\tilde{e}\,\hat{S}_*\right)_z}{\tilde{\gamma}_z} \;=\; \nabla_n\cdot\left(\tilde{\gamma}_z^{-1}K\nabla_n\hat{S}_*\right) \;+\; \frac{\left(D\hat{S}_{*_z}\right)_z}{\tilde{\gamma}_z}\,. \qquad (3.20.4\_S^*)$$

where the thickness-weighted value of Preformed Salinity is given by

$$\hat{S}_* \equiv \tilde{\gamma}_z\overline{\left(S_*/\gamma_z\right)\Big|_\gamma}\,. \qquad \text{(thickness\_weighted\_average)}$$

The advective form of Eqn. (3.20.4_S*) is

$$\frac{\partial\hat{S}_*}{\partial t}\bigg|_n + \hat{\mathbf{v}}\cdot\nabla_n\hat{S}_* + \tilde{e}\frac{\partial\hat{S}_*}{\partial z} \;=\; \frac{\hat{\mathrm{d}}\hat{S}_*}{\mathrm{d}t} \;=\; \tilde{\gamma}_z\nabla_n\cdot\left(\tilde{\gamma}_z^{-1}K\nabla_n\hat{S}_*\right) + \left(D\frac{\partial\hat{S}_*}{\partial z}\right)_z. \qquad (A.21.7)$$

The left-hand side is the material derivative of the thickness-weighted Preformed Salinity with respect to the thickness-weighted horizontal velocity $\hat{\mathbf{v}}$ and the temporally averaged dianeutral velocity $\tilde{e}$ of density coordinates. The right-hand side is the divergence of the turbulent fluxes of Preformed Salinity; the fact that the lateral diffusion term is the divergence of a flux can be seen when it is transformed to Cartesian coordinates. The turbulent eddy fluxes are here parameterized with the turbulent eddy diffusivities K and D.

The epineutral eddy diffusive flux is related to the correlations of eddy perturbation quantities by

$$\overline{\left(\frac{\mathbf{v}''S_*''}{\gamma_z}\right)\bigg|_\gamma} \;=\; -\,K\tilde{\gamma}_z^{-1}\nabla_\gamma\hat{S}_*\,. \qquad \text{(lateral\_eddy\_flux)}$$

Here the double-primed quantities are the deviation of the instantaneous value of the quantity from the thickness-weighted mean value.

In this course we are assuming Absolute Salinity to be a conservative variable, so it too satisfies a conservation equation identical to Eqn. (A.21.7), that is,

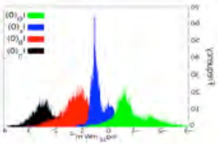
$$\boxed{\frac{\partial\hat{S}_\mathrm{A}}{\partial t}\bigg|_n + \hat{\mathbf{v}}\cdot\nabla_n\hat{S}_\mathrm{A} + \tilde{e}\frac{\partial\hat{S}_\mathrm{A}}{\partial z} \;=\; \tilde{\gamma}_z\nabla_n\cdot\left(\tilde{\gamma}_z^{-1}K\nabla_n\hat{S}_\mathrm{A}\right) + \left(D\hat{S}_{\mathrm{A}_z}\right)_z.} \qquad \underline{(A.21.11)}$$

The left-hand side is the material derivative of the thickness-weighted Absolute Salinity, written with respect to the neutral tangent plane so that it involves the thickness-weighted horizontal velocity $\hat{\mathbf{v}}$ and the temporally averaged dianeutral velocity $\tilde{e}$ of density coordinates.

Notice that the turbulent mixing has all originated from the left-hand side of the instantaneous conservation equation (A.21.1). This is the nature of turbulent mixing and its parameterization; it all comes from the eddying advection of "potential" variables (the correlation of primed variables). The molecular diffusivities are relegated to the role of destroying the tracer variance that is created by the turbulent flux of tracer.

We turn now to consider the material derivative of Conservative Temperature in a turbulent ocean. From Eqns. (A.13.5) and (A.21.8) the instantaneous material derivative of Θ is, without approximation,

$$\rho c_p^0\frac{\mathrm{d}\Theta}{\mathrm{d}t} \;=\; \frac{\left(T_0+\theta\right)}{\left(T_0+t\right)}\left(-\nabla\cdot\mathbf{F}^\mathrm{R} - \nabla\cdot\mathbf{F}^\mathrm{Q} + \rho\varepsilon\right) \;+\; \left[\frac{\left(T_0+\theta\right)}{\left(T_0+t\right)}\mu\left(p\right) - \mu\left(0\right)\right]\nabla\cdot\mathbf{F}^\mathrm{S}. \qquad (A.21.13)$$

The fact that the right-hand side of Eqn. (A.21.13) is not the divergence of a flux means that Θ is not a 100% conservative variable. However, our previous finite-amplitude analysis of mixing pairs of seawater parcels has shown that the non-constant coefficients of the divergences of the molecular fluxes of heat $-\nabla\cdot\mathbf{F}^\mathrm{Q}$ and salt $-\nabla\cdot\mathbf{F}^{\mathrm{S}}$ appearing on the right-hand side of Eqn. (A.21.13) are of no practical consequence as they cause an error in Conservative Temperature of no more than 1.2 mK (see Figure A.18.1). These non-ideal terms on the right-hand side of Eqn. (A.21.13) in a turbulent ocean have been shown to be an order of magnitude less than the dissipation term $\rho\varepsilon$ which is also justifiably neglected in oceanography (Graham and McDougall, 2013); see the histogram  on page ~57 of these lecture notes.

Hence with negligible error, the right-hand side of Eqn. (A.21.13) may be regarded as the sum of the ideal molecular flux of heat term $-\nabla\cdot\mathbf{F}^{\mathrm{Q}}$ and the term due to the boundary and radiative heat fluxes, $-(T_0+\theta)\nabla\cdot\mathbf{F}^{\mathrm{R}}\big/(T_0+t)$. At the sea surface the potential temperature θ and *in situ* temperature t are equal so that this last term is simply $-\nabla\cdot\mathbf{F}^{\mathrm{R}}$ so that there are no approximations with treating the air-sea sensible, latent and radiative heat fluxes as being fluxes of $c_p^0\Theta$. There is an issue at the sea floor where the boundary heat flux (the geothermal heat flux) affects Conservative Temperature through the "heat capacity" $(T_0+t)c_p^0\big/(T_0+\theta)$ rather than simply c_p^0. That is, the input of a certain amount of geothermal heat flux will cause a local change in Θ as though the seawater had the "specific heat capacity" $(T_0+t)c_p^0\big/(T_0+\theta)$ rather than c_p^0. These two specific heat capacities differ from each other by no more than 0.15% at a pressure of 4000 dbar. If this small percentage change in the effective "specific heat capacity" was ever considered important, it could be corrected by artificially multiplying the geothermal heat flux at the sea floor by $(T_0+\theta)\big/\left([T_0+t]c_p^0\right)$, so becoming the geothermal flux of Conservative Temperature.

We conclude that for the purpose of accounting for the transport of "heat" in the ocean it is sufficiently accurate to assume that Conservative Temperature is in fact conservative and that its instantaneous conservation equation is

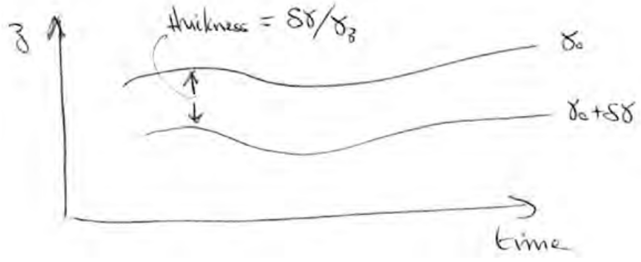
$$c_p^0\left(\rho\Theta\right)_t + c_p^0\nabla\cdot\left(\rho\Theta\mathbf{u}\right) = \rho c_p^0\frac{\mathrm{d}\Theta}{\mathrm{d}t} = -\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}}. \qquad \text{(A.21.14)}$$

Now we perform the same two-stage averaging procedure as outlined above in the case of Preformed Salinity. The Boussinesq form of the mesoscale-averaged equation is (analogous to Eqns. (A.21.7) or (A.21.11))

$$\boxed{\hat{\Theta}_t\Big|_n + \hat{\mathbf{v}}\cdot\nabla_n\hat{\Theta} + \tilde{e}\frac{\partial\hat{\Theta}}{\partial z} = \tilde{\gamma}_z\nabla_n\cdot\left(\tilde{\gamma}_z^{-1}K\nabla_n\hat{\Theta}\right) + \left(D\hat{\Theta}_z - F^{\mathrm{bound}}\right)_z.} \qquad \text{(A.21.15)}$$

As in the case of the S_{A} equation (A.21.11), the molecular flux of heat has been ignored in comparison with the turbulent fluxes of Conservative Temperature. The air-sea fluxes of sensible and latent heat, the radiative and the geothermal heat fluxes remain in Eqn. (A.21.15) in the vertical heat flux F^{bound} which is the sum of these boundary heat fluxes divided by $\rho_0 c_p^0$.

Equations (A.21.11) and (A.21.15) are the appropriately averaged conservation equations for "salinity and temperature" in physical oceanography. Remember, they have been thickness-weighted averaged in "density" coordinates.



The dianeutral velocity $\tilde e$

Just as the lateral gradients of Absolute Salinity and Conservative Temperature are compensating in terms of density when measured along the neutral tangent plane, so too are the temporal derivatives when measured along the neutral tangent plane. That is, we have not only

$$\alpha^{\Theta}\nabla_n\hat\Theta - \beta^{\Theta}\nabla_n\hat S_{\mathrm{A}} = \mathbf{0} \qquad (3.11.12)$$

but also

$$\alpha^{\Theta}\,\hat\Theta_t\Big|_n - \beta^{\Theta}\,\hat S_{\mathrm{A}_t}\Big|_n = 0\ . \qquad \text{(Neutral\_temporal)}$$

Now here are our S_{A} and Θ conservation equations to look at as we take the next step.

$$\boxed{\left.\frac{\partial \hat S_{\mathrm{A}}}{\partial t}\right|_n + \hat{\mathbf{v}}\cdot\nabla_n\hat S_{\mathrm{A}} + \tilde e\frac{\partial \hat S_{\mathrm{A}}}{\partial z} = \tilde\gamma_z\nabla_n\cdot\left(\tilde\gamma_z^{-1}K\nabla_n\hat S_{\mathrm{A}}\right) + \left(D\hat S_{\mathrm{A}_z}\right)_z .} \qquad \text{(A.21.11)}$$

$$\boxed{\hat\Theta_t\Big|_n + \hat{\mathbf{v}}\cdot\nabla_n\hat\Theta + \tilde e\frac{\partial\hat\Theta}{\partial z} = \tilde\gamma_z\nabla_n\cdot\left(\tilde\gamma_z^{-1}K\nabla_n\hat\Theta\right) + \left(D\hat\Theta_z - F^{\mathrm{bound}}\right)_z .} \qquad \text{(A.21.15)}$$

Now take α^{Θ} times the conservation equation (A.21.15) for $\hat\Theta$ minus β^{Θ} times the conservation equation (A.21.11) for Absolute Salinity $\hat S_{\mathrm{A}}$, and use the above two neutral relationships, Eqn. (3.11.12) and Eqn. (Neutral_temporal), to find the following equation for the dianeutral velocity $\tilde e$ (note that the boundary heat flux F^{bound} also needs to be included for fluid volumes that abut the sea surface)

$$\begin{aligned}\tilde e\left(\alpha^{\Theta}\hat\Theta_z - \beta^{\Theta}\hat S_{\mathrm{A}_z}\right) &= \alpha^{\Theta}\tilde\gamma_z\nabla_n\cdot\left(\tilde\gamma_z^{-1}K\nabla_n\hat\Theta\right) - \beta^{\Theta}\tilde\gamma_z\nabla_n\cdot\left(\tilde\gamma_z^{-1}K\nabla_n\hat S_{\mathrm{A}}\right)\\ &\quad + \alpha^{\Theta}\left(D\hat\Theta_z\right)_z - \beta^{\Theta}\left(D\hat S_{\mathrm{A}_z}\right)_z .\end{aligned} \qquad (A.22.3)$$

The left-hand side is equal to $\tilde e\,g^{-1}N^2$ and the first two terms on the right hand side would sum to zero if the equation of state were linear, that is, if both α^{Θ} and β^{Θ} were constant. Note that $\tilde e$ is the temporally averaged vertical velocity through the neutral tangent plane at a given longitude and latitude; it has not been thickness-weighted when it was averaged.

This equation for $\tilde e\,g^{-1}N^2$ can be rewritten in the following form

$$\boxed{\tilde e\,g^{-1}N^2 = -K\left(C_{\mathrm{b}}^{\Theta}\nabla_n\hat\Theta\cdot\nabla_n\hat\Theta + T_{\mathrm{b}}^{\Theta}\nabla_n\hat\Theta\cdot\nabla_n P\right) + \alpha^{\Theta}\left(D\hat\Theta_z\right)_z - \beta^{\Theta}\left(D\hat S_{\mathrm{A}_z}\right)_z .} \qquad \textbf{(A.22.4)}$$

where the cabbeling coefficient is defined as

$$C_{\mathrm{b}}^{\Theta} = \left.\frac{\partial\alpha^{\Theta}}{\partial\Theta}\right|_{S_{\mathrm{A}},p} + 2\frac{\alpha^{\Theta}}{\beta^{\Theta}}\left.\frac{\partial\alpha^{\Theta}}{\partial S_{\mathrm{A}}}\right|_{\Theta,p} - \left(\frac{\alpha^{\Theta}}{\beta^{\Theta}}\right)^2\left.\frac{\partial\beta^{\Theta}}{\partial S_{\mathrm{A}}}\right|_{\Theta,p} , \qquad (3.9.2)$$

and the thermobaric coefficient is defined as

$$T_{\mathrm{b}}^{\Theta} = \beta^{\Theta}\left.\frac{\partial\left(\alpha^{\Theta}/\beta^{\Theta}\right)}{\partial P}\right|_{S_{\mathrm{A}},\Theta} = \left.\frac{\partial\alpha^{\Theta}}{\partial P}\right|_{S_{\mathrm{A}},\Theta} - \frac{\alpha^{\Theta}}{\beta^{\Theta}}\left.\frac{\partial\beta^{\Theta}}{\partial P}\right|_{S_{\mathrm{A}},\Theta} . \qquad (3.8.2)$$

The cabbeling nonlinearity (the C_{b}^{Θ} term) always causes "densification", that is, it always causes a negative dianeutral velocity, $\tilde e$, while the thermobaric nonlinearity (the T_{b}^{Θ} term) can cause either dianeutral upwelling or downwelling.

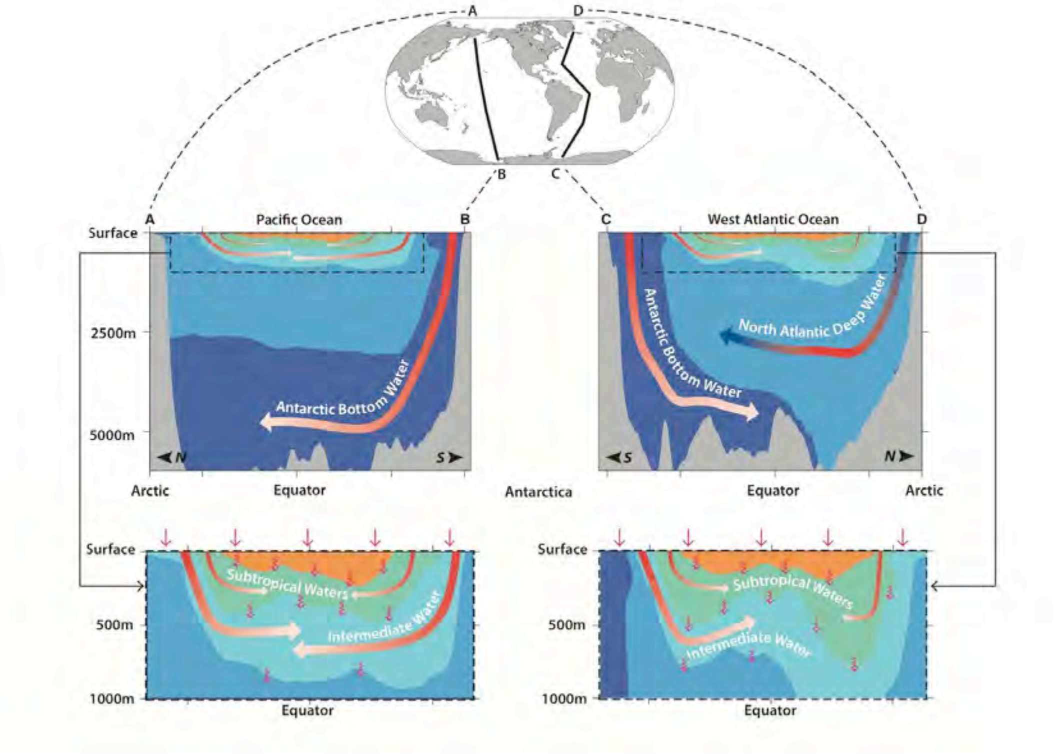
The vertical turbulent diffusion terms can be re-expressed in terms of DN^2 so that Eqn. (A.22.4) becomes

$$\tilde{e}\,N^2 = -\,gK\left(C_{\mathrm{b}}^{\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n\hat{\Theta} + T_{\mathrm{b}}^{\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n P\right) + \left(DN^2\right)_z - DN^2\frac{R_\rho}{\left(R_\rho-1\right)}\left[\frac{\alpha_z^{\Theta}}{\alpha^{\Theta}} - \frac{\beta_z^{\Theta}}{\beta^{\Theta}}\frac{1}{R_\rho}\right]. \qquad \text{(A.22.5)}$$

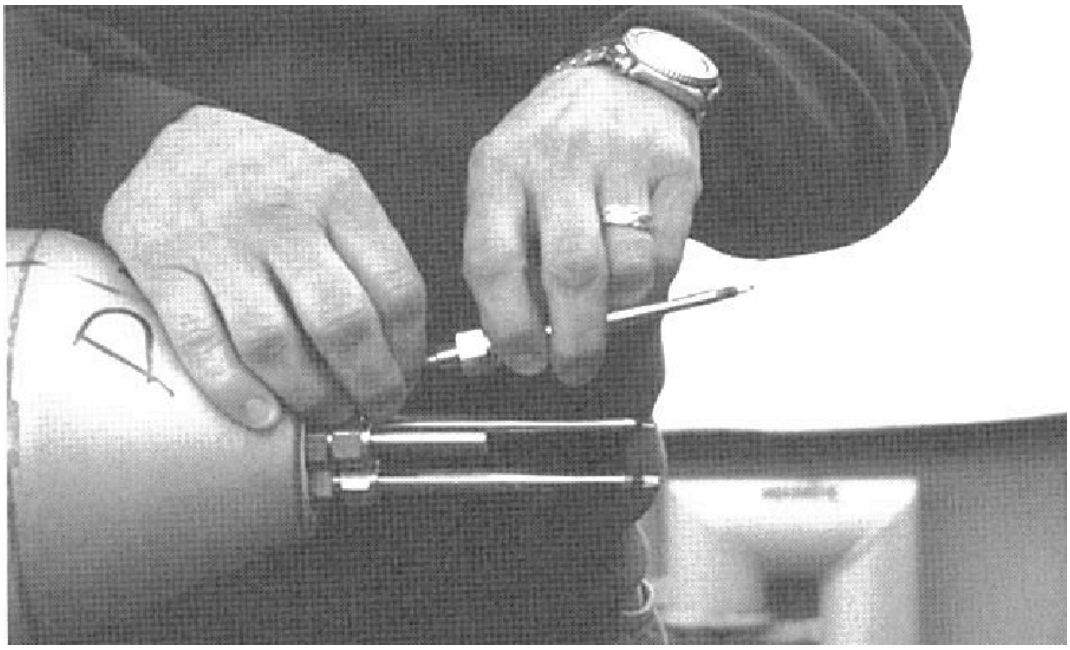
The Osborn (1980) relation $DN^2 = \Gamma\varepsilon \approx 0.2\,\varepsilon$ can be used in the second line of Eqn. (A.22.5) to relate upwelling $\tilde{e}$ to the vertical gradient of the dissipation of turbulent kinetic energy, ε. But when doing this, one should not ignore the last term in the above equation, nor the cabbeling and thermobaric advection terms.

It is important to realize that the dianeutral velocity $\tilde{e}$ is not a separate mixing process, but rather is a direct result of mixing processes such as (i) small-scale turbulent mixing as parameterized by the diffusivity D, and (ii) lateral turbulent mixing of heat and salt along the neutral tangent plane (as parameterized by the lateral turbulent diffusivity K) acting in conjunction with the cabbeling and thermobaric nonlinearities of the equation of state.

The importance of the dianeutral velocity $\tilde{e}$ in the deep ocean



Measuring the dissipation of kinetic energy: shear probes



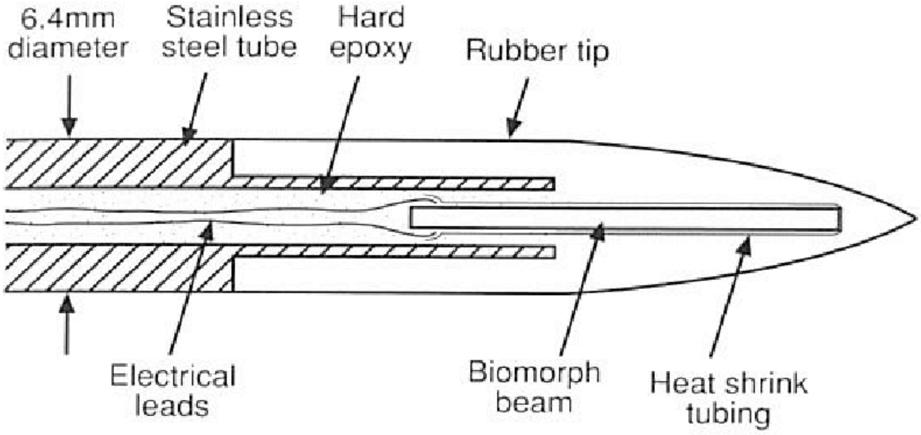
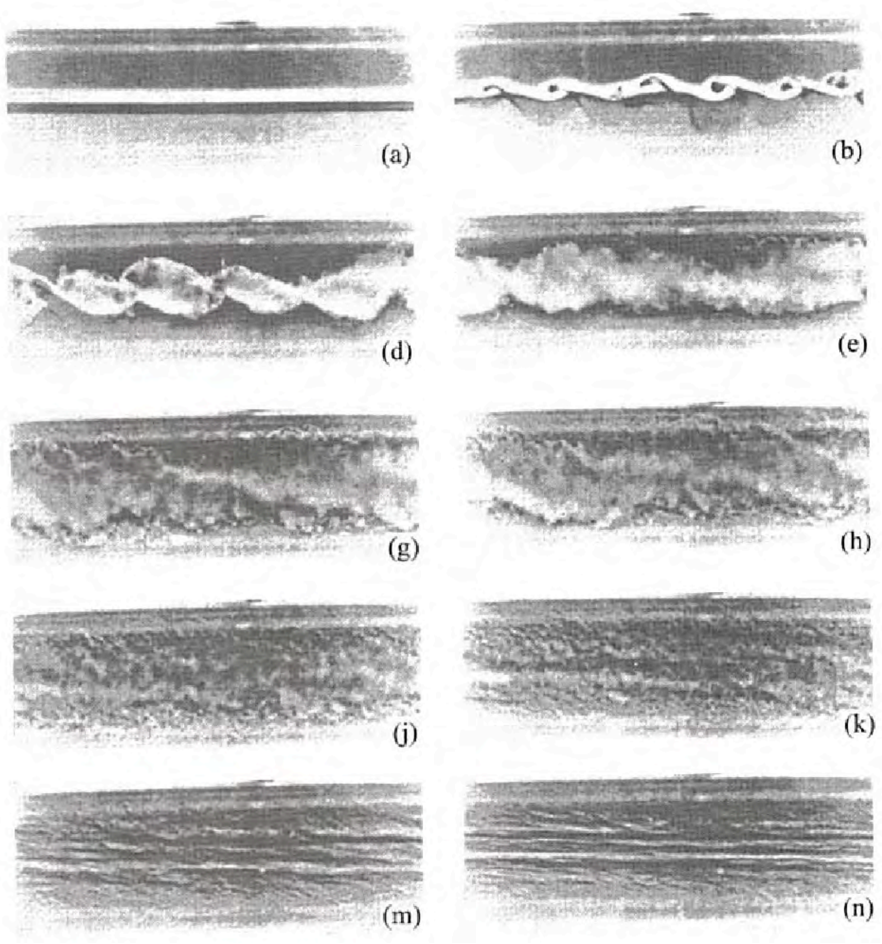


Figure 2.10. The piezoelectric air-foil shear probe designed by Osborn (1974). It has a diameter of 6.4 mm. Lateral forces caused by turbulence motion as the probe moves steadily through the water are converted into electrical signals that are calibrated to determine the relative turbulent velocity normal to the probe as a function of time.

Breaking internal gravity waves; the main process causing D



Dianeutral advection by Thermobaricity and cabbeling

We have seen the dianeutral advection arising from lateral diffusion in conjunction with the thermobaric and cabbeling nonlinearities of the equation of state in the $\tilde{e}$ evolution equation

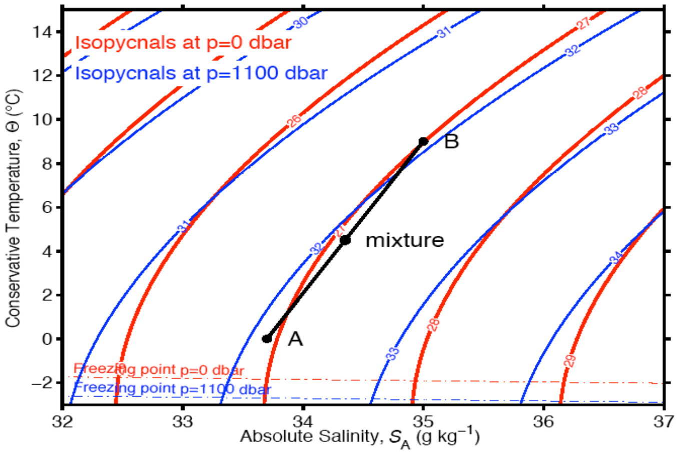
$$\boxed{\tilde{e}\, g^{-1} N^2 \;=\; -\,K\left(C_{\mathrm{b}}^{\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n\hat{\Theta} \;+\; T_{\mathrm{b}}^{\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n P\right) + \alpha^{\Theta}\left(D\hat{\Theta}_z\right)_z - \beta^{\Theta}\left(D\hat{S}_{\mathrm{A}_z}\right)_z .} \qquad \textbf{(A.22.4)}$$

where the thermobaric and cabbeling coefficients are given by

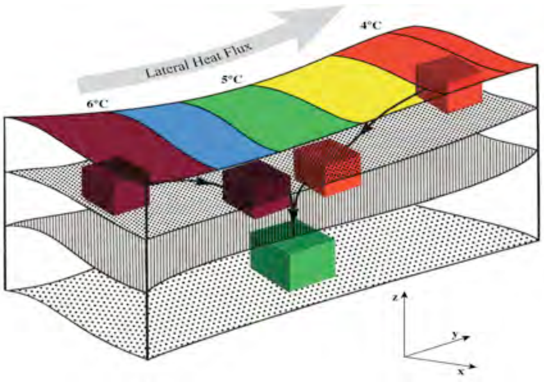
$$T_{\mathrm{b}}^{\Theta} \;=\; \beta^{\Theta}\left.\frac{\partial\left(\alpha^{\Theta}/\beta^{\Theta}\right)}{\partial P}\right|_{S_{\mathrm{A}},\Theta} \;=\; \left.\frac{\partial\alpha^{\Theta}}{\partial P}\right|_{S_{\mathrm{A}},\Theta} - \;\frac{\alpha^{\Theta}}{\beta^{\Theta}}\left.\frac{\partial\beta^{\Theta}}{\partial P}\right|_{S_{\mathrm{A}},\Theta} , \qquad (3.8.2)$$

$$C_{\mathrm{b}}^{\Theta} \;=\; \left.\frac{\partial\alpha^{\Theta}}{\partial\Theta}\right|_{S_{\mathrm{A}},p} \;+\; 2\frac{\alpha^{\Theta}}{\beta^{\Theta}}\left.\frac{\partial\alpha^{\Theta}}{\partial S_{\mathrm{A}}}\right|_{\Theta,p} \;-\; \left(\frac{\alpha^{\Theta}}{\beta^{\Theta}}\right)^{2}\left.\frac{\partial\beta^{\Theta}}{\partial S_{\mathrm{A}}}\right|_{\Theta,p} . \qquad (3.9.2)$$

What are thermobaricity and cabbeling; how do these processes work?

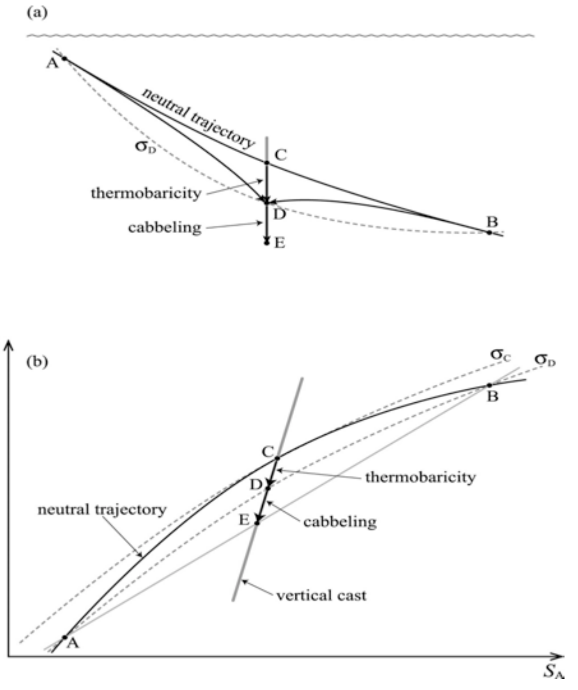


Cabbeling can be understood by looking at the isolines of potential density above. Consider the curved red lines (and ignore parcels A and B for now). A mixture of two parcels that both lie of a red potential contour will result in a mixed parcel that is denser than the original density. This is cabbeling.



The cabbeling processes requires the intimate mixing, at the molecular level, whereas the dianeutral motion of thermobaricity occurs during the isentropic advection of the two fluid parcels (and is made permanent by the intimate molecular diffusion which leads to the green fluid of the deepest cube above).

The dianeutral motion of thermobaricity occurs because the two parcels in the insulating plastic bags have a different compressibility to that of the ocean that surrounds them on their journey. So pressure changes result in a different change in density and hence a different vertical trajectory.



Note that

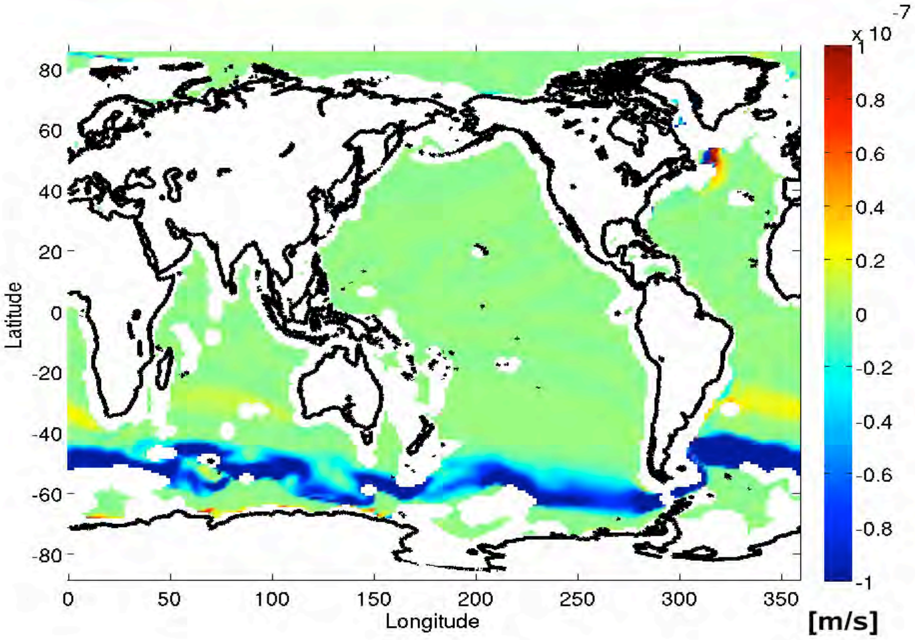
$$\alpha^{\Theta}\nabla_n^2\hat{\Theta} - \beta^{\Theta}\nabla_n^2\hat{S}_A = -\left(C_b^{\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n\hat{\Theta} + T_b^{\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n P\right), \qquad \text{(Epineutral\_K)}$$

so that unless α^{Θ} and β^{Θ} are constant, it is not possible that both $\nabla_n^2\hat{\Theta}$ and $\nabla_n^2\hat{S}_A$ are zero. This can be understood as follows. The nature of the neutral constraint on the lateral mixing process means that $\nabla_n\hat{S}_A = \left(\alpha^{\Theta}/\beta^{\Theta}\right)\nabla_n\hat{\Theta}$ so even if $\nabla_n^2\hat{\Theta} = 0$ (which is consistent with the epineutral gradient of $\hat{\Theta}$, $\nabla_n\hat{\Theta}$, being spatially constant), the epineutral gradient of $\hat{S}_A$, $\nabla_n\hat{S}_A$, must vary in space according to $\nabla_n\cdot\nabla_n\hat{S}_A = \nabla_n^2\hat{S}_A = \nabla_n\left(\alpha^{\Theta}/\beta^{\Theta}\right)\cdot\nabla_n\hat{\Theta}$. This leads to a dianeutral velocity $\tilde{e}$ which affects the conservation equation of both $\hat{S}_A$ and $\hat{\Theta}$. It is the nature of the neutral mixing constraint, $\alpha^{\Theta}\nabla_n\hat{\Theta} = \beta^{\Theta}\nabla_n\hat{S}_A$, that guarantees that both $\nabla_n^2\hat{\Theta}$ and $\nabla_n^2\hat{S}_A$ cannot be zero simultaneously.

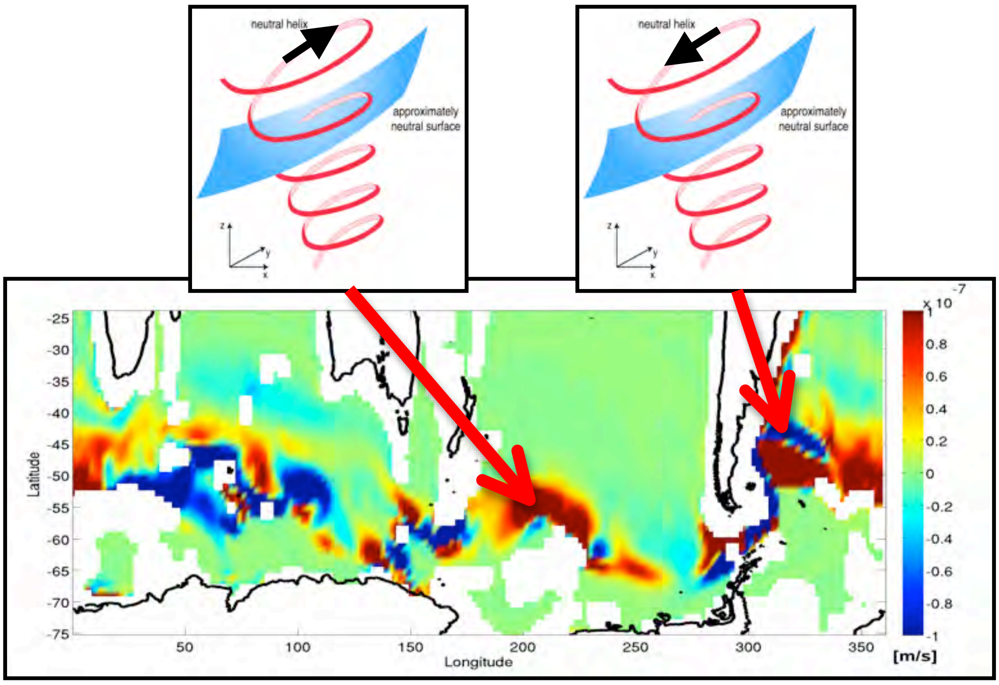
Note that both the thermobaric and cabbeling dianeutral advection is proportional to the mesoscale eddy flux per unit area of "heat" along the neutral tangent plane, $-c_p^0 K\nabla_n\Theta$, and is independent of the amount of small-scale (dianeutral) turbulent mixing and hence is also independent of the dissipation of mechanical energy ε. So here we have two processes that cause mean vertical motion through "density surfaces" but have no signature in the observations that are made to measure vertical mixing processes; no signature in the dissipation of mechanical energy ε.

Interestingly, for given magnitudes of the epineutral gradients of pressure and Conservative Temperature, the dianeutral advection of thermobaricity is maximized when these gradients are parallel, while neutral helicity is maximized when these gradients are perpendicular, since neutral helicity is proportional to $T_b^{\Theta}\left(\nabla_n P\times\nabla_n\Theta\right)\cdot\mathbf{k}$ (see Eqn. (3.13.2)).

When the cabbeling and thermobaricity processes are analyzed by considering the mixing of two fluid parcels one finds that the density change is proportional to the square of the property (Θ and/or p) contrasts between the two fluid parcels. This leads to the thought that if an ocean front is split up into a series of many less intense fronts then the effects of cabbeling and thermobaricity might be reduced in proportion to the number of such fronts. Actually, this is not the case. Rather, the total dianeutral transport across a frontal region depends on the product of the lateral flux of heat passing through the front and the contrast in temperature and/or pressure across the front, but is independent of the sharpness of the front. This can be understood by noting from above that the dianeutral velocity due to cabbeling, $e^{\mathrm{Cab}} = -gN^{-2}K\,C_{\mathrm{b}}^{\Theta}\nabla_n\Theta\cdot\nabla_n\Theta$, is proportional to the scalar product of the epineutral flux of heat $-c_p^0 K\nabla_n\Theta$ and the epineutral temperature gradient $\nabla_n\Theta$. We note that while the epineutral diffusivity K varies strongly in space, commonly the epineutral heat flux $-c_p^0 K\nabla_n\Theta$ varies less fast in space than K. When spatially integrating the dianeutral advection velocity over the area of the frontal region, one can exploit the slowly varying nature of $-c_p^0 K\nabla_n\Theta$ to find that the total dianeutral transport is approximately proportional to the lateral heat flux times the difference in temperature across the frontal region (in the case of cabbeling) or the difference in pressure across the frontal region (in the case of thermobaricity).

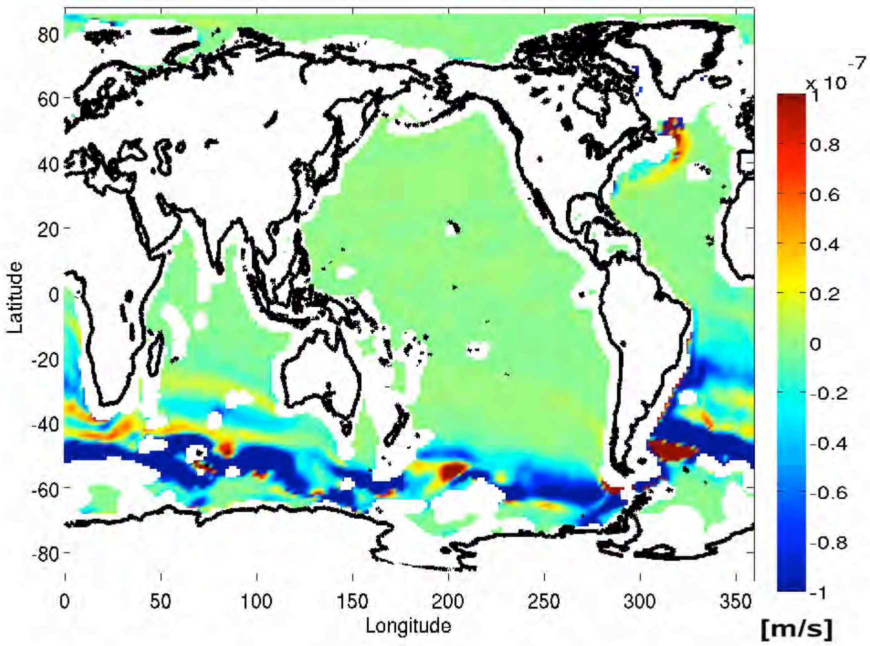


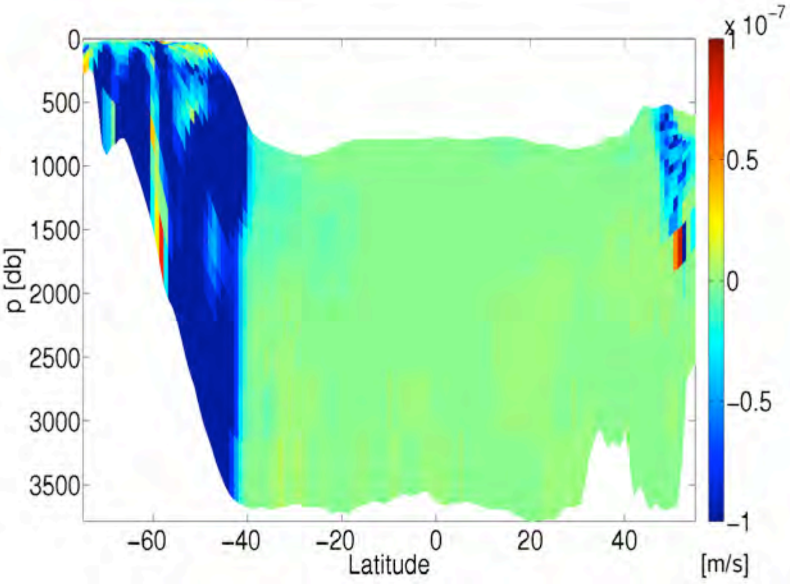
This figure is of the dianeutral velocity due to thermobaricity. In the Southern Ocean this is a dominant mixing process, being larger than the canonical diapycnal upwelling velocity of $10^{-7}\ \mathrm{m\ s^{-1}}$ of Munk (1966).



The figure above shows the vertical velocity through an approximately neutral surface caused by neutral helicity. That is, this is the actual vertical flow caused by the helical nature of neutral trajectories. The magnitude in the Southern Ocean is at leading order of $10^{-7}\ \mathrm{m\ s^{-1}}$, this being the canonical diapycnal velocity, dating back to Munk (1966).

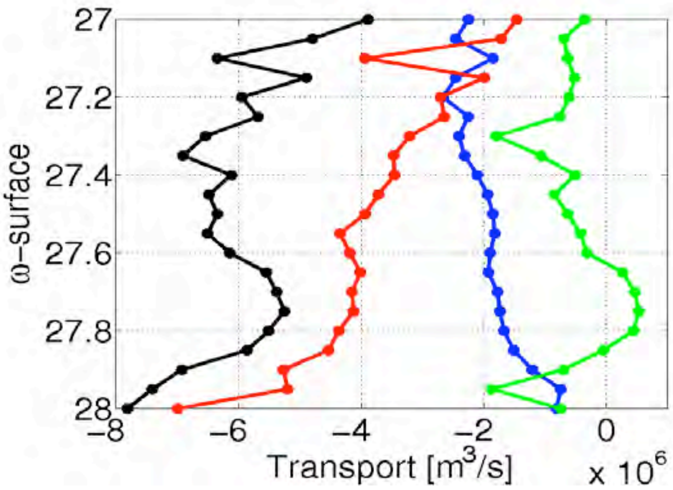
The figure below is the total dianeutral velocity for all non-linear equation-of-state processes, namely thermobaricity, cabbeling and the helical nature of neutral trajectories.





This figure is of the zonally-averaged dianeutral velocity due to the sum of thermobaricity, cabbeling and another strange process that is due to the thermobaric coefficient T_b^Θ, the helical nature of neutral trajectories. In the Southern Ocean these non-linear processes are the dominant mixing process, being larger than the canonical diapycnal upwelling velocity of $10^{-7}\ \mathrm{m\,s^{-1}}$ of Munk (1966).

When these dianeutral velocities are spatially integrated over the whole world's oceans, we find, as a function of Neutral Density,



In green is the mean dianeutral transport from the ill-defined nature of "neutral surfaces", blue is the dianeutral transport due to cabbeling, red due to thermobaricity, and black is the total global dianeutral transport due to the sum of these three non-linear processes.

These transports are to compared with the production rate of Deep and Bottom Water in the world ocean of about $(15-20)\times10^6\ \mathrm{m^3\,s^{-1}}$. The conclusion is that these dianeutral advection processes due to the nonlinear nature of the equation of state of seawater are not insignificant processes.

Double-diffusive convection; "salt-fingers"

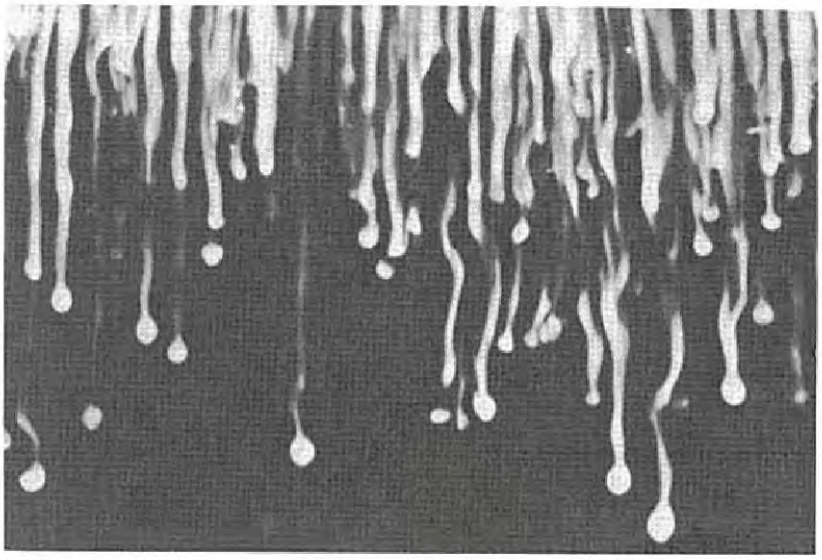


Figure 4.17. Salt fingers. These are formed in the laboratory by carefully allowing a warm weak brine solution containing a fluorescent dye to spread over a cold fresh layer of water. A vertical sheet of light is used to cause the dye to emit light and so make the developing fingers visible in this horizontal view. The 'fingers' are typically 2 mm in width in the laboratory experiment, but in the ocean fingers may be some few centimetres wide. (From Huppert and Turner, 1981.)

The "budget method" of estimating the vertical diffusivity *D*

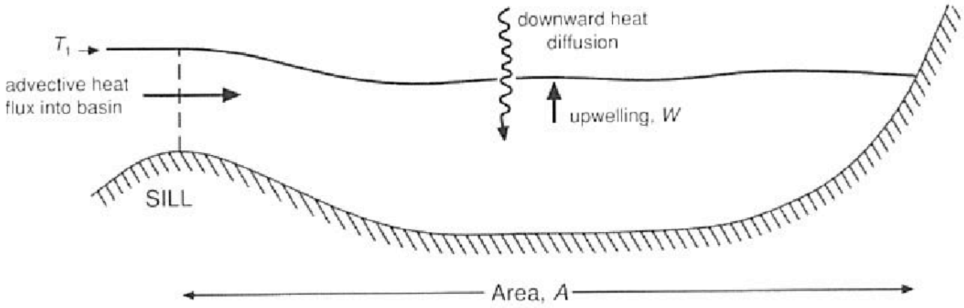


Figure 4.22. Heat balance in a deep-ocean basin. Flow enters a deep-ocean basin over a sill on the left. The basin is closed on the right. There is a downward flux of heat by diffusion from water of higher temperature above the T_1 isotherm and upward (upwelling) motion at speed, w, within the basin at the level of the T_1 isotherm, maintaining a steady state.

This "budget method" is a way of estimating the vertical diffusivity across the isotherm without measuring the properties of the turbulence at the centimeter scale.

The water-mass transformation equation

It is instructive to substitute Eqn. (A.22.4) for $\tilde{e}$ into the expression (A.21.15) for the material derivative of $\hat{\Theta}$, thus eliminating $\tilde{e}$ and obtaining the following equation for the temporal and spatial evolution of $\hat{\Theta}$ along the neutral tangent plane (McDougall (1984))

$$\boxed{\begin{aligned}\hat{\Theta}_t\Big|_n + \hat{\mathbf{v}}\cdot\nabla_n\hat{\Theta} \;=\; &\tilde{\gamma}_z\nabla_n\cdot\left(\tilde{\gamma}_z^{-1}K\nabla_n\hat{\Theta}\right) + KgN^{-2}\hat{\Theta}_z\left(C_{\mathrm{b}}^{\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n\hat{\Theta} + T_{\mathrm{b}}^{\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n P\right)\\ &+ D\beta^{\Theta}gN^{-2}\hat{\Theta}_z^{3}\,\frac{d^2\hat{S}_{\mathrm{A}}}{d\hat{\Theta}^2}\,.\end{aligned}} \qquad \textbf{(A.23.1)}$$

The term involving D has been written as proportional to the curvature of the $\hat{S}_{\mathrm{A}}-\hat{\Theta}$ diagram of a vertical cast; this term can also be written as $D\beta^{\Theta}gN^{-2}\left(\hat{\Theta}_z\hat{S}_{\mathrm{A}_{zz}}-\hat{S}_{\mathrm{A}_z}\hat{\Theta}_{zz}\right)$. The form of Eqn. (A.23.1) illustrates that when analyzed in density coordinates, Conservative Temperature (and Absolute Salinity)

(i) are affected not only by the expected lateral diffusion process along density surfaces but also by the nonlinear dianeutral advection processes, cabbeling and thermobaricity,

(ii) are affected by diapycnal turbulent mixing only to the extent that the vertical $\hat{S}_{\mathrm{A}}-\hat{\Theta}$ diagram is not locally straight, and

(iii) are not influenced by the vertical variation of D since D_z does not appear in this equation.

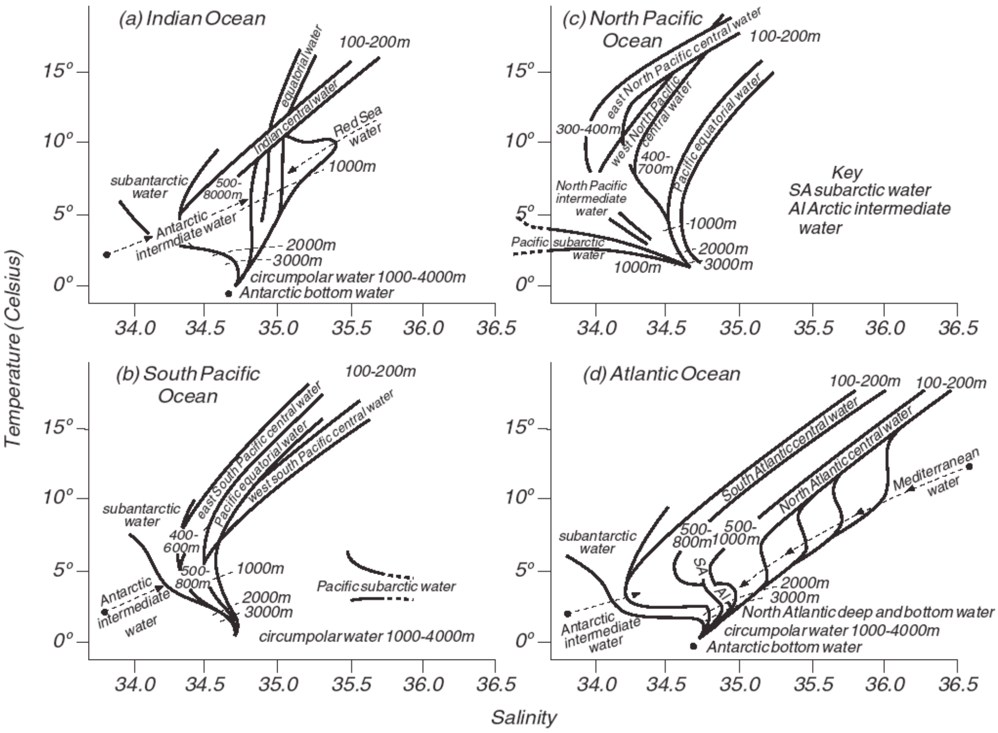


Figure 13.11 T-S plots of water in the various ocean basins. After Tolmazin (1985: 138).

A review of our basic conservation equations

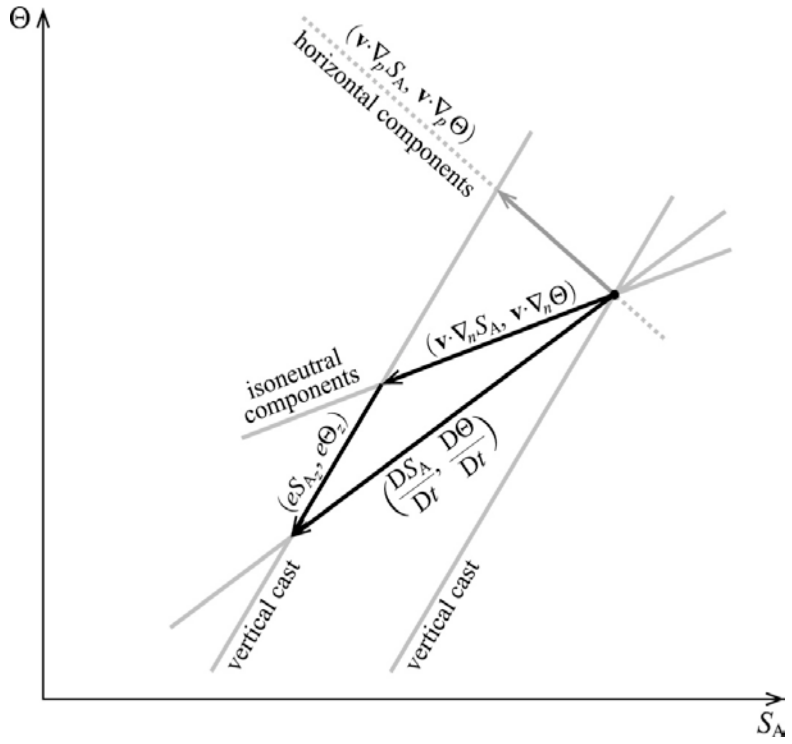
$$\boxed{\left.\frac{\partial \hat{S}_{\mathrm{A}}}{\partial t}\right|_n + \hat{\mathbf{v}}\cdot\nabla_n \hat{S}_{\mathrm{A}} + \tilde{e}\frac{\partial \hat{S}_{\mathrm{A}}}{\partial z} = \tilde{\gamma}_z \nabla_n \cdot\left(\tilde{\gamma}_z^{-1} K \nabla_n \hat{S}_{\mathrm{A}}\right) + \left(D\frac{\partial \hat{S}_{\mathrm{A}}}{\partial z}\right)_z .} \qquad \text{(A.21.11)}$$

$$\boxed{\left.\hat{\Theta}_t\right|_n + \hat{\mathbf{v}}\cdot\nabla_n \hat{\Theta} + \tilde{e}\frac{\partial \hat{\Theta}}{\partial z} = \tilde{\gamma}_z \nabla_n \cdot\left(\tilde{\gamma}_z^{-1} K \nabla_n \hat{\Theta}\right) + \left(D\hat{\Theta}_z\right)_z .} \qquad \text{(A.21.15)}$$

$$\boxed{\tilde{e}\, g^{-1} N^2 = -K\left(C_{\mathrm{b}}^{\Theta}\nabla_n \hat{\Theta}\cdot\nabla_n \hat{\Theta} + T_{\mathrm{b}}^{\Theta}\nabla_n \hat{\Theta}\cdot\nabla_n P\right) + \alpha^{\Theta}\left(D\hat{\Theta}_z\right)_z - \beta^{\Theta}\left(D\hat{S}_{\mathrm{A}_z}\right)_z .} \qquad \textbf{(A.22.4)}$$

$$\boxed{\begin{aligned}\left.\hat{\Theta}_t\right|_n + \hat{\mathbf{v}}\cdot\nabla_n \hat{\Theta} &= \tilde{\gamma}_z \nabla_n \cdot\left(\tilde{\gamma}_z^{-1} K \nabla_n \hat{\Theta}\right) + KgN^{-2}\hat{\Theta}_z\left(C_{\mathrm{b}}^{\Theta}\nabla_n \hat{\Theta}\cdot\nabla_n \hat{\Theta} + T_{\mathrm{b}}^{\Theta}\nabla_n \hat{\Theta}\cdot\nabla_n P\right)\\ &\quad + D\beta^{\Theta} g N^{-2}\hat{\Theta}_z^3 \frac{d^2 \hat{S}_{\mathrm{A}}}{d\hat{\Theta}^2} .\end{aligned}} \qquad \textbf{(A.23.1)}$$

Equations (A.21.11) and (A.21.15) are the fundamental evolution equations of Absolute Salinity and Conservative Temperature in a turbulent ocean, and the pair of equations **(A.22.4)** and **(A.23.1)** are simply derived as linear combinations of Eqns. (A.21.11) and (A.21.15). The "density" conservation equation **(A.22.4)** and the "water-mass transformation" equation **(A.23.1)** are in some sense the "normal modes" of Eqns. (A.21.11) and (A.21.15). That is, Eqn. **(A.22.4)** expresses how mixing processes contribute to the mean vertical velocity $\tilde{e}$ through the neutral tangent plane, while **(A.23.1)** expresses how the tracer called "Conservative Temperature measured along the neutral direction" is affected by mixing processes; this equation does not contain $\tilde{e}$.



For completeness, the water-mass conservation equation for Absolute Salinity that corresponds to Eqn. (A.23.1) is

$$\left.\frac{\partial \hat{S}_{\mathrm{A}}}{\partial t}\right|_{n} + \hat{\mathbf{v}}\cdot\nabla_{n}\hat{S}_{\mathrm{A}} = \tilde{\gamma}_{z}\nabla_{n}\cdot\left(\tilde{\gamma}_{z}^{-1}K\nabla_{n}\hat{S}_{\mathrm{A}}\right) + K\,gN^{-2}\,\hat{S}_{\mathrm{A}_{z}}\left(C_{\mathrm{b}}^{\Theta}\nabla_{n}\hat{\Theta}\cdot\nabla_{n}\hat{\Theta} + T_{\mathrm{b}}^{\Theta}\nabla_{n}\hat{\Theta}\cdot\nabla_{n}P\right)$$
$$+ D\alpha^{\Theta}gN^{-2}\hat{\Theta}_{z}^{3}\frac{d^{2}\hat{S}_{\mathrm{A}}}{d\hat{\Theta}^{2}}\,, \qquad \text{(A.23.2)}$$

and it easy to show that α^{Θ} times the right-hand side of Eqn. (A.23.1) is equal to β^{Θ} times the right-hand side of Eqn. (A.23.2).

Potential density ρ^{Θ} or ρ^{θ}

Potential density ρ^{θ} is the density that a fluid parcel would have if its pressure were changed to a fixed reference pressure p_{r} in an isentropic and isohaline manner. Potential density referred to reference pressure p_{r} can be written as

$$\rho^{\theta}\left(S_{\mathrm{A}},t,p,p_{\mathrm{r}}\right) = \rho\left(S_{\mathrm{A}},\theta[S_{\mathrm{A}},t,p,p_{\mathrm{r}}],p_{\mathrm{r}}\right) = g_{P}^{-1}\left(S_{\mathrm{A}},\theta[S_{\mathrm{A}},t,p,p_{\mathrm{r}}],p_{\mathrm{r}}\right). \qquad (3.4.2)$$

Using the functional forms of either $\rho = \tilde{\rho}\left(S_{\mathrm{A}},\theta,p\right)$ or $\rho = \hat{\rho}\left(S_{\mathrm{A}},\Theta,p\right)$, potential density with respect to reference pressure p_{r} (e. g. 1000 dbar) can be evaluated more easily as

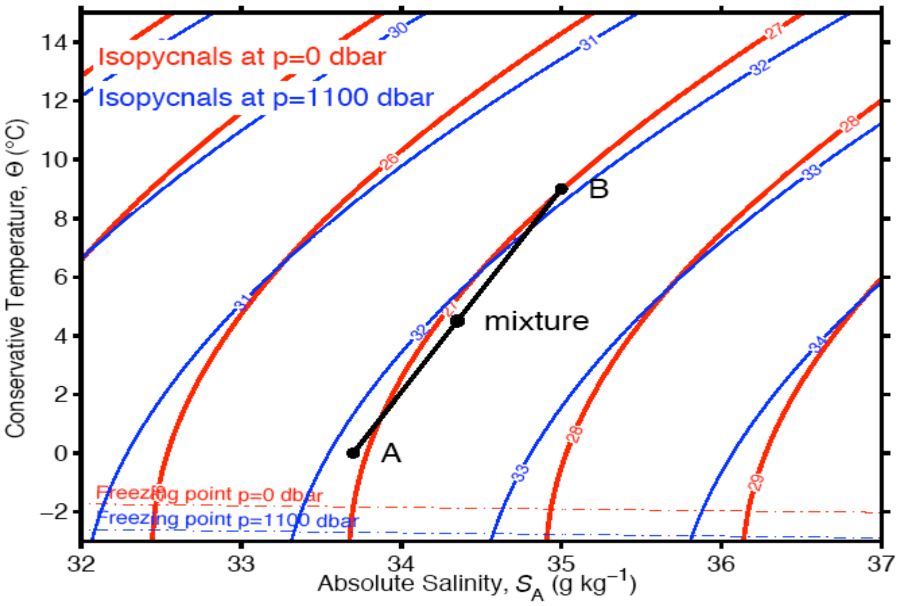
$$\rho^{\Theta}\left(S_{\mathrm{A}},t,p,p_{\mathrm{r}}\right) = \bar{\rho}\left(S_{\mathrm{A}},\eta,\,p_{\mathrm{r}}\right) = \tilde{\rho}\left(S_{\mathrm{A}},\theta,\,p_{\mathrm{r}}\right) = \hat{\rho}\left(S_{\mathrm{A}},\Theta,\,p_{\mathrm{r}}\right), \qquad (3.4.3)$$

where we note that the potential temperature θ in the penultimate expression is the potential temperature with respect to $0\,\mathrm{dbar}$. Once the reference pressure is fixed, potential density is a function only of Absolute Salinity and Conservative Temperature (or equivalently, of Absolute Salinity and potential temperature). Note that it is equally correct to label potential density as ρ^{θ} or ρ^{Θ} (or indeed as ρ^{η}) because η, θ and Θ are constant during the isentropic and isohaline pressure change from p to p_{r}; that is, these variables posses the "potential" property.

Since we know that $v = g_{P} = \tilde{h}_{P} = \hat{h}_{P}$, potential density may also be expressed in terms of the pressure derivative of the expressions $h = \tilde{h}\left(S_{\mathrm{A}},\theta,p\right)$ and $h = \hat{h}\left(S_{\mathrm{A}},\Theta,p\right)$ as

$$\rho^{\Theta}\left(S_{\mathrm{A}},t,p,p_{\mathrm{r}}\right) = \left[\tilde{h}_{P}\left(S_{\mathrm{A}},\theta,\,p{=}\,p_{\mathrm{r}}\right)\right]^{-1} = \left[\hat{h}_{P}\left(S_{\mathrm{A}},\Theta,\,p{=}\,p_{\mathrm{r}}\right)\right]^{-1}. \qquad (3.4.4)$$

The figure below shows contours of constant potential density on the $S_{\mathrm{A}}-\Theta$ diagram. The red contours have $p_{\mathrm{r}} = 0\,\mathrm{dbar}$ while the blue contours are with respect to the reference pressure $p_{\mathrm{r}} = 1100\,\mathrm{dbar}$. Notice particularly that on this $S_{\mathrm{A}}-\Theta$ diagram the contours rotate with increasing reference pressure.



An important consequence of this rotation can be deduced by considering the two seawater parcels A and B. If parcels A and B were at the sea surface (that is, at $0\ \text{dbar}$) then parcel B would be denser than parcel A. However, if both seawater parcels were at $1100\ \text{dbar}$ then the reverse is the case; now parcel A is denser than parcel B. Therein lies a whole level of complication in physical oceanography, all caused by the thermobaric non-linearity of the equation of state of seawater.

The symbol σ_1 is used for $\hat{\rho}^{\Theta}\left(S_{\text{A}}, \Theta, p_{\text{r}}\!=\!1000\ \text{dbar}\right) - 1000\ \text{kg m}^{-3}$ and similarly for σ_0, σ_2 and σ_4, and these are called "potential density anomaly".

Here is another figure illustrating the rotation of the potential density contours with pressure.

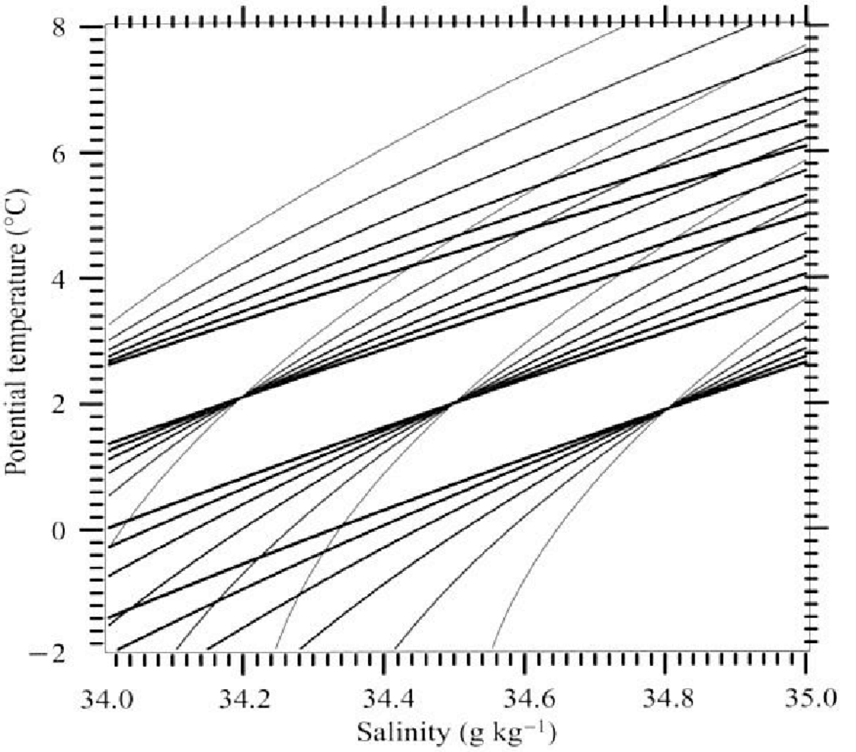


Figure 2.1. Equation of state for sea water. Contours of the density difference $\rho(p, \theta, S) - \rho(p, 2\,^{\circ}\text{C}, 34, 5\ \text{psu})$ are shown in the (θ, S)-plane for different values of pressure corresponding to depths of 0 m (*thin lines*) to 5 km (*thick lines*) in 1 km intervals. The contour interval is $0.25\ \text{kg m}^{-3}$. The equation of state is nonlinear. The contours (isopycnals) are *curved* and their slope *turns* with pressure. Courtesy of Ernst Maier-Reimer.

Calculating the thermodynamic properties of seawater using the GSW Oceanographic Toolbox

The computer software needed to evaluate the thermodynamic properties of seawater is available from the web site www.TEOS-10.org The GSW Oceanographic Toolbox (GSW stands for Gibbs SeaWater) can be downloaded in a variety of computer languages. The list

http://www.teos-10.org/pubs/GSW_Toolbox_list.pdf

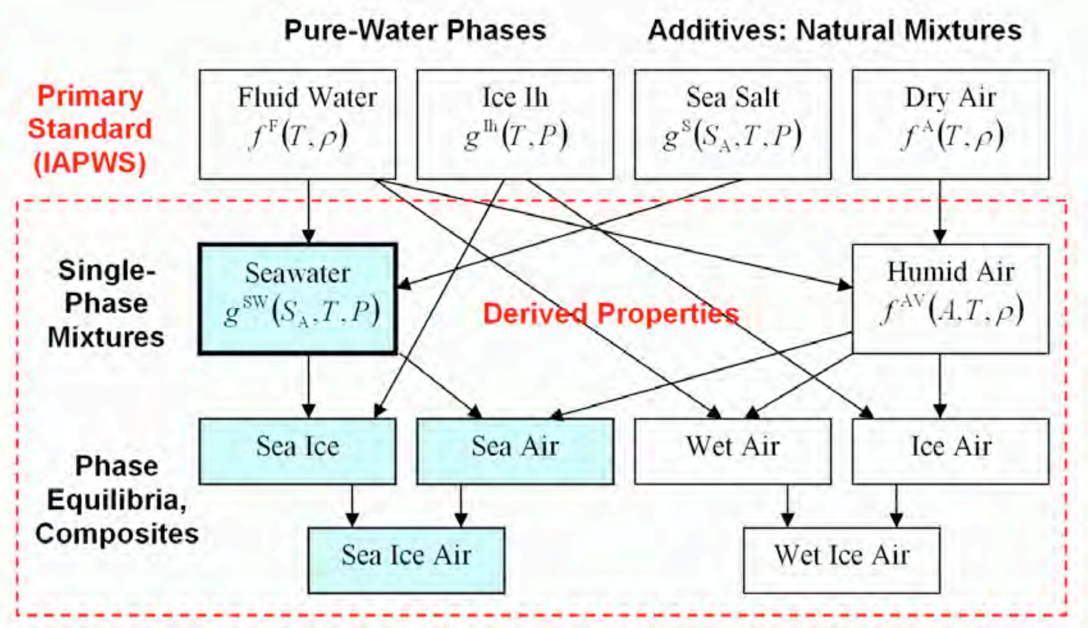
lists all the available algorithms.

For the past thirty years we have taken the "raw" data of Practical Salinity S_{P} (PSS-78), *in situ* temperature t (now ITS-90) and pressure p and we have used an algorithm to calculate potential temperature θ in order to analyze and publish water-mass characteristics on the $S_{\mathrm{P}} - \theta$ diagram. On this $S_{\mathrm{P}} - \theta$ diagram we have been able to draw curved contours of potential density using EOS-80 which has been the international standard for seawater from 1980-2009.

Under TEOS-10 this practice has now changed:- density and potential density (and all types of geostrophic streamfunction including dynamic height anomaly) are now not functions of Practical Salinity S_{P} but rather are functions of Absolute Salinity S_{A}.

In summary, under EOS-80 we have used the observed variables $\left(S_{\mathrm{P}}, t, p\right)$ to first form potential temperature θ and then we have analyzed water masses on the $S_{\mathrm{P}} - \theta$ diagram, and we have been able to draw curved contours of potential density on this same $S_{\mathrm{P}} - \theta$ diagram. Under TEOS-10, the observed variables $\left(S_{\mathrm{P}}, t, p\right)$, together with longitude and latitude, are used to first form Absolute Salinity S_{A} using **gsw_SA_from_SP**, and then Conservative Temperature Θ is calculated using **gsw_CT_from_t**. Oceanographic water masses are then analyzed on the $S_{\mathrm{A}} - \Theta$ diagram (using **gsw_SA_CT_plot**), and potential density contours can be drawn on this $S_{\mathrm{A}} - \Theta$ diagram using **gsw_rho**(SA,CT,p_ref).

So the first steps with analyzing observed oceanographic data is to calculate and store Absolute Salinity S_{A} and Conservative Temperature Θ. Thereafter, all the analysis uses these variables and does not make any further use of the observed Practical Salinity S_{P}, nor of the *in situ* temperature t, nor of the potential temperature θ.



Formulas for properties of seawater and ice expressed in terms of the Gibbs functions $g(S_\mathrm{A}, T, p)$ for seawater and $g(T, p)$ for ice.

Property	**Symbol**	**Expression in $g(S, T, p)$ of seawater**	**Expression in $g(T, p)$ of ice**
specific Gibbs energy	g	g	g
specific enthalpy	h	$g - T g_T$	$g - T g_T$
specific Helmholtz energy	f	$g - p g_p$	$g - p g_p$
specific internal energy	u	$g - T g_T - p g_p$	$g - T g_T - p g_p$
Specific entropy	s	$- g_T$	$- g_T$
pressure	p	p	p
density	ρ	$1 / g_p$	$1 / g_p$
specific isobaric heat capacity	c_p	$-T g_{TT}$	$-T g_{TT}$
thermal expansion	α	g_{Tp} / g_p	g_{Tp} / g_p
isothermal compressibility	κ_T	$-g_{pp} / g_p$	$-g_{pp} / g_p$
isentropic compressibility	κ_s	$\left(g_{tp}^2 - g_{tt} g_{pp}\right) / \left(g_p g_{tt}\right)$	$\left(g_{tp}^2 - g_{tt} g_{pp}\right) / \left(g_p g_{tt}\right)$
Sound speed	w	$g_p \sqrt{g_{tt} / \left(g_{tp}^2 - g_{tt} g_{pp}\right)}$	–
chemical potential of water	μ_W	$g - S_\mathrm{A} g_S$	g
pressure coefficient for ice	β	–	$-g_{Tp} / g_{pp}$

Freezing temperature and isobaric melting enthalpy

As an example of the use of more than one of the above thermodynamic potentials, consider the process of the melting (or freezing) of ice into seawater.

Thermodynamic theory tells us that freezing occurs at the temperature t_f at which the chemical potential of water in seawater μ^W equals the chemical potential of ice μ^Ih. Thus, the freezing temperature t_f is found by solving the implicit equation

$$\mu^\mathrm{W}\left(S_\mathrm{A}, t_\mathrm{f}, p\right) = \mu^\mathrm{Ih}\left(t_\mathrm{f}, p\right) \tag{3.33.1}$$

or equivalently, in terms of the two Gibbs functions,

$$g\left(S_\mathrm{A}, t_\mathrm{f}, p\right) - S_\mathrm{A}\, g_{S_\mathrm{A}}\left(S_\mathrm{A}, t_\mathrm{f}, p\right) = g^\mathrm{Ih}\left(t_\mathrm{f}, p\right). \tag{3.33.2}$$

The Gibbs function for ice Ih, $g^\mathrm{Ih}\left(t, p\right)$, is defined as part of TEOS-10, so we have very accurate freezing temperatures which are functions of Absolute Salinity and pressure.

Knowledge of the Gibbs functions of seawater and of ice also lead to very accurate values for the latent heat of melting (isobaric melting enthalpy), namely

$$L_p^\mathrm{SI}\left(S_\mathrm{A}, p\right) = h - S_\mathrm{A} \left.\frac{\partial h}{\partial S_\mathrm{A}}\right|_{T,p} - h^\mathrm{Ih} = h - S_\mathrm{A}\left(\mu - T\mu_T\right) - h^\mathrm{Ih}, \tag{3.34.6}$$

which is actually the difference between the partial specific enthalpies of water in seawater and of ice.

I should go into this more, exactly how to calculate the isobaric melting enthalpy.

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The vertical gradient of potential density

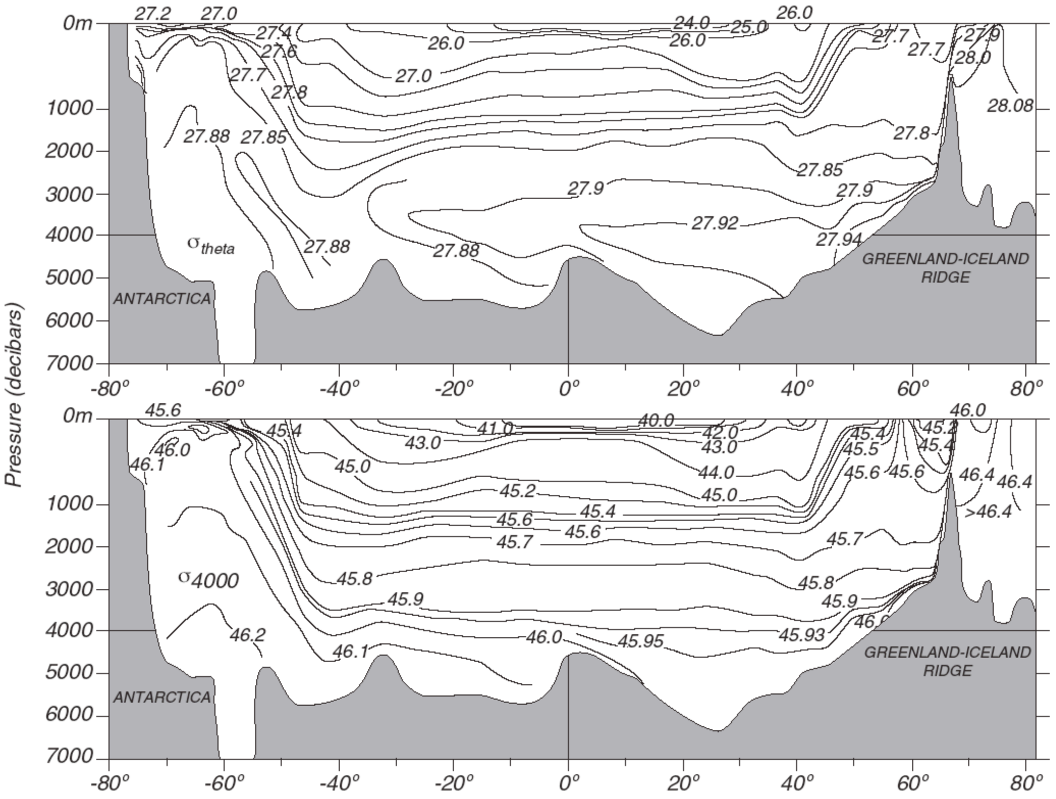


Figure 6.10 Vertical sections of density in the western Atlantic. Note that the depth scale changes at 1000 m depth. **Upper**: σ_Θ, showing an apparent density inversion below 3,000 m. **Lower**: σ_4 showing continuous increase in density with depth. After Lynn and Reid (1968).

The potential density of a seawater sample $\left(S_\mathrm{A},\Theta,p\right)$, referenced to reference pressure p_r is given by $\rho^\Theta\left(S_\mathrm{A},\Theta\right) = \hat{\rho}\left(S_\mathrm{A},\Theta,p_\mathrm{r}\right)$. The vertical gradient of the natural logarithm of potential density is $\beta^\Theta\left(p_\mathrm{r}\right)$ times the vertical gradient of Absolute Salinity minus $\alpha^\Theta\left(p_\mathrm{r}\right)$ times the vertical gradient of Conservative Temperature,

$$\frac{1}{\rho^\Theta}\frac{\partial\rho^\Theta}{\partial z} = \beta^\Theta\left(p_\mathrm{r}\right)S_{\mathrm{A}_z} - \alpha^\Theta\left(p_\mathrm{r}\right)\Theta_z . \qquad \text{(A.26.2)}$$

The ratio of this vertical gradient of potential density to the square of the buoyancy frequency is given by (Tutorial exercise)

$$\frac{-g\rho^{-1}\rho_z^\Theta}{N^2} = \frac{\beta^\Theta\left(p_\mathrm{r}\right)}{\beta^\Theta\left(p\right)}\frac{\left[R_\rho/r-1\right]}{\left[R_\rho-1\right]} = \frac{\beta^\Theta\left(p_\mathrm{r}\right)}{\beta^\Theta\left(p\right)}\frac{1}{G^\Theta} \approx \frac{1}{G^\Theta} , \qquad \text{(3.20.5)}$$

where r is the ratio of the slope on the $S_\mathrm{A}-\Theta$ diagram of an isoline of potential density with reference pressure p_r to the slope of a potential density surface with reference pressure p, and is defined by

$$r = \frac{\alpha^\Theta\left(S_\mathrm{A},\Theta,p\right)/\beta^\Theta\left(S_\mathrm{A},\Theta,p\right)}{\alpha^\Theta\left(S_\mathrm{A},\Theta,p_\mathrm{r}\right)/\beta^\Theta\left(S_\mathrm{A},\Theta,p_\mathrm{r}\right)} , \qquad \text{(3.17.2)}$$

and the "isopycnal temperature gradient ratio" G^Θ is defined by

$$G^\Theta \equiv \frac{\left[R_\rho-1\right]}{\left[R_\rho/r-1\right]} \qquad \text{where} \qquad R_\rho = \frac{\alpha^\Theta\Theta_z}{\beta^\Theta\left(S_\mathrm{A}\right)_z} \qquad \text{(3.17.4)}$$

is the ratio of the vertical contribution from Conservative Temperature to that from Absolute Salinity to the static stability N^2 of the water column. The name "isopycnal temperature gradient ratio" is chosen for G^Θ because it can be shown that G^{Θ} is the ratio of the gradient of Conservative Temperature in a potential density surface to that in a neutral tangent plane (Tutorial exercise),

$$\nabla_{\sigma}\Theta \;=\; G^{\Theta}\nabla_{n}\Theta \;. \qquad (3.17.3)$$

The saline contraction coefficient $\beta^{\Theta}\big(S_{\mathrm{A}},\Theta,p\big)$ does not vary very much from a constant value compared with variation of the thermal expansion coefficient $\alpha^{\Theta}\big(S_{\mathrm{A}},\Theta,p\big)$. That is, you make a 10% - 20% error by approximating r as

$$r \;\approx\; \frac{\alpha^{\Theta}\big(S_{\mathrm{A}},\Theta,p\big)}{\alpha^{\Theta}\big(S_{\mathrm{A}},\Theta,p_{\mathrm{r}}\big)}\;. \qquad (3.17.2\_approx)$$

There is never any reason to actually make this approximation in numerical work, rather this approximation can aid in thinking about what causes what in the ocean. [You can check that this is a good approximation by inspection of the red and blue potential density contours on the above $S_{\mathrm{A}} - \Theta$ diagram.]

Also, the slope difference between that of a neutral tangent plane and a potential density surface is given by (Tutorial exercise)

$$\begin{aligned}\nabla_{n}z - \nabla_{\sigma}z \;&=\; \frac{\nabla_{n}\Theta - \nabla_{\sigma}\Theta}{\Theta_{z}} \;=\; \Big(1 - G^{\Theta}\Big)\frac{\nabla_{n}\Theta}{\Theta_{z}} \\ &=\; \frac{R_{\rho}\big[1-r\big]}{\big[R_{\rho}-r\big]}\frac{\nabla_{n}\Theta}{\Theta_{z}} \;=\; \frac{R_{\rho}\big[1-r\big]}{r\big[R_{\rho}-1\big]}\frac{\nabla_{\sigma}\Theta}{\Theta_{z}}.\end{aligned} \qquad (3.18.1)$$

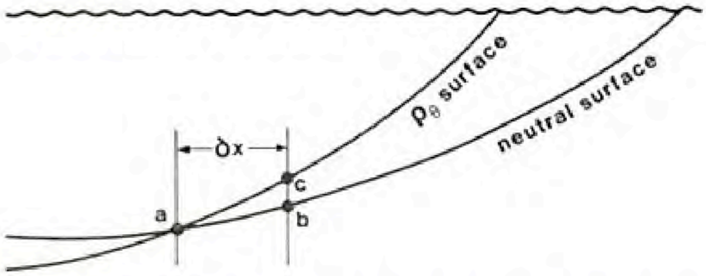


FIG. 1. Sketch of a cross section through the ocean showing a neutral surface and a potential density surface passing through point a. At a horizontal distance δx from point a, a vertical cast cuts the two surfaces at points b and c.

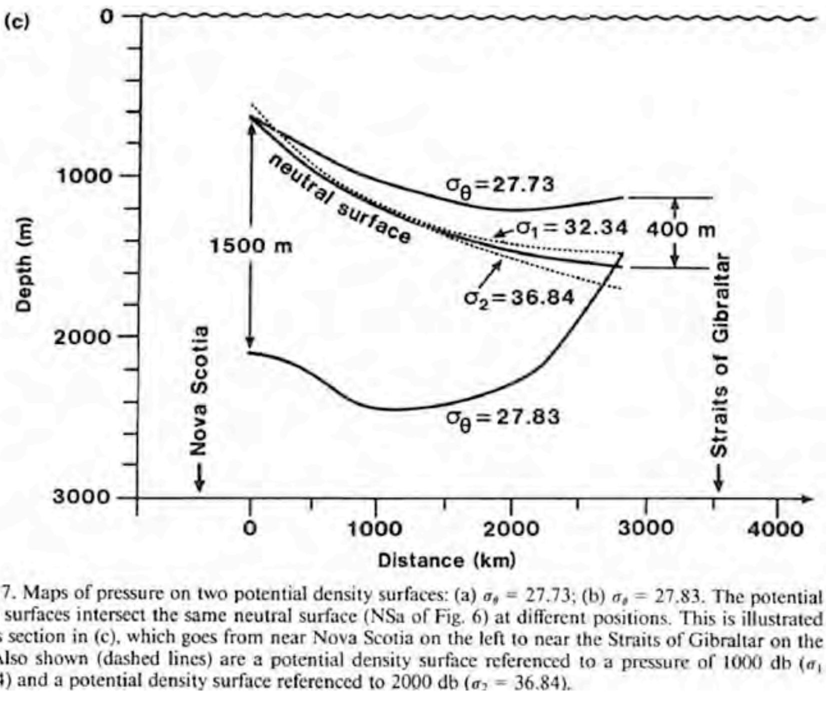
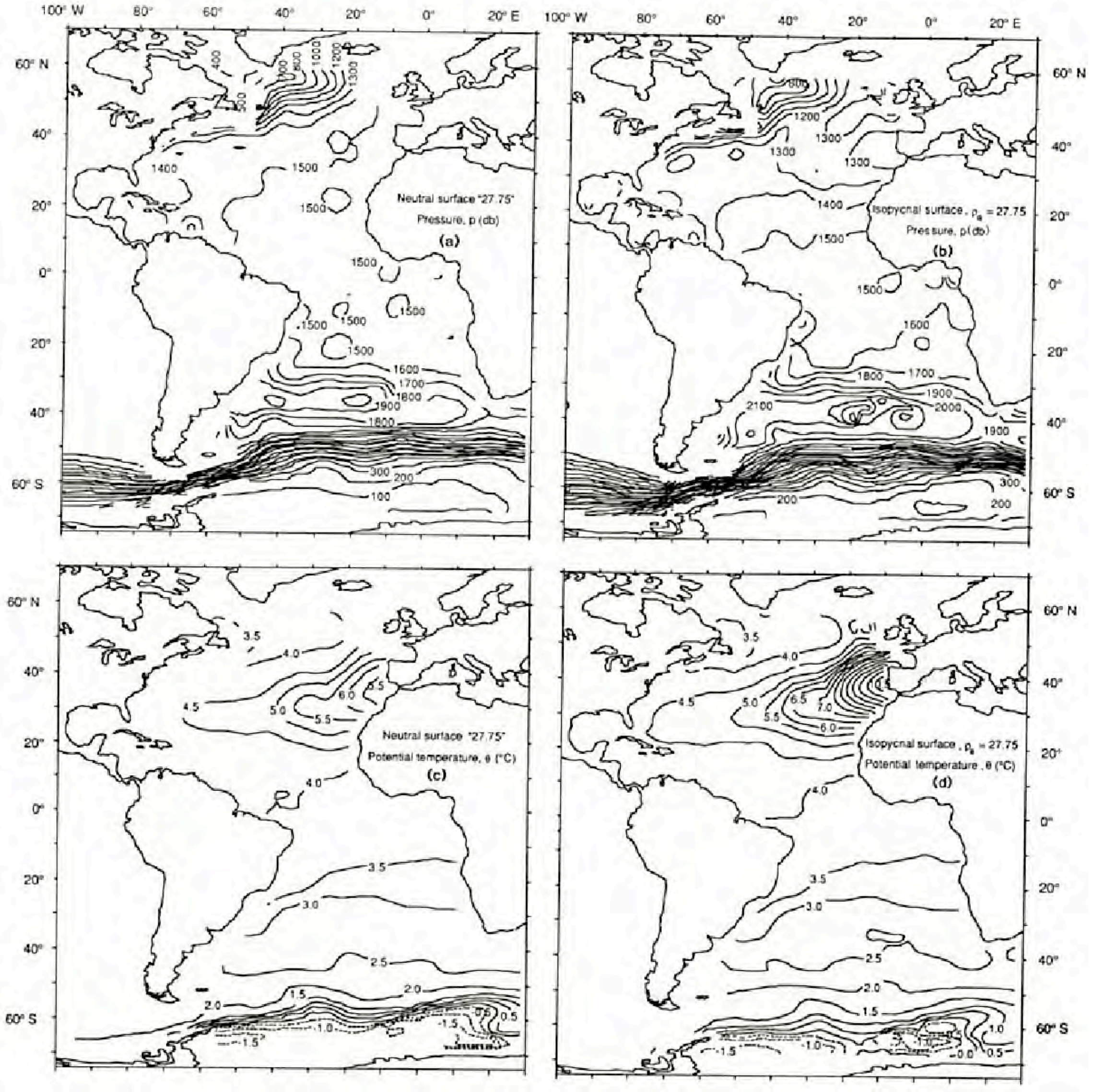


FIG. 7. Maps of pressure on two potential density surfaces: (a) σ_{θ} = 27.73; (b) σ_{θ} = 27.83. The potential density surfaces intersect the same neutral surface (NSa of Fig. 6) at different positions. This is illustrated in cross section in (c), which goes from near Nova Scotia on the left to near the Straits of Gibraltar on the right. Also shown (dashed lines) are a potential density surface referenced to a pressure of 1000 db (σ_1 = 32.34) and a potential density surface referenced to 2000 db (σ_2 = 36.84).



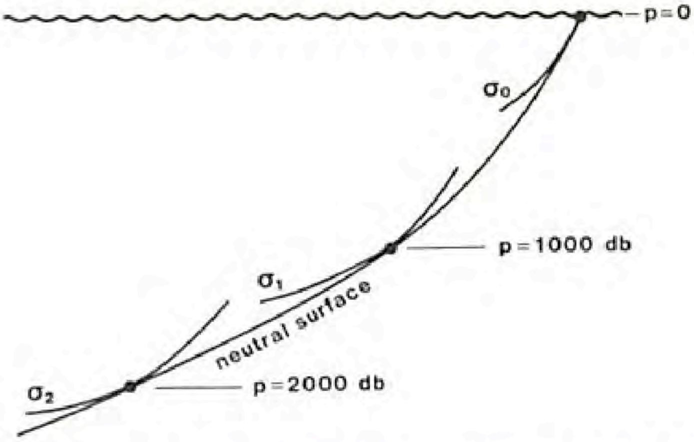
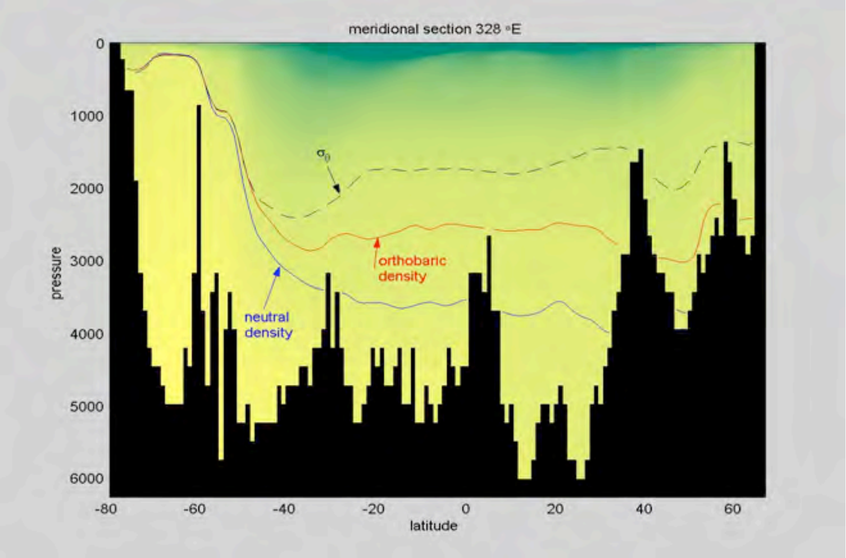
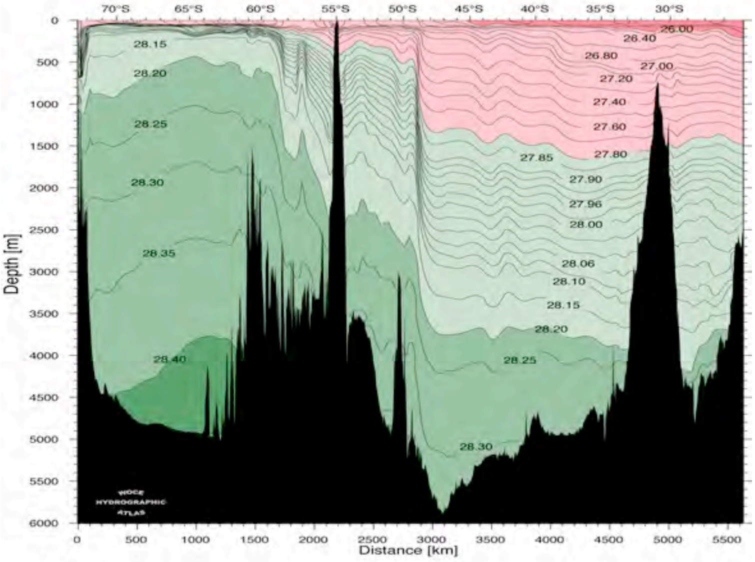
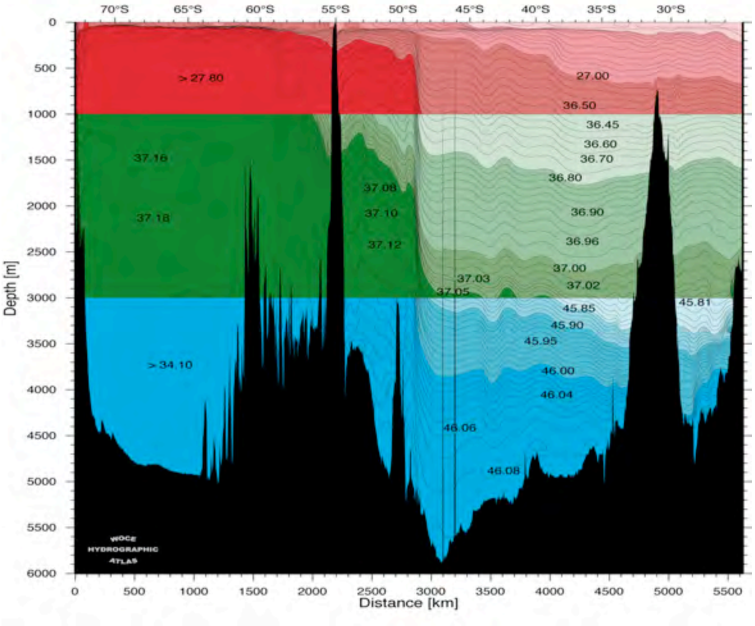


FIG. 2. Sketch of a neutral surface and three different potential density surfaces, referenced to 0 db, 1000 db and 2000 db. The neutral surface is tangential to potential density surfaces only at the reference pressure of those potential density surfaces. In this way, the neutral surface can be regarded as the envelope curve of many locally referenced potential density surfaces with continually changing reference pressures. The definition of a neutral surface adopted in this paper avoids the concept of potential density and in particular, avoids the changing reference pressure which is endemic to a neutral surface defined in terms of potential density concepts.



Below is a cross-section of Neutral Density in the Southern Ocean.





Before Neutral Density was available, cross-sections of density used potential density referenced to three different reference pressures, 0 dbar , 2000 dbar , and 4000 dbar , as shown above.

Geostrophic, hydrostatic and "thermal wind" equations

The geostrophic approximation to the horizontal momentum equations (Eqn. (B9)) equates the Coriolis term to the horizontal pressure gradient $\nabla_z P$ so that the geostrophic equation is

$$f\,\mathbf{k}\times\rho\mathbf{u} = -\nabla_z P \qquad \text{or} \qquad f\mathbf{v} = \tfrac{1}{\rho}\,\mathbf{k}\times\nabla_z P = g\,\mathbf{k}\times\nabla_p z\,, \tag{3.12.1}$$

where $\mathbf{u}$ is the three dimensional velocity and $\mathbf{v} = -\mathbf{k}\times(\mathbf{k}\times\mathbf{u})$ is the horizontal velocity where $\mathbf{k}$ is the vertical unit vector (pointing upwards) and f is the Coriolis parameter. The last part of the above equation has used $\nabla_z P = -P_z \nabla_p z$ from Eqn. (3.12.4b) below and the hydrostatic approximation, which is the following approximation to the vertical momentum equation (B9),

$$P_z = -g\rho. \tag{3.12.2}$$

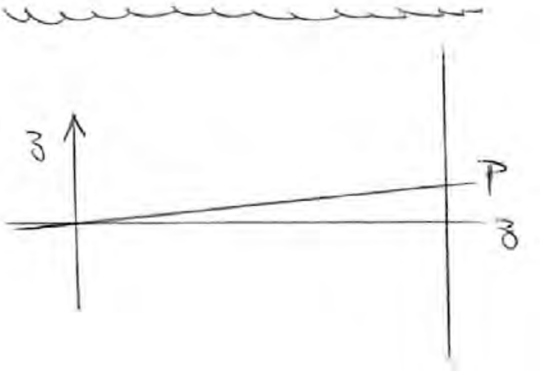
The use of P in these equations rather than p serves to remind us that in order to retain the usual units for height, density and the gravitational acceleration, pressure in these dynamical equations must be expressed in Pa not dbar.

The so called "thermal wind" equation is an equation for the vertical gradient of the horizontal velocity under the geostrophic approximation. Vertically differentiating Eqn. (3.12.1) and using the hydrostatic equation Eqn. (3.12.2), the thermal wind can be written

$$\boxed{f\,\mathbf{v}_z = \left(\tfrac{1}{\rho}\right)_z \mathbf{k}\times\nabla_z P + \tfrac{1}{\rho}\mathbf{k}\times\nabla_z\left(P_z\right) = -\tfrac{g}{\rho}\,\mathbf{k}\times\nabla_p\rho = \tfrac{N^2}{g\rho}\,\mathbf{k}\times\nabla_n P,} \tag{3.12.3}$$

where ∇_p is the projected lateral gradient operator in the isobaric surface (see Eqn. (3.11.3)). The last part of this equation relates the "thermal wind", $f\,\mathbf{v}_z$, to the pressure gradient in the neutral tangent plane. Note that the Boussinesq approximation has not been made to derive any part of Eqn. (3.12.3). Under the Boussinesq approximation, $\nabla_p\rho$ is approximated by $\nabla_z\rho$, and the last term in Eqn. (3.12.3) is approximated as $-N^2\,\mathbf{k}\times\nabla_n z$. The derivation of Eqn. (3.12.3) proceeds as follows. To go from the second part of Eqn. (3.12.3) to the third part use is made of

$$\nabla_p\rho = \nabla_z\rho + \rho_z\nabla_p z \quad \text{and} \quad \nabla_p P = \mathbf{0} = \nabla_z P + P_z\nabla_p z\,. \tag{3.12.4a,b}$$



To go from the third part of Eqn. (3.12.3) to the final part, use is made of Eqn. (3.12.4a) and $\nabla_n\rho = \nabla_z\rho + \rho_z\nabla_n z$, which, when combined gives

$$\nabla_p\rho = \nabla_n\rho - \rho_z\left(\nabla_n z - \nabla_p z\right). \tag{3.12.5}$$

Now Eqn. (3.12.4b) is used together with $\nabla_n P = \nabla_z P + P_z\nabla_n z$ to find

$$\nabla_n P = P_z\left(\nabla_n z - \nabla_p z\right), \tag{3.12.6}$$

and this is substituted into Eqn. (3.12.5) to find

$$\nabla_p\rho = \nabla_n\rho - \rho_z\nabla_n P/P_z\,. \tag{3.12.7}$$

Now along a neutral tangent plane we know that $\nabla_n\rho = \rho\kappa\nabla_n P$ (κ is the isentropic and isohaline compressibility of seawater) and substituting this into

Eqn. (3.12.7) leads to the final expression of Eqn. (3.12.3), namely $\frac{N^2}{g\rho}\,\mathbf{k}\times\nabla_n P$ (recognizing that the buoyancy frequency is defined by $N^2 = g\left(\kappa P_z - \frac{1}{\rho}\rho_z\right)$).

Neutral helicity

From page 94 of these lecture notes we know that the normal $\mathbf{n}$ to the neutral tangent plane is given by

$$\begin{aligned} g^{-1} N^2 \mathbf{n} \;&=\; -\rho^{-1}\nabla\rho + \kappa\nabla P \;=\; -\rho^{-1}\left(\nabla\rho - \nabla P / c^2\right) \\ &=\; \alpha^{\Theta}\nabla\Theta - \beta^{\Theta}\,\nabla S_{\mathrm{A}} . \end{aligned} \qquad (3.11.1)$$

It is natural to think that all these little tangent planes would link up and form a well-defined surface, but this is not actually the case in the ocean. In order to understand why the ocean chooses to be so ornery [bad-tempered] we need to understand what property the normal $\mathbf{n}$ to a surface must fulfill in order that the surface exists. We will find that this property is that the scalar product of the normal of the surface $\mathbf{n}$ and the curl of $\mathbf{n}$ must be zero everywhere on the surface; that is $\mathbf{n}\cdot\nabla\times\mathbf{n}$ must be zero everywhere on the surface.

In general, for a surface to exist in (x,y,z) space there must be a function $\phi(x,y,z)$ that is constant on the surface and whose gradient $\nabla\phi$ is in the direction of the normal to the surface, $\mathbf{n}$. That is, there must be an integrating factor $b(x,y,z)$ such that $\nabla\phi = b\mathbf{n}$. Assuming now that the surface does exist, consider a line integral of $b\mathbf{n}$ along a closed curved path in the surface. Since the line element of the integration path is everywhere normal to $\mathbf{n}$, the closed line integral is zero, and by Stokes's theorem, the area integral of $\nabla\times(b\mathbf{n})$ must be zero over the area enclosed by the closed curved path. Since the area element of integration $d\mathbf{A}$ is in the direction $\mathbf{n}$, it is clear that $\nabla\times(b\mathbf{n})\cdot d\mathbf{A}$ is proportional to $\nabla\times(b\mathbf{n})\cdot\mathbf{n}$. The only way that this area integral can be guaranteed to be zero for all such closed paths is if the integrand is zero everywhere on the surface, that is, if $\nabla\times(b\mathbf{n})\cdot\mathbf{n} = (\nabla b\times\mathbf{n})\cdot\mathbf{n} + b(\nabla\times\mathbf{n})\cdot\mathbf{n} = 0$, that is, if $\mathbf{n}\cdot\nabla\times\mathbf{n} = 0$ at all locations on the surface.

For the case in hand, the normal to the neutral tangent plane is in the direction $\alpha^{\Theta}\nabla\Theta - \beta^{\Theta}\,\nabla S_{\mathrm{A}}$ and we define the neutral helicity H^{n} as the scalar product of $\alpha^{\Theta}\nabla\Theta - \beta^{\Theta}\,\nabla S_{\mathrm{A}}$ with its curl,

$$H^{\mathrm{n}} \;\equiv\; \left(\alpha^{\Theta}\nabla\Theta - \beta^{\Theta}\,\nabla S_{\mathrm{A}}\right)\cdot\nabla\times\left(\alpha^{\Theta}\nabla\Theta - \beta^{\Theta}\,\nabla S_{\mathrm{A}}\right) . \qquad (3.13.1)$$

Neutral tangent planes (which do exist) do not link up in space to form a well-defined neutral surface unless the neutral helicity H^{n} is everywhere zero on the surface.

Recognizing that both the thermal expansion coefficient and the saline contraction coefficient are functions of $(S_{\mathrm{A}},\Theta,p)$, neutral helicity H^{n} may be expressed as the following four expressions, all of which are proportional to the thermobaric coefficient T_{b}^{Θ} of the equation of state,

$$\begin{aligned} H^{\mathrm{n}} \;&=\; \beta^{\Theta}\,T_{\mathrm{b}}^{\Theta}\,\nabla P\cdot\nabla S_{\mathrm{A}}\times\nabla\Theta \\ &=\; P_z\,\beta^{\Theta}\,T_{\mathrm{b}}^{\Theta}\left(\nabla_p S_{\mathrm{A}}\times\nabla_p\Theta\right)\cdot\mathbf{k} \\ &=\; g^{-1}\,N^2 T_{\mathrm{b}}^{\Theta}\left(\nabla_n P\times\nabla_n\Theta\right)\cdot\mathbf{k} \\ &\approx\; g^{-1}\,N^2 T_{\mathrm{b}}^{\Theta}\left(\nabla_a P\times\nabla_a\Theta\right)\cdot\mathbf{k} \end{aligned} \qquad (3.13.2)$$

where P_z is simply the vertical gradient of pressure ($\mathrm{Pa\ m^{-1}}$) and $\nabla_n\Theta$ and $\nabla_p\Theta$ are the two-dimensional gradients of Θ in the neural tangent plane and in the horizontal plane (actually the isobaric surface) respectively. The gradients $\nabla_a P$ and $\nabla_a\Theta$ are taken in an approximately neutral surface. Neutral helicity has units of $\mathrm{m^{-3}}$. Recall that the thermobaric coefficient is given by

$$T_{\mathrm{b}}^{\Theta} \;=\; \beta^{\Theta}\left(\alpha^{\Theta}/\beta^{\Theta}\right)_P \;=\; \alpha_P^{\Theta} - \left(\alpha^{\Theta}/\beta^{\Theta}\right)\beta_P^{\Theta} . \qquad (3.8.2)$$

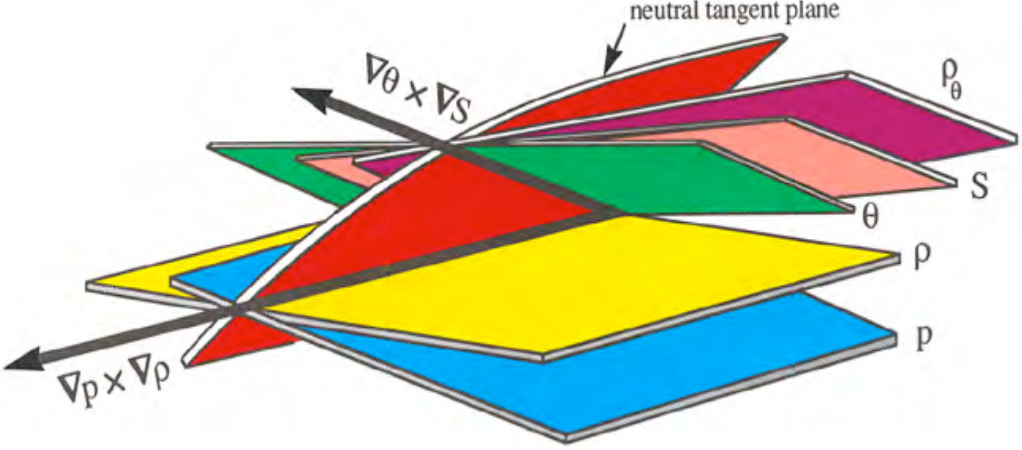
The geometrical interpretation of neutral helicity

How can we understand neutral helicity H^{n} geometrically? Recall the definition of a neutral tangent plane, Eqn. (3.11.2), namely

$$-\rho^{-1}\nabla_n\rho+\kappa\nabla_n P \;=\; \alpha^{\Theta}\nabla_n\Theta-\beta^{\Theta}\nabla_n S_{\mathrm{A}} \;=\; \mathbf{0}. \tag{3.11.2}$$

This implies that the two lines $\nabla P\times\nabla\rho$ and $\nabla\Theta\times\nabla S_{\mathrm{A}}$ both lie in the neutral tangent plane. This is because along the line $\nabla P\times\nabla\rho$ both pressure and *in situ* density are constant, and along this line the neutral property is satisfied. Similarly, along the line $\nabla\Theta\times\nabla S_{\mathrm{A}}$ both Conservative Temperature and Absolute Salinity are constant, which certainly describes a line in the neutral tangent plane. Hence the picture emerges below of the geometry in (x,y,z) space of six planes, intersecting in one of the two lines $\nabla P\times\nabla\rho$ and $\nabla\Theta\times\nabla S_{\mathrm{A}}$. The neutral tangent plane is the only plane that includes both of these desirable lines.

Why are these lines "desirable"? Well $\nabla P\times\nabla\rho$ is desirable because it is the direction of the "thermal wind", and $\nabla\Theta\times\nabla S_{\mathrm{A}}$ is desirable because adiabatic and isohaline motion occurs along this line; a necessary attribute of a well-bred "mixing" plane such as the neutral tangent plane.



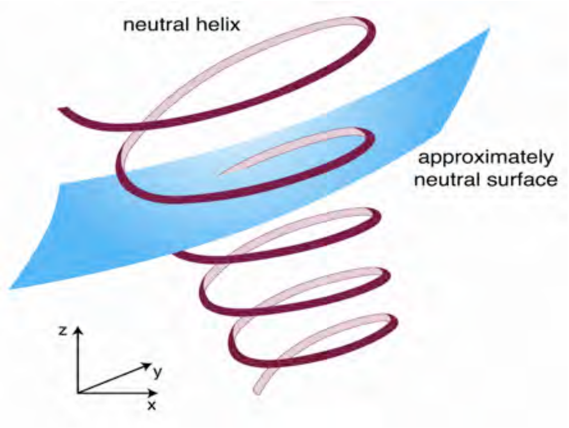
Prolonged gazing at the above figure while examining the definition of neutral helicity, H^{n}, Eqn. (3.13.2), shows that neutral helicity vanishes when the two vectors $\nabla P\times\nabla\rho$ and $\nabla\Theta\times\nabla S_{\mathrm{A}}$ coincide, and that this occurs when the two-dimensional gradients $\nabla_n\Theta$ are $\nabla_n P$ parallel.

Neutral helicity is proportional to the component of the vertical shear of the geostrophic velocity ($\mathbf{v}_z$, the "thermal wind") in the direction of the temperature gradient along the neutral tangent plane $\nabla_n\Theta$, since, from Eqn. (3.12.3) and the third line of (3.13.2) we find that

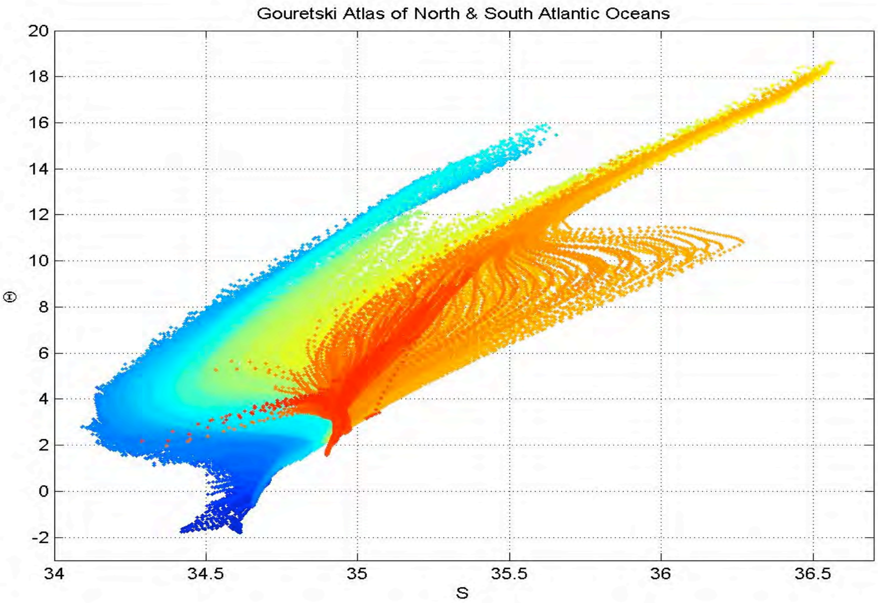
$$H^{\mathrm{n}}=\rho T_{\mathrm{b}}^{\Theta} f\mathbf{v}_z\cdot\nabla_n\Theta\,. \tag{3.13.3}$$

Interestingly, for given magnitudes of the epineutral gradients of pressure and Conservative Temperature, neutral helicity is maximized when these gradients are perpendicular since neutral helicity is proportional to $T_{\mathrm{b}}^{\Theta}\left(\nabla_n P\times\nabla_n\Theta\right)\cdot\mathbf{k}$ (see Eqn. (3.13.2)), while the dianeutral advection of thermobaricity, $e^{\mathrm{Tb}}=-gN^{-2}K\,T_{\mathrm{b}}^{\Theta}\nabla_n\Theta\cdot\nabla_n P$, is maximized when $\nabla_n\Theta$ and $\nabla_n P$ are parallel (see Eqn. **(A.22.4)**).

Because of the non-zero neutral helicity, H^{n}, in the ocean, lateral motion following neutral tangent planes has the character of helical motion. That is, if we ignore the effects of diapycnal mixing processes (as well as ignoring cabbeling and thermobaricity), the mean flow around ocean gyres still passes through any well-defined "density" surface because of the helical nature of neutral trajectories, caused in turn by the non-zero neutral helicity. We will return to this mean vertical motion caused by the ill-defined nature of "neutral surfaces" in a few pages.

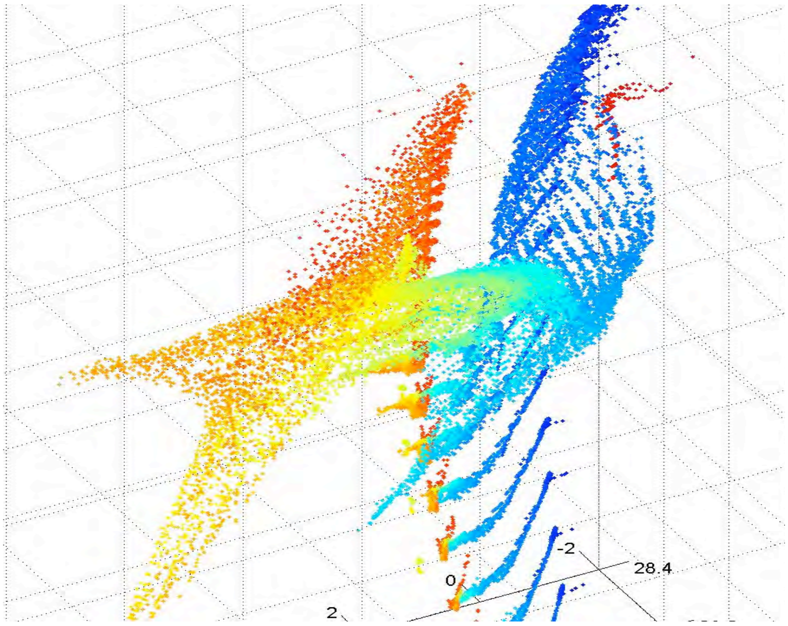


The skinny nature of the ocean; why is the ocean 95% empty?



The above diagram contains all of the ocean hydrography below 200 dbar from both the North and South Atlantic ocean. The colour represents the latitude, with blue in the south, red in the north and green in the equatorial region. It is seen that the data fill the area on this $S_A - \Theta$ diagram, leaving no holes.

When considering the plotting of this same data on a three-dimensional $S_A - \Theta - p$ "plot", one could be forgiven for thinking that the data would fill in a solid shape in these three dimensions. But this is not observed. Rather than the $S_A - \Theta - p$ data occupying the volume inside, say, a packet of Toblerone chocolate, instead, the data resides on the cardboard of the Toblerone packet and the chocolate is missing.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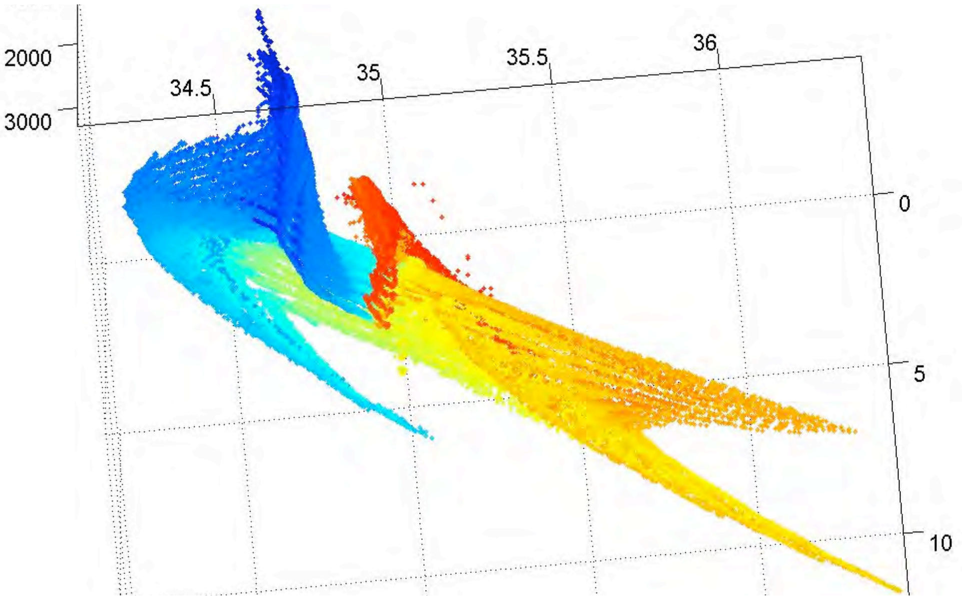
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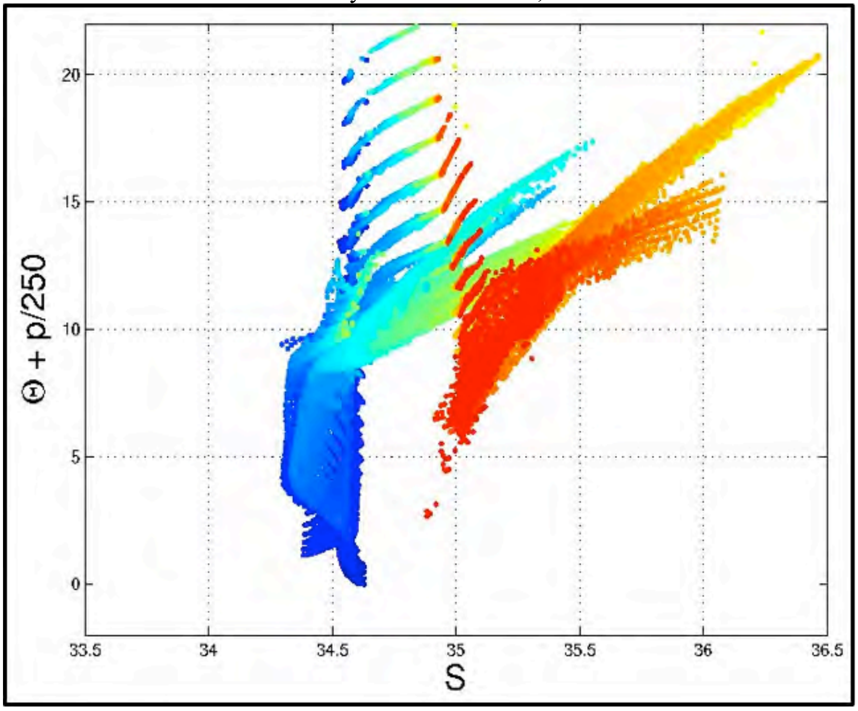
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The skinny nature of the ocean; implication for neutral helicity

If all the $\left(S_\mathrm{A},\Theta,p\right)$ data from the whole global ocean were to lie exactly on a single surface in $\left(S_\mathrm{A},\Theta,p\right)$ space, we will prove that this requires $\nabla S_\mathrm{A}\times\nabla\Theta\cdot\nabla P = 0$ everywhere in physical $\left(x,y,z\right)$ space. That is, we will prove that the skinniness of the ocean hydrography in $\left(S_\mathrm{A},\Theta,p\right)$ space is a direct indication of the smallness of neutral helicity H^n.

Since, under our assumption, all the $\left(S_\mathrm{A},\Theta,p\right)$ data from the whole global ocean lies on the single surface in $\left(S_\mathrm{A},\Theta,p\right)$ space we have

$$f\left(S_\mathrm{A},\Theta,p\right) = 0 \qquad \text{(Twiggy\_01)}$$

for every $\left(S_\mathrm{A},\Theta,p\right)$ observation drawn for the whole global ocean in physical $\left(x,y,z\right)$ space. Taking the spatial gradient of this equation in physical $\left(x,y,z\right)$ space we have $\nabla f = 0$ since f is zero at every point in physical $\left(x,y,z\right)$ space. Expanding ∇f in terms of the spatial gradients ∇S_A, $\nabla\Theta$, and ∇P, and taking the scalar product with $\nabla S_\mathrm{A}\times\nabla\Theta$ we find that

$$\left.\frac{\partial f}{\partial P}\right|_{S_\mathrm{A},\Theta}\nabla P\cdot\nabla S_\mathrm{A}\times\nabla\Theta = 0\,. \qquad \text{(Twiggy\_02)}$$

In the general case of $f_P \neq 0$, the result $\nabla P\cdot\nabla S_\mathrm{A}\times\nabla\Theta = 0$ is proven. In the special case $f_P = 0$, f is independent of P so that we have a simpler equation for the surface f, being

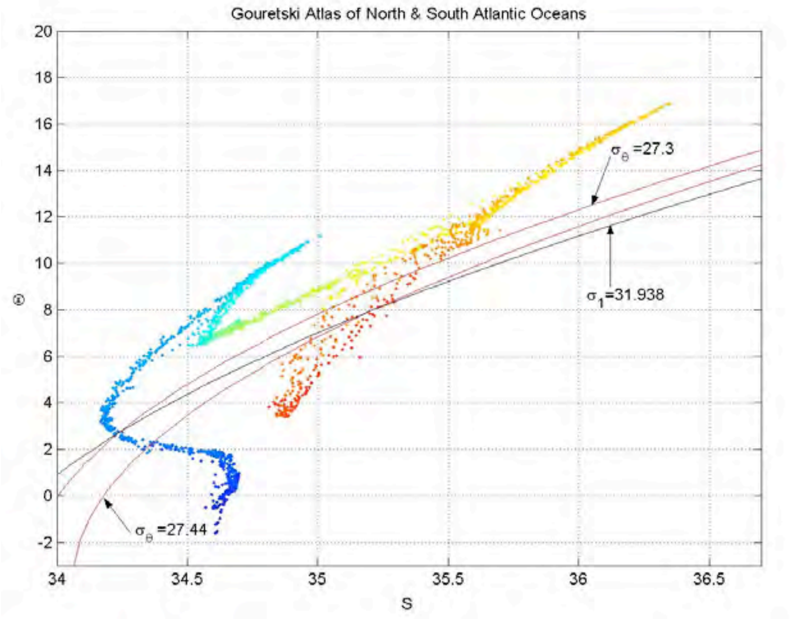
$$f\left(S_\mathrm{A},\Theta\right) = 0\,, \qquad \text{(Twiggy\_03)}$$

which is the equation for a single line on the $\left(S_\mathrm{A},\Theta\right)$ diagram; a single "water-mass" for the whole world ocean. In this case, changes in S_A are locally proportional to those of Θ so that $\nabla S_\mathrm{A}\times\nabla\Theta = \mathbf{0}$ which also guarantees our required relation $\nabla P\cdot\nabla S_\mathrm{A}\times\nabla\Theta = 0$.

Hence we have proven that the skinniness of the ocean hydrography in $\left(S_\mathrm{A},\Theta,p\right)$ space is a direct indication of the smallness of neutral helicity $H^\mathrm{n} = \beta^\Theta T_\mathrm{b}^\Theta\nabla P\cdot\nabla S_\mathrm{A}\times\nabla\Theta$.

The skinny nature of the ocean; demonstrated from data at constant pressure

The diagram below is a cut at constant pressure through the above three-dimensional $S_{\mathrm{A}} - \Theta - p$ data. The cut is at a pressure of 500 dbar. This diagram illustrates the smallness of neutral helicity from the perspective of the equation $H^{\mathrm{n}} \;=\; P_z \beta^{\Theta} T_{\mathrm{b}}^{\Theta} \left(\nabla_n S_{\mathrm{A}} \times \nabla_n \Theta \right) \cdot \mathbf{k}$.



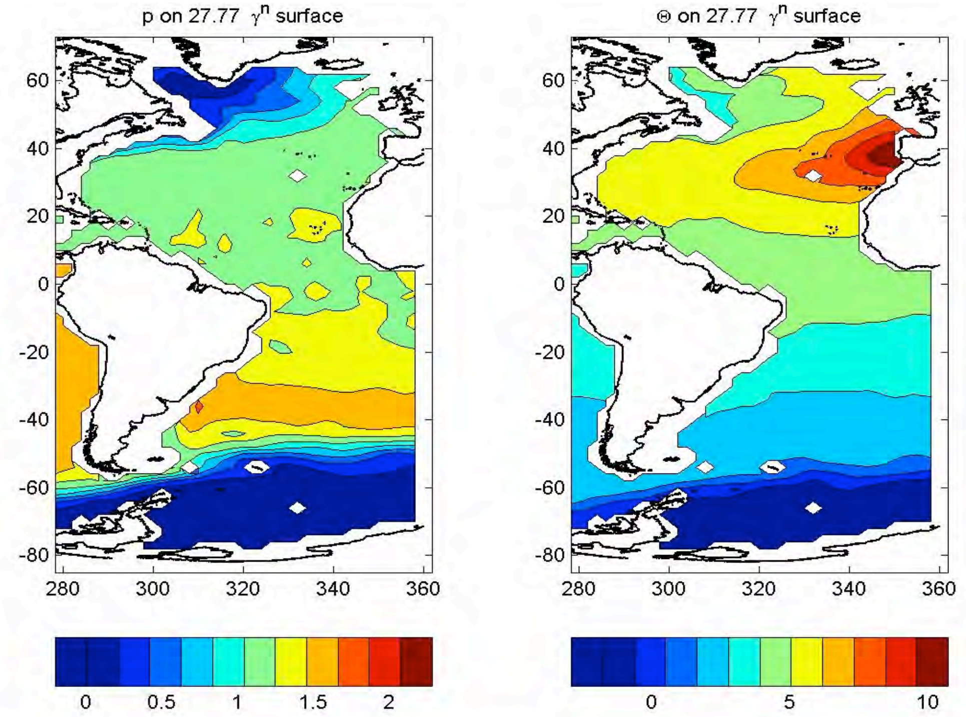
The skinny nature of the ocean; demonstrated from data on Neutral Density surfaces

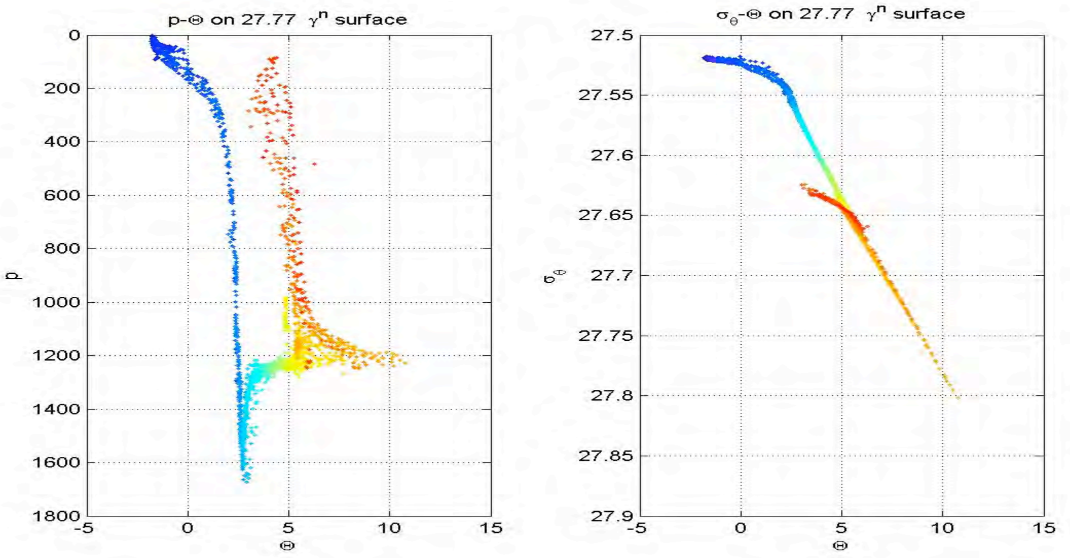
Here the "skinny" nature of the ocean will be demonstrated by looking at data on approximately neutral surfaces; Neutral Density γ^{n} surfaces. The following lines of the equation for neutral helicity

$$\begin{aligned} H^{\mathrm{n}} &= g^{-1} N^2 T_{\mathrm{b}}^{\Theta} \left(\nabla_n P \times \nabla_n \Theta \right) \cdot \mathbf{k} \\ &\approx g^{-1} N^2 T_{\mathrm{b}}^{\Theta} \left(\nabla_a P \times \nabla_a \Theta \right) \cdot \mathbf{k} \end{aligned} \qquad (3.13.2)$$

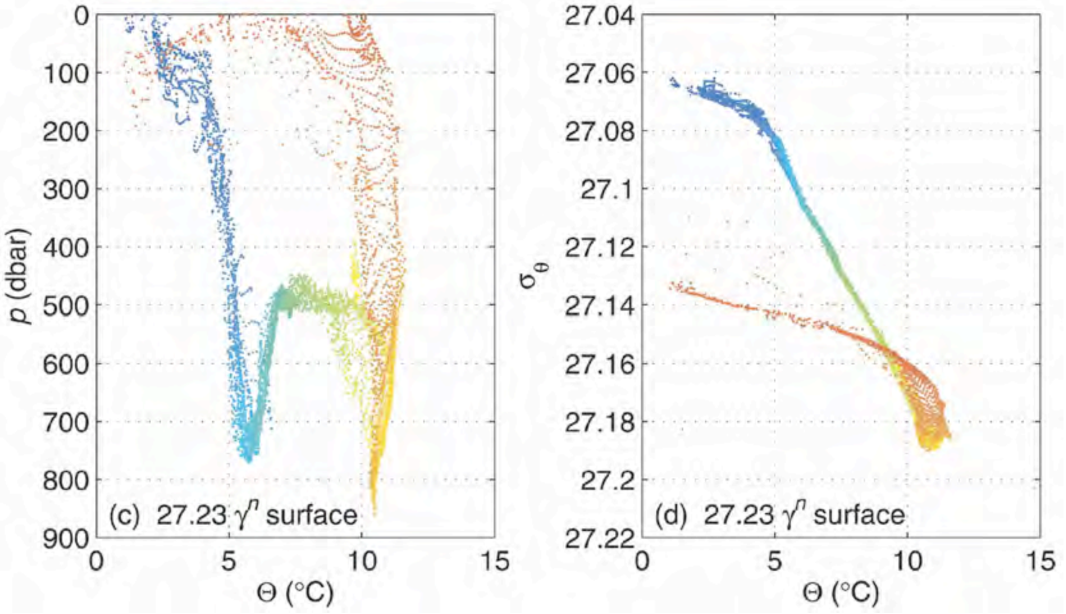
show that neutral helicity H^{n} will be small if the contours of P and of Θ on a γ^{n} surface are lined up; that is if $\nabla_a P$ and $\nabla_a \Theta$ are parallel.

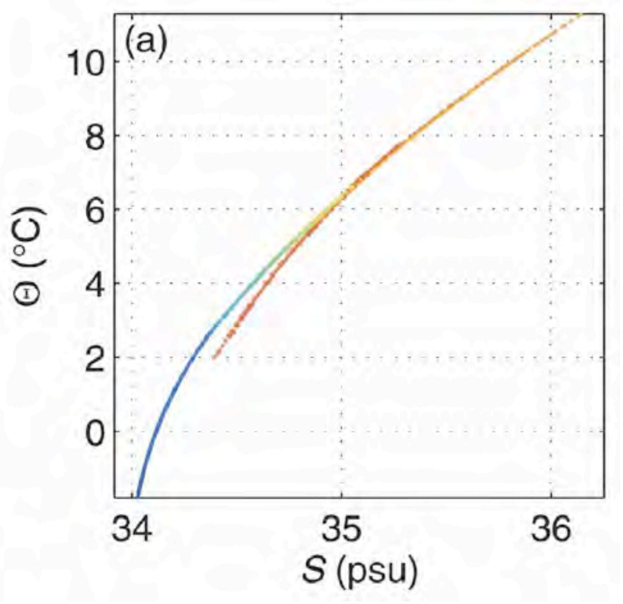
The ocean seems desperate to minimize H^{n}; either $\nabla_a P$ and $\nabla_a \Theta$ are parallel or where they are not parallel, one of $\nabla_a P$ or $\nabla_a \Theta$ is tiny.





Notice the rather large range of potential density of $0.28\,\mathrm{kg\,m^{-3}}$ on this Neutral Density surface. Also, the value of potential density at the northern hemisphere outcrop is larger than that at the southern hemisphere outcrop by about $0.1\,\mathrm{kg\,m^{-3}}$.





The above plots confirm that the ocean is rather "skinny" in $\left(S_{\mathrm{A}}, \Theta, p\right)$ space and hence that neutral helicity H^{n} is small in some sense (small compared to what?).

Note that while for some purposes a zero-neutral-helicity ocean,

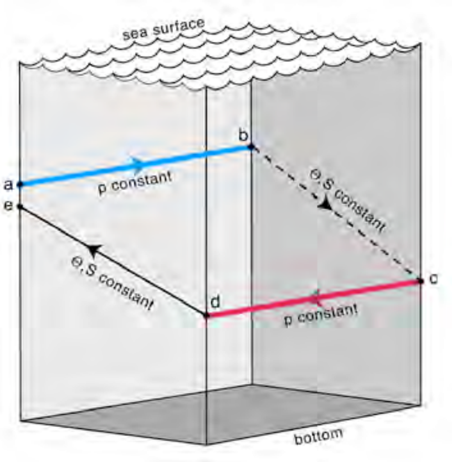
$$f\left(S_{\mathrm{A}}, \Theta, p\right) = 0 \qquad \text{(Twiggy\_01)}$$

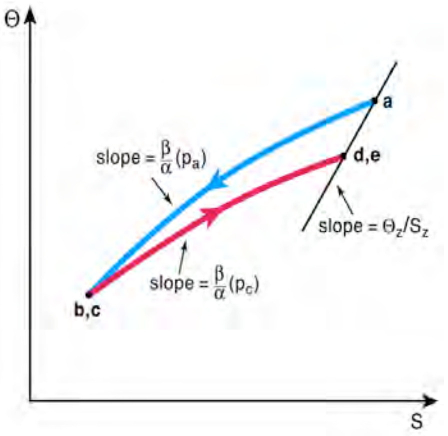
might be a reasonable approximation, this $f\left(S_{\mathrm{A}}, \Theta, p\right) = 0$ surface is multi-valued along any particular axis. We saw this on the rotating view of the data in three $\left(S_{\mathrm{A}}, \Theta, p\right)$ dimensions. This multi-valued nature is also apparent on the last figure which is of only one approximately neutral surface. A slightly denser surface would have the same $\left(S_{\mathrm{A}}, \Theta\right)$ values in the Southern Atlantic as the above plot has in the North Atlantic.

Note also in the above figures that where a particular Neutral Density surface comes to the surface (outcrops) in the North Atlantic, it has a greater potential density than in the Southern Ocean by between 0.07 kg m^{-3} and 0.14 kg m^{-3}. This is a general feature of the ocean; approximately neutral surfaces have different potential densities even at the reference pressure of that potential density. The northern hemisphere and southern hemisphere parts of a single ocean are separate branches in these multi-valued spaces.

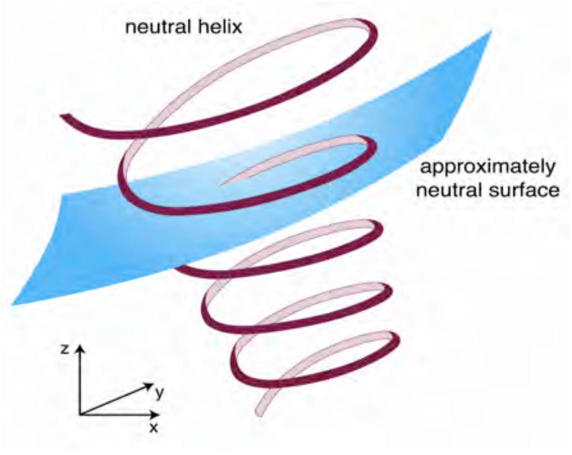
Consequences of non-zero neutral helicity

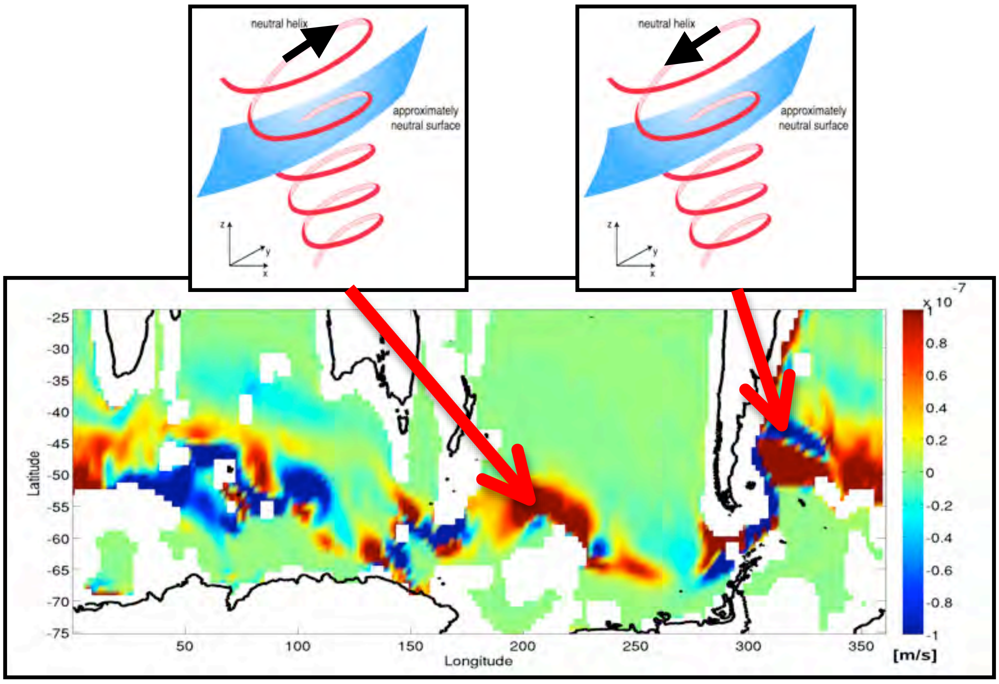
This diagram below is a simple example of the ill-defined nature of a "neutral surface" and the implication for mean dianeutral motion. The lateral mixing which causes the changes of S_A and Θ along this path occur at very different pressures. It is the rotation of the isopycnals on the $S_\mathrm{A} - \Theta$ diagram (because of the different pressures) that causes the ill-defined nature of "neutral surfaces", that is, the helical nature of neutral trajectories. In this example $\nabla_a P$ and $\nabla_a \Theta$ are at right angles, that is, $\nabla_a P \cdot \nabla_a \Theta = 0$.





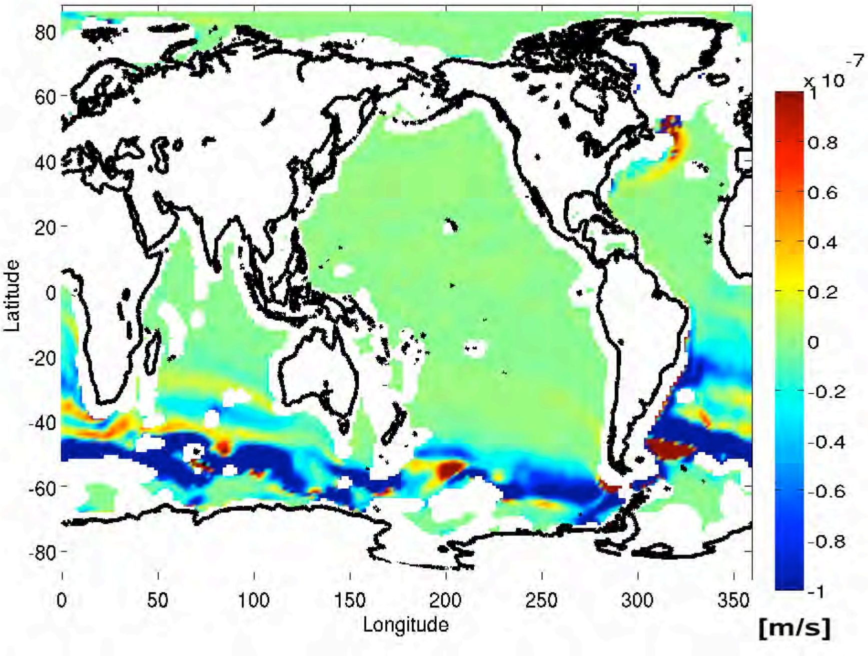
The cork-screwing motion as fluid flows along a helical neutral trajectory causes vertical dia-surface flow through any well-defined density surface. This mean diapycnal flow occurs in the absence of any vertical mixing process. That is, this mean vertical advection occurs in the absence of the dissipation of turbulent kinetic energy, and is additional to the other dianeutral advection processes, thermobaricity and cabbeling.

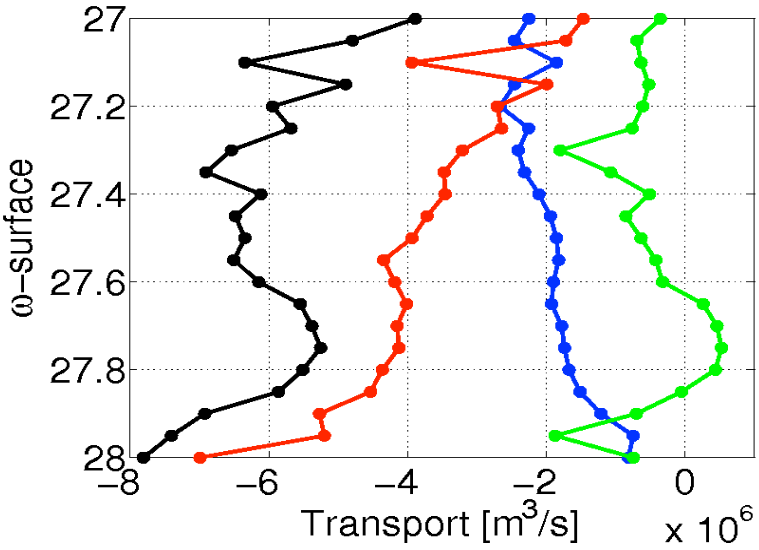




The figure above shows the vertical velocity through an approximately neutral surface caused by neutral helicity. That is, this is the actual vertical flow caused by the helical nature of neutral trajectories. The magnitude in the Southern Ocean is at leading order of $10^{-7}\ \mathrm{m\,s^{-1}}$, this being the canonical diapycnal velocity, dating back to Munk (1966).

The figure below is the total dianeutral velocity for all non-linear equation-of-state processes, namely thermobaricity, cabbeling and the helical nature of neutral trajectories.





When globally integrated over complete density surfaces, the total transport due to these non-linear processes can be calculated. In green is the mean dianeutral transport from the ill-defined nature of "neutral surfaces", blue is the dianeutral transport due to cabbeling, red due to thermobaricity, and black is the total global dianeutral transport due to the sum of these three non-linear processes.

We conclude from this that while the mean dianeutral transport from the ill-defined nature of "neutral surfaces" is of leading order locally, it spatially averages to a very small transport over a complete density surface. By contrast, cabbeling and thermobaricity are predominantly downwards advection everywhere, so there is little such cancellation on area integration with these processes.

Rotation of the horizontal velocity with height

Define the angle φ (measured counter-clockwise with respect to due east) of the horizontal velocity $\mathbf{v}$ so that

$$\mathbf{v} = |\mathbf{v}|(\cos\varphi, \sin\varphi) \; . \qquad \text{(V\_rotate\_01)}$$

Vertically differentiate this equation and take the cross product with $\mathbf{v}$ to obtain

$$\mathbf{v}\times\mathbf{v}_z = \mathbf{k}\varphi_z|\mathbf{v}|^2 , \qquad \text{(V\_rotate\_02)}$$

which shows that the rate of spiraling of the horizontal velocity vector in the vertical, φ_z, is proportional to the amount by which this velocity is not parallel to the direction of the "thermal wind" shear $\mathbf{v}_z$. The last equation can be rewritten as

$$\varphi_z|\mathbf{v}|^2 = \mathbf{k}\cdot\mathbf{v}\times\mathbf{v}_z = uv_z - vu_z = -\,\mathbf{v}\cdot\mathbf{k}\times\mathbf{v}_z = -\,\mathbf{v}\cdot\nabla\times\mathbf{v} \; , \qquad \text{(V\_rotate\_03)}$$

which demonstrates that the rotation of the horizontal velocity with height is proportional to the helicity of the horizontal velocity, $\mathbf{v}\cdot\nabla\times\mathbf{v}$.

Now, substituting Eqn. (3.12.3) for the "thermal wind" $\mathbf{v}_z$, namely

$$\boxed{f\,\mathbf{v}_z = \left(\tfrac{1}{\rho}\right)_z \mathbf{k}\times\nabla_z P + \tfrac{1}{\rho}\mathbf{k}\times\nabla_z\left(P_z\right) = -\tfrac{g}{\rho}\,\mathbf{k}\times\nabla_p\,\rho = \tfrac{N^2}{g\rho}\,\mathbf{k}\times\nabla_n P,} \qquad (3.12.3)$$

into Eqn. (V_rotate_03) we find

$$\varphi_z|\mathbf{v}|^2 = -\,\mathbf{v}\cdot\mathbf{k}\times\mathbf{v}_z = \tfrac{N^2}{fg\rho}\,\mathbf{v}\cdot\nabla_n P \, . \qquad \text{(V\_rotate\_04)}$$

Under the usual Boussinesq approximation $-\left(g\rho\right)^{-1}\nabla_n P$ is set equal to the slope of the neutral tangent plane, $\nabla_n z$, so that we have

$$\varphi_z|\mathbf{v}|^2 \approx -\tfrac{N^2}{f}\,\mathbf{v}\cdot\nabla_n z \, , \qquad \text{(V\_rotate\_05)}$$

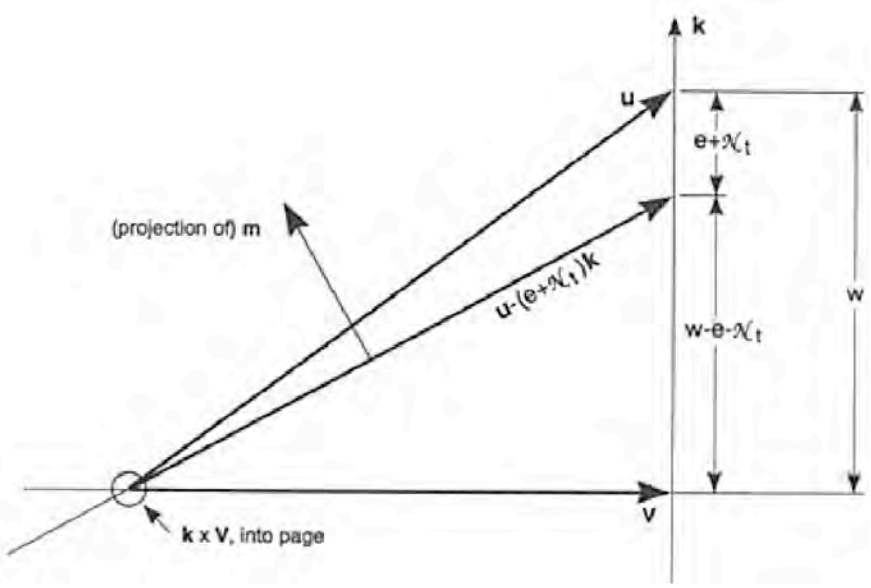
and since the vertical velocity through a geopotential, w, is given by the simple geometrical equation (where e is the dianeutral velocity, that is, the vertical velocity through the neutral tangent plane),

$$w = z_t\big|_n + \mathbf{v}\cdot\nabla_n z + e \, , \qquad \text{(V\_rotate\_06)}$$

we have

$$\boxed{\varphi_z|\mathbf{v}|^2 \approx -\tfrac{N^2}{f}\left(w - e - z_t\big|_n\right),} \qquad \text{(V\_rotate\_07)}$$

showing that the rotation of the horizontal velocity vector with height is not simply proportional to the vertical velocity of the flow but rather only to the sliding motion along the neutral tangent plane, $\mathbf{v}\cdot\nabla_n z$.



The absolute velocity vector in the ocean

Neutral helicity is proportional to the component of the vertical shear of the geostrophic velocity ($\mathbf{v}_z$, the "thermal wind") in the direction of the temperature gradient along the neutral tangent plane $\nabla_n\Theta$, since, from Eqn. (3.12.3), namely $f\,\mathbf{v}_z = \tfrac{N^2}{g\rho}\,\mathbf{k}\times\nabla_n P$, and the third line of (3.13.2), namely $H^{\mathrm{n}} = g^{-1}N^2 T_{\mathrm{b}}^{\Theta}\left(\nabla_n P\times\nabla_n\Theta\right)\cdot\mathbf{k}$, we find that

$$H^{\mathrm{n}} = \rho T_{\mathrm{b}}^{\Theta} f\mathbf{v}_z\cdot\nabla_n\Theta. \qquad (3.13.4)$$

This connection between neutral helicity and an aspect of the horizontal velocity vector motivates the idea that the mean velocity might be somehow linked to neutral helicity, and this link is established in this section.

The absolute velocity vector in the ocean can be written as a closed expression involving the neutral helicity, and this expression is derived as follows. First the Eulerian-mean horizontal velocity is related directly to mixing processes by invoking the water-mass transformation equation (A.23.1), so that

$$\begin{aligned}\overline{\mathbf{v}}\cdot\nabla_n\hat{\Theta} \;=\; & \tilde{\gamma}_z\nabla_n\cdot\left(\tilde{\gamma}_z^{-1}K\nabla_n\hat{\Theta}\right)+KgN^{-2}\hat{\Theta}_z\left(C_{\mathrm{b}}^{\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n\hat{\Theta}\;+T_{\mathrm{b}}^{\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n P\right)\\ & +D\beta^{\Theta}gN^{-2}\hat{\Theta}_z^3\frac{d^2\hat{S}_{\mathrm{A}}}{d\hat{\Theta}^2}\;-\;\mathbf{\Psi}_z\cdot\nabla_n\hat{\Theta}\;-\;\hat{\Theta}_t\Big|_n,\end{aligned} \qquad (3.13.7)$$

where the thickness-weighted mean velocity of density-coordinate averaging, $\hat{\mathbf{v}}$, has been written as $\hat{\mathbf{v}} = \overline{\mathbf{v}}+\mathbf{\Psi}_z$, that is, as the sum of the Eulerian-mean horizontal velocity $\overline{\mathbf{v}}$ and the quasi-Stokes eddy-induced horizontal velocity $\mathbf{\Psi}_z$ (McDougall and McIntosh (2001)). The quasi-Stokes vector streamfunction $\mathbf{\Psi}$ is usually expressed in terms of an imposed lateral diffusivity and the slope of the locally-referenced potential density surface (Gent *et al.*, (1995)). More generally, at least in a steady state when $\hat{\Theta}_t\big|_n$ is zero, the right-hand side of Eqn. (3.13.7) is due only to mixing processes and once the form of the lateral and vertical diffusivities are known, these terms are known in terms of the ocean's hydrography. Eqn. (3.13.7) is written more compactly as

$$\overline{\mathbf{v}}\cdot\boldsymbol{\tau} \;=\; v^{\perp} \qquad \text{where} \qquad \boldsymbol{\tau} \;\equiv\; \nabla_n\hat{\Theta}\big/\left|\nabla_n\hat{\Theta}\right|, \qquad (3.13.8)$$

and $v^{\perp}$ is interpreted as being due to mixing processes.

Following Needler (1985) and McDougall (1995) the mean horizontal velocity $\overline{\mathbf{v}}$ is split into components along and across the contours of $\hat{\Theta}$ on the neutral tangent plane, so that

$$\overline{\mathbf{v}} \;=\; v^{\parallel}\boldsymbol{\tau}\times\mathbf{k} \;+\; v^{\perp}\boldsymbol{\tau}\;, \qquad (3.13.9)$$

where $v^{\parallel} = \overline{\mathbf{v}}\cdot\boldsymbol{\tau}\times\mathbf{k}$. Note that if $\boldsymbol{\tau}$ points northwards then $\boldsymbol{\tau}\times\mathbf{k}$ points eastward. The expression $\overline{\mathbf{v}}\cdot\boldsymbol{\tau} \;=\; v^{\perp}$ of Eqn. (3.13.8) is now vertically differentiated to obtain

$$\overline{\mathbf{v}}\cdot\boldsymbol{\tau}_z \;=\; -\overline{\mathbf{v}}_z\cdot\boldsymbol{\tau} \;+\; v_z^{\perp} \;=\; -\tfrac{N^2}{fg\rho}\,\mathbf{k}\times\nabla_n P\cdot\boldsymbol{\tau} \;+\; v_z^{\perp}, \qquad (3.13.10)$$

where we have used the "thermal wind" equation (3.12.3), $\overline{\mathbf{v}}_z \;=\; \tfrac{N^2}{fg\rho}\,\mathbf{k}\times\nabla_n P$. We will now show that the left-hand side of this equation is $-\phi_z v^{\parallel}$ where ϕ_z is the rate of rotation of the direction of the unit vector $\boldsymbol{\tau}$ with respect to height (in radians per metre). By expressing the two-dimensional unit vector $\boldsymbol{\tau}$ in terms of the angle ϕ (measured counter-clockwise) of $\boldsymbol{\tau}$ with respect to due east so that $\boldsymbol{\tau} = \left(\cos\phi, \sin\phi\right)$, we see that $\boldsymbol{\tau}\times\mathbf{k} = \left(\sin\phi, -\cos\phi\right)$, $\boldsymbol{\tau}_z \;=\; -\,\phi_z\,\boldsymbol{\tau}\times\mathbf{k}$ and $\mathbf{k}\cdot\boldsymbol{\tau}\times\boldsymbol{\tau}_z \;=\; \phi_z$. Interestingly, ϕ_z is also equal to minus the helicity of $\boldsymbol{\tau}$ (and to minus the helicity of $\boldsymbol{\tau}\times\mathbf{k}$), that is, $\phi_z \;=\; -\,\boldsymbol{\tau}\cdot\nabla\times\boldsymbol{\tau} \;=\; -\left(\boldsymbol{\tau}\times\mathbf{k}\right)\cdot\nabla\times\left(\boldsymbol{\tau}\times\mathbf{k}\right)$, where the helicity of a vector is defined to be the scalar product of the vector with its curl. From the velocity decomposition (3.13.9) and the equation $\boldsymbol{\tau}_z = -\phi_z \boldsymbol{\tau}\times\mathbf{k}$ we see that the left-hand side of Eqn. (3.13.10), $\bar{\mathbf{v}}\cdot\boldsymbol{\tau}_z$, is $-\phi_z v^{\parallel}$, hence $v^{\parallel}$ can be expressed as

$$v^{\parallel} = \frac{N^2}{fg\rho}\,\frac{\mathbf{k}\cdot\nabla_n P\times\boldsymbol{\tau}}{\phi_z} - \frac{v_z^{\perp}}{\phi_z} \qquad \text{or} \qquad v^{\parallel} = \frac{H^{\mathrm{n}}}{\phi_z \rho f T_{\mathrm{b}}^{\Theta}\left|\nabla_n \hat{\Theta}\right|} - \frac{v_z^{\perp}}{\phi_z}, \tag{3.13.11}$$

where we have used the definition of neutral helicity H^{n}, Eqn. (3.13.2). The expression for both horizontal components of the Eulerian-mean horizontal velocity vector $\bar{\mathbf{v}}$ is

$$\boxed{\bar{\mathbf{v}} = \left\{\frac{N^2}{fg\rho}\,\frac{\mathbf{k}\cdot\nabla_n P\times\boldsymbol{\tau}}{\phi_z} - \frac{v_z^{\perp}}{\phi_z}\right\}\boldsymbol{\tau}\times\mathbf{k} + v^{\perp}\boldsymbol{\tau},} \tag{3.13.12}$$

and the horizontal velocity due to solely the two mixing terms can be expressed as

$$-\frac{v_z^{\perp}}{\phi_z}\,\boldsymbol{\tau}\times\mathbf{k} + v^{\perp}\boldsymbol{\tau} = \frac{(v^{\perp})^2}{\phi_z}\left(\frac{\boldsymbol{\tau}\times\mathbf{k}}{v^{\perp}}\right)_z, \tag{3.13.13}$$

which has the magnitude $\left|\frac{1}{\phi_z}\left(v^{\perp}\boldsymbol{\tau}\times\mathbf{k}\right)_z\right| = \left|\frac{1}{\phi_z}\left(v^{\perp}\boldsymbol{\tau}\right)_z\right| = \left|\left(v^{\perp}\boldsymbol{\tau}\right)_{\phi}\right|$.

Equation (3.13.12) for the Eulerian-mean horizontal velocity $\bar{\mathbf{v}}$ shows that in the absence of mixing processes (so that $v^{\perp} = v_z^{\perp} = 0$) and so long as

(i) the epineutral $\hat{\Theta}$ contours do spiral in the vertical (i.e. $\phi_z \neq 0$) and

(ii) $\left|\nabla_n \hat{\Theta}\right|$ is not zero,

then neutral helicity H^{n} (which is proportional to $\mathbf{k}\cdot\nabla_n P\times\boldsymbol{\tau}$) is required to be non-zero in the ocean whenever the ocean is not motionless. Neutral helicity arises in this context because it is proportional to the component of the thermal wind vector $\bar{\mathbf{v}}_z$ in the direction across the $\hat{\Theta}$ contour on the neutral tangent plane (see Eqn. (3.13.4)).

Planetary potential vorticity

Planetary potential vorticity is the Coriolis parameter f times the vertical gradient of a suitable variable. Potential density is sometimes used for that variable but using potential density (i) involves an inaccurate separation between lateral and diapycnal advection because potential density surfaces are not a good approximation to neutral tangent planes and (ii) incurs the non-conservative baroclinic production term of Eqn. (3.13.5). Using approximately neutral surfaces, "ans", (such as Neutral Density surfaces) provides an optimal separation between the effects of lateral and diapycnal mixing in the potential vorticity equation. In this case the potential vorticity variable is proportional to the reciprocal of the thickness between a pair of closely spaced approximately neutral surfaces.

The evolution equation for planetary potential vorticity is derived by first taking the epineutral "divergence" $\nabla_n\cdot$ of the geostrophic relationship from Eqn. (3.12.1), namely $f\mathbf{v} = g\mathbf{k}\times\nabla_p z$. The projected "divergences" of a two-dimensional vector $\mathbf{a}$ in the neutral tangent plane and in an isobaric surface, are $\nabla_n\cdot\mathbf{a} = \nabla_z\cdot\mathbf{a} + \mathbf{a}_z\cdot\nabla_n z$ and $\nabla_p\cdot\mathbf{a} = \nabla_z\cdot\mathbf{a} + \mathbf{a}_z\cdot\nabla_p z$ from which we find (using Eqn. (3.12.6), $\nabla_n z - \nabla_p z = \nabla_n P/P_z$)

$$\nabla_n\cdot\mathbf{a} = \nabla_p\cdot\mathbf{a} + \mathbf{a}_z\cdot\nabla_n P/P_z. \tag{3.20.1}$$

Applying this relationship to the two-dimensional vector $f\mathbf{v} = g\mathbf{k}\times\nabla_p z$ we have

$$\nabla_n \cdot \left(f\mathbf{v} \right) \;=\; g\,\nabla_p \cdot \left(\mathbf{k} \times \nabla_p z \right) \;+\; f\mathbf{v}_z \cdot \nabla_n P / P_z \;=\; 0\,. \qquad (3.20.2)$$

The first part of this expression can be seen to be zero by simply calculating its components, and the second part is zero because the thermal wind vector $\mathbf{v}_z$ points in the direction $\mathbf{k} \times \nabla_n P$ (see Eqn. (3.12.3)). It can be shown that $\nabla_r \cdot \left(f\mathbf{v} \right) \;=\; 0$ in any surface r which contains the line $\nabla P \times \nabla \rho$.

Eqn. (3.20.2), namely $\nabla_n \cdot \left(f\mathbf{v} \right) \;=\; 0$, can be interpreted as the divergence form of the evolution equation of planetary potential vorticity since

$$\nabla_n \cdot \left(f\mathbf{v} \right) \;=\; \nabla_n \cdot \left(\frac{q\,\mathbf{v}}{\gamma_z} \right) \;=\; 0\;, \qquad (3.20.3)$$

where $q = f\gamma_z$ is the planetary potential vorticity, being the Coriolis parameter times the vertical gradient of Neutral Density. This instantaneous equation can be averaged in a thickness-weighted sense in density coordinates yielding

$$\boxed{\nabla_n \cdot \left(\frac{\hat{q}\,\hat{\mathbf{v}}}{\tilde{\gamma}_z} \right) \;=\; -\nabla_n \cdot \overline{\left(\frac{\mathbf{v}''q''}{\gamma_z} \right)} \;=\; \nabla_n \cdot \left(\tilde{\gamma}_z^{-1} K \nabla_n \hat{q} \right)}\;, \qquad (3.20.4)$$

where the double-primed quantities are deviations of the instantaneous values from the thickness-weighted mean quantities. Here the epineutral eddy flux of planetary potential vorticity per unit area has been taken to be down the epineutral gradient of $\hat{q}$ with the epineutral diffusivity K . The thickness-weighted mean planetary potential vorticity is

$$\hat{q} \;\equiv\; \tilde{\gamma}_z \left. \overline{\left(\frac{q}{\gamma_z} \right)} \right|_{\gamma} \;=\; f\tilde{\gamma}_z\;, \qquad (3.20.5)$$

and the averaging in the above equations is consistent with the difference between the thickness-weighted mean velocity and the velocity averaged *on* the Neutral Density surface, $\hat{\mathbf{v}} - \tilde{\mathbf{v}}$ (the bolus velocity), being $\hat{\mathbf{v}} - \tilde{\mathbf{v}} \;=\; K\,\nabla_n \ln\left(\hat{q} \right)$, since Eqn. (3.20.4) can be written as $\nabla_n \cdot \left(f\hat{\mathbf{v}} \right) = \nabla_n \cdot \left(\tilde{\gamma}_z^{-1} K \nabla_n \hat{q} \right)$ while the epineutral temporal average of Eqn. (3.20.3) is $\nabla_n \cdot \left(f\tilde{\mathbf{v}} \right) = 0$.

The divergence form of the mean planetary potential vorticity evolution equation, Eqn. (3.20.4), is quite different to that of a normal conservative variable such as Absolute Salinity or Conservative Temperature,

$$\left(\left. \frac{\hat{\Theta}}{\tilde{\gamma}_z} \right|_n \right)_t \;+\; \nabla_n \cdot \left(\frac{\hat{\Theta}\,\hat{\mathbf{v}}}{\tilde{\gamma}_z} \right) \;+\; \frac{\left(\tilde{e}\,\hat{\Theta} \right)_z}{\tilde{\gamma}_z} \;=\; \nabla_n \cdot \left(\tilde{\gamma}_z^{-1} K \nabla_n \hat{\Theta} \right) \;+\; \frac{\left(D\hat{\Theta}_z \right)_z}{\tilde{\gamma}_z}\;, \qquad (\hat{\Theta}\text{\_Eqn.})$$

because in Eqn. (3.20.4) the following three terms are missing; (i) the vertical diffusion of $\hat{q}$ with diffusivity D (ii) the dianeutral advection of $\hat{q}$ by the dianeutral velocity $\tilde{e}$, and (iii) the temporal tendency term.

The mean planetary potential vorticity equation (3.20.4) may be put into the advective form by subtracting $\hat{q}$ times the mean continuity equation,

$$\left(\left. \frac{1}{\tilde{\gamma}_z} \right|_n \right)_t \;+\; \nabla_n \cdot \left(\frac{\hat{\mathbf{v}}}{\tilde{\gamma}_z} \right) \;+\; \frac{\tilde{e}_z}{\tilde{\gamma}_z} \;=\; 0\;, \qquad (3.20.6)$$

from Eqn. (3.20.4), yielding ($\tilde{\gamma}_z^{-1}$ times)

$$\left. \hat{q}_t \right|_n \;+\; \hat{\mathbf{v}} \cdot \nabla_n \hat{q} \;=\; \tilde{\gamma}_z \nabla_n \cdot \left(\tilde{\gamma}_z^{-1} K \nabla_n \hat{q} \right) \;+\; \hat{q}\tilde{e}_z\;, \qquad (3.20.7)$$

or

$$\boxed{\left. \hat{q}_t \right|_n \;+\; \hat{\mathbf{v}} \cdot \nabla_n \hat{q} \;+\; \tilde{e}\hat{q}_z \;=\; \frac{\mathrm{d}\hat{q}}{\mathrm{d}t} \;=\; \tilde{\gamma}_z \nabla_n \cdot \left(\tilde{\gamma}_z^{-1} K \nabla_n \hat{q} \right) \;+\; \left(\hat{q}\tilde{e} \right)_z}\,. \qquad (3.20.8)$$

In this form, it is clear that planetary potential vorticity behaves like a conservative variable as far as epineutral mixing is concerned, but it is quite unlike a normal conservative variable as far as vertical mixing is concerned; contrast Eqn. (3.20.8) with the conservation equation for Conservative Temperature,

$$\boxed{\hat{\Theta}_t\Big|_n + \hat{\mathbf{v}}\cdot\nabla_n\hat{\Theta} + \tilde{e}\hat{\Theta}_z = \frac{\mathrm{d}\hat{\Theta}}{\mathrm{d}t} = \tilde{\gamma}_z\nabla_n\cdot\left(\tilde{\gamma}_z^{-1}K\nabla_n\hat{\Theta}\right)+\left(D\hat{\Theta}_z\right)_z}\,. \qquad \underline{\text{(A.21.15)}}$$

If $\hat{q}$ were a normal conservative variable the last term in Eqn. (3.20.8) would be $\left(D\hat{q}_z\right)_z$ where D is the vertical diffusivity. The term that actually appears in Eqn. (3.20.8), $\left(\hat{q}\tilde{e}\right)_z$, is different to $\left(D\hat{q}_z\right)_z$ by $\left(\hat{q}\tilde{e} - D\hat{q}_z\right)_z = f\left(\tilde{e}\tilde{\gamma}_z - D\tilde{\gamma}_{zz}\right)_z$. Equation (A.22.4) for the mean dianeutral velocity $\tilde{e}$ can be expressed as $\tilde{e} \approx D_z + D\tilde{\gamma}_{zz}/\tilde{\gamma}_z$ if the following three aspects of the non-linear equation of state are ignored; (1) cabbeling and thermobaricity, (2) the vertical variation of the thermal expansion coefficient and the saline contraction coefficient, and (3) the vertical variation of the integrating factor $b(x,y,z)$ of Eqns. (3.20.10) - (3.20.15) below. Even when ignoring these three different implications of the nonlinear equation of state, the evolution equations (3.20.7) and (3.20.8) of $\hat{q}$ are unlike normal conservation equations because of the extra term

$$\left(\hat{q}\tilde{e} - D\hat{q}_z\right)_z = f\left(\tilde{e}\tilde{\gamma}_z - D\tilde{\gamma}_{zz}\right)_z \approx f\left(D_z\tilde{\gamma}_z\right)_z = \left(D_z\hat{q}\right)_z \qquad (3.20.9)$$

on their right-hand sides. This presence of this additional term can result in "unmixing" of $\hat{q}$ in the vertical. Consider a situation where both $\hat{q}$ and $\hat{\Theta}$ are locally linear functions of $\hat{S}_{\mathrm{A}}$ down a vertical water column, so that the $\hat{S}_{\mathrm{A}} - \hat{q}$ and $\hat{S}_{\mathrm{A}} - \hat{\Theta}$ diagrams are both locally straight lines, exhibiting no curvature. Imposing a large amount of vertical mixing at one height (e. g. a delta function of D) will not change the $\hat{S}_{\mathrm{A}} - \hat{\Theta}$ diagram because of the zero $\hat{S}_{\mathrm{A}} - \hat{\Theta}$ curvature (see the water-mass transformation equation (A.23.1)). However, the additional term $\left(D_z\hat{q}\right)_z$ of Eqn. (3.20.9) means that there will be a change in $\hat{q}$ of $\left(D_z\hat{q}\right)_z = \hat{q}D_{zz} + \hat{q}_z D_z \approx \hat{q}D_{zz}$. This is $\hat{q}$ times a negative anomaly at the central height of the extra vertical diffusion, and is $\hat{q}$ times a positive anomaly on the flanking heights above and below the central height. In this way, a delta function of extra vertical diffusion induces structure in the initially straight $\hat{S}_{\mathrm{A}} - \hat{q}$ line which is a telltale sign of "unmixing".

This planetary potential vorticity variable, $\hat{q} = f\tilde{\gamma}_z$, is often mapped on Neutral Density surfaces to give insight into the mean circulation of the ocean on density surfaces. The reasoning is that if the influence of dianeutral advection (the last term in Eqn. (3.20.7)) is small, and the epineutral mixing of $\hat{q}$ is also small, then in a steady ocean $\hat{\mathbf{v}}\cdot\nabla_n\hat{q} = 0$ and the thickness-weighted mean flow on density surfaces $\hat{\mathbf{v}}$ will be along contours of thickness-weighted planetary potential vorticity $\hat{q} = f\tilde{\gamma}_z$.

Because the square of the buoyancy frequency, N^2, accurately represents the vertical static stability of a water column, there is a strong urge to regard fN^2 as the appropriate planetary potential vorticity variable, and to map its contours on Neutral Density surfaces. This urge must be resisted, as spatial maps of fN^2 are significantly different to those of $\hat{q} = f\tilde{\gamma}_z$. To see why this is the case the relationship between the epineutral gradients of $\hat{q}$ and fN^2 will be derived.

For the present purposes Neutral Helicity will be assumed sufficiently small that the existence of neutral surfaces is a good approximation, and we seek the integrating factor $b = b(x,y,z)$ which allows the construction of Neutral Density surfaces (γ surfaces) according to

$$\frac{\nabla\gamma}{\gamma} \;=\; b\left(\beta^{\Theta}\nabla S_{\mathrm{A}} - \alpha^{\Theta}\nabla\Theta\right) \;=\; b\left(\frac{\nabla\rho}{\rho} - \kappa\nabla P\right). \qquad (3.20.10)$$

Taking the curl of this equation gives

$$\frac{\nabla b}{b}\times\left(\kappa\nabla P - \frac{\nabla\rho}{\rho}\right) \;=\; -\,\nabla\kappa\times\nabla P. \qquad (3.20.11)$$

The bracket on the left-hand side is normal to the neutral tangent plane and points in the direction $\mathbf{n} = -\nabla_n z + \mathbf{k}$ and is $g^{-1}N^2\left(-\nabla_n z + \mathbf{k}\right)$. Taking the component of Eqn. (3.20.11) in the direction of the normal to the neutral tangent plane, $\mathbf{n}$, we find

$$\begin{aligned} 0 \;&=\; \nabla\kappa\times\nabla P\cdot\mathbf{n} \;=\; \left(\nabla_n\kappa + \kappa_z\mathbf{n}\right)\times\left(\nabla_n P + P_z\mathbf{n}\right)\cdot\mathbf{n} \\ &=\; \nabla_n\kappa\times\nabla_n P\cdot\mathbf{n} \;=\; \nabla_n\kappa\times\nabla_n P\cdot\mathbf{k} \;=\; \left(\kappa_{S_{\mathrm{A}}}\nabla_n S_{\mathrm{A}} + \kappa_{\Theta}\nabla_n\Theta\right)\times\nabla_n P\cdot\mathbf{k} \qquad (3.20.12) \\ &=\; T_{\mathrm{b}}^{\Theta}\nabla_n P\times\nabla_n\Theta\cdot\mathbf{k} \;=\; g\,N^{-2}H^{\mathrm{n}}, \end{aligned}$$

which simply says that the neutral helicity H^{n} must be zero in order for the dianeutral component of Eqn. (3.20.11) to hold, that is, $\nabla_n P\times\nabla_n\Theta\cdot\mathbf{k}$ must be zero. Here the equalities $\kappa_{S_{\mathrm{A}}} = \beta_P^{\Theta}$ and $\kappa_{\Theta} = -\,\alpha_P^{\Theta}$ have been used.

Since ∇b can be written as $\nabla b = \nabla_n b + b_z\mathbf{n}$, Eqn. (3.20.11) becomes

$$g^{-1}N^2\,\nabla_n \ln b\times\left(-\nabla_n z + \mathbf{k}\right) \;=\; -\,P_z\nabla_p\kappa\times\left(-\nabla_p z + \mathbf{k}\right), \qquad (3.20.13)$$

where $\nabla P = P_z\left(-\nabla_p z + \mathbf{k}\right)$ has been used on the right-hand side, $\left(-\nabla_p z + \mathbf{k}\right)$ being the normal to the isobaric surface. Concentrating on the horizontal components of this equation, $g^{-1}N^2\,\nabla_n \ln b \;=\; -\,P_z\nabla_p\kappa$, and using the hydrostatic equation $P_z = -\,g\rho$ gives

$$\boxed{\nabla_n \ln b \;=\; \rho g^2 N^{-2}\,\nabla_p\kappa \;=\; -\,\rho g^2 N^{-2}\left(\alpha_P^{\Theta}\nabla_p\Theta - \beta_P^{\Theta}\nabla_p S_{\mathrm{A}}\right)}. \qquad (3.20.14)$$

The integrating factor b defined by Eqn. (3.20.10), that is $b \equiv -gN^{-2}\gamma^{-1}\nabla\gamma\cdot\mathbf{n}/(\mathbf{n}\cdot\mathbf{n}) = -gN^{-2}\gamma^{-1}\nabla\gamma\cdot\mathbf{n}/(1+\nabla_n z\cdot\nabla_n z)$, allows spatial integrals of $b\,(\beta^{\Theta}\nabla S_{\mathrm{A}} - \alpha^{\Theta}\nabla\Theta) \approx \nabla\ln\gamma$ to be approximately independent of path for "vertical paths", that is, for paths in planes whose normal has zero vertical component.

By analogy with fN^2, the Neutral Surface Potential Vorticity ($NSPV$) is defined as $-g\gamma^{-1}$ times $\hat{q} = f\tilde{\gamma}_z$, so that $NSPV = b\,fN^2$ (having used the vertical component of Eqn. (3.20.10)), so that the ratio of $NSPV$ to fN^2 is found by spatially integrating Eqn. (3.20.14) to be

$$\begin{aligned} \frac{NSPV}{fN^2} \;=\; b \;&=\; \exp\left\{-\int_{\mathrm{ans}}\rho g^2\,N^{-2}\left(\alpha_P^{\Theta}\nabla_p\Theta - \beta_P^{\Theta}\nabla_p S_{\mathrm{A}}\right)\cdot d\boldsymbol{l}\right\} \\ &=\; \exp\left\{\int_{\mathrm{ans}}\rho g^2\,N^{-2}\nabla_p\kappa\cdot d\boldsymbol{l}\right\}. \end{aligned} \qquad (3.20.15)$$

The integral here is taken along an <u>a</u>pproximately <u>n</u>eutral <u>s</u>urface (such as a Neutral Density surface) from a location where $NSPV$ is equal to fN^2.

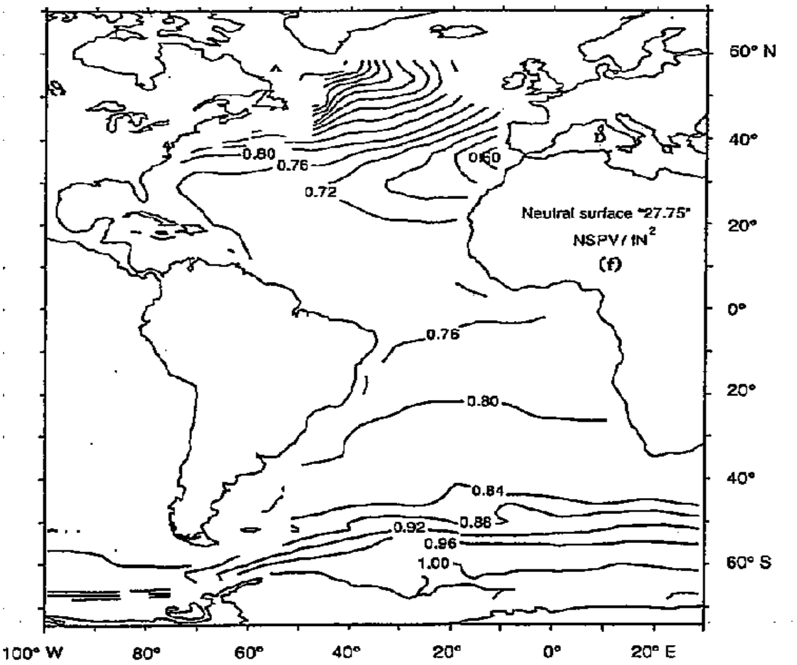


Figure. Map of NSPV versus fN². Plot of the ratio of NSPV to fN^2 on a Neutral Density surface in the Atlantic.

The deficiencies of fN^2 as a form of planetary potential vorticity have not been widely appreciated. Even in a lake, the use of fN^2 as planetary potential vorticity is inaccurate since the right-hand side of (3.20.14) is then

$$-\rho g^2 N^{-2} \alpha_P^\Theta \nabla_p \Theta \;=\; \rho g^2 N^{-2} \alpha_P^\Theta \Theta_z \nabla_\Theta P / P_z \;=\; -\frac{\alpha_P^\Theta}{\alpha^\Theta} \nabla_\Theta P, \qquad (3.20.16)$$

where the geometrical relationship $\nabla_p \Theta = -\Theta_z \nabla_\Theta P / P_z$ has been used along with the hydrostatic equation. The mere fact that the Conservative Temperature surfaces in the lake have a slope (i. e. $\nabla_\Theta P \neq \mathbf{0}$) means that the spatial variation of contours of fN^2 on a Θ surface will not be the same as for the contours of $NSPV$ on a Θ surface in a lake.

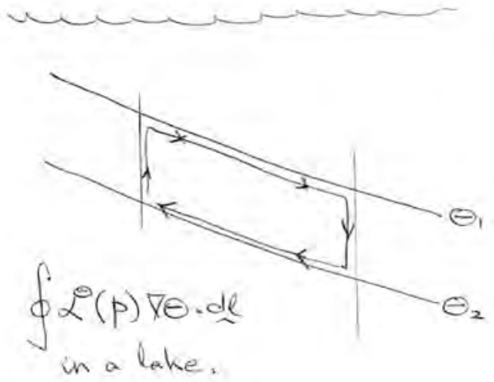


Figure. NSPV versus fN² in a lake. Because the thermal expansion coefficient is a function of pressure, the vertical integral of N^2 on the two vertical parts of the closed loop are not equal, even in a lake.

In the situation where there is no gradient of Conservative Temperature along a Neutral Density surface ($\nabla_\gamma \Theta = \mathbf{0}$) the contours of $NSPV$ along the Neutral Density surface coincide with those of isopycnal-potential-vorticity (IPV), the potential vorticity defined with respect to the vertical gradient of potential density by $IPV = -fg\rho^{-1}\rho_z^{\Theta}$. IPV is related to fN^2 by (McDougall (1988))

$$\frac{IPV}{fN^2} \equiv \frac{-g\rho^{-1}\rho_z^{\Theta}}{N^2} = \frac{\beta^{\Theta}(p_{\mathrm{r}})}{\beta^{\Theta}(p)}\frac{\left[R_\rho/r-1\right]}{\left[R_\rho-1\right]} = \frac{\beta^{\Theta}(p_{\mathrm{r}})}{\beta^{\Theta}(p)}\frac{1}{G^{\Theta}} \approx \frac{1}{G^{\Theta}}, \qquad (3.20.17)$$

so that the ratio of $NSPV$ to IPV, evaluated on an approximately neutral surface, is

$$\frac{NSPV}{IPV} = \frac{\beta^{\Theta}(p)}{\beta^{\Theta}(p_{\mathrm{r}})}\frac{\left[R_\rho-1\right]}{\left[R_\rho/r-1\right]}\exp\left\{\int_{\mathrm{ans}} g^2 N^{-2}\nabla_P(\rho\kappa)\cdot d\boldsymbol{l}\right\}. \qquad (3.20.18)$$

The sketch below indicates why $NSPV$ is different to IPV; it is the highly differentiated nature of potential vorticity that causes the isolines of IPV and $NSPV$ to not coincide even at the reference pressure p_{r} of the potential density variable. $NSPV$, fN^2 and IPV have the units s^{-3}.

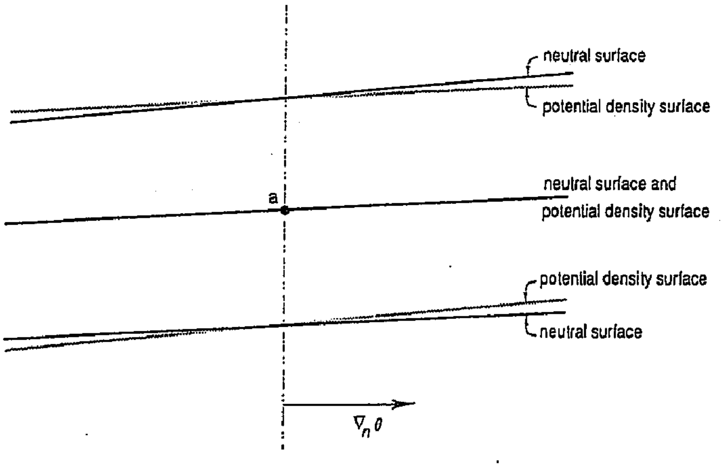


Fig. 14. A vertical cross section through three neutral surfaces and three potential density surfaces. The reference pressure of the potential density is the pressure of the central point, a. The neutral surface and potential density surface that pass though this point are parallel. The slopes of the other pairs of surfaces are different.

Production of entropy when ice melts into seawater

The general case we consider in this section has the seawater temperature above its freezing temperature, while the ice, in order to be ice, needs to be at or below the freezing temperature of pure water (i.e., seawater having zero Absolute Salinity). Note that this condition permits situations in which the initial ice temperature (say, -1 °C) is higher than or equal to that of seawater (say, -1.5 °C), as is often the case for floating ice sheets.

In other words, the general case we are considering is not an equilibrium situation in which certain amounts of ice and seawater co-exist without further melting or freezing. Rather, we consider a very small mass of ice in contact with a large mass of seawater. Without exchange of heat or matter with its surroundings, the initial non-equilibrium two-phase state is assumed to always turn irreversibly into a final ice-free equilibrium state after requisite relaxation time. During the melting of ice Ih into seawater at fixed pressure, entropy increases (or in one special case, is constant) while three quantities are conserved; mass, salt and enthalpy. While this process is adiabatic it is not isentropic.

The equations representing the budgets of mass, salt, enthalpy h and entropy η during this adiabatic melting event at constant pressure are

$$m_{\mathrm{SW}}^{\mathrm{f}} = m_{\mathrm{SW}}^{\mathrm{i}} + m_{\mathrm{Ih}}\,, \qquad \text{(Entropy\_1)}$$

$$m_{\mathrm{SW}}^{\mathrm{f}} S_{\mathrm{A}}^{\mathrm{f}} = m_{\mathrm{SW}}^{\mathrm{i}} S_{\mathrm{A}}^{\mathrm{i}}\,, \qquad \text{(Entropy\_2)}$$

$$m_{\mathrm{SW}}^{\mathrm{f}} h^{\mathrm{f}} = m_{\mathrm{SW}}^{\mathrm{i}} h^{\mathrm{i}} + m_{\mathrm{Ih}} h^{\mathrm{Ih}}\,. \qquad \text{(Entropy\_3)}$$

$$m_{\mathrm{SW}}^{\mathrm{f}} \eta^{\mathrm{f}} = m_{\mathrm{SW}}^{\mathrm{i}} \eta^{\mathrm{i}} + m_{\mathrm{Ih}} \eta^{\mathrm{Ih}} + m_{\mathrm{Ih}}\delta\eta\,. \qquad \text{(Entropy\_4)}$$

The superscripts i and f stand for the "initial" and "final" values, that is, the values before and after the melting event, while the subscripts SW and Ih stand for "seawater" and "ice Ih".

When we considered the production of entropy on mixing between pairs of seawater parcels the nonlinear production term was written as being proportional to the mass of the sum of the two seawater parcels, that is as $m_{\mathrm{SW}}^{\mathrm{f}}\delta\eta$, but in the present situation it seems sensible to write the production of entropy term as proportional to the mass of ice being melted, that is as $m_{\mathrm{Ih}}\delta\eta$, since the production of entropy is proportional to m_{Ih}. Hence we will take $\delta\eta$ to be the non-conservative production of entropy on melting *per unit mass of ice*.

The mass, salinity and enthalpy conservation equations and the entropy evolution equation, (Entropy_1) – (Entropy_4), can be combined to give the following expressions for the differences in the Absolute Salinity, the specific enthalpy and the specific entropy of the seawater phase due to the melting of the ice,

$$\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right) = -\frac{m_{\mathrm{Ih}}}{m_{\mathrm{SW}}^{\mathrm{f}}} S_{\mathrm{A}}^{\mathrm{i}} = -\,w^{\mathrm{Ih}} S_{\mathrm{A}}^{\mathrm{i}}\,, \qquad \text{(Entropy\_5)}$$

$$\left(h^{\mathrm{f}} - h^{\mathrm{i}}\right) = -\,w^{\mathrm{Ih}}\left(h^{\mathrm{i}} - h^{\mathrm{Ih}}\right), \qquad \text{(Entropy\_6)}$$

$$\left(\eta^{\mathrm{f}} - \eta^{\mathrm{i}}\right) = -\,w^{\mathrm{Ih}}\left(\eta^{\mathrm{i}} - \eta^{\mathrm{Ih}}\right) + w^{\mathrm{Ih}}\delta\eta\,, \qquad \text{(Entropy\_7)}$$

where we have defined the mass fraction of melted ice Ih $m_{\mathrm{Ih}}/m_{\mathrm{SW}}^{\mathrm{f}}$ as w^{Ih}. The initial and final values of the specific enthalpy of seawater are given by

$h^{\mathrm{i}} = h\left(S_{\mathrm{A}}^{\mathrm{i}}, t^{\mathrm{i}}, p\right) = \hat{h}\left(S_{\mathrm{A}}^{\mathrm{i}}, \Theta^{\mathrm{i}}, p\right)$ and $h^{\mathrm{f}} = h\left(S_{\mathrm{A}}^{\mathrm{f}}, t^{\mathrm{f}}, p\right) = \hat{h}\left(S_{\mathrm{A}}^{\mathrm{f}}, \Theta^{\mathrm{f}}, p\right)$, where the specific enthalpy of seawater has been written in two different functional forms, one being a function of *in situ* temperature and the other being a function of Conservative Temperature. Similarly, the initial and final values of the specific entropy of seawater are given by $\eta^{\mathrm{i}} = \eta\left(S_{\mathrm{A}}^{\mathrm{i}}, t^{\mathrm{i}}, p\right) = \hat{\eta}\left(S_{\mathrm{A}}^{\mathrm{i}}, \Theta^{\mathrm{i}}\right)$ and $\eta^{\mathrm{i}} = \eta\left(S_{\mathrm{A}}^{\mathrm{i}}, t^{\mathrm{i}}, p\right) = \hat{\eta}\left(S_{\mathrm{A}}^{\mathrm{i}}, \Theta^{\mathrm{i}}\right)$, noting that when expressed in terms of Conservative Temperature, the specific entropy of seawater is not separately a function of pressure.

We have illustrated the use of Eqns. (Entropy_5) and (Entropy_6) in Fig. Ice_4(a), Ice_5 and Ice_6. Note that at $p = 0\,\mathrm{dbar}$ Eqn. (Entropy_6) becomes simply $\Theta^{\mathrm{f}} - \Theta^{\mathrm{i}} = -\, w^{\mathrm{Ih}}\left(\Theta^{\mathrm{i}} - h^{\mathrm{Ih}}/c_p^0\right)$.

Rearranging Eqn. (Entropy_7) we find the following expression for the production of entropy on melting, $\delta\eta$,

$$\boxed{\delta\eta \;=\; \frac{\left(\eta^{\mathrm{f}} - \eta^{\mathrm{i}}\right)}{w^{\mathrm{Ih}}} \;+\; \left(\eta^{\mathrm{i}} - \eta^{\mathrm{Ih}}\right)}. \qquad \text{(Entropy\_8)}$$

Another way of expressing this uses Eqn. (Entropy_6) to arrive at

$$\boxed{\delta\eta \;=\; -\left(\eta^{\mathrm{f}} - \eta^{\mathrm{i}}\right)\frac{\left(h^{\mathrm{i}} - h^{\mathrm{Ih}}\right)}{\left(h^{\mathrm{f}} - h^{\mathrm{i}}\right)} \;+\; \left(\eta^{\mathrm{i}} - \eta^{\mathrm{Ih}}\right)}. \qquad \text{(Entropy\_9)}$$

This equation provides a way of calculating the non-conservative production of entropy because for given input parameter values we know how to calculate the final values of Absolute Salinity and enthalpy, and hence the final value of both *in situ* and Conservative Temperatures. Hence we can calculate the final value of entropy η^{f} and then use Eqn. (Entropy_9) to evaluate $\delta\eta$. But before we do this, we will use the above equations to explore the situation near thermodynamic equilibrium.

Entropy production as equilibrium conditions are approached

Here we prove that as equilibrium conditions are approached, the production of entropy on melting tends to zero. That is, as the temperature of both the seawater and the ice approach the freezing temperature, the production of entropy per unit mass of ice that melts, $\delta\eta$, approaches zero. The specific entropy of seawater is regarded as being a function of specific enthalpy, that is, in the functional form $\eta = \breve{\eta}\left(S_{\mathrm{A}}, h, p\right)$, and the entropy difference between the initial and final entropies of seawater, $\eta^{\mathrm{f}} - \eta^{\mathrm{i}}$, is expanded as a Taylor series in Absolute Salinity and specific enthalpy at fixed pressure about the initial properties at $\left(S_{\mathrm{A}}^{\mathrm{i}}, h^{\mathrm{i}}, p\right)$ as

$$\begin{aligned} \eta^{\mathrm{f}} - \eta^{\mathrm{i}} \;=\;& \breve{\eta}_{S_{\mathrm{A}}}\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right) + \breve{\eta}_{h}\left(h^{\mathrm{f}} - h^{\mathrm{i}}\right) \\ &+ \tfrac{1}{2}\breve{\eta}_{S_{\mathrm{A}}S_{\mathrm{A}}}\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right)^2 + \breve{\eta}_{hS_{\mathrm{A}}}\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right)\left(h^{\mathrm{f}} - h^{\mathrm{i}}\right) + \tfrac{1}{2}\breve{\eta}_{hh}\left(h^{\mathrm{f}} - h^{\mathrm{i}}\right)^2 \;+\; \text{h.o.t.}, \end{aligned} \qquad \text{(Entropy\_10)}$$

where h.o.t. stands for "higher order terms". Using Eqns. (Entropy_5) and (Entropy_6) to express the property differences $\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right)$ and $\left(h^{\mathrm{f}} - h^{\mathrm{i}}\right)$ of Eqn. (Entropy_9) in terms of the known properties of the initial state, $w^{\mathrm{Ih}} S_{\mathrm{A}}^{\mathrm{i}}$ and $w^{\mathrm{Ih}}\left(h^{\mathrm{i}} - h^{\mathrm{Ih}}\right)$, we find the following Taylor series expression for the production of entropy $\delta\eta$ (from substituting Eqn. (Entropy_10) into Eqn. (Entropy_8))

$$\begin{aligned}\delta\eta \;=\; & -\breve{\eta}_{S_\mathrm{A}} S_\mathrm{A}^\mathrm{i} - \breve{\eta}_h\left(h^\mathrm{i}-h^\mathrm{Ih}\right) + \left(\eta^\mathrm{i}-\eta^\mathrm{Ih}\right) \\ & + w^\mathrm{Ih}\left[\tfrac{1}{2}\breve{\eta}_{S_\mathrm{A}S_\mathrm{A}}\left(S_\mathrm{A}^\mathrm{i}\right)^2 + \breve{\eta}_{hS_\mathrm{A}} S_\mathrm{A}^\mathrm{i}\left(h^\mathrm{i}-h^\mathrm{Ih}\right) + \tfrac{1}{2}\breve{\eta}_{hh}\left(h^\mathrm{i}-h^\mathrm{Ih}\right)^2\right] + \text{h.o.t.}\end{aligned} \qquad \text{(Entropy\_11)}$$

The terms on the right-hand side of this equation are all in terms of properties of the initial state, before melting occurs, and the partial derivatives are all evaluated at $\left(S_\mathrm{A}^\mathrm{i}, h^\mathrm{i}, p\right)$.

From the Fundamental Thermodynamic Relation, $\mathrm{d}h - v\,\mathrm{d}P = \left(T_0+t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_\mathrm{A}$, we note that the partial derivatives of specific entropy that appear in Eqn. (Entropy_11) are given by

$$\breve{\eta}_{S_\mathrm{A}} = -\mu/T \quad \text{and} \quad \breve{\eta}_h = 1/T\,, \qquad \text{(Entropy\_12a,b)}$$

where $T = T_0+t$ is the Absolute Temperature and μ is the relative chemical potential of seawater. Substituting these expressions for $\breve{\eta}_{S_\mathrm{A}}$ and $\breve{\eta}_h$ into Eqn. (Entropy_11) gives

$$\begin{aligned}\delta\eta \;=\; & \frac{\mu^\mathrm{i}}{T^\mathrm{i}} S_\mathrm{A}^\mathrm{i} - \frac{1}{T^\mathrm{i}}\left(h^\mathrm{i}-h^\mathrm{Ih}\right) + \left(\eta^\mathrm{i}-\eta^\mathrm{Ih}\right) \\ & + w^\mathrm{Ih}\left[\tfrac{1}{2}\breve{\eta}_{S_\mathrm{A}S_\mathrm{A}}\left(S_\mathrm{A}^\mathrm{i}\right)^2 + \breve{\eta}_{hS_\mathrm{A}} S_\mathrm{A}^\mathrm{i}\left(h^\mathrm{i}-h^\mathrm{Ih}\right) + \tfrac{1}{2}\breve{\eta}_{hh}\left(h^\mathrm{i}-h^\mathrm{Ih}\right)^2\right] + \text{h.o.t.}\end{aligned} \qquad \text{(Entropy\_13)}$$

As equilibrium conditions are approached, the mass fraction w^Ih of ice that can melt in seawater approaches zero (because the temperature of the seawater approaches the freezing temperature and has little excess enthalpy available to melt much ice). Hence, as equilibrium conditions are approached, the terms proportional to w^Ih in Eqn. (Entropy_13) can be ignored.

The enthalpy of seawater is defined in terms of the Gibbs function of seawater by $h = g - Tg_T$, and the enthalpy of ice Ih is given in term of the Gibbs function of ice Ih by $h^\mathrm{Ih} = g^\mathrm{Ih} - T^\mathrm{Ih} g_T^\mathrm{Ih}$. Correspondingly, the entropies of seawater and of ice Ih are the negatives of their respective temperature derivatives, that is, $\eta = -g_T$ and $\eta^\mathrm{Ih} = -g_T^\mathrm{Ih}$. Also, the relative chemical potential of seawater μ is the derivative of the Gibbs function of seawater with respect to Absolute Salinity, $\mu = g_{S_\mathrm{A}}$, the chemical potential of ice Ih is $\mu^\mathrm{Ih} = g^\mathrm{Ih}$ and the chemical potential of water in seawater is $\mu^\mathrm{W} = g - S_\mathrm{A} g_{S_\mathrm{A}} = g - S_\mathrm{A}\mu$. Considering the case where the mass fraction of ice tends to zero, the right-hand side of Eqn. (Entropy_13) becomes

$$\boxed{\begin{aligned}\left.\delta\eta\right|_{w^\mathrm{Ih}\to 0} &= \frac{\mu^\mathrm{i}}{T^\mathrm{i}} S_\mathrm{A}^\mathrm{i} - \frac{1}{T^\mathrm{i}}\left(h^\mathrm{i}-h^\mathrm{Ih}\right) + \left(\eta^\mathrm{i}-\eta^\mathrm{Ih}\right) \\ &= \frac{1}{T^\mathrm{i}}\left(g^\mathrm{Ih} - g^\mathrm{i} + \mu^\mathrm{i} S_\mathrm{A}^\mathrm{i}\right) - \eta^\mathrm{Ih}\left(1 - \frac{T^\mathrm{Ih}}{T^\mathrm{i}}\right) \\ &= \frac{1}{T^\mathrm{i}}\left(\mu^\mathrm{Ih} - \mu^\mathrm{Wi} - \eta^\mathrm{Ih}\left[T^\mathrm{i} - T^\mathrm{Ih}\right]\right).\end{aligned}} \qquad \text{(Entropy\_14)}$$

This equation is a remarkably simple expression that applies for arbitrary temperatures of seawater and of ice and is 100% accurate in the $w^\mathrm{Ih} \to 0$ limit. Eqn. (Entropy_14) has been plotted on the same axes as Figures Ice_16(a) and Ice_17(a) below and the plots are indistinguishable (since these panels of these figures were for vanishingly small ice mass fraction).

As we have learnt, and as described in IOC *et al.* (2010), the equilibrium between seawater and ice occurs at the temperature T_freeze at which the chemical potential of water in seawater μ^W equals the chemical potential of ice μ^Ih, that is, when $g^{\mathrm{Ih}} - g^{\mathrm{i}} + \mu^{\mathrm{i}} S_{\mathrm{A}}^{\mathrm{i}}$ is zero. As equilibrium conditions are approached, that is, as the temperature of both the seawater and the ice Ih approach the freezing temperature at given seawater salinity and pressure, we have that $\left[T^{\mathrm{i}} - T^{\mathrm{Ih}}\right] \rightarrow 0$, and since both $\left(\mu^{\mathrm{Ih}} - \mu^{\mathrm{Wi}}\right) \rightarrow 0$ and $w^{\mathrm{Ih}} \rightarrow 0$ in this limit, we see by combing Eqns. (Entropy_13) and (Entropy_14) that $\delta\eta \rightarrow 0$.

This completes the proof that as equilibrium conditions are approached, the non-conservative production of entropy on melting per unit mass of ice melted, $\delta\eta$, tends to zero.

Entropy production for arbitrary seawater and ice temperatures

Returning to the equation for the non-conservative production of entropy, namely Eqn. (Entropy_8) or (Entropy_9), we have plotted $\delta\eta$ for three different values of the ice mass fraction w^{Ih} on the seawater temperature – ice temperature plot, and for $S_{\mathrm{A}} = S_{\mathrm{SO}} = 35.16504 \text{ g kg}^{-1}$ at $p = 0 \text{ dbar}$ in both Figures Ice_16 and Ice_17. As noted above, as $w^{\mathrm{Ih}} \rightarrow 0$, Eqn. (Entropy_9) and Eqn. (Entropy_14) give the same results for $\delta\eta$.

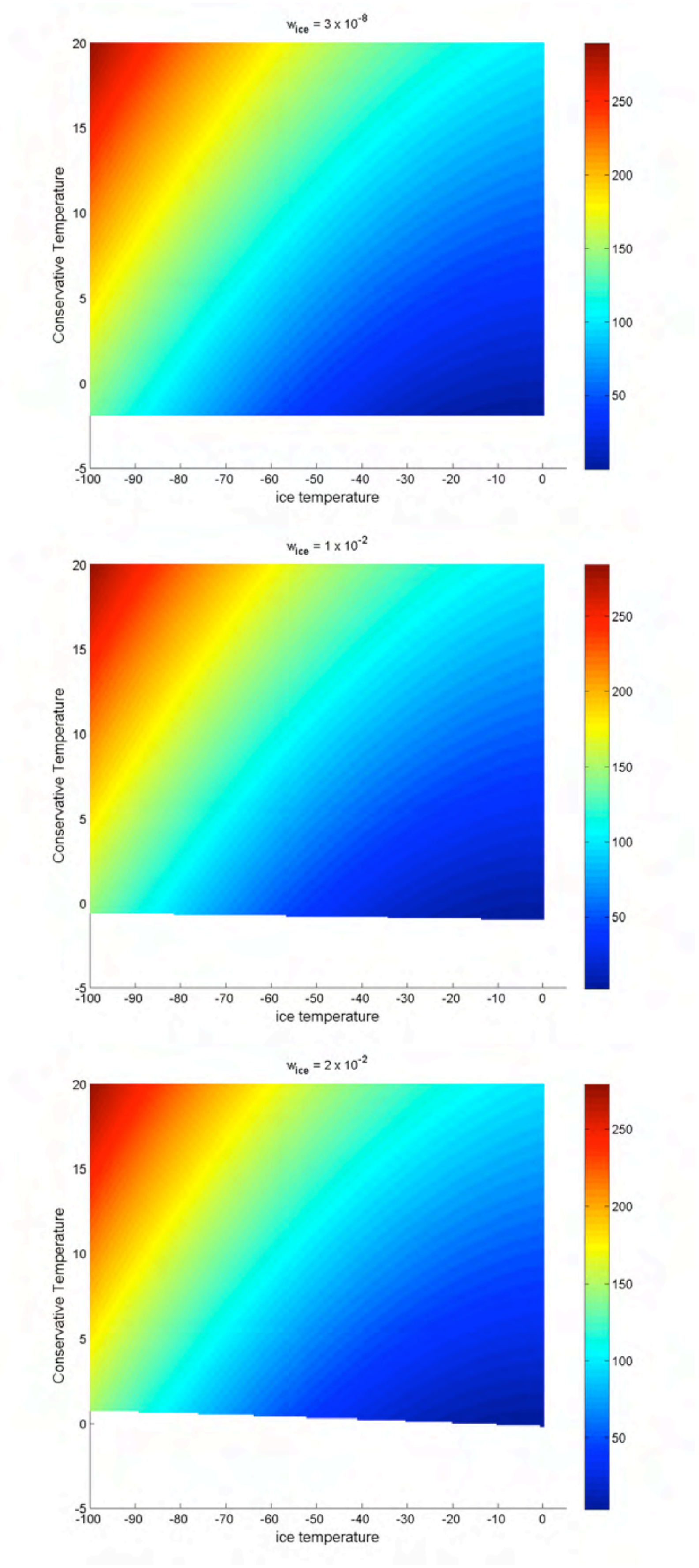


Figure Ice_16. The production of entropy $(\mathrm{J\,K^{-1}}(\mathrm{kg\ ice\ Ih})^{-1})$ from Eqn. (Entropy_9) for three different values of w^{Ih} and for $S_{\mathrm{A}} = S_{\mathrm{SO}} = 35.16504\ \mathrm{g\,kg^{-1}}$ at $p = 0\ \mathrm{dbar}$.

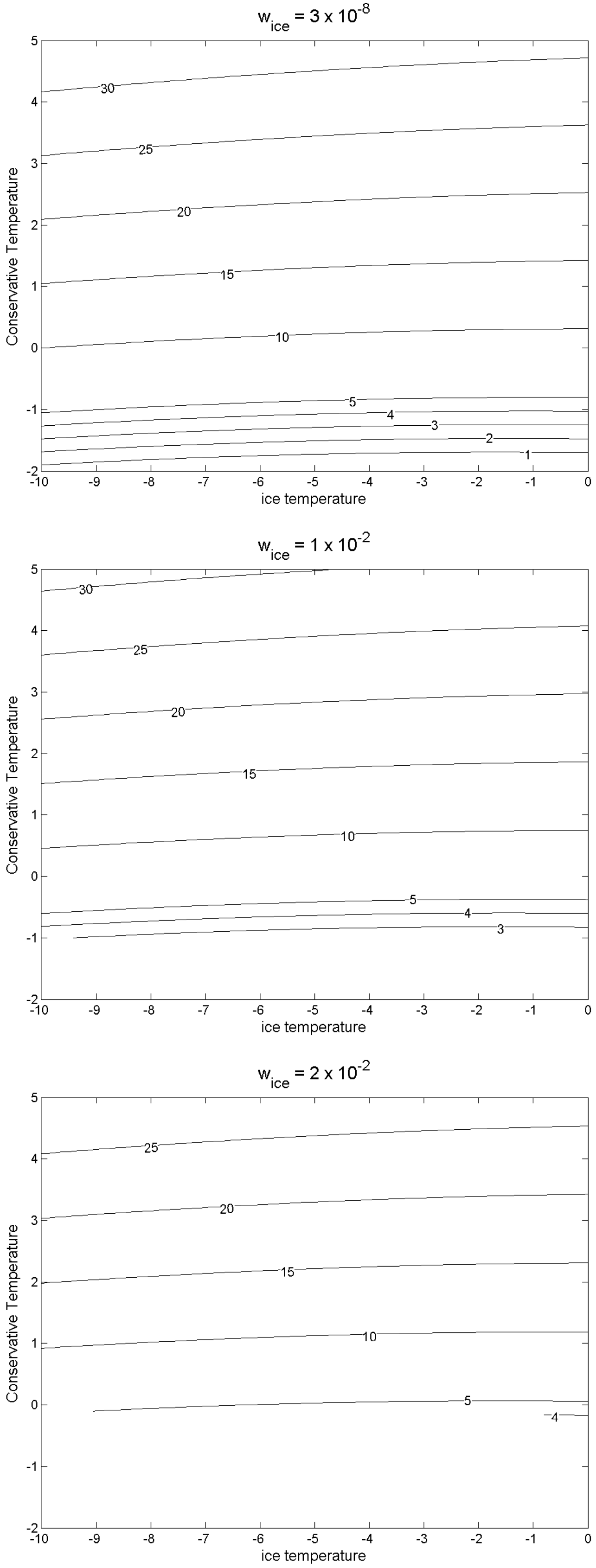


Figure Ice_17. The production of entropy ($\mathrm{J\,K^{-1}}\left(\mathrm{kg\ ice\ Ih}\right)^{-1}$) from Eqn. (Entropy_9) for three different values of w^{Ih} and for $S_{\mathrm{A}} = S_{\mathrm{SO}} = 35.16504\ \mathrm{g\ kg^{-1}}$ at $p = 0\ \mathrm{dbar}$. This is the same as Figure Ice_16, but for restricted temperature ranges.

Discussion of the LINEAR dependence of the production of entropy on seawater temperature

These numerical results indicate that the production of entropy depends on the square of the difference between the ice temperature and the freezing temperature, but surprisingly, it depends LINEARLY on the difference between the seawater temperature and the freezing temperature. A Taylor series analysis of Eqn. (Entropy_13) conforms this linear dependence on $\left[T^{\mathrm{i}} - T_{\mathrm{freeze}} \right]$.

Here we attempt to understand why does the production of entropy depends linearly on the seawater temperature difference $\left[T^{\mathrm{i}} - T_{\mathrm{freeze}} \right]$, since it is normal to find that the production of entropy is proportional to the square of property differences. In this regard, recall that (i) the non-conservative production of entropy when seawater parcels are turbulently mixed to uniformity is proportional to the square of the property differences,

$$\delta\eta \;=\; -\tfrac{1}{2}\frac{m_1 m_2}{m^2}\left\{ \breve{\eta}_{hh}\left(\Delta h\right)^2 + 2\breve{\eta}_{hS_{\mathrm{A}}}\,\Delta h\,\Delta S_{\mathrm{A}} + \breve{\eta}_{S_{\mathrm{A}}S_{\mathrm{A}}}\left(\Delta S_{\mathrm{A}}\right)^2 \right\}, \qquad \text{(A.16.6)}$$

and (ii) the corresponding non-conservative production of entropy expressed in terms of the molecular fluxes is given by the second line of the following equation,

$$\begin{aligned} \rho\frac{\mathrm{d}\eta}{\mathrm{d}t} \;=\; \left(\rho\eta\right)_t + \nabla\cdot\left(\rho\mathbf{u}\eta\right) \;&=\; -\nabla\cdot\left(\frac{1}{T}\mathbf{F}^{\mathrm{Q}} - \frac{\mu}{T}\mathbf{F}^{\mathrm{S}}\right) \\ &\quad + \mathbf{F}^{\mathrm{Q}}\cdot\nabla\left(\frac{1}{T}\right) + \mathbf{F}^{\mathrm{S}}\cdot\nabla\left(\frac{-\mu}{T}\right). \end{aligned} \qquad \text{(B.24)}$$

Since the molecular flux of heat $\mathbf{F}^{\mathrm{Q}}$ is approximately proportional to the gradient of temperature, we see that both the laminar and turbulent cases have the production of entropy being proportional to the square of either property differences or of property gradients.

So how is it that we have found that for the process of ice melting into seawater (or indeed water) that the non-conservative production of entropy $\delta\eta$ is linearly proportional to the seawater temperature (that exceeds the freezing temperature)?

We can find the answer by doing a Taylor series expansion of Eqn. (Entropy_13) about the equilibrium point. The lowest-order term in temperature differences to $\delta\eta$ is

$$\begin{aligned} &\left[\frac{\left(h^{\mathrm{i}} - h^{\mathrm{Ih}}\right)}{\left(T^{\mathrm{i}}\right)^2} + \left(\frac{\mu^{\mathrm{i}}}{T^{\mathrm{i}}}\right)_T S_{\mathrm{A}}^{\mathrm{i}} \right]\left[T^{\mathrm{i}} - T_{\mathrm{freeze}} \right] + \ldots. \\ &= \left[h^{\mathrm{i}} - h^{\mathrm{Ih}} - S_{\mathrm{A}}^{\mathrm{i}} h_{S_{\mathrm{A}}}^{\mathrm{i}} \right]\frac{\left[T^{\mathrm{i}} - T_{\mathrm{freeze}} \right]}{\left(T^{\mathrm{i}}\right)^2} + \ldots. \end{aligned} \qquad \text{(Entropy\_15)}$$

The enthalpy flux $\left[h^{\mathrm{i}} - h^{\mathrm{Ih}} - S_{\mathrm{A}}^{\mathrm{i}} h_{S_{\mathrm{A}}}^{\mathrm{i}} \right]$, per unit mass of ice Ih melted, is familiar; it is the amount of enthalpy that effectively departs the seawater and enters the ice (in order to convert the ice to seawater), and it includes the change in enthalpy due to the change in the seawater salinity due to melting. So Eqn. (Entropy_15) does seem to have the usual form of a flux of enthalpy times a difference of $1/T$, just the same as the second line of Eqn. (B.24). So the form is actually the same as usual, it is just that with the phase change, there is an enthalpy flux per unit mass $\left[h^{\mathrm{i}} - h^{\mathrm{Ih}} - S_{\mathrm{A}}^{\mathrm{i}} h_{S_{\mathrm{A}}}^{\mathrm{i}} \right]$ that is approximately independent of the temperature differences.

Melting and freezing:- an entropy production pump

When ice melts into seawater that is warmer than the freezing temperature, we have shown that there is a non-conservative production of entropy. What happens during the reverse process, when ice forms? Well, when ice forms, it forms at the freezing temperature, so the freezing occurs near equilibrium conditions, so there is nearly zero production of entropy. So we seem to have a one-way valve, or an entropy pump, in which entropy is produced on melting, but is not produced (or consumed) on freezing.

Melting into an intermediate mass of seawater

First, consider the melting of say 1 kg of ice into 999 kg of seawater. Second, consider the following two-stage process where we initially melt the 1 kg of ice into just 499kg of the same seawater, and then in a second stage, mix this 500kg of diluted and cooled seawater with the remaining 500kg of original seawater. We would hope that the production of entropy via this two-stage process would be the same as in the one-stage melting process, and it can be shown that this is the case.

THREE-DIMENSIONAL RESIDUAL-MEAN THEORY

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Abstract

Mesoscale eddies act to mix fluid parcels in a way that is highly constrained by the stratified nature of the fluid. The residual-mean theory provides the link between the different views that are apparent from averaging these turbulent flow fields in height coordinates and in density coordinates. It reduces the parameterization problem from three dimensions to two dimensions and it shows how the eddy fluxes are skew-symmetric in height coordinates so that the total advection velocity can be adiabatic.

1. Introduction

The residual-mean theory of Andrews and McIntyre (1976) was developed for the zonal averaging operator. It was realized that the Eulerian-mean northward velocity was not a reliable indicator of the mean velocity at which heat and tracers were advected meridionally. The zonal-residual-mean theory involves a revised total velocity field, called the residual-mean velocity field, which better represents the velocity at which heat and tracers were advected by the "mean" atmospheric circulation. This zonal-residual-mean theory has been extended to the oceanic case (where continents interrupt the zonal integrals) by McIntosh and McDougall (1996).

The task of parameterizing unresolved mesoscale eddy motions in a forward ocean model is significantly more complicated than forming an appropriate zonally-averaged velocity field. There are two principal reasons for the added complexity. First, the mean flow field in a forward ocean model is three dimensional and is of zeroth order in perturbation amplitude (in contrast to the two-dimensional velocity field of the zonally-averaged problem where the Eulerian-mean flow is of second order in perturbation amplitude), and second, one needs to account for unresolved fields in both

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space and time. The temporal-residual-mean (TRM) theory addresses the first issue, while there is as yet no published solution to the second issue (a potential solution to this problem is sketched below).

We begin by summarizing the TRM theory, first emphasizing its advective nature, then examining the vector decomposition of the eddy density flux that is inherent in the TRM approach. This is followed by a physical interpretation of the TRM conservation equations as being equivalent to the corresponding equations averaged in density coordinates. The TRM theory provides the physical interpretation of the quasi-Stokes (or eddy-induced) streamfunction of a method such as that of Gent *et al.* (1995). This streamfunction is the contribution of eddies to the horizontal transport of water of a certain density class, and this physical interpretation assists in applying boundary conditions to the quasi-Stokes streamfunction.

This article concentrates on theoretical features of residual-mean theory and we argue that the Gent and McWilliams (1990) scheme for advecting tracers in models is not equivalent to down-gradient diffusion of thickness despite this being the original justification of the scheme. The construction of the vertical component of the eddy-induced velocity assumes that the eddy-induced velocity is three-dimensionally non-divergent and this means that the eddy-induced velocity cannot be proportional to the down-gradient flux of thickness. This also is apparent in the diapycnal nature of the resolved-scale velocity in such ocean models, and we argue that the resolved-scale velocity in these models is the Eulerian-mean velocity, that is, it is the velocity averaged at constant height, not at constant density as we have previously stated (Gent *et al.*, 1995). In this way, it is argued that the Gent *et al.* (1995) scheme is really a parameterization of the quasi-Stokes velocity of the TRM theory. This realization points to the route for improved parameterizations, and it also has implications for how we must interpret the model variables in such coarse-resolution models.

Coarse resolution ocean models suffer from two separate problems because of their lack of horizontal resolution. The first problem is that they do not exhibit mesoscale eddy activity and the temporal-residual-mean (TRM) theory addresses this issue. In this way we can imagine a model that has fine horizontal resolution but, for whatever reason, does not have mesoscale eddies (perhaps because the model is too viscous). The addition of the skew diffusion of the TRM theory can correct for the effects of the missing mesoscale eddies. The second problem is that these models have no knowledge of the spatial correlations of properties on scales smaller than their resolution. This second problem would arise whether mesoscale eddies and temporal perturbations were present or not. In this article, a tentative solution to this lack of horizontal resolution is advanced. The end result of this procedure is to suggest more terms that should be added to the quasi-Stokes streamfunction. These extra contributions effectively put into a coarse resolution model the missing horizontal spatial correlations. The extra contributions do not require any parameterization since they are already written in terms of the variables carried by the coarse resolution model.

This article concentrates on the theory of three-dimensional residual-mean circulations and it does not discuss the state of the art in actually parameterizing the quasi-Stokes streamfunction of the TRM circulation, although a few remarks are made along these lines in the concluding section. Nor does this article concentrate on the significant advantages that have been identified to date when eddy-induced advection is included in coarse-resolution ocean models.

2. Review of the TRM Mean Density Equation

In what follows the averaging operator (the overbar) is defined to be a low-pass temporal average and primed quantities are the deviations from this low-passed value. In developing the theory it is convenient to deal with the density conservation equation and to ignore any non-linearity in the equation of state. In practice ocean models do not carry a conservation equation for density but rather for conservative tracers such as salinity and potential temperature. Diapycnal mixing in the ocean is relatively weak and it proves very useful to develop the residual-mean theory for the density conservation equation and to treat density as a conservative variable for this purpose. The usual conservation equations for Eulerian-averaged density and for half the density variance are

$$\bar{D}_t\bar{\gamma} = \bar{Q} - \nabla \cdot \left(\overline{\boldsymbol{U}'\gamma'}\right) \tag{1}$$

and

$$\bar{D}_t\bar{\phi} = \overline{Q'\gamma'} - \overline{\boldsymbol{U}'\gamma'} \cdot \nabla\bar{\gamma} + O\left(\alpha^3\right) \tag{2}$$

Here $\bar{\phi} \equiv \frac{1}{2}\overline{\gamma'^2}$ is half the density variance measured at a fixed point in space and the terminology $O\left(\alpha^3\right)$ indicates terms that are of cubic or higher order in perturbation amplitude.

In order to develop residual-mean conservation equations that apply to unsteady flows we need to admit the possibility that the Eulerian-mean density may not be the most appropriate mean density to appear in the mean density conservation equation. For example, the Eulerian-mean density, $\bar{\gamma}(x, y, z, t)$, describes a density surface whose average height is not that of the original Eulerian averaging, z. The appropriate mean density is the one whose surface is, on average, at the height of the averaging. This density can be expressed in terms of $\bar{\gamma}$ and $\bar{\phi}$ by

$$\tilde{\gamma} = \bar{\gamma} - \left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right)_z + O\left(\alpha^3\right) \tag{3}$$

The distinction here is between averaging density at a given height, z, and averaging the height of a given density surface $\gamma = \tilde{\gamma}$. McDougall and McIntosh (1998a) used the density variance equation, (2), to rewrite the mean density conservation equation, (1), in terms of this new mean density, $\tilde{\gamma}$, the TRM velocity, $\bar{\boldsymbol{U}}^{\#}$ and a new "diabatic" term, $\bar{Q}^{\#}$ as

$$\bar{D}_t^{\#}\tilde{\gamma} \equiv \tilde{\gamma}_t + \bar{\boldsymbol{U}}^{\#} \cdot \nabla\tilde{\gamma} = \bar{Q}^{\#} + O\left(\alpha^3\right) \tag{4}$$

where

$$\bar{\boldsymbol{U}}^{\#} \equiv \bar{\boldsymbol{U}} + \boldsymbol{U}^{+}; \quad \boldsymbol{U}^{+} \equiv \nabla \times (\boldsymbol{\Psi} \times \mathbf{k}) = \boldsymbol{\Psi}_z - \mathbf{k}\left(\nabla_H \cdot \boldsymbol{\Psi}\right) \tag{5}$$

$$\boldsymbol{\Psi} \equiv -\frac{\overline{\boldsymbol{V}'\gamma'}}{\bar{\gamma}_z} + \frac{\bar{\boldsymbol{V}}_z}{\bar{\gamma}_z}\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right) \tag{6}$$

and

$$\bar{Q}^{\#} = \bar{Q} + \left[-\frac{\overline{Q'\gamma'}}{\bar{\gamma}_z} + \frac{\bar{Q}_z}{\bar{\gamma}_z}\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right)\right]_z \tag{7}$$

We will return to a detailed discussion of these expressions, but first the TRM density conservation, (4), will be derived a little differently; this time examining the nature of the eddy density flux itself rather than simply its divergence.

3. Vector Decomposition of the Eddy Density Flux

Combining (3) and (1), the conservation equation for $\tilde{\gamma}$ can be written as

$$\tilde{\gamma}_t + \nabla \cdot \left(\bar{\boldsymbol{U}}\tilde{\gamma}\right) = \bar{Q}^{\#} - \nabla \cdot \boldsymbol{F}^M + O\left(\alpha^3\right) \tag{8}$$

where the modified density flux, $\boldsymbol{F}^M$, is

$$\boldsymbol{F}^M = \overline{\boldsymbol{U}'\gamma'} + \bar{\boldsymbol{U}}\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right)_z + \mathbf{k}\left\{\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right)_t - \frac{\overline{Q'\gamma'}}{\bar{\gamma}_z} + \frac{\bar{Q}_z}{\bar{\gamma}_z}\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right)\right\} \tag{9}$$

Now the density variance equation, (2), is used to eliminate $\overline{w'\gamma'}$ from the expression (9), and guided by the results above, the modified density flux, can be expressed as

$$\boldsymbol{F}^M = -\boldsymbol{A}\nabla\tilde{\gamma} + \boldsymbol{N} + O\left(\alpha^3\right) \tag{10}$$

where the asymmetric matrix $\boldsymbol{A}$ is defined in terms of the two components of the quasi-Stokes streamfunction, $\boldsymbol{\Psi} = (\Psi^x, \Psi^y)$, as

$$\boldsymbol{A} \equiv \begin{bmatrix} 0 & 0 & \Psi^x \\ 0 & 0 & \Psi^y \\ -\Psi^x & -\Psi^y & 0 \end{bmatrix} \tag{11}$$

and the non-divergent density flux, $\boldsymbol{N}$, is given by

$$\boldsymbol{N} \equiv \left(\frac{\bar{\boldsymbol{V}}\bar{\phi}}{\bar{\gamma}_z}\right)_z - \mathbf{k}\nabla_H \cdot \left(\frac{\bar{\boldsymbol{V}}\bar{\phi}}{\bar{\gamma}_z}\right) = \nabla \times \left[\left(\frac{\bar{\boldsymbol{V}}\bar{\phi}}{\bar{\gamma}_z}\right) \times \mathbf{k}\right] \tag{12}$$

The density variance equation, (2), can be written in terms of the modified density flux, $\boldsymbol{F}^M$, as (subscripts denote differentiation)

$$\bar{D}_t\bar{\phi} = -\boldsymbol{F}^M \cdot \nabla\tilde{\gamma} + \left\{\bar{\gamma}_z\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right)_t - \tilde{\gamma}_t\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right)_z + \left(\frac{\bar{Q}\bar{\phi}}{\bar{\gamma}_z}\right)_z\right\} + O\left(\alpha^3\right) \tag{13}$$

Apart from the three terms in curly brackets (the two unsteady terms and the diabatic term), it is apparent that the advection of density variance by the mean flow is balanced by the diapycnal component of the modified density flux. Furthermore, the vector decomposition, (10), shows that the diapycnal component of $\boldsymbol{F}^M$ is due only to the non-divergent flux, $\boldsymbol{N}$, since the skew flux is directed in the density surface (see Figure 1c). That is, apart from the diabatic and unsteady terms, we have $\bar{D}_t\bar{\phi} = -\boldsymbol{N}\cdot\nabla\tilde{\gamma} + O\left(\alpha^3\right)$. In the same three-dimensional turbulent situation as we are considering, Marshall and Shutts (1981) have found that the horizontal advection of variance is balanced by a non-divergent two-dimensional flux. This finding was subject to the assumption that the mean flow in the horizontal plane follows the mean density contours. Without having to invoke such an assumption, the present result generalizes Marshall and Shutt's finding to three dimensions, involving the advection of variance by the three-dimensional mean flow, $\bar{D}_t\bar{\phi}$, and the non-divergent part, $\boldsymbol{N}$, of the three-dimensional modified density flux. However, this result appears to be of no real use but rather is in the nature of a truism because neither side of $\bar{D}_t\bar{\phi} = -\boldsymbol{N} \cdot \nabla\tilde{\gamma} + O\left(\alpha^3\right)$ involves the eddy density flux.

4. Discussion of the TRM Density Equation

It is apparent that the modified density flux, $\boldsymbol{F}^M$, represents the eddy forcing of the mean density equation, (8). The TRM theory (McDougall and McIntosh, 1998a) shows

- that $\boldsymbol{F}^M$ is the sum of a skew flux, $-\boldsymbol{A}\nabla\tilde{\gamma}$ plus some non-gradient-terms,

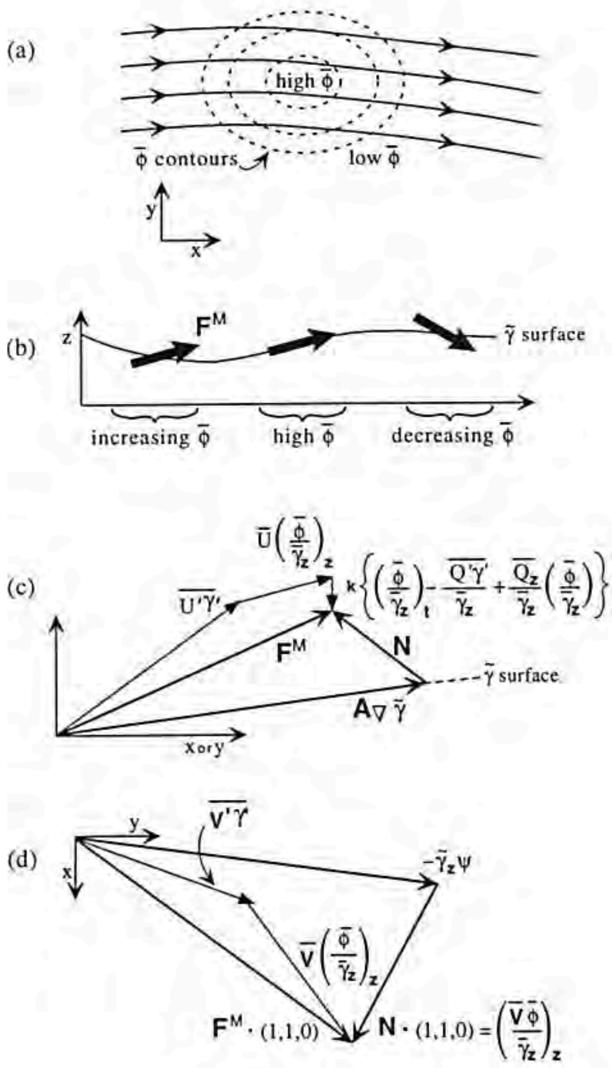

Figure 1. As the mean flow moves through a region of increasing density variance (panel (a)) the modified density flux, $\boldsymbol{F}^M$, must have an upwards directed diapycnal component (panel (b), where it is assumed that the unsteady and diabatic terms in (13) do not dominate). This diapycnal component of $\boldsymbol{F}^M$ is supplied by only the non-divergent flux, $\boldsymbol{N}$, since the skew flux is directed in the density surface [panel (c)]. Panel (c) also indicates the construction of the modified density flux according to its definition, (9). The TRM decomposition of the modified density flux into the two parts $\boldsymbol{A}\nabla\tilde{\gamma}$ and $\boldsymbol{N}$ is fascinating as it is only the skew flux that affects the mean density equation, while it is only the non-divergent flux that affects the density variance equation. Panel (d) shows just the horizontal components of the full three-dimensional vectors that are sketched in panel (c).

- that these non-gradient-terms are non-divergent and so do not affect the mean density equation,
- that the diapycnal component of $\boldsymbol{F}^M$ is due only to the non-divergent flux, $\boldsymbol{N}$,
- that the skew flux, $-\boldsymbol{A}\nabla\tilde{\gamma}$, does not contribute to the density variance equation,
- that the symmetric diffusion tensor, $\boldsymbol{S}$, (which we anticipate exists and causes diffusion of passive tracers along density surfaces) must be such that it does not cause a density flux, that is, $\boldsymbol{S}\nabla\tilde{\gamma} = \mathbf{0}$, consistent with current practice in ocean GCMs (beginning with Redi, 1982), and
- that the divergence of the skew flux is the advection of density by the extra (quasi-Stokes) velocity, that is, $\nabla \cdot (\boldsymbol{A}\nabla\tilde{\gamma}) = -\boldsymbol{U}^{+} \cdot \nabla\tilde{\gamma}$.

These points are illustrated in Figure 1.

The above has involved various manipulations of (i) the mean density equation, (ii) the density variance equation, and (iii), the continuity equation. Apart from simply writing these equations in different forms, what has been achieved? One achievement can be described as a major simplification. In the original Reynolds-averaged mean density equation, (1), the task of parameterizing the eddy density flux is daunting and has never been done successfully because each of the three components of the eddy flux, $\overline{\boldsymbol{U}'\gamma'}$, needs to be parameterized and one has no intuition about how much of this flux should be divergent, how much should be diapycnal or what form the non-gradient terms might take. An indication of how difficult it would be to parameterize $\overline{\boldsymbol{U}'\gamma'}$ directly can be obtained by combining (9) and (10) to write $\overline{\boldsymbol{U}'\gamma'}$ as

$$\overline{\boldsymbol{U}'\gamma'} = -\boldsymbol{A}\nabla\tilde{\gamma} + \boldsymbol{N} - \bar{\boldsymbol{U}}\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right)_z - \mathbf{k}\left\{\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right)_t - \frac{\overline{Q'\gamma'}}{\bar{\gamma}_z} + \frac{\bar{Q}_z}{\bar{\gamma}_z}\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right)\right\} + O\left(\alpha^3\right) \tag{14}$$

All terms except the first are non-gradient terms; that is, they are not of the form of a diffusion tensor operating on the appropriate mean density gradient, $\nabla\tilde{\gamma}$. How would one have guessed the nature of these non-gradient terms without the TRM theory? In contrast, all that needs to be parameterized in the TRM density conservation (4) or (8) is the quasi-Stokes streamfunction, $\boldsymbol{\Psi}$. It is expected that it will be substantially easier to parameterize this two-dimensional vector rather than having to parameterize the three-dimensional vector $\overline{\boldsymbol{U}'\gamma'}$.

Another major achievement of TRM theory (and equally of the Gent and McWilliams (1990) eddy parameterization scheme) is that even if the parameterization of $\boldsymbol{\Psi}$ is imperfect, because the parameterized term enters the density conservation equation as a skew flux which is equivalent to an extra advection of density, the total velocity, the TRM velocity,

$\bar{\boldsymbol{U}}^{\#} = \bar{\boldsymbol{U}} + \boldsymbol{\Psi}_z - \mathbf{k}\,(\nabla_H \cdot \boldsymbol{\Psi})$, will have a diapycnal component only if the diabatic source term, $\bar{Q}^{\#}$, is non-zero. That is, uncertainty in the parameterization of the quasi-Stokes streamfunction will not cause unwanted changes in water masses. This feature occurs because the TRM theory shows that the symmetric diffusion tensor does not cause any flux of density, which provides belated proof of this assumption in the rotated symmetric diffusion tensor of Redi (1982) and Griffies *et al.* (1998).

Hand-in-hand with this progress in understanding the mean density equation has come the realization that the conservation equations should be written in terms of the modified density variable, $\tilde{\gamma}$, or equivalently, that this is the correct interpretation for the mean density that is carried by an eddyless general circulation model. Also, just as the mean density field and the total advection velocity are re-interpreted in the TRM approach, so too the appropriate diabatic source term is changed from $\bar{Q}$ to $\bar{Q}^{\#}$. The need for this change is best understood by averaging the conservation equation in density coordinates, and this is discussed in the next section.

There are other approaches to developing mean conservation equations in turbulent stratified fluids. The generalized-Lagrangian-mean approach (Andrews and McIntyre, 1978) is an exact theory but it has not proved of practical use because the Lagrangian-mean velocity and the Stokes velocity are both divergent at leading order (second order) in perturbation quantities. This is the reason why we call our additional velocity, $\boldsymbol{U}^{+}$, the "quasi-Stokes" velocity because not only is it an approximation to the true Stokes velocity, but also the divergence of the quasi-Stokes velocity is identically zero and so differs from the divergence of the true Stokes velocity at leading order. Plumb and Mahlman (1987) have pursued a Lagrangian perturbation analysis of the tracer conservation equations under the zonal averaging operator and we have extended this technique to the density equation under temporal averaging in three dimensions (this is not discussed here), but to date we have not been successful in applying Plumb and Mahlman's "effective transport" method to the tracer equations under temporal averaging in three dimensions. The "effective" density conservation equation has much in common with the TRM density conservation equation in that the density variable is different to $\tilde{\gamma}$ and, like the TRM velocity, the effective velocity is non-divergent. The "effective" approach is however less attractive that the TRM approach because of the difficulty in evaluating the correlations between Lagrangian perturbation quantities as compared to the TRM approach where the correlations are between perturbation quantities evaluated at fixed points in space.

5. The Isopycnal Interpretation of TRM

With errors that are cubic in perturbation quantities, it is possible to show that the TRM approach of forming averaged quantities for use in height coordinates corresponds to temporally averaging the instantaneous conservation equations in density coordinates. McDougall and McIntosh (1998b) have proven that the quasi-Stokes streamfunction, $\boldsymbol{\Psi}$, is the contribution of perturbations to the horizontal transport of fluid that is denser than $\tilde{\gamma}(z)$, the density of the density surface whose average height is z. Their approach consisted of writing a vertical Taylor series expression for the horizontal transport of fluid of this density class, and is illustrated in Figure 2a and by the equation

$$\boldsymbol{\Psi} \equiv -\frac{\overline{\boldsymbol{V}'\gamma'}}{\bar{\gamma}_z} + \frac{\bar{\boldsymbol{V}}_z}{\bar{\gamma}_z}\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right) = \overline{\left(\boldsymbol{V} + \frac{1}{2}\boldsymbol{V}_z\eta'\right)\eta'} + O\left(\alpha^3\right) \tag{15}$$

where η' is the perturbation height of the density surface, so that $\overline{\eta'} \equiv 0$ and $\eta' = -\gamma'|_z/\bar{\gamma}_z + O(\alpha^3)$. The velocity $\left(\boldsymbol{V} + \frac{1}{2}\boldsymbol{V}_z\eta'\right)$ is the instantaneous velocity at the height mid way between the fixed height, z, and the instantaneous height of the density surface, $z+\eta'$, so that the quasi-Stokes streamfunction is the average horizontal transport of fluid between these same two heights as indicated in Figure 2a. It is this horizontal transport of fluid that must be added to the volume transport found by using the Eulerian-averaged velocity in order to correctly represent the transport of shaded fluid in Figure 2a.

The Taylor series approach also shows that the thickness-weighted value, $\hat{A}$ of any quantity, A, obtained by averaging A between a pair of closely-spaced $\tilde{\gamma}$ surfaces is

$$\hat{A} \equiv \tilde{\gamma_z}\overline{\left(\frac{A}{\gamma_z}\right)\bigg|_{\tilde{\gamma}}} \equiv \tilde{A} + \overline{A'|_{\tilde{\gamma}}\eta'_z} = \bar{A} + \left(-\frac{\overline{A'\gamma'}}{\bar{\gamma}_z} + \frac{\bar{A}_z}{\bar{\gamma}_z}\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right)\right)_z + O\left(\alpha^3\right) \tag{16}$$

where $\tilde{A}$ is the value averaged on the density surface (not thickness-weighted) and $\overline{A'|_{\tilde{\gamma}}\,\eta'_z}$ is due to the correlations between perturbations evaluated on a density surface and the thickness between two closely-spaced surfaces. With A equal to the horizontal velocity vector, $\boldsymbol{V}$, (16) shows that

$$\hat{\boldsymbol{V}} \equiv \tilde{\boldsymbol{V}} + \boldsymbol{V}^B = \bar{\boldsymbol{V}} + \boldsymbol{\Psi}_z + O\left(\alpha^3\right) = \bar{\boldsymbol{V}}^{\#} + O\left(\alpha^3\right) \tag{17}$$

where the bolus velocity, $\boldsymbol{V}^B = \overline{\boldsymbol{V}'|_{\tilde{\gamma}}\,\eta'_z}$, is due to correlations between the horizontal velocity evaluated on the density surface and the thickness between density surfaces. Hence the thickness-weighted horizontal velocity

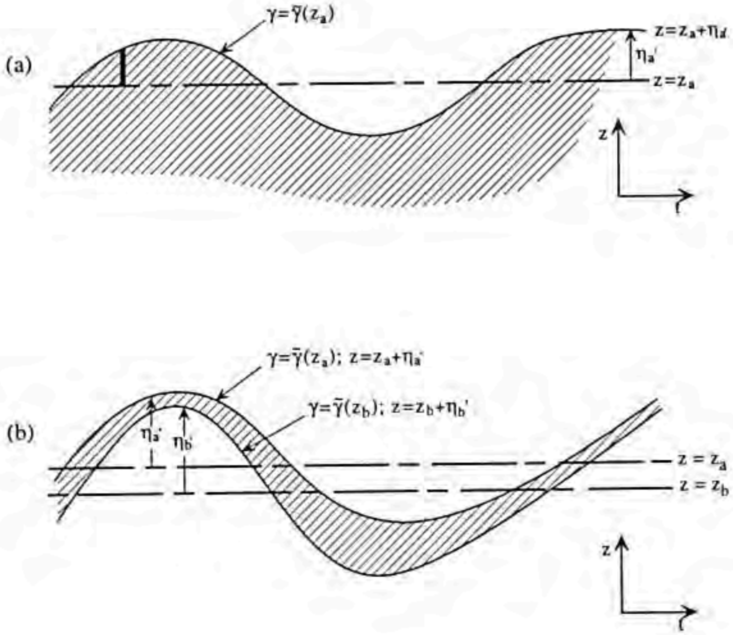

Figure 2. (a) Sketch of the height of a $\tilde{\gamma}$ density surface as a function of time at a given latitude and longitude. The quasi-Stokes streamfunction, $\boldsymbol{\Psi}$, is equal to the horizontal volume transport between the fixed height, $z = z_a$, and the instantaneous height of this density surface. This volume flux is equal to the temporal average of the perturbation height, η', and the velocity appropriate to the column of fluid shown, namely, $\left(\boldsymbol{V} + \frac{1}{2}\boldsymbol{V}_z\eta'\right)$ where both $\boldsymbol{V}$ and $\boldsymbol{V}_z$ are evaluated at the fixed height, $z = z_a$. It is this volume transport that must be added to the volume transport found by using the horizontal Eulerian-mean velocity in order to correctly estimate the transport of the shaded fluid that is more dense than $\tilde{\gamma}(z)$. (b) The thickness-weighted horizontal velocity of density coordinates, $\hat{\boldsymbol{V}}$, is defined to be the average horizontal velocity of the the shaded fluid, and this is equal to the horizontal TRM velocity, $\bar{\boldsymbol{V}}^{\#} \equiv \bar{\boldsymbol{V}} + \boldsymbol{\Psi}_z$, with an error that is cubic in the amplitude of the temporal perturbations.

obtained by averaging in density coordinates is equal to the horizontal TRM velocity, $\bar{\boldsymbol{V}}^{\#}$, up to error terms of cubic order in perturbation quantities.

When the instantaneous density conservation equation, $D_t\gamma = Q$, is averaged in density coordinates, one finds that the time-averaged diapycnal velocity, $\tilde{e} \equiv \overline{e|_{\tilde{\gamma}}}$, is given by

$$\tilde{e} \equiv \overline{\left(\frac{Q}{\gamma_z}\right)\Big|_{\tilde{\gamma}}} \equiv \frac{\hat{Q}}{\tilde{\gamma}_z} = \frac{\bar{Q}^{\#}}{\tilde{\gamma}_z} + O\left(\alpha^3\right) \tag{18}$$

where the last part of this expression has used the general thickness-weighted relationship, (16), and it is noted (from (4)) that $\bar{Q}^{\#}/\tilde{\gamma}_z$ is also the diapycnal component, $\bar{e}^{\#}$, of the TRM velocity, $\bar{\boldsymbol{U}}^{\#}$. That is, $\bar{D}_t^{\#}\tilde{\gamma} = \bar{e}^{\#}\tilde{\gamma}_z = \bar{Q}^{\#} + O\left(\alpha^3\right)$.

These results, (17) and (18), derived by McDougall and McIntosh (1998b) from a Taylor series approach, show that both the horizontal and the diapycnal components of the TRM velocity, $\bar{\boldsymbol{U}}^{\#}$, are the same as those obtained by averaging the instantaneous flow with respect to $\tilde{\gamma}$ surfaces (within cubic errors in perturbation amplitude). In this way, it is clear that the TRM theory is the way of representing in height coordinates the relevant terms that arise from averaging in density coordinates. The reason why the TRM approach is needed in height coordinates is that unless significant changes are made to the horizontal momentum equations, the resolved-scale velocity in height-coordinate models is the Eulerian-mean velocity.

The above results have errors that are cubic in the amplitude of perturbation quantities and so the question arises whether these errors may be significant. On the basis of the corresponding zonal-residual-mean theory, we have reason to believe that the cubic terms will be quite small. McIntosh and McDougall (1996) extended the zonal-residual-mean theory of Andrews and McIntyre (1976) to the oceanic situation where the continents interrupt the zonal integrals, and they showed that the zonally-thickness-weighted circulation (evaluated by zonally averaging in density coordinates) was well approximated by the zonal-residual-mean circulation which was evaluated in height coordinates. This close correspondence occurred despite the fact that at a constant latitude in the Southern ocean, density surfaces vary in height by about 1,500 m. In the TRM case of temporal averaging at a given latitude and longitude, density surfaces undulate much less than 1,500 m, with root-mean-square vertical excursions of 150 m being more typical. Hence we expect that ignoring the cubic terms in perturbation amplitude will be quite adequate for our purposes in the TRM theory.

6. The TRM Tracer Conservation Equation

The divergence form of the instantaneous tracer conservation equation is $(\tau/\gamma_z)_t + \nabla_\gamma \cdot (\boldsymbol{V}\tau/\gamma_z) + (e\tau)_\gamma = X/\gamma_z$, where the temporal derivative is taken following a density surface, e is the diapycnal velocity and X is the source term which represents local production or consumption, as well as the flux divergence of unresolved mixing processes. Temporally averaging this tracer equation yields

$$\left(\frac{\hat{\tau}}{\tilde{\gamma}_z}\right)_t + \nabla_{\tilde{\gamma}} \cdot \left(\frac{\hat{\boldsymbol{V}}\hat{\tau}}{\tilde{\gamma}_z}\right) + (\tilde{e}\hat{\tau})_{\tilde{\gamma}} = \frac{\hat{X}}{\tilde{\gamma}_z} - \overline{\left(\frac{Q''\tau''}{\gamma_z}\right)_{\tilde{\gamma}}} - \nabla_{\tilde{\gamma}} \cdot \overline{\left(\frac{\boldsymbol{V}''\tau''}{\gamma_z}\right)} \qquad (19)$$

where both the overbars on the right represent quantities averaged at constant density and subscripts denote differentiation. Here the mean value of the tracer is the thickness-weighted tracer value, with the double primed variables being the deviation of the instantaneous variables from their thickness-weighted values. These variables obey

$$\hat{\tau} \equiv \tilde{\gamma}_z \left(\overline{\left.\frac{\tau}{\gamma_z}\right|_{\tilde{\gamma}}} \right) \quad \text{and} \quad \overline{\left.\frac{\tau''}{\gamma_z}\right|_{\tilde{\gamma}}} \equiv 0 \tag{20}$$

To make progress it is necessary to assume that the eddy fluxes of tracer in (19) are representable as a diffusion tensor operating on the gradient of thickness-weighted tracer. McDougall and McIntosh (1998b) assume that the first two terms on the right-hand side of (19) amount to $(1/\tilde{\gamma}_z)$ times the divergence of a diapycnal diffusivity, D, operating on the diapycnal gradient of $\hat{\tau}$. That is, the sum of these two terms are regarded as $(1/\tilde{\gamma}_z)\left(D\hat{\tau}_z\right)_z$. The epipycnal flux (*i.e.* the flux directed along a density surface) in (19) is also assumed to take a Fickian form, namely, $\overline{\left(\frac{\boldsymbol{V}''\tau''}{\gamma_z}\right)} = -\frac{K}{\tilde{\gamma}_z}\nabla_{\tilde{\gamma}}\hat{\tau}$. These assumptions mean that the right-hand side of (19) can be written in height coordinates as $(1/\tilde{\gamma}_z)\,\nabla\cdot(\boldsymbol{S}\nabla\hat{\tau})$, where $\boldsymbol{S}$ is the symmetric diffusion tensor of Redi (1982). It is worth noting that these Fickian assumptions have not yet been proven for temporal averaging of three-dimensional flow. Under the simpler zonal averaging operator, Plumb and Mahlman (1987) expanded perturbation quantities in terms of linearized Lagrangian displacements and they were able to establish the diffusive nature of the fluxes for the tracer equation in that case. To date such an approach has not been successful for temporal averaging in three dimensions in either Cartesian or density coordinates.

The left-hand side of (19) is now transformed into height coordinates, using (17) to equate $\hat{\boldsymbol{V}}$ to $\bar{\boldsymbol{V}}^{\#}$ and (18) to equate $\tilde{e}$ to $\bar{Q}^{\#}/\tilde{\gamma}_z$ which from (4) is seen to be the diapycnal component, $\bar{e}^{\#}$, of the TRM velocity. The result of this transformation is

$$\hat{\tau}_t|_z + \nabla_H \cdot \left(\bar{\boldsymbol{V}}^{\#}\hat{\tau}\right) + \left(\bar{w}^{\#}\hat{\tau}\right)_z = \nabla\cdot(\boldsymbol{S}\nabla\hat{\tau}) + O\left(\alpha^3\right) \tag{21}$$

or

$$\hat{\tau}_t|_z + \nabla_H \cdot (\bar{\boldsymbol{V}}\hat{\tau}) + (\bar{w}\hat{\tau})_z = \nabla\cdot([\boldsymbol{S}+\boldsymbol{A}]\nabla\hat{\tau}) + O\left(\alpha^3\right) \tag{22}$$

This conservation equation is of exactly the same form as is solved in modern GCMs of the ocean. The form (21) applies when the quasi-Stokes streamfunction is used to form the quasi-Stokes velocity whereas the form (22) uses the quasi-Stokes streamfunction in the antisymmetric diffusion tensor, $\boldsymbol{A}$. Griffies (1998) has pointed out that adopting the skew-diffusion approach, (22), is preferable numerically because the quasi-Stokes streamfunction is spatially differentiated one less time in comparison with (21). It is perhaps worth noting that while the skew flux, $-\boldsymbol{A}\nabla\hat{\tau} = -\hat{\tau}_z\boldsymbol{\Psi} + \mathbf{k}\left[\boldsymbol{\Psi}\cdot\nabla_H\hat{\tau}\right]$ has no component in the direction of $\nabla\hat{\tau}$ the horizontal and vertical components of the skew flux are often down-gradient and up-gradient respectively (see Plumb, 1979).

There are two major conclusions to take away from the TRM tracer conservation equation, (22). First, one needs to not only diffuse the tracer with a symmetric diffusion tensor, but also with the asymmetric diffusion tensor, $\boldsymbol{A}$, defined by (11) and (6). This ensures that the tracer is transported with the TRM velocity. The second point is that the mean tracer is not the Eulerian-averaged tracer value. If one wanted to insist that the model's tracer value was the Eulerian-mean tracer value, then one would need to impose an additional flux divergence in the tracer equation as follows,

$$\bar{\tau}_t|_z + \nabla_H\cdot\left(\bar{\boldsymbol{V}}\bar{\tau}\right) + \left(\bar{w}\bar{\tau}\right)_z = \nabla\cdot\left(\left[\boldsymbol{S}+\boldsymbol{A}\right]\nabla\bar{\tau}\right) - \nabla\cdot\boldsymbol{E} + O\left(\alpha^3\right) \qquad (23)$$

where the additional flux, $\boldsymbol{E}$, is (using (16)),

$$\boldsymbol{E} = \mathbf{k}\left(-\frac{\overline{\tau'\gamma'}}{\bar{\gamma}_z} + \frac{\bar{\tau}_z}{\bar{\gamma}_z}\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right)\right)_t + \bar{\boldsymbol{U}}\left(-\frac{\overline{\tau'\gamma'}}{\bar{\gamma}_z} + \frac{\bar{\tau}_z}{\bar{\gamma}_z}\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right)\right)_z \qquad (24)$$

Such non-gradient terms would be very difficult to parameterize.

It is perhaps surprising, but also fortunate, that the tracer that is naturally carried by an eddyless height-coordinate model should be interpreted in exactly the same way as the tracer carried by an eddyless density-coordinate model, namely, as the thickness-weighted tracer value, $\hat{\tau}$. Lozier *et al.* (1994) have drawn attention to the damage that can be done to water masses by averaging salinity and potential temperature data at fixed height. The theoretical result presented in this section dictates that tracer data should be averaged between density surfaces not only for the purposes of forming atlases of hydrographic data, but also for comparing with the output of ocean models, for the assimilation of observed data into ocean models and before using data in inverse models.

While the tracer variables in height-coordinate and density-coordinate models should be interpreted identically, the same cannot be said of the velocity vectors. The resolved-scale horizontal velocity in a height-coordinate model is the Eulerian-mean velocity, $\bar{\boldsymbol{V}}$, whereas the resolved-scale horizontal velocity in a density coordinate model is the horizontal velocity averaged on a density surface, $\tilde{\boldsymbol{V}}$. This interpretation of the horizontal velocities in the two different coordinates is consistent (through geostrophy) with the manner in which the horizontal pressure gradient is calculated in height-coordinates and the isopycnal gradient of the Montgomery potential is evaluated in density coordinates.

7. The Diapycnal Nature of the Eulerian-mean Velocity

The advection of $\tilde{\gamma}$ by the Eulerian-mean flow is given by (from (8) using (10) and (11))

$$\begin{aligned}\tilde{\gamma}_t + \bar{\boldsymbol{U}} \cdot \nabla\tilde{\gamma} &= \bar{Q}^{\#} + \nabla\cdot(\boldsymbol{A}\nabla\tilde{\gamma}) + O\left(\alpha^3\right) \\ &= \bar{Q}^{\#} - \boldsymbol{U}^{+} \cdot \nabla\tilde{\gamma} + O\left(\alpha^3\right) \\ &= \bar{Q}^{\#} + \tilde{\gamma}_z \nabla_{\tilde{\gamma}} \cdot \boldsymbol{\Psi} + O\left(\alpha^3\right)\end{aligned} \tag{25}$$

where $\nabla_{\tilde{\gamma}}$ is the spatial gradient operator in a $\tilde{\gamma}$ surface. Hence the diapycnal component of the Eulerian-mean velocity, $\bar{e}$ is

$$\bar{e} = \bar{Q}^{\#}/\tilde{\gamma}_z + \nabla_{\tilde{\gamma}} \cdot \boldsymbol{\Psi} + O\left(\alpha^3\right) \tag{26}$$

This is a compact way of expressing how the eddy forcing affects the Eulerian-mean density equation:- namely by the epipycnal divergence of the quasi-Stokes streamfunction, $\nabla_{\tilde{\gamma}} \cdot \boldsymbol{\Psi}$. Since the physical interpretation of the quasi-Stokes streamfunction is the contribution of eddy motions to the transport of water of a certain density class, it is perhaps not surprising to see the epineutral divergence of this same physical quantity appear as a diapycnal advection. (Note that we use the word "diapycnal" to mean the part of the vertical velocity that flows through the $\tilde{\gamma}$ surface, not through the $\bar{\gamma}$ surface.)

In contrast to the Eulerian-mean flow, the diapycnal component of the TRM velocity, $\bar{e}^{\#}$ is

$$\bar{e}^{\#} = \bar{Q}^{\#}/\tilde{\gamma}_z + O\left(\alpha^3\right) \tag{27}$$

Gent and McWilliams (1990) realized that their suggested parameterization of eddies caused the resolved-scale velocity to have a diapycnal component and for several years this feature was considered a weakness of their scheme. This was considered a sufficiently negative feature that it was emphasised that the areal average of this diapycnal velocity component was zero. Now, of course, we realise that the Eulerian-mean velocity should have a diapycnal component caused by mesoscale eddies. Gent *et al.* (1995) pointed out that the relevant velocity at which tracers are advected was the total velocity (which we are now interpreting as the TRM velocity, $\bar{\boldsymbol{U}}^{\#}$) and they showed that this TRM velocity was diapycnal only to the extent of explicit diapycnal mixing processes, as is evident in (27). A good way of illustrating the diapycnal nature of the Eulerian-mean flow is to consider the relaxation of the density front of section 6 of Gent *et al.* (1995). There the Eulerian-mean flow is zero and so the advection of density following the Eulerian-mean flow is simply the temporal change of density at a point in space. As the front relaxes, the density at a fixed point certainly changes and this occurs [see (25)] due to the variation of the quasi-Stokes streamfunction along density surfaces. If one were to interpret these changes of density following the Eulerian-mean flow as a symmetric diffusion of density then it would be as often up-gradient as down-gradient. The key is to realize that these density changes are not due to diffusion in the normal sense of the word, but rather they are due to the divergence of a skew-diffusive density flux. This realization is totally equivalent to viewing the process with respect to the TRM velocity, when one finds that the front relaxes adiabatically; this being the explanation advanced by Gent *et al.* (1995).

The vector relationship between the velocity vectors $\bar{\boldsymbol{U}}$, $\boldsymbol{U}^{+}$ and $\bar{\boldsymbol{U}}^{\#}$ is illustrated in Figure 3. The positions of a given density surface are shown at an initial time and at a later time and the labelled velocity vectors are actually the displacements achieved by those velocities in this time interval. The vertical component of the Eulerian-mean velocity is due to the sum of (i) the sliding along the density surface due to its slope, $-\bar{\boldsymbol{V}} \cdot \nabla_H \tilde{\gamma}/\tilde{\gamma}_z$, (ii), the vertical advection of the density surface, $-\tilde{\gamma}_t/\tilde{\gamma}_z$, (iii), diabatic mixing processes, $\bar{Q}^{\#}/\tilde{\gamma}_z$, and (iv), the diapycnal eddy forcing of the Eulerian-mean flow, $\nabla_{\tilde{\gamma}} \cdot \boldsymbol{\Psi}$. The vertical component of the TRM velocity has no diapycnal eddy forcing but rather is the sum of just three terms, namely (i) the sliding along the density surface due to its slope, $-\bar{\boldsymbol{V}}^{\#} \cdot \nabla_H \tilde{\gamma}/\tilde{\gamma}_z$, (ii), the vertical advection of the density surface, $-\tilde{\gamma}_t/\tilde{\gamma}_z$ and (iii), the diabatic mixing processes, $\bar{Q}^{\#}/\tilde{\gamma}_z$. The cubic terms in perturbation quantities are not included on this figure as they are of higher order and are believed to be unimportant.

The eddy forcing of the mean density equation can be expressed as $-\boldsymbol{U}^{+} \cdot \nabla\tilde{\gamma}$ [see the middle line of (25)] and the relative contribution of the vertical quasi-Stokes velocity to this is

$$\frac{-w^{+}\tilde{\gamma}_z}{-\boldsymbol{U}^{+} \cdot \nabla\tilde{\gamma}} = \frac{\nabla_H \cdot \boldsymbol{\Psi}}{\nabla_{\tilde{\gamma}} \cdot \boldsymbol{\Psi}} \tag{28}$$

In the quasi-geostrophic (QG) limit this ratio is assumed to be unity because only the vertical component of the extra velocity appears as eddy forcing in the density equation (see Tréguier *et al.*, 1997). This equation shows that the QG limit is equivalent to assuming that the quasi-Stokes streamfunction varies much more strongly with horizontal position than with height. To the extent that QG theory is applicable to the real ocean,

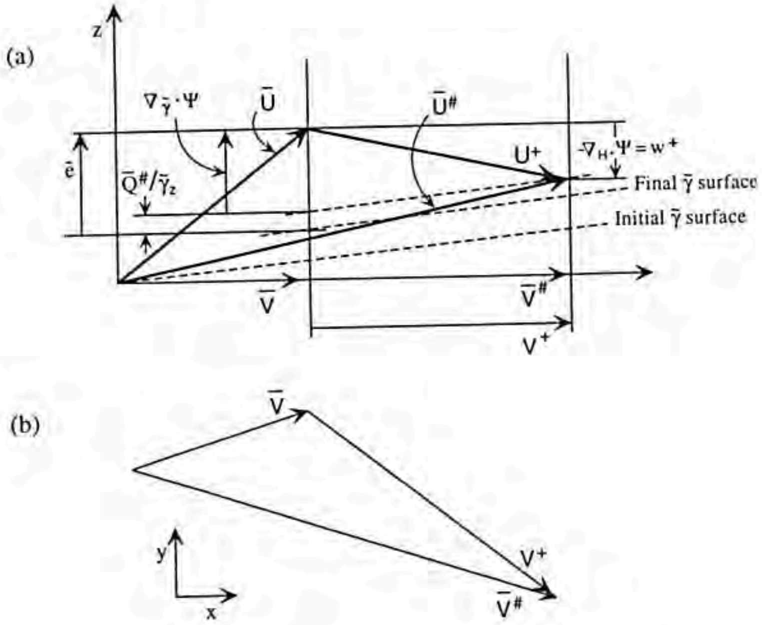

Figure 3. (a) Sketch of the Eulerian-mean velocity, $\bar{\boldsymbol{U}}$, the quasi-Stokes velocity, $\boldsymbol{U}^+$, and the TRM velocity, $\bar{\boldsymbol{U}}^{\#}$. (b) The horizontal components of the same three velocities.

the implication would be that the horizontal quasi-Stokes velocity is unimportant. The following argument suggests that this implication of QG theory is inappropriate to the real ocean. McDougall (1995) pointed out that while the eddy-induced horizontal velocity, $\boldsymbol{V}^+$, might be small (rarely larger than 1 mm/s), the fact that it tends to point in a direction across the mean epipycnal property gradients means that it can be the dominant term in a conservation equation. Also, GCM experiments with the Gent and McWilliams (1990) scheme show that the quasi-Stokes circulation accounts for up to 0.5 PW of meridional heat flux in the Southern Ocean (Danabasoglu and McWilliams, 1995). Hence it seems that this aspect of QG theory is inappropriate to the problem of parameterizing eddies in the ocean.

Ocean GCM simulations using the Gent and McWilliams (1990) scheme have found large diapycnal transports in the Southern Ocean for both the Eulerian-mean flow and the quasi-Stokes circulation. Hirst and McDougall (1998) specifically plotted the zonally-averaged streamfunctions of the Eulerian-mean flow and the quasi-Stokes flow in density coordinates to illustrate the diapycnal nature of both circulations (their figure 6), and they found about 14Sv of zonally-averaged diapycnal transport in the Southern

Ocean in both the Eulerian-mean and the quasi-Stokes circulations. The sum of these circulations was much smaller. The Gent and McWilliams (1990) scheme is often described as being a parameterization of "bolus transport", but if this were the case one would expect the extra advection of the Gent *et al.* (1995) scheme to have no diapycnal transport. In Gent *et al.* (1995) we also assumed that the resolved-scale velocity of an eddy-less ocean model could be interpreted as the velocity averaged on density surfaces, but the large diapycnal transport of the resolved-scale velocity illustrates that this is not the case. Rather the resolved-scale velocity in such models is the Eulerian-mean velocity. The observation that the quasi-Stokes advection has substantial diapycnal transport raises the important question:- "in what sense can we regard the quasi-Stokes velocity as bolus transport?" This question sets the scene for section 10 of this paper.

8. The Quasi-Stokes Velocity is not Due to the Down-gradient Thickness Flux

The aim of Gent and McWilliams (1990) and of Gent *et al.* (1995) was to provide a parameterization for the bolus velocity and it was argued that this should be directed down the isopycnal gradient of thickness so that the extra horizontal velocity would be $\kappa\left(\nabla_H\tilde{\gamma}/\tilde{\gamma}_z\right)_z$. However, in order to make the streamfunction a locally-determined quantity, the diffusivity was moved inside the vertical derivative so that the streamfunction of Gent *et al.* (1995) became $\kappa\nabla_H\tilde{\gamma}/\tilde{\gamma}_z$. This form also allowed the boundary conditions at the top and bottom of the ocean to be easily satisfied by having the diffusivity go to zero.

An immediate consequence of the TRM theory is that it justifies the appearance of κ inside the vertical derivative and so provides theoretical support for a closure of the Gent and McWilliams (1990) form. This is seen by making the most elementary assumption about the horizontal density flux in the expression, (6), for the quasi-Stokes streamfunction. If one assumes that the horizontal density flux is directed down the horizontal gradient of $\tilde{\gamma}$ with diffusivity κ (that is, $\overline{\mathbf{V}'\gamma'} = -\kappa\nabla_H\tilde{\gamma}$) and if one ignores the second term in the quasi-Stokes streamfunction, then (6) becomes $\mathbf{\Psi} = \kappa\nabla_H\tilde{\gamma}/\tilde{\gamma}_z$ exactly as in Gent *et al.* (1995) and as used by many other authors.

It was realized by Gent *et al.* (1995) that in many situations it was crucial that the diffusivity be located inside the vertical derivative in the expression for the eddy-induced velocity. For example, in the Eady problem (and to a good approximation also in the Southern Ocean), the slopes of density surfaces are independent of height so that the original idea of down-gradient thickness flux would mean that the eddy-induced horizontal velocity was zero at all heights except for delta functions of eddy-induced horizontal velocity at the top and bottom. With the diffusivity inside the vertical derivative, and with the streamfunction set to zero on all boundaries, the Gent and McWilliams (1990) parameterization quite naturally gives boundary layers of eddy-induced advection at the top and bottom of the ocean just as in the Eady problem, and the thickness of these boundary layers can be readily controlled by the height over which the diffusivity is tapered to zero. It is in fact these boundary layers that carry most of the meridional circulation of the quasi-Stokes velocity in GCM simulations of the Southern Ocean because in this region the northward slope of density surfaces tends to be almost independent of depth.

Quite apart from the issue of having the diffusivity inside the vertical derivative, there are two other compelling reasons why the eddy-induced velocity of Gent *et al.* (1995) (which we are interpreting as the quasi-Stokes velocity) is not the down-gradient thickness flux. The first of these is that the quasi-Stokes velocity is three-dimensionally non-divergent whereas the epipycnal flux of thickness is divergent. The second (which has been discussed above) is that the epipycnal thickness flux has no diapycnal component whereas the quasi-Stokes velocity has a large diapycnal component. These differences arise through the use of the streamfunction (that is, the continuity equation) to construct the vertical component of the quasi-Stokes velocity.

9. Boundary Conditions on the Quasi-Stokes Streamfunction

The physical interpretation of the quasi-Stokes streamfunction, as described in section 5 above, provides guidance on the boundary conditions that should be imposed at the top and bottom of the ocean. Figure 4 displays the temporal variations in the heights of three different $\tilde{\gamma}$ surfaces (panels (a) to (c)) when the ocean's density field displays harmonic temporal variations. When a given density is less than any in the ocean at that time, the height of that density surface is taken to be at the sea surface. The modified density, $\tilde{\gamma}$, appropriate to each height has the property (by definition) that the height of this $\tilde{\gamma}$ surface averages to zero, as is indicated by the shading in Figure 4 (the shaded fluid appearing below the mean height is equal to the shaded fluid above the mean height). As the sea surface (or the ocean floor) is approached, the shaded area reduces to zero and so the correlation of velocity and thickness in this shaded region also must tend to zero. That is, the contribution of eddies to the transport of water that is more dense than $\tilde{\gamma}$ reduces to zero as the sea surface (or ocean floor) is approached. By definition, this transport is the quasi-Stokes streamfunction and so it must approach zero smoothly at the top and bottom boundary.

In the absence of a horizontal boundary one would estimate that a fluid

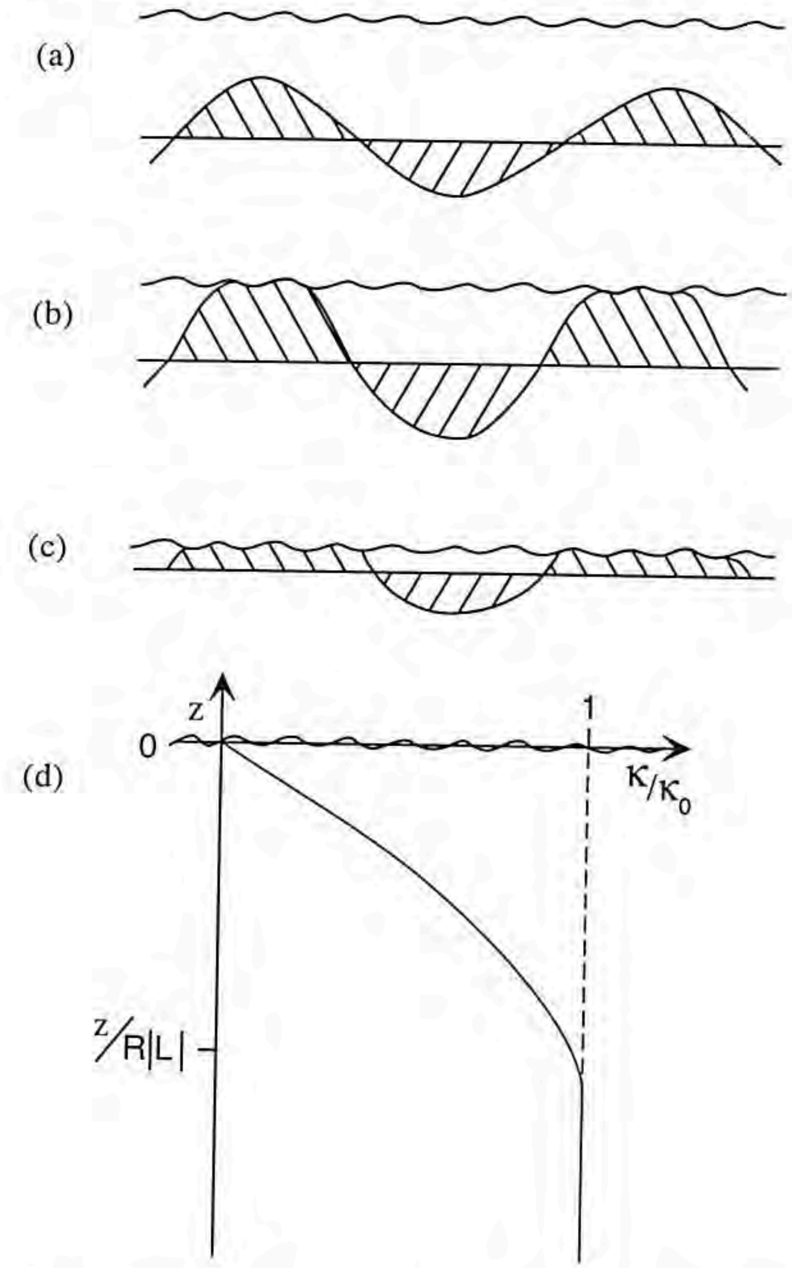

Figure 4. Sketch of the temporal variation of the heights of three different $\tilde{\gamma}$ surfaces as the sea surface is approached. Panel (d) sketches the implication for the vertical tapering of the diffusivity.

parcel in a mesoscale eddy would undergo vertical excursions (of height) that would scale with the Rossby radius, R, multiplied by the magnitude of the slope of the density surface, $|\boldsymbol{L}| = |\nabla_H \tilde{\gamma} / \tilde{\gamma}_z|$. Both R and $|\boldsymbol{L}|$ can be estimated locally at every point in a GCM. One would estimate that if $R|\boldsymbol{L}|$ were greater than the depth of a certain grid-point, then the density surface, $\tilde{\gamma}$, appropriate to that point would have begun to clip the sea surface as indicated in Figure 4b and 4c. This suggests that the quasi-Stokes streamfunction (or a diffusivity that is used to parameterize the quasi-Stokes streamfunction) should be tapered to zero according to the scaled height, $z/(R|\boldsymbol{L}|)$ (as sketched in Figure 4d) and such a procedure is already in use (see appendix B of Large *et al.*, 1997). The physical interpretation of the quasi-Stokes streamfunction makes it possible to justify this procedure.

Edmon *et al.* (1980) have contoured the divergence of the Eliassen-Palm flux of the zonally-averaged flow and have shown that for a finite amplitude situation (their figure 3d), the contours are not all bunched into surface boundary layers as one might expect from the linear solution to the Eady problem. These several lines of evidence lead us to conclude that in addition to numerical convenience, there are good physical justifications for tapering of the quasi-Stokes streamfunction over several hundred metres when approaching a horizontal boundary. Tréguier *et al.* (1997) have also suggested that the explicit horizontal diffusion should be increased as the diffusivity of the quasi-Stokes streamfunction is decreased in these boundary layers, and this appears to be a suggestion worth trying.

With no-slip boundary conditions it is clear that the quasi-Stokes streamfunction should be put equal to zero on all vertical boundaries. Mesoscale eddies would actually feel the presence of the vertical boundary when they were within a few Rossby radii of the boundary, so this would be a good choice of distance for the horizontal tapering of the quasi-Stokes streamfunction of the TRM circulation.

10. The Quasi-Stokes Velocity is not the Bolus Velocity

The horizontal quasi-Stokes velocity is the vertical derivative of the quasi-Stokes streamfunction, and we vertically differentiate the second expression in (15) to find that

$$\begin{aligned} \boldsymbol{V}^{+} = \boldsymbol{\Psi}_z &= \overline{\left(\boldsymbol{V}' + \bar{\boldsymbol{V}}_z \eta'\right) \eta'_z} + \overline{\left(\boldsymbol{V}_z + \frac{1}{2} \boldsymbol{V}_{zz} \eta'\right) \eta'} + O\left(\alpha^3\right) \\ &= \quad \boldsymbol{V}^B \quad + \quad \left(\tilde{\boldsymbol{V}} - \bar{\boldsymbol{V}}\right) \quad + O\left(\alpha^3\right) \end{aligned} \tag{29}$$

The expression $(\boldsymbol{V}' + \bar{\boldsymbol{V}}_z \eta')$ is the first-order Taylor series expansion for the velocity perturbation at constant density, $\boldsymbol{V}'|_{\tilde{\gamma}}$ so that the first term of (29) is the bolus velocity, $\boldsymbol{V}^B$ to within an error that is third order in perturbation quantities. At leading order, the expression $\left(\boldsymbol{V}_z + \frac{1}{2}\boldsymbol{V}_{zz}\eta'\right)$ is the instantaneous shear half way between the fixed height and the instantaneous height of the density surface so that the second term in (29) is equal to the difference between the horizontal velocities averaged at constant density and at constant height, $\left(\tilde{\boldsymbol{V}} - \bar{\boldsymbol{V}}\right)$.

It is apparent from (29) that the task of the quasi-Stokes streamfunction is not only to parameterize the bolus velocity, but also to take account of $\left(\tilde{\boldsymbol{V}} - \bar{\boldsymbol{V}}\right)$. The reason why this dual role exists for the quasi-Stokes streamfunction is that it is to be used in a model that has a vertical coordinate whose height does not vary in time. That is, the TRM theory applies to height-coordinate models and sigma-coordinate models such as SPEM. The momentum equations in this type of model dictate that the model's horizontal velocity in the Eulerian-mean velocity, $\bar{\boldsymbol{V}}$.

The task of parameterizing the effects of mesoscale eddies is very different for isopycnal models than for height-coordinate models. In an isopycnal model the extra horizontal velocity that is needed is indeed the bolus velocity. The sum of the bolus velocity and the resolved-scale horizontal velocity of an isopycnal model, $\tilde{\boldsymbol{V}}$, gives the thickness-weighted velocity of isopycnal coordinates, $\hat{\boldsymbol{V}}$. In stark contrast to the large diapycnal component of the quasi-Stokes velocity of height-coordinate models, the bolus advection that is needed in isopycnal models has zero diapycnal component. Also, the resolved scale velocity, $\tilde{\boldsymbol{V}}$, has no diapycnal component except for explicitly imposed small-scale mixing processes. A further important contrast is that whereas both $\bar{\boldsymbol{U}}$ and $\boldsymbol{U}^+$ of height-coordinate models are non-divergent, both $\tilde{\boldsymbol{V}}$ and $\boldsymbol{V}^B$ of isopycnal models are divergent (while their sum is not). It is this divergent nature of the two velocities in density coordinates that resolves the "curious point" raised by Tréguier, Held and Larichev (1997) (on their page 571). For the above three reasons it is clear that the task of parameterizing the effects of eddies on the transport of tracers in height-coordinate models is different to the corresponding task in isopycnal coordinates.

The following approximate expression can be found for $\left(\tilde{\boldsymbol{V}} - \bar{\boldsymbol{V}}\right)$ using the thermal wind relation, $\boldsymbol{V}_z = -\left(g/f\rho_o\right)\mathbf{k}\times\nabla_H\gamma$, which applies to both the mean and the perturbation fields.

$$\left(\tilde{\boldsymbol{V}} - \bar{\boldsymbol{V}}\right) = \left(\frac{g}{f\rho_o}\right)\mathbf{k}\times\nabla_H\left(\frac{\bar{\phi}}{\bar{\gamma}_z}\right) + O\left(\alpha^3\right) \tag{30}$$

Taking a maximum expected value of half the density variance of 10^{-2} kg^2m^{-6} (equivalent to an rms vertical heaving by meso-scale eddies of about 150 m) and assuming the epineutral gradient of $(\bar{\phi}/\bar{\gamma}_z)$ to vary by its own magnitude in a horizontal distance of 10^6 m, we find from (30) that $\left(\tilde{V} - \bar{V}\right)$ is about 10^{-3} m/s. One assumes that it is sufficiently accurate to use the geostrophic approximation (thermal wind) in this estimation. While this estimate of $\left(\tilde{V} - \bar{V}\right)$ is quite large, it must be noticed that this velocity is directed along the (usually closed) contours of $(\bar{\phi}/\bar{\gamma}_z)$ in the horizontal plane. Because of this, when the normal component of $\left(\tilde{V} - \bar{V}\right)$ is integrated along a closed path (for example, a path that encircles the globe passing through Drake Passage) then the average of the normal component of $\left(\tilde{V} - \bar{V}\right)$ is zero. This term can contribute to zonally-averaged tracer budgets if there is a correlation between the tracer values and the locations where $\left(\tilde{V} - \bar{V}\right)$ is northward or southward, but this is unlikely to be of leading order importance.

Another consequence of the form (30) is that the horizontal divergence of $\left(\tilde{V} - \bar{V}\right)$ is zero except for a small term due to the beta effect (as pointed out by Tréguier *et al.* (1997) for the QG case). This implies that if the quasi-Stokes streamfunction was made to satisfy $\boldsymbol{\Psi}_z \approx \boldsymbol{V}^B$ rather than (29), this approximation would not affect the determination of the correct vertical quasi-Stokes velocity, w^+.

Hence we conclude that while it may well be sufficiently accurate for many purposes to regard the horizontal quasi-Stokes velocity of the TRM circulation as the bolus velocity, the eddy forcing of the mean density equation, (25), is caused by the part of the quasi-Stokes velocity that is directed normal to the density surfaces, $-\boldsymbol{U}^+ \cdot \nabla\tilde{\gamma}$ and this is just the part that would be zero if the three-dimensional quasi-Stokes velocity were in fact the bolus velocity. It is the construction of the vertical component of the quasi-Stokes velocity that causes the full three-dimensional quasi-Stokes velocity to have a component normal to density surfaces. This construction uses the non-divergent nature of the quasi-Stokes velocity, and this is the key assumption that makes it different to the bolus velocity which is three-dimensionally divergent.

It is concluded that the eddy-induced velocities that are needed in eddy-less models are quite different in isopycnal models than in height-coordinate models. In isopycnal models the extra velocity that is needed is the bolus velocity which has no diapycnal component and is three-dimensionally divergent. In direct contrast, in height coordinates the eddy-induced velocity is non-divergent and has a substantial diapycnal component. Despite these differences, it seems that if one achieves a close correspondence between the horizontal bolus velocity and the vertical derivative of the quasi-Stokes streamfunction, the very nature of the residual-mean approach will ensure a good three-dimensional flow.

11. How Important is the Second Part of the Expression for $\mathbf{\Psi}$?

Here we investigate the contribution to the mean density equation of the second term in the expression, (6), for the quasi-Stokes streamfunction, $(\bar{\mathbf{V}}_z/\bar{\gamma}_z)\,(\bar{\phi}/\bar{\gamma}_z)$. From (25), the forcing of the density equation due to the presence of mesoscale eddy motions is $\tilde{\gamma}_z \nabla_{\tilde{\gamma}} \cdot \mathbf{\Psi}$ so that the second term of the quasi-Stokes streamfunction contributes to the eddy forcing of the mean density equation the amount

$$\tilde{\gamma}_z \nabla_{\tilde{\gamma}} \cdot \left(\frac{\bar{\mathbf{V}}_z}{\bar{\gamma}_z} \frac{\bar{\phi}}{\bar{\gamma}_z} \right) \tag{31}$$

The geostrophic relationship in density coordinates implies that $\nabla_{\tilde{\gamma}} \cdot (f\tilde{\mathbf{V}}) = 0$ so that we have $\nabla_{\tilde{\gamma}} \cdot (f\tilde{\mathbf{V}}) = O\left(\alpha^2\right)$, and taking the derivative with respect to $\tilde{\gamma}$ of this expression we have

$$\nabla_{\tilde{\gamma}} \cdot \left(f \bar{\mathbf{V}}_{\tilde{\gamma}}\right) = \nabla_{\tilde{\gamma}} \cdot \left(\frac{f \bar{\mathbf{V}}_z}{\bar{\gamma}_z} \right) + O\left(\alpha^2\right) = O\left(\alpha^2\right) \tag{32}$$

This equation is used in (31) to show that

$$\tilde{\gamma}_z \nabla_{\tilde{\gamma}} \cdot \left(\frac{\bar{\mathbf{V}}_z}{\bar{\gamma}_z} \frac{\bar{\phi}}{\bar{\gamma}_z} \right) = f \bar{\mathbf{V}}_z \cdot \nabla_{\tilde{\gamma}} \left(\frac{\bar{\phi}}{f \bar{\gamma}_z} \right) + O\left(\alpha^4\right) \tag{33}$$

and the mean thermal wind equation, $\bar{\mathbf{V}}_z = -\left(g/f\rho_o\right) \mathbf{k} \times \nabla_H \bar{\gamma}$, is used to show that

$$\tilde{\gamma}_z \nabla_{\tilde{\gamma}} \cdot \left(\frac{\bar{\mathbf{V}}_z}{\bar{\gamma}_z} \frac{\bar{\phi}}{\bar{\gamma}_z} \right) = \left(\frac{g}{f\rho_o} \right) \mathbf{k} \times \nabla_H \left(\frac{\bar{\phi}}{\bar{\gamma}_z} \right) \cdot \nabla_H \bar{\gamma} + O\left(\alpha^4\right) \tag{34}$$

plus a smaller term that is proportional to the variation of the Coriolis parameter with latitude. This expression is unlikely to make a significant contribution to the mean density equation. One way of seeing this is to write (34) as $(g/f\rho_o)\,\mathbf{k} \cdot \nabla_H \times \left(\left[\bar{\phi}/\bar{\gamma}_z\right] \nabla_H \bar{\gamma}\right) + O\left(\alpha^4\right)$ and Stokes' theorem can be used to relate the contribution of this term in a closed region in a horizontal plane to the values of $\left[\bar{\phi}/\bar{\gamma}_z\right]$ and of $\bar{\gamma}$ around the periphery of the closed area. This leads to the conclusion that the expression (34) will oscillate in sign in neighbouring spatial regions so that its areal average will be small.

Interestingly, this contribution, (34), of the second term in the streamfunction to $\tilde{\gamma}_z \nabla_{\tilde{\gamma}} \cdot \mathbf{\Psi}$ is the same expression but of opposite sign to the contribution of $\left(\tilde{V}-\bar{V}\right)$ to the eddy forcing of the mean density equation, namely $-\left(\tilde{V}-\bar{V}\right)\cdot\nabla_H\bar{\gamma}$ [see (25)]. That is, these two different parts of the eddy forcing of the mean density equation are not simply two different ways of viewing the same process, rather, one is the negative of the other. We would not have expected the two contributions to the density equation to be the same since, from (29), the second term in the streamfunction is seen to contribute to both V^B and $\left(\tilde{V}-\bar{V}\right)$. However, to find that the terms are of the same magnitude but of opposite sign seems coincidental.

Taking the result of this section and the previous section together, it is concluded that as far as the eddy forcing of the mean density equation is concerned, one can ignore the second term in the expression, (6), for the streamfunction, so that it is sufficiently accurate to seek a parameterization of $-\overline{V'\gamma'}/\bar{\gamma}_z$ and to regard this as the quasi-Stokes streamfunction, Ψ. Alternatively, if a good parameterization can be found for the horizontal bolus velocity, V^B (perhaps by way of the potential vorticity equation) then it is sufficiently accurate to equate this to Ψ_z and, together with suitable boundary conditions, the quasi-Stokes streamfunction can be estimated in this manner. Hence there appear to be at least these two equally good routes to obtain approximate parameterizations of the quasi-Stokes streamfunction.

12. The Horizontal-&-Temporal-Residual-Mean Circulation

So far the averaging operator has been a low-pass temporal average and the aim of the temporal-residual-mean theory has been to incorporate in eddyless models the effects of the missing temporal correlations of variables. Such temporal correlations can be thought of as being caused by mesoscale eddies. Coarse resolution models also lack knowledge of spatial correlations between variables on scales smaller than the grid scale. The best-known example of this is in western boundary currents, where, as pointed out by Rintoul and Wunsch (1991), the spatial correlations of northward velocity and temperature (at a given height) in the Gulf Stream is an important contributor to the northward heat flux. This section summarises a preliminary attack on this issue. Note that the parameterization of these spatial correlations would be necessary even for a stratified fluid that contained no eddies, that is, for a completely steady and laminar ocean.

The physical motivation for the total quasi-Stokes streamfunction of the horizontal and temporal residual-mean (H&TRM) circulation remains the same as for the quasi-Stokes streamfunction of the temporal-residual-mean circulation. That is, we seek a two-dimensional streamfunction so that the sum of it and the vertical integral of the Eulerian mean velocity gives the horizontal transport, per unit horizontal distance, of water that is denser than $\tilde{\gamma}$. Equivalently, we seek the horizontal velocity at which tracers are advected given both the lack of mesoscale eddies and the limited horizontal resolution, and we want this horizontal velocity to be given by the sum of the Eulerian mean horizontal velocity plus the vertical derivative of the total quasi-Stokes streamfunction.

Figure 5a shows the height of a particular density surface, $\tilde{\gamma}\,(< z_a >)$ as a function of x at various times and we call the fluid that is denser than $\tilde{\gamma}$ "marked fluid". This particular density surface is chosen so that its temporal and x-average height is at the known height, $< z_a >$. At each location, x, the temporal mean height of the same density surface is at $z_a(x)$ and the instantaneous height of the density surface is $z = z_a(x) + \eta'_a(x,t)$ so that $\overline{\eta'_a(x,t)} = 0$. The spatial average of $z_a(x)$ in the x direction in the range $-\frac{1}{2}\Delta x < x < \frac{1}{2}\Delta x$ is labelled $< z_a >$. The horizontal distance over which the spatial averaging is being performed is Δx which corresponds to the horizontal grid size of an eddyless height-coordinate model in the east-west direction. The temporal average of the northward transport of "marked fluid" integrated over the width, Δx of this box is

$$\text{Mean Northward Transport of Marked Fluid} = \int_{-\Delta x/2}^{\Delta x/2} \overline{\int_{-H}^{z_a(x)+\eta'_a(x,t)} v \, dzdx} \tag{35}$$

where the bottom of the ocean is at $z = -H$. The overbar continues to represents a low-pass temporal average and the angle brackets denotes a box-car x-average over the distance Δx. The inner vertical integral in (35) is split into three separate integrals so that (35) becomes

$$\int_{-\Delta x/2}^{\Delta x/2} \int_{-H}^{<z_a>} \bar{v} \, dzdx + \int_{-\Delta x/2}^{\Delta x/2} \int_{<z_a>}^{z_a(x)} \bar{v} \, dzdx + \int_{-\Delta x/2}^{\Delta x/2} \overline{\int_{<z_a>}^{z_a(x)+\eta'_a(x,t)} v \, dzdx} \tag{36}$$

Because the limits of the vertical integration in the first two terms are independent of time, the temporal averaging operator has been applied to the integrand so that the northward velocity that enters the first two terms is the Eulerian mean northward velocity, $\bar{v}$.

Figure 5a shows several snapshots of the height of the density surface as a function of x across this face of a box and when the height of this density surface is temporally averaged, the resulting average height, $z = z_a(x)$ is sketched as a function of x in Figure 5b. The figure indicates that this mean height is a linear function of x but in the subsequent analysis this is not a necessary requirement. If a higher order spatial function of x is included in the function $z_a(x)$, the resulting expression for the volume transport merely contains higher order terms that we subsequently ignore. The important feature is that the spatially and temporally averaged height of this density

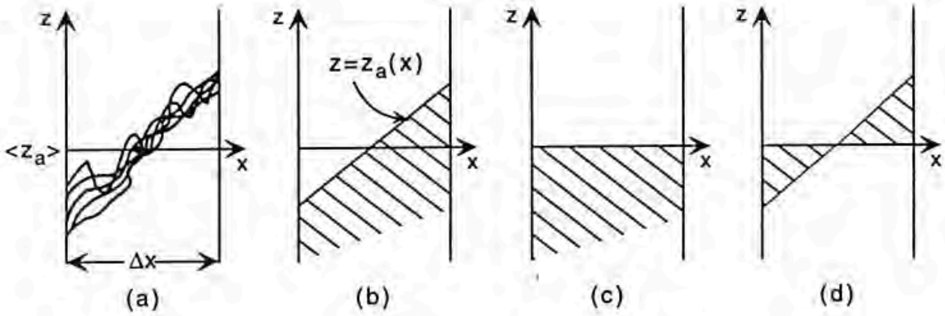

Figure 5. (a) Snapshots at various times of the height of a particular density surface are sketched as a function of the distance, x, across the face of a box of a coarse-resolution model. When the height of this density surface is temporally averaged, the smooth curve in panel (b) is found, and the northward transport of shaded water in (b) can be calculated as the sum of the transports of shaded water in panels (c) and (d).

surface is the known height, $< z_a >$. Figures 5c and 5d illustrate how the vertical integral up to the height $z = z_a(x)$ in Figure 5b can be decomposed into the first two terms in (36), namely the first integral whose integration limits are not a function of x and the second whose integration limits are a function of x. We now discuss each of the three terms in (36) in turn.

The order of integration of the first term in (36) is reversed showing that it is

$$\Delta x \int_{-H}^{<z_a>} < \bar{v} > dz \tag{37}$$

and the model's resolved-scale northward velocity is interpreted as the box-car x-average of the temporal mean velocity at fixed height, $< \bar{v} >$. Note that the geostrophic relationship inherently yields the spatially averaged velocity rather than say the velocity at the centre of the face, so the interpretation of the model's resolved-scale northward velocity as $< \bar{v} >$ is the only interpretation of the model's velocity that is consistent with geostrophy. We conclude that the first term in (36) is the northward flux of marked fluid that can be calculated using the model's resolved-scale velocity.

In order to evaluate the second term in (36), the Eulerian-mean northward velocity, $\bar{v}$ is written as a spatial Taylor series as

$$\bar{v} = \bar{v}\,(x, z) = \bar{v_o} + \bar{v_x}x + \bar{v_z}[z - < z_a >] + \ldots \tag{38}$$

where $\bar{v_x}$ and $\bar{v_z}$ are understood to be evaluated at $z =< z_a >$ and at the centre of the box in the x direction, that is, at $x = 0$, while $\bar{v_o}$ is independent of both x and z. Substituting this Taylor series into the middle term in (36) it can be shown to be

$$\begin{aligned}\int_{-\Delta x/2}^{\Delta x/2}\int_{<z_a>}^{z_a(x)} \bar{v}\, dzdx &= \frac{1}{12} < \bar{v} >_x L^x[\Delta x]^3 + \frac{1}{24} < \bar{v} >_z (L^x)^2 [\Delta x]^3 \\ &+ O\left([\Delta x]^4\right) \qquad (39)\end{aligned}$$

where L^x is the mean slope of the density surface in the x direction, $L^x = -\tilde{\gamma}_x / \tilde{\gamma}_z$.

The inner integral of the third term in (36) is what appears in the Taylor series analysis of McDougall and McIntosh (1998b) so that we can write this integral as

$$\overline{\int_{z_a(x)}^{z_a(x)+\eta'_a(x,t)} v dz} = \left(-\frac{\overline{v'\gamma'}}{\bar{\gamma}_z} + \frac{\bar{v}_z}{\bar{\gamma}_z}\frac{\bar{\phi}}{\bar{\gamma}_z} \right)\Bigg|_{z=z_a(x)} + O\left(\alpha^3\right) \qquad (40)$$

which is the northward component of the quasi-Stokes streamfunction of the purely temporal-residual-mean circulation, evaluated at the height $z = z_a(x)$. Hence the last term in (36) is Δx times the spatial average of the streamfunction, (40), along the sloping density surface, $z = z_a(x)$, plus higher order error terms. It is readily shown that evaluating the streamfunction, (40), at the fixed height, $z =< z_a >$ incurs only higher order error terms.

Dividing (36) by Δx and subtracting the vertical integral of the model's resolved-scale velocity, $< \bar{v} >$ gives the expression for the northward component of the new quasi-Stokes streamfunction:- the quasi-Stokes streamfunction that now includes the effects of both temporal and spatial averaging, namely

$$\begin{aligned}\frac{1}{12} < \bar{v} >_x L^x[\Delta x]^2 + \frac{1}{24} < \bar{v} >_z (L^x)^2 [\Delta x]^2 &+ \left(-\frac{\overline{v'\gamma'}}{\bar{\gamma}_z} + \frac{< \bar{v} >_z}{\bar{\gamma}_z}\frac{\bar{\phi}}{\bar{\gamma}_z} \right) \\ &+ O\left(\alpha^3, [\Delta x]^3\right) \qquad (41)\end{aligned}$$

and the eastward component of the new quasi-Stokes streamfunction, where the spatial box-car averaging is over the northward length scale Δy is

$$\begin{aligned}\frac{1}{12} < \bar{u} >_x L^y[\Delta y]^2 + \frac{1}{24} < \bar{u} >_z (L^y)^2 [\Delta y]^2 &+ \left(-\frac{\overline{u'\gamma'}}{\bar{\gamma}_z} + \frac{< \bar{u} >_z}{\bar{\gamma}_z}\frac{\bar{\phi}}{\bar{\gamma}_z} \right) \\ &+ O\left(\alpha^3, [\Delta y]^3\right) \qquad (42)\end{aligned}$$

Having defined the total quasi-Stokes streamfunction so that it has the quasi-Lagrangian property (transport of fluid denser than $\tilde{\gamma}$), it is clear that the difference between two such streamfunctions in the vertical gives the contributions of both temporal and horizontal box-car averaging to the appropriate thickness-weighted mean velocity. It is this horizontal velocity that is required in the layered continuity equation and in the layered tracer conservation equation. The total quasi-Stokes streamfunction whose northward and eastward components are (41) and (42) must be made to satisfy the same boundary conditions as discussed earlier for the quasi-Stokes streamfunction of the TRM circulation.

We can make some preliminary remarks about the direction of the extra quasi-Stokes streamfunction whose role is to overcome the inherent horizontal box-car averaging of coarse resolution models. Consider the situation where $L^x = 0$ and $\partial L^x/\partial z = 0$ so that the density surface slopes to the north or south and, from (41), there is no contribution from the "spatial averaging terms" to the total northward velocity. Even though the density surface does not slope to the east, there is a contribution from the horizontal averaging part of (42) to the eastward velocity. This example implies that, contrary to temporal averaging, the terms that correct for the box-car horizontal averaging of coarse resolution models do not necessarily cause a contribution to the total quasi-Stokes streamfunction in the down-gradient direction of the horizontal density gradient, but can cause a contribution normal to this direction.

In the Gulf Stream and the East Australian Current, I expect that it will be the first term in (41) that will dominate. The first two terms in (41) correspond to the northward heat flux due to the unresolved spatial correlations of northward velocity and potential temperature, as discussed by Rintoul and Wunsch (1991). The sign of the first term in (41) is such as to cause an increase in the northward flux of heat, and when the expression, (41), is used in a coarse resolution model, this flux of heat will be represented by an additional northward flux of "marked" water, just as it would appear in an eddy-resolving isopycnal model of the same region. This is a case where the extra advection velocity that must be added to a coarse-resolution model is not down the horizontal density gradient and so one would not normally think that it is important because the extra advection will not tend to contribute to the local heat or salt conservation equation. Despite this, the transport of water of certain density classes clearly is important for the section-averaged heat and fresh-water fluxes. The mixing that is required to transform one water mass into another can occur at locations very distant to the section across which the poleward heat flux is being budgeted.

At face value it appears that the terms in (41) and (42) that correct for the horizontal box-car averaging should not be important because the numerical discretization involved in writing conservation equations on a grid of boxes has errors that are quadratic in the grid size of the model. The first two terms in (41) and (42) are also quadratic in the grid size and so it seems inconsistent to be including terms at this order. However, in western boundary currents, the horizontal shear of the northward velocity actually scales as the reciprocal of the grid resolution so that the first term in (41) is really one order of lower than it appears (Bill Dewar, personal communication, 1997).

Notice that in the quasi-Stokes streamfunction of TRM we need to parameterize the horizontal flux of density, $\overline{\boldsymbol{V}'\gamma'}$ whereas in the horizontal box-car averaging parts of the H&TRM quasi-Stokes streamfunction, no parameterization is required. That is, the quantities that appear in the first two terms in (41) and (42) are already known to the coarse-resolution model. This is because we have chosen to do the temporal averaging first, followed by the box-car horizontal averaging, so that the variables that are being considered at the stage of box-car horizontal averaging are assumed to be smooth in space. They key assumption appears to be that the temporally-averaged velocity field is sufficiently smooth that the Taylor series, (38), converges and can be approximated by the leading linear terms.

13. Concluding Remarks

This article has concentrated on theoretical aspects of residual-mean theory as applied to scalar conservation equations in three-dimensions. Little has been said about the important issue of obtaining a practical parameterization of the quasi-Stokes streamfunction of the TRM circulation, and the few remarks below will not be comprehensive in this regard.

Tréguier (1998) has analysed a primitive equation model for the zonally-averaged bolus velocity and has found a small diffusivity for use in the Gent *et al.* (1995) scheme. If it can be shown that it is appropriate to use a such a small diffusivity for the quasi-Stokes streamfunction then this should have some benefits so long as the models remain stable with these smaller diffusivities. The two benefits that come to mind are avoiding the slowing of the horizontal circulation of the sub-tropical gyres that occurs with the larger values of the quasi-Stokes diffusivity, and reducing the intrusion of Antarctic Bottom Water into the North Atlantic which is too strong with present values of the quasi-Stokes diffusivity (Hirst and McDougall, 1998).

To date coarse resolution models have mainly been run with diffusivities that are independent of space, but the work of Visbeck *et al.* (1997) suggests that the diffusivity should depend on the slope of the density surfaces and so should be a rather strong function of space. It is hoped that by having the diffusivity be an increasing function of the slope of density sufaces, it may be possible to avoid numerical instabilities while having a much smaller diffusivity in most of the ocean. In this way it may be possible to avoid numerical instabilities, which tend to occur on boundaries, while having the strength of the skew diffusion of the H&TRM circulation set at realistically small values in the ocean interior such as in the Antarctic Circumpolar Current.

As discussed in section 8 above, the Gent and McWilliams (1990) parameterization scheme is essentially equivalent to the TRM theory under the assumption that the horizontal flux of density is directed down the horizontal density gradient. While this is a common assumption, several authors have recently made the point that there is probably better theoretical support for the flux of potential vorticity along neutral density surfaces being directed down the epineutral gradient of potential vorticity. This naturally leads to a parameterization for the bolus velocity and then one has to address the questions of applying boundary conditions at the top and bottom of the ocean and of avoiding a singularity at the equator. Killworth (1998) has made great strides with the issue of boundary conditions, but so far only for one horizontal dimension. When the extra horizontal dimension is added, another constraint arises that such a scheme must satisfy. These constraints are automatically satisfied by the robust Gent *et al.* (1995) implementation of the TRM circulation.

The theory of Killworth (1998) and parameterization schemes based on the down-epineutral-gradient of potential vorticity are, by construction, applicable to the parameterization of eddies in eddyless density-coordinate models. In such density-coordinate models, the additional velocity that is required is the bolus velocity and this velocity is three-dimensionally divergent and adiabatic. It is not obvious a priori that such a parameterization scheme should be applied to a z-coordinate model where the use of the continuity equation ensures that whatever choice is made for its horizontal components, the extra velocity is three-dimensionally non-divergent and most importantly, diabatic at leading order. One may indeed be able to get away with using the horizontal velocity of one theory in the three-dimensional parameterization machinery of another, but one must be aware of the fact that one is mixing apples and oranges in the process.

It seems that the topic of parameterization is in its infancy. We have a robust scheme that has been used to date with a diffusivity that may be too large in many places. We also have some ideas about how to develop a parameterization based on the assumption that the epineutral flux of potential vorticity is down-gradient, but this has not yet matured into a robust scheme in three dimensions. In addition to the issues of temporal averaging, there is the issue of the lack of horizontal resolution, and in this article it has been argued that this should be treated separately from the

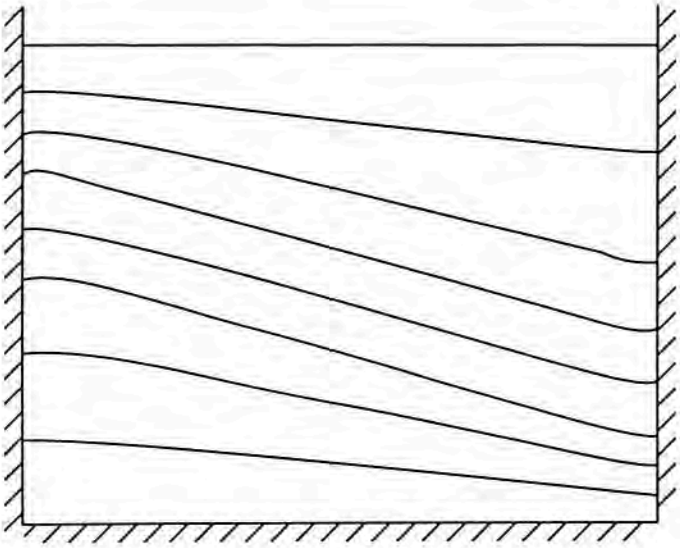

Figure 6. Sketch of a vertical section showing several density contours.

issue of parameterizing the effects of the missing mesoscale eddies.

The actual scheme that is used for down-gradient thickness diffusion in the MICOM isopycnic model seems to have very different characteristics to the Gent and McWilliams (1990) scheme. Consider an ocean section as sketched in Figure 6 where the slope of a given density surface is constant in the interior. The Gent and McWilliams (1990) scheme will act on this structure to destroy the available potential energy and to relax the isopycnals towards a final (flat) state of rest. This is achieved by a large-scale overturning motion as described in Gent *et al.* (1995). However the MICOM scheme (as described by Bleck *et al.*, 1992) acts to smooth the interface heights and as these are already smooth in the ocean interior, the scheme has no effect there, but will lead to some motion only near the edges of Figure 6. The reasons for this different behaviour are not entirely clear at this time, but it seems that the Gent and McWilliams (1990) method, by supplying an extra velocity field, has the ability of achieving a far field effect whereas the MICOM scheme that is implemented only in the thickness equation seems to respond only to the small-scale variations in layer thickness. A valid scheme in isopycnal coordinates would provide an estimate of the bolus velocity and this extra velocity would be inserted into all the conservation statements.

Another issue concerns the mechanical (sum of potential and kinetic) energy equation. Work in progress with Professor Jürgen Willebrand shows that the expected extraction of energy by baroclinic instability is guaranteed if $\Psi \cdot \nabla_H \tilde{\gamma} < 0$. The Gent *et al.* (1995) scheme for Ψ satisfies this requirement at every point in space, and indeed this ability of mesoscale eddies to deplete available potential energy was a key motivation of the original work of Gent and McWilliams (1990). In contrast, a parameterization scheme based on the down-epineutral-gradient flux of potential vorticity does not satisfy this requirement at every point. One then will have to rely on other sensible features of the scheme to achieve a global extraction of energy by baroclinic instability. The terms in the quasi-Stokes streamfunction of the H&TRM circulation that correct for the inherent box-car horizontal averaging of coarse resolution models also do not satisfy this energy requirement at every point in space.

Finally, there is the issue of whether the present implementation of the TRM circulation in ocean models is displaying improvements for the correct reasons. Several authors have described substantial improvements including greatly improved deep water masses, less unwanted deep convection and less drift in coupled atmosphere-ocean models (see Hirst *et al.*, 1996). An important common element of these improvements is that the bottom water of the world's oceans has been able to sink from the surface to the ocean bottom with very little dilution. In fact, in the work of Hirst and McDougall (1996) it was found that there was insufficient diapycnal mixing occurring in the overflow regions. Previously such a result had only been possible using a density-coordinate model. In this way, a height-coordinate model has been shown to be sufficiently "adiabatic" for the purposes of climate modelling.

In practice this vertical motion of the Deep and Bottom Water occurs in canyons and across sills which are not part of the coarse resolution models. The TRM advection scheme achieves this "adiabatic" sinking motion because of two almost equal effects, as demonstrated by Hirst and McDougall (1996). First, the unwanted horizontal diffusion is eliminated, and second, an extra advection (or skew diffusion) is added which assists in the transport of water from the surface to the deep. The elimination of horizontal diffusion is thought to be physically required, but the extra advection at the bottom of the ocean seems to be more an artefact of the bottom boundary condition on the quasi-Stokes streamfunction than a representation of the actual boundary current mechanisms that achieve the transport of bottom water. In this way it may be that half of the benefits that we are seeing to date have been obtained by stealth:- obtaining the right results for the wrong reasons. If so, what fraction of this half will respond incorrectly to changing boundary conditions associated with, for example, climate change?

In summary, this article has shown how the three-dimensional residual-mean theory allows coarse-resolution models to incorporate the effects of temporal eddies and of limited spatial resolution. By seeking a parameterization for the quasi-Stokes streamfunction, (6), and adding this to the components shown in (41) and (42) that account for the limited horizontal resolution, an extra skew diffusive flux, (see (10) and (11)), can be added to a coarse-resolution ocean model. The equivalence of this procedure to averaging the instantaneous flow in density coordinates has been demonstrated, and this equivalence provides the physical motivation for the H&TRM theory.

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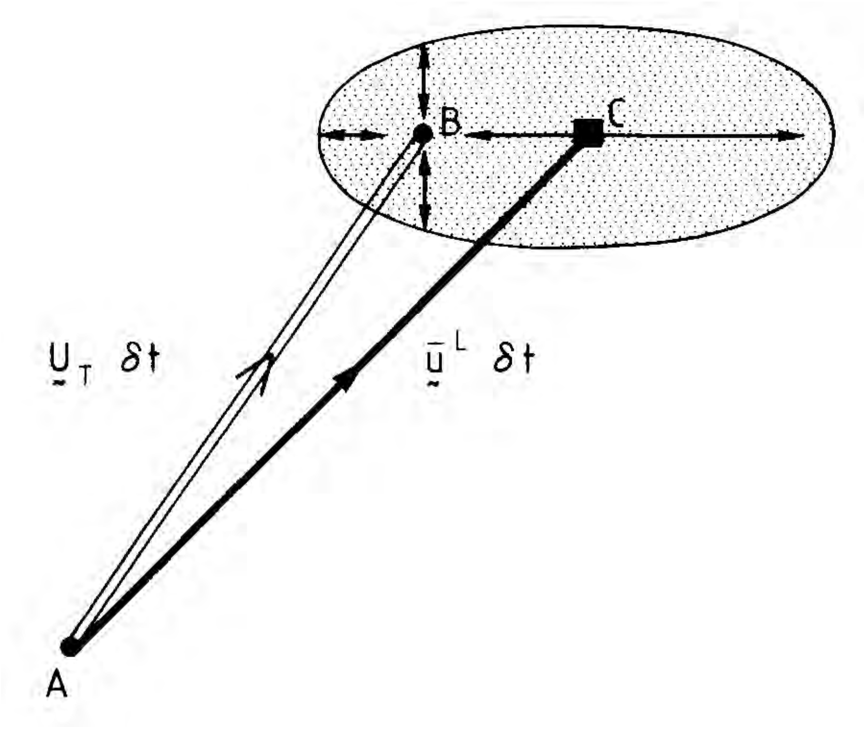
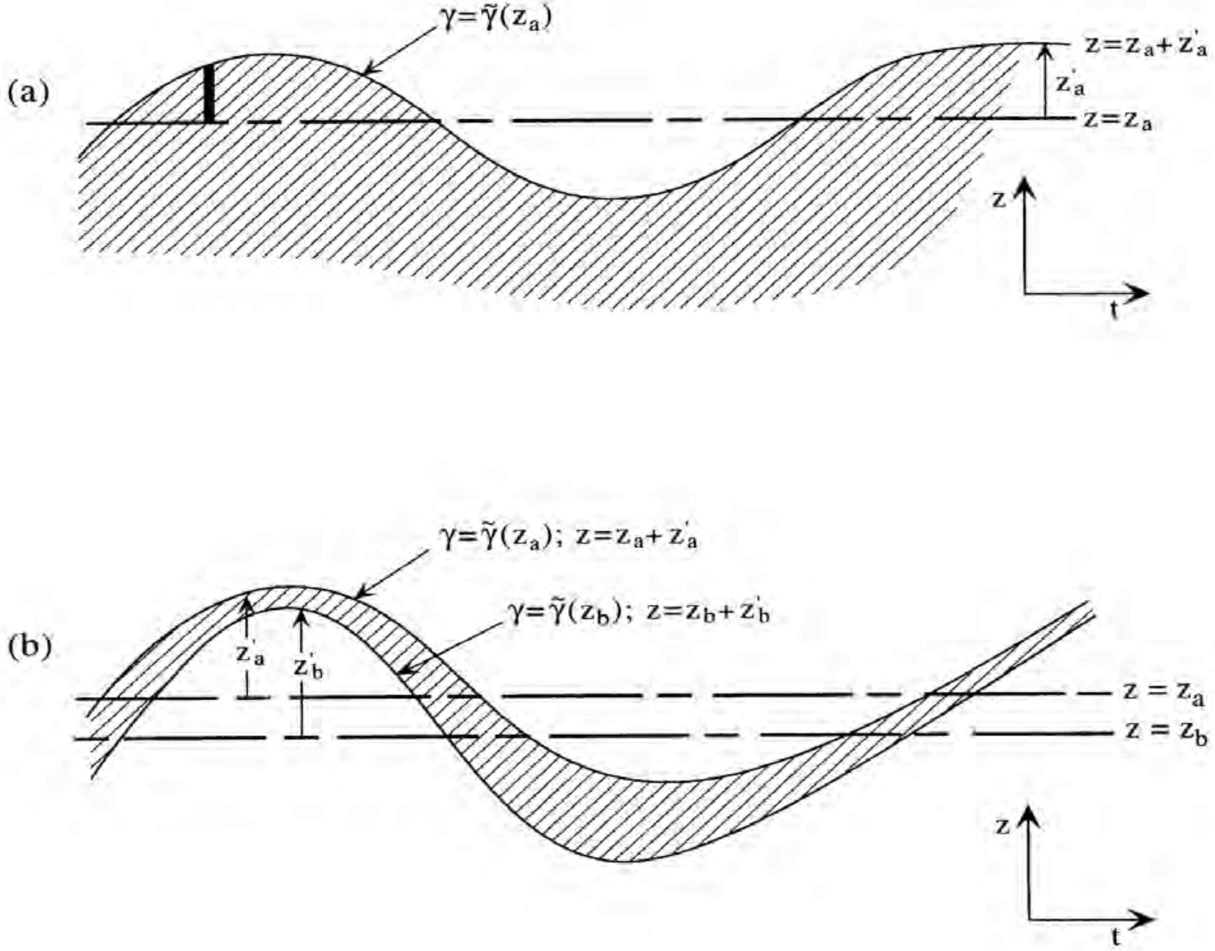
What is an appropriate **average** velocity?



Transport of water of given *density* classes



The overturning streamfunction of Gent et al (1995)

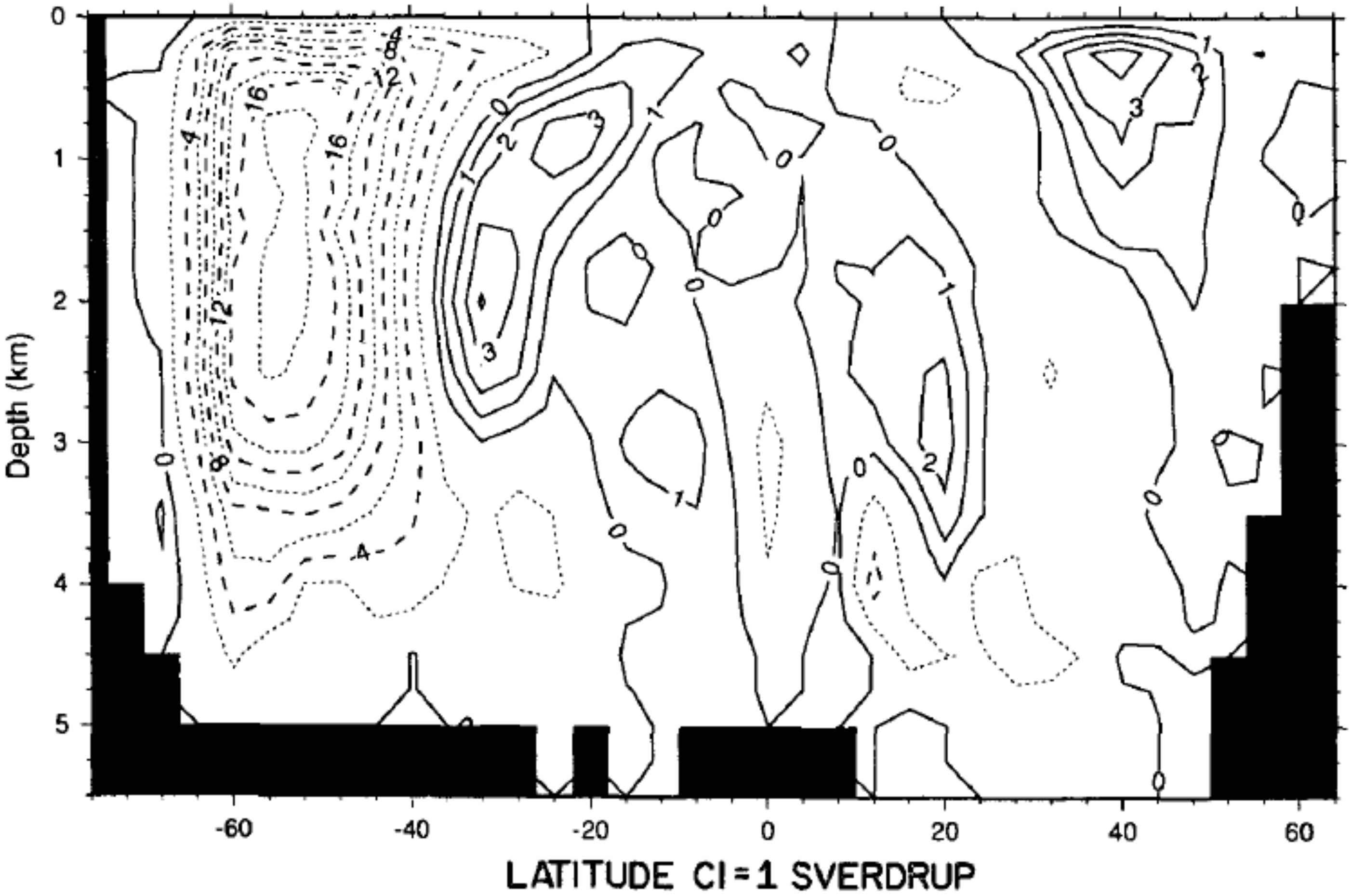
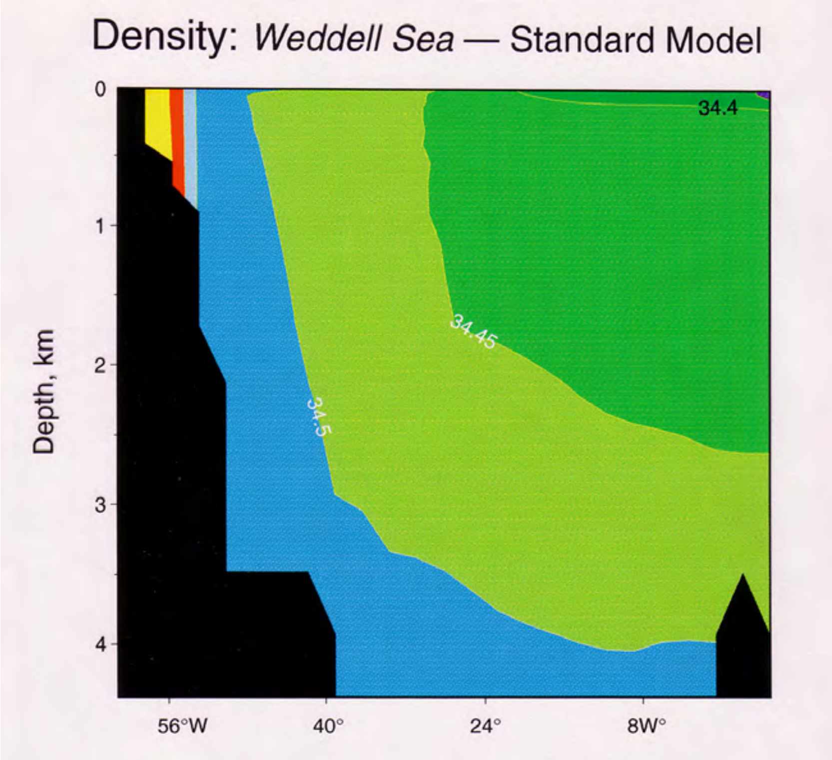
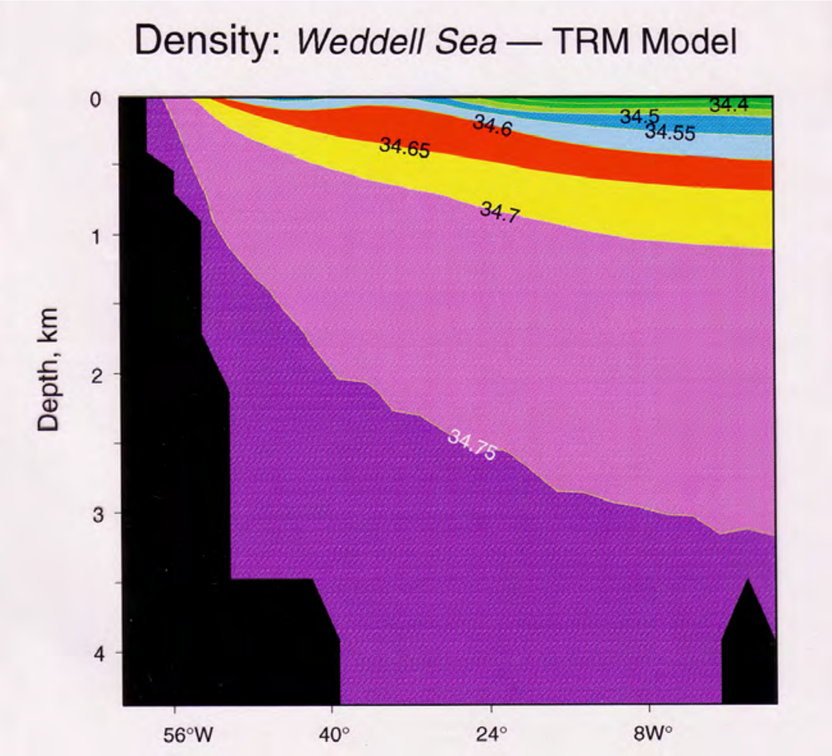


FIG. 6. Zonally averaged meridional overturning streamfunction $\int \kappa \rho_y / \rho_z dx$ in Sverdrups calculated from Levitus (1982) data where the average is over all ocean basins: $\kappa = 10^3 \text{ m}^2 \text{ s}^{-1}$ and is constant.

Transport of water of given *density* classes

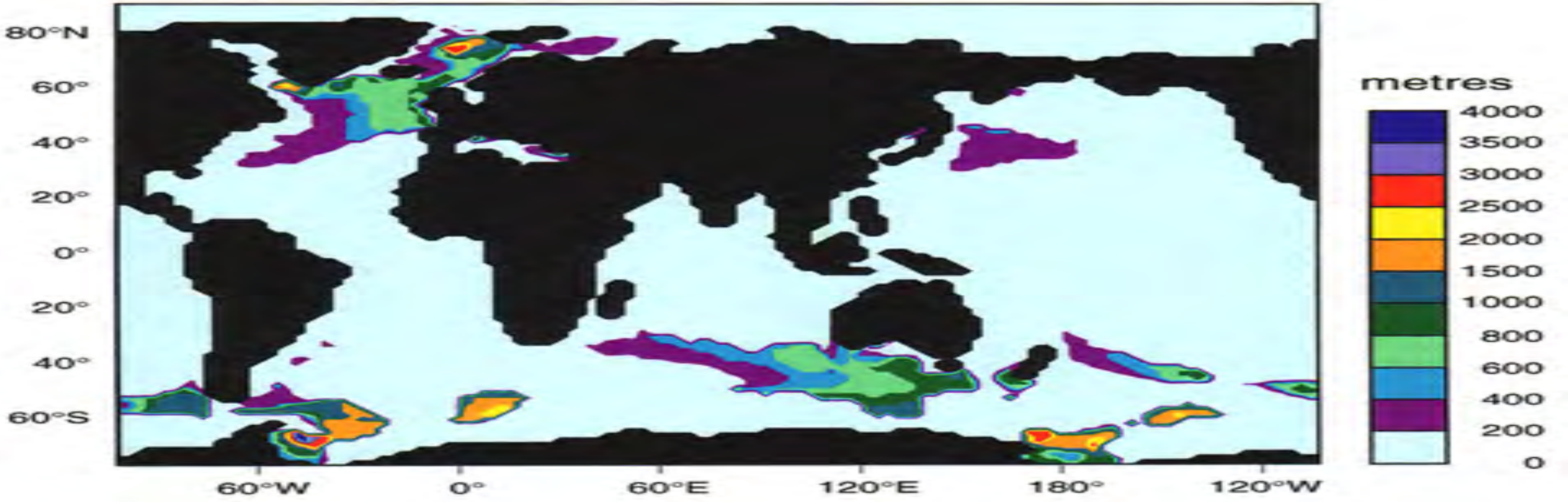


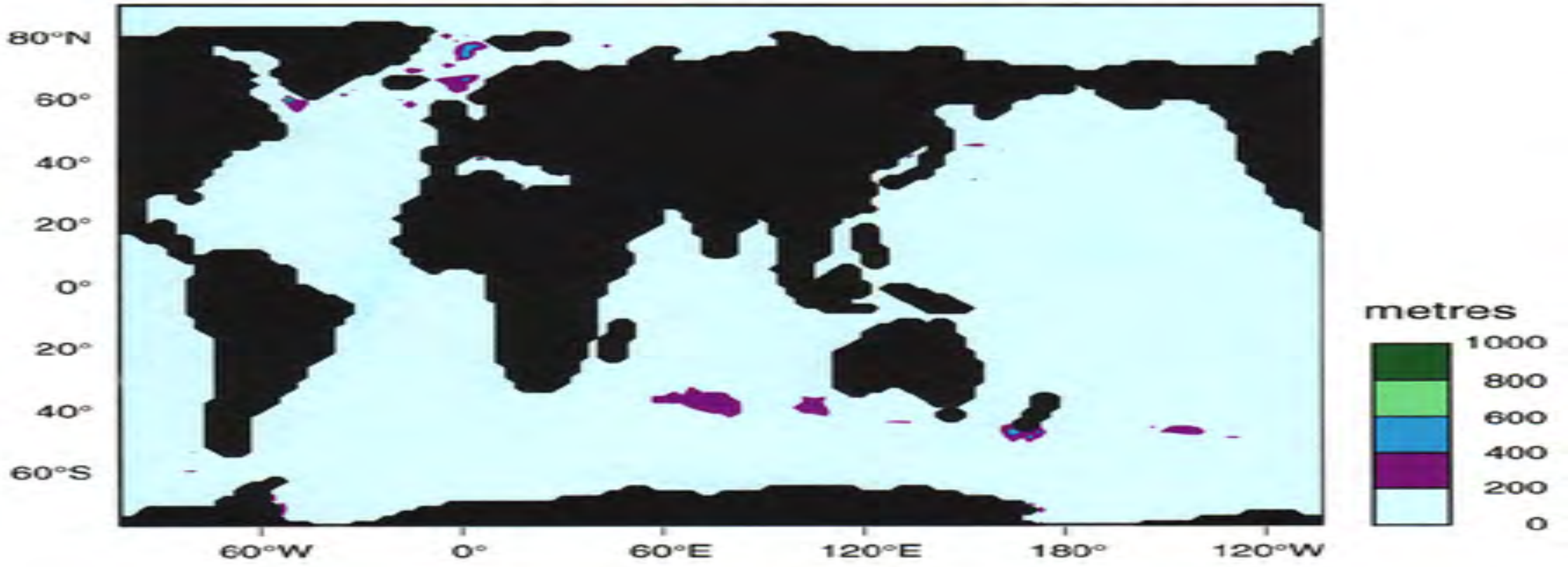
Density: *Weddell Sea* — Standard Model



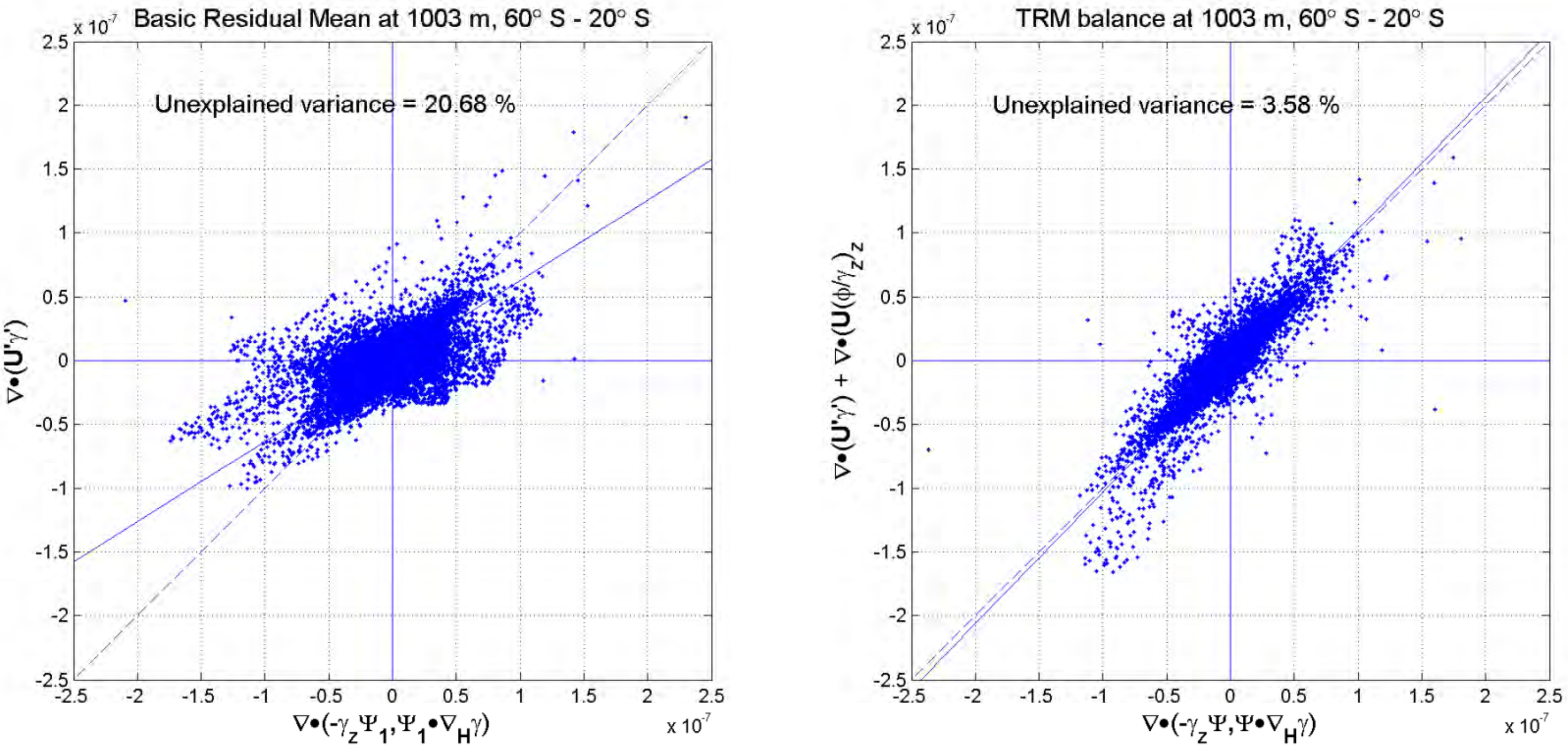
Density: *Weddell Sea* — TRM Model

Hirst & McDougall (1996)


Mixed Layer Depth — Standard Model

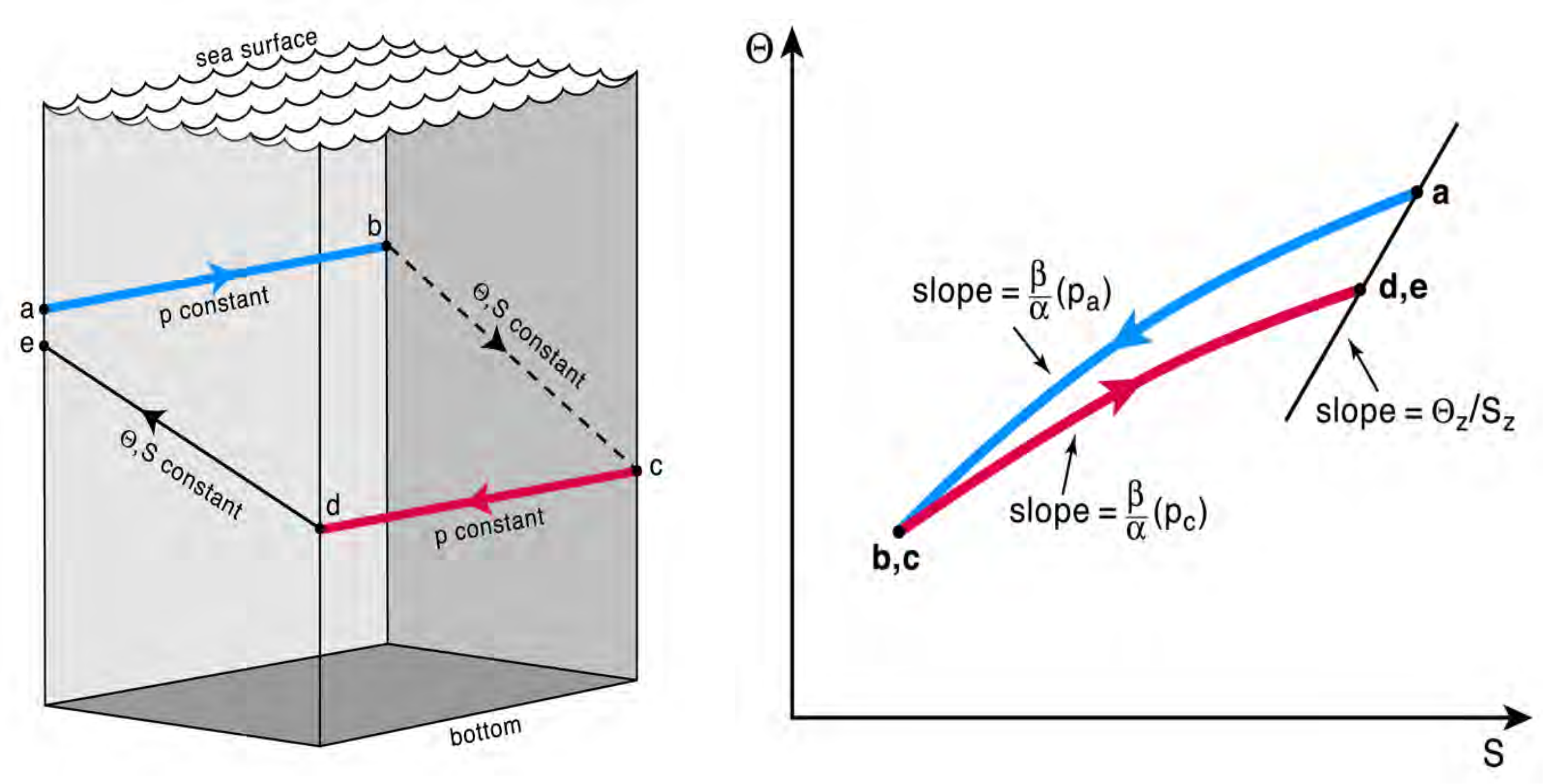

Mixed Layer Depth — TRM Model

The TRM eddy flux balance in an eddy-resolving model



- The basic residual-mean balance misses 21% of the effects of eddy fluxes. The TRM theory only misses 4% of the action, and so provides a more accurate springboard to pursue eddy parameterization.

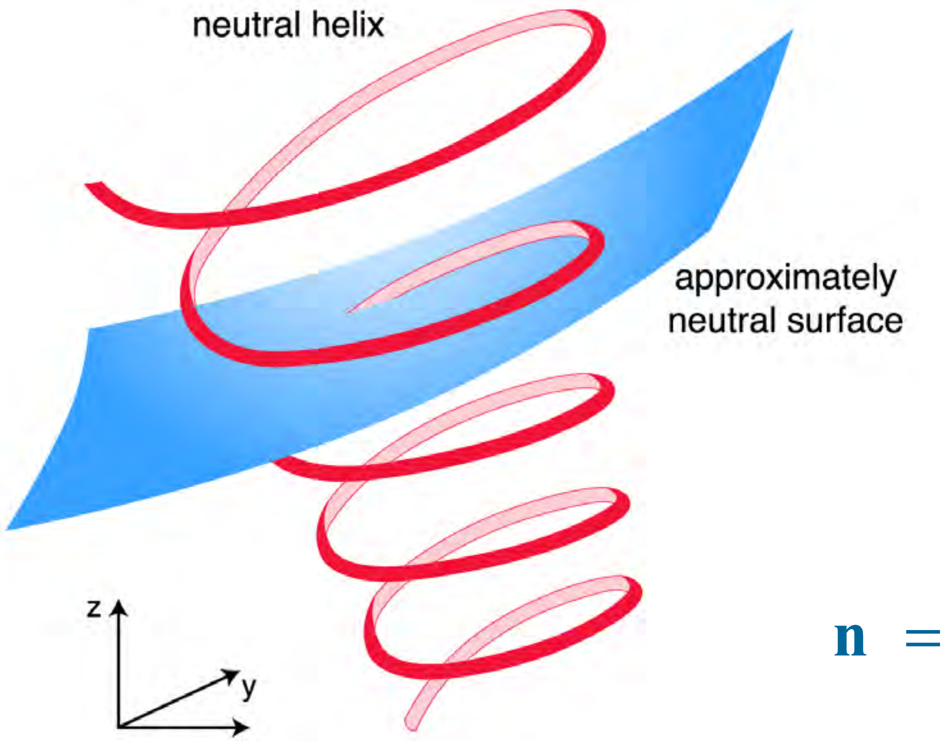
The ill-defined nature of "neutral surfaces"



The local direction of neutral mixing is the plane that is normal to

$$\mathbf{n} = \alpha\nabla\Theta - \beta\nabla S_{\mathrm{A}}$$

The helical nature of neutral trajectories



$$\mathbf{n} = \alpha \nabla \Theta - \beta \nabla S_{\mathrm{A}}$$

For a neutral surface to be well-defined, Neutral Helicity, $H = \mathbf{n} \cdot \nabla \times \mathbf{n}$ has to be zero.

Neutral Helicity

The neutral tangent plane is the plane in which an in situ fluid parcel can be moved small distances without feeling a buoyant restoring force.

The normal to the neutral tangent plane is in the direction $\alpha \nabla \Theta - \beta \nabla S_{\mathrm{A}}$ where α is the thermal expansion coefficient and β is the saline contraction coefficient. (This recognizes that $\rho = \rho\left(S_{\mathrm{A}}, \Theta, p\right)$)

These neutral tangent planes link up to form a well-defined neutral surface only if the helicity, *H,* is zero, where

$$H \equiv \left(\alpha \nabla \Theta - \beta \nabla S_{\mathrm{A}}\right) \cdot \nabla \times \left(\alpha \nabla \Theta - \beta \nabla S_{\mathrm{A}}\right)$$

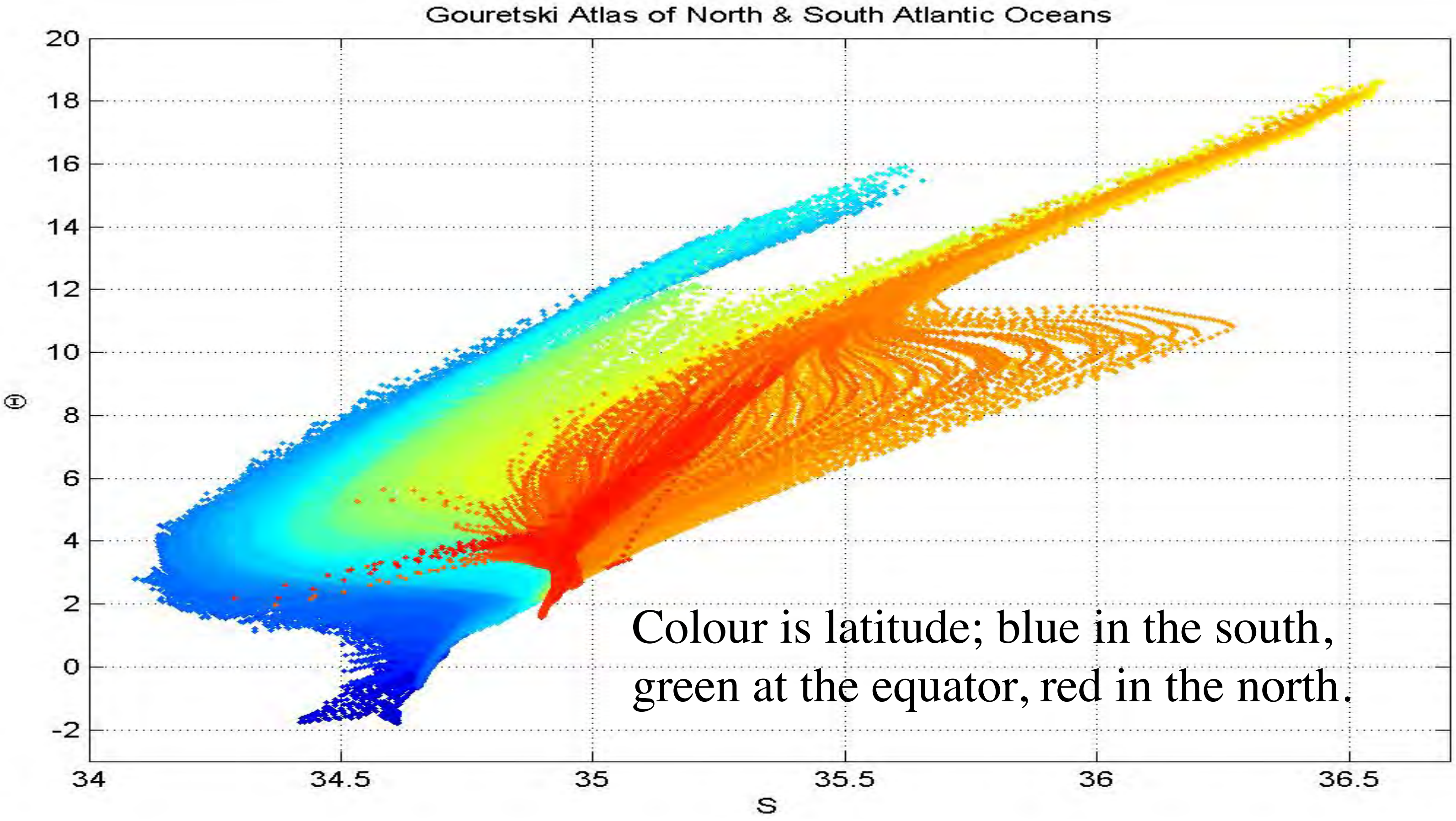
If helicity were exactly zero everywhere then the entire global ocean data would lie on a single surface in $S_{\mathrm{A}} - \Theta - p$ space rather than filling a volume in this space. That is, if $H = 0$ everywhere, then the data all lie on a surface $f\left(S_{\mathrm{A}}, \Theta, p\right) = 0$.

The ocean is very thin, like Twiggy

We are still searching for a convincing explanation for why the world ocean is 95% empty.

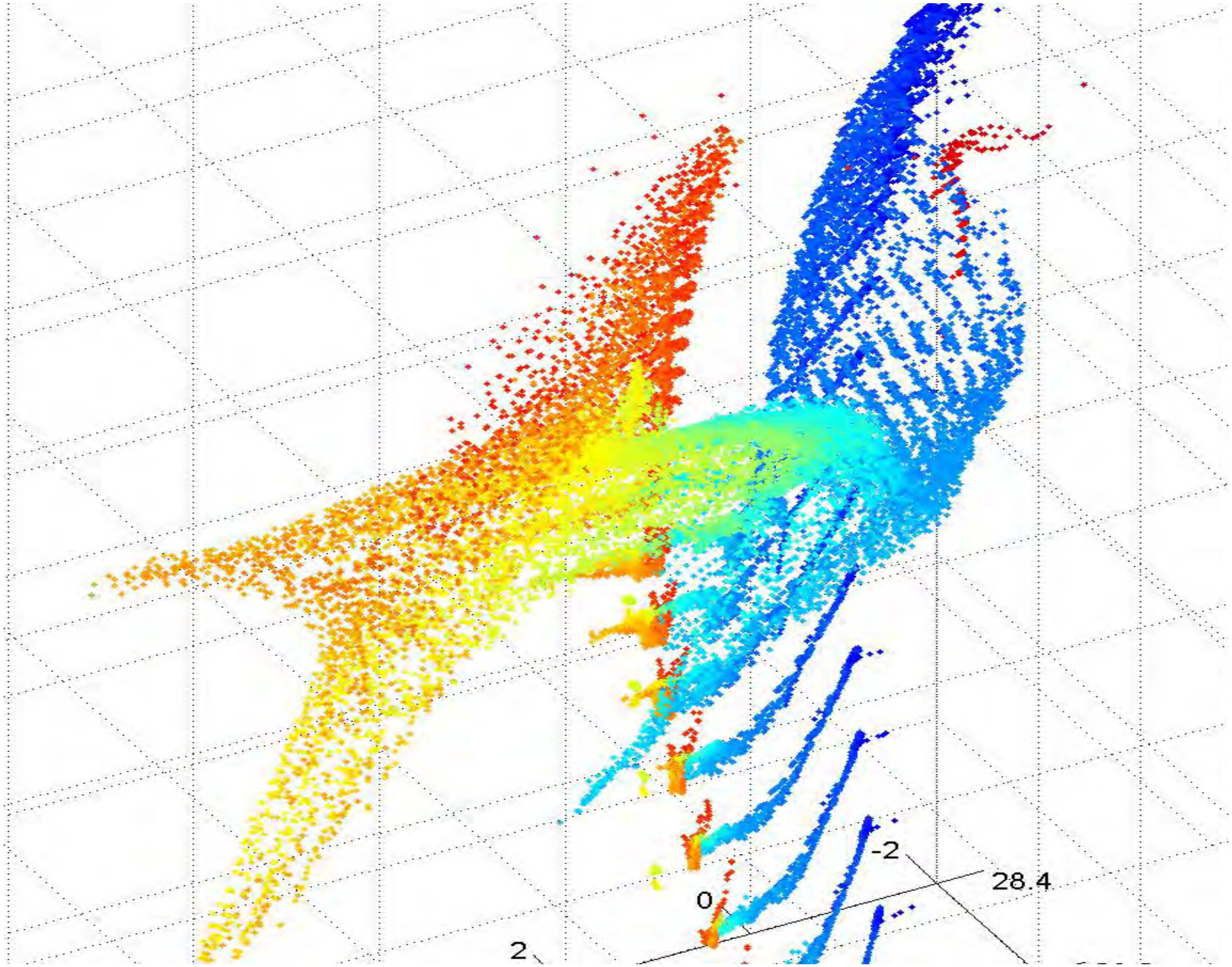
The $S_A - \Theta$ diagram for the Atlantic, 250 dbar to the bottom

While this plot of all the data from both the North & South Atlantic looks “solid” or “full” on the $S_A - \Theta$ diagram, …

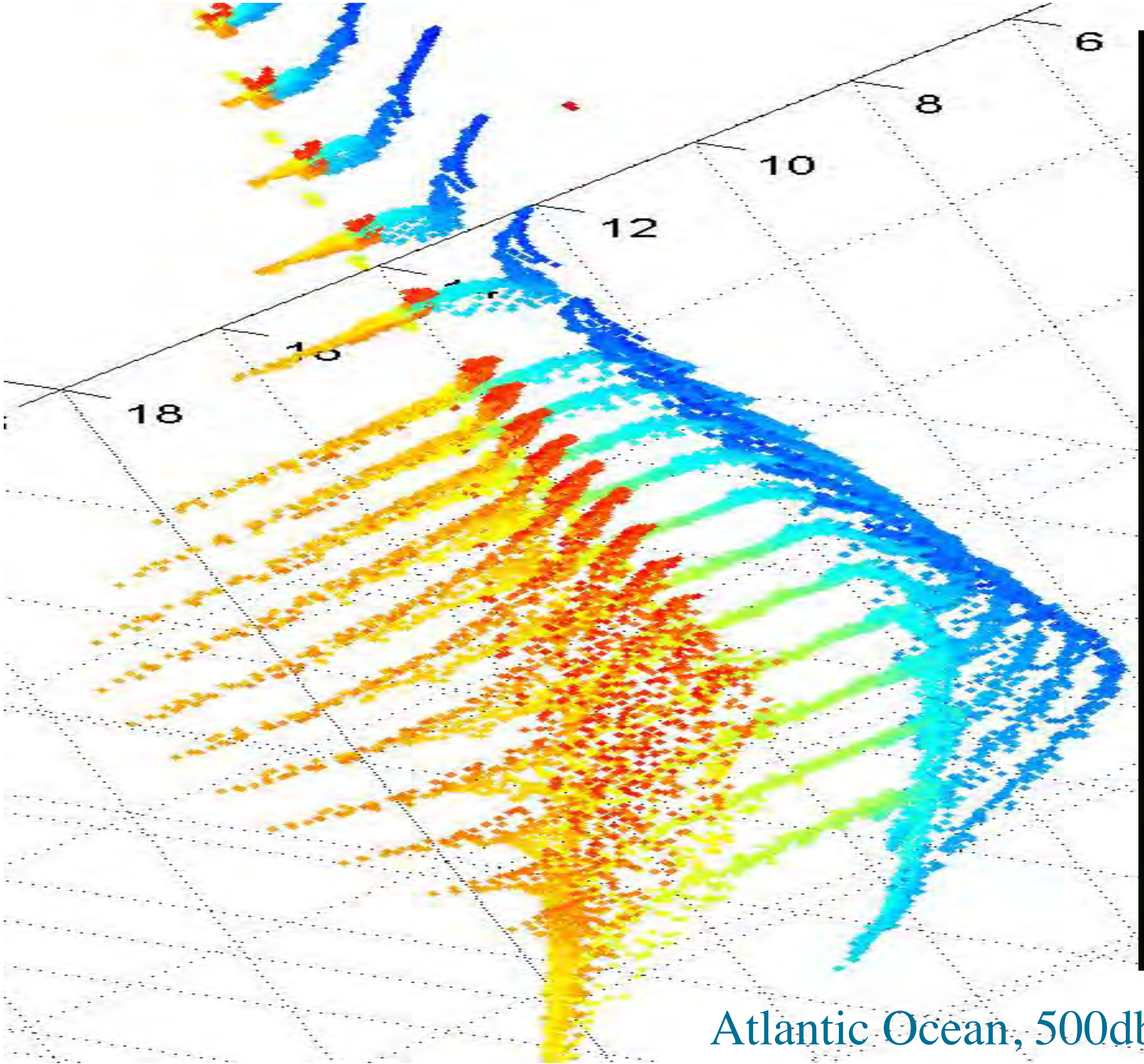


Colour is latitude; blue in the south, green at the equator, red in the north.

…the ocean is actually quite “**thin**” in $S_{\mathrm{A}} - \Theta - p$ space.

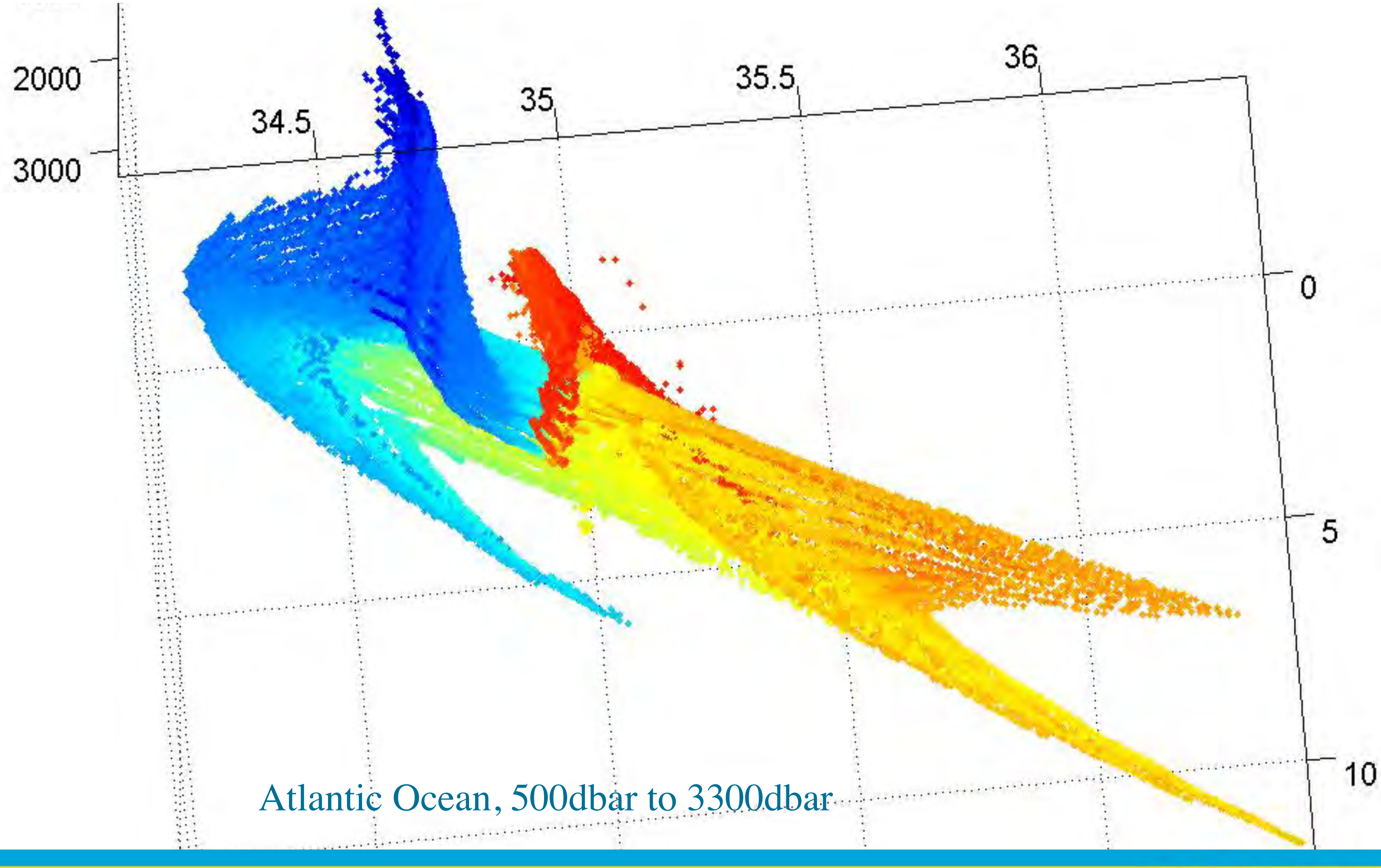


Call the World Ocean “twiggy”; it’s all skin and bone



Atlantic Ocean, 500dbar to 3300dbar

An end view of the Atlantic "twiggy"

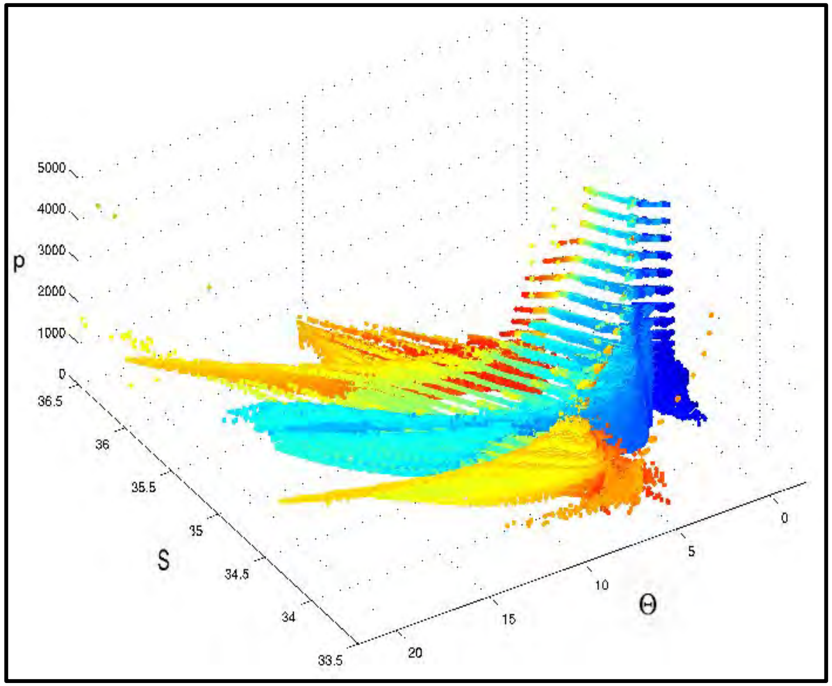


Atlantic Ocean, 500dbar to 3300dbar

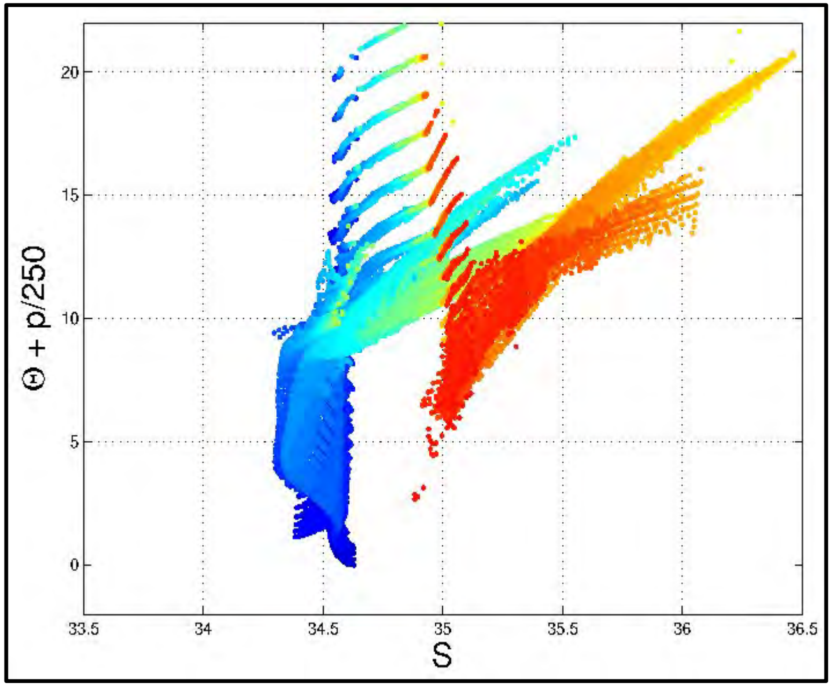
The global ocean is quite “thin” in $S_A - \Theta - p$ space.

The world's oceans take up a fair amount of space in $S_A - \Theta$ space but in $S_A - \Theta - p$ space it lies near a single surface:

The Global Ocean



The North Atlantic



colour is latitude – red is north and blue is south

The ill-defined nature of "neutral surfaces"

Neutral helicity $H = \left(\alpha\nabla\Theta - \beta\nabla S_\mathrm{A}\right)\cdot\nabla\times\left(\alpha\nabla\Theta - \beta\nabla S_\mathrm{A}\right)$ can be written as

$$\begin{aligned} H &= \beta T_b \nabla p \cdot \nabla S_\mathrm{A} \times \nabla\Theta \\ &= g^{-1} N^2 T_b \nabla_n p \times \nabla_n \Theta \cdot \mathbf{k} \\ &= p_z \beta T_b \nabla_p S_\mathrm{A} \times \nabla_p \Theta \cdot \mathbf{k} \end{aligned}$$

where the thermobaric coefficient is $T_b = \alpha_p - \left(\alpha/\beta\right)\beta_p$.

H being zero implies

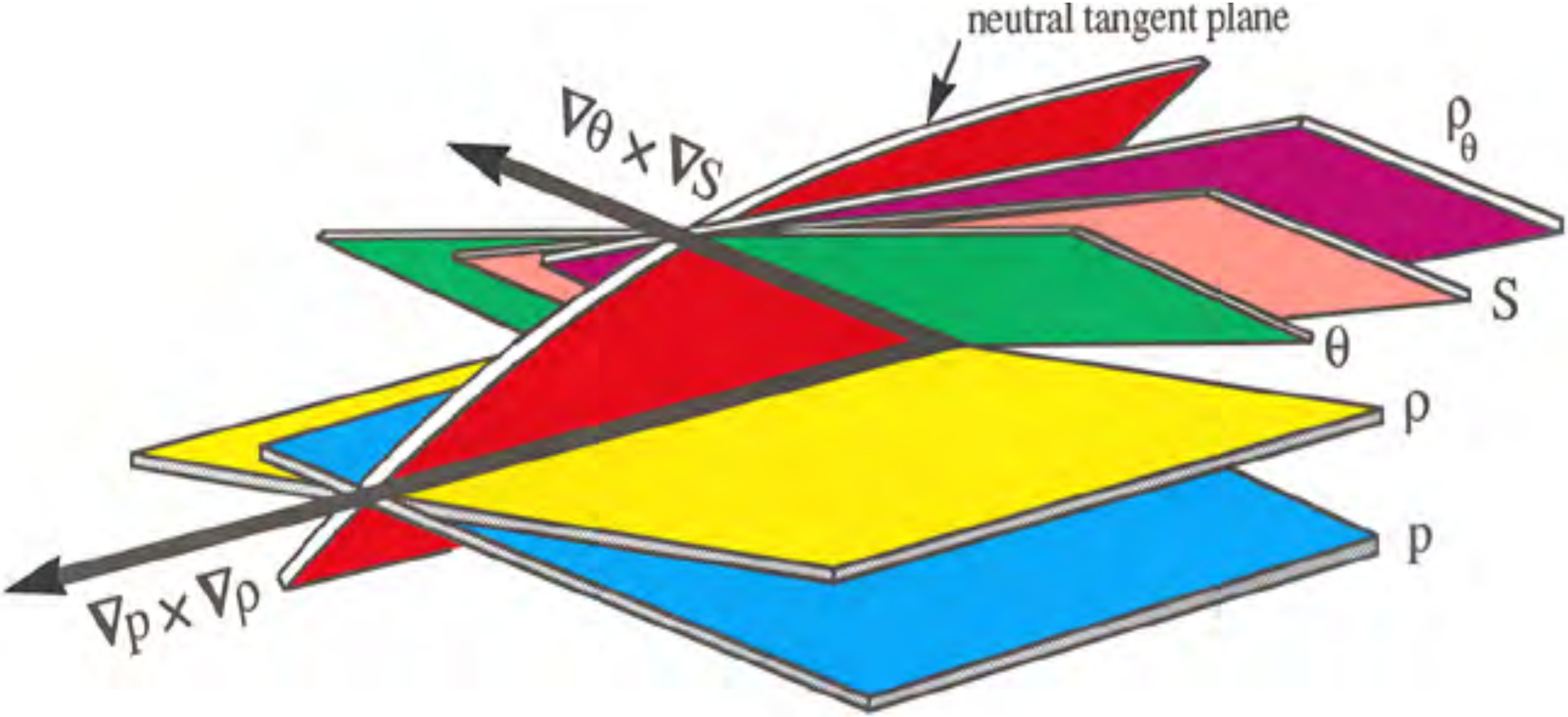
(a) that the line $\nabla S_\mathrm{A} \times \nabla\Theta$ lies in an isobaric surface, and

(b) that contours of p and Θ in a neutral tangent plane are parallel, and

(c) that S_A and Θ data in an isobaric surface describe a line (rather than an area) on the $S_\mathrm{A} - \Theta$ diagram.

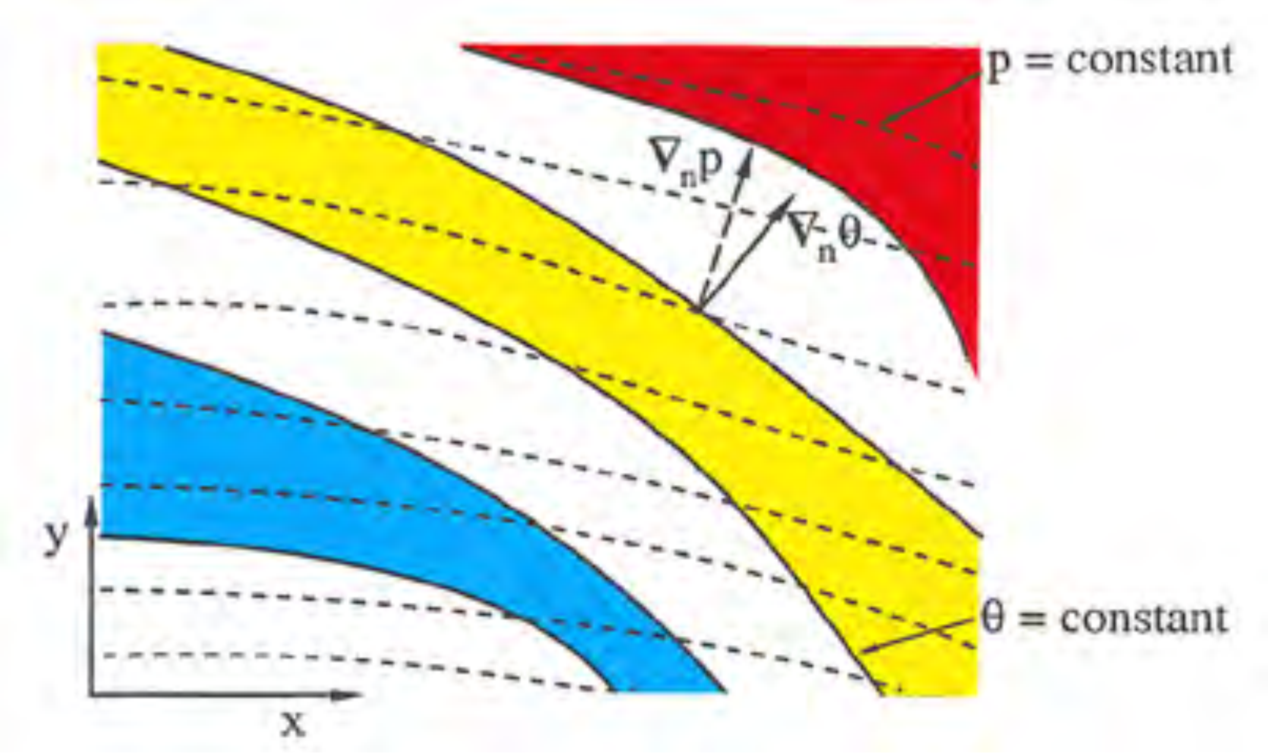
The ill-defined nature of "neutral surfaces"

(a) Zero helicity requires that $\nabla S_{\mathrm{A}} \times \nabla \Theta$ lie in the p surface since $\nabla p \cdot \nabla S_{\mathrm{A}} \times \nabla \Theta$ has to be zero.



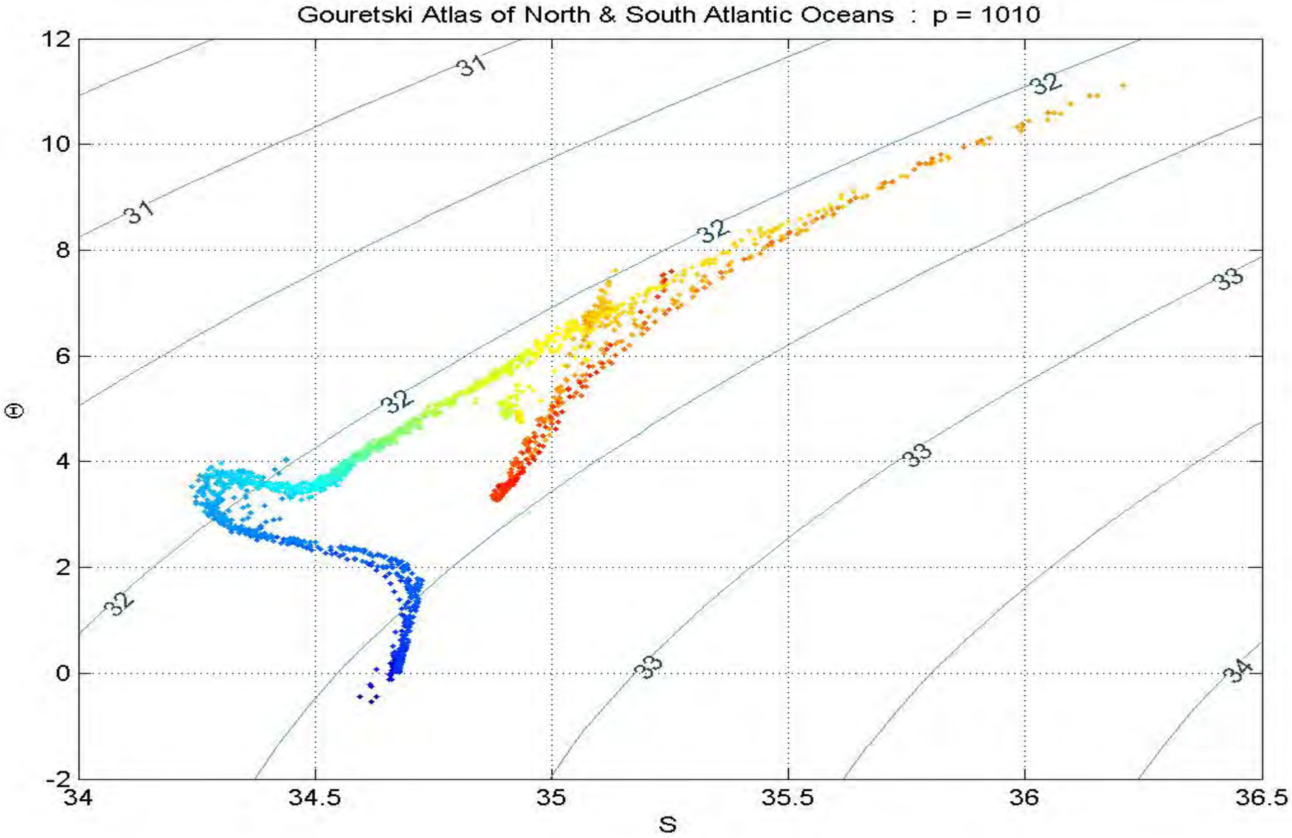
The ill-defined nature of "neutral surfaces"

(b) Zero helicity requires that the contours of constant p and Θ be parallel in a neutral tangent plane, that is, $\nabla_n p \times \nabla_n \Theta = \mathbf{0}$.

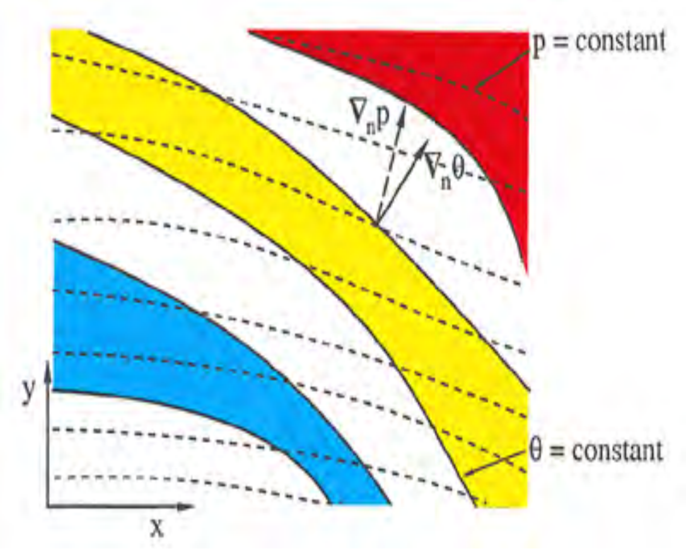


The ill-defined nature of "neutral surfaces"

(c) Zero helicity requires that the contours of constant S_A and Θ be parallel in an isobaric surface, that is, $\nabla_p S_\mathrm{A} \times \nabla_p \Theta = \mathbf{0}$.



why is the oceanic twiggy so thin?



Recall that zero helicity requires that the contours of constant p and Θ be parallel in a neutral tangent plane, that is,

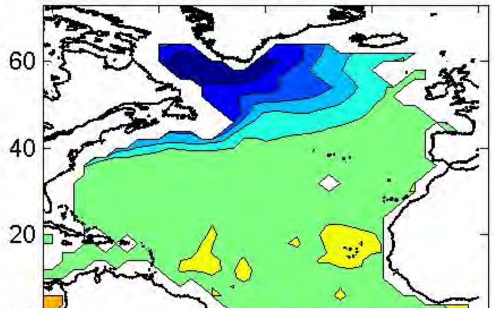
$$\nabla_n p \times \nabla_n \Theta = \mathbf{0}$$

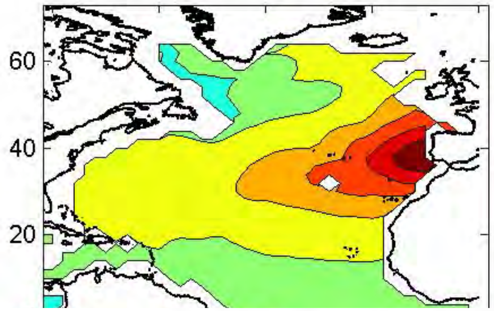
The Mediterranean Water happens to enter the North Atlantic at a location and depth where the neutral density surfaces are approximately flat (no thermal wind), that is, $\nabla_n p = \mathbf{0}$, so that there is no possibility of $\nabla_n p \times \nabla_n \Theta$ being significant. The same applies to the entry of the Red Sea Water into the Indian Ocean.

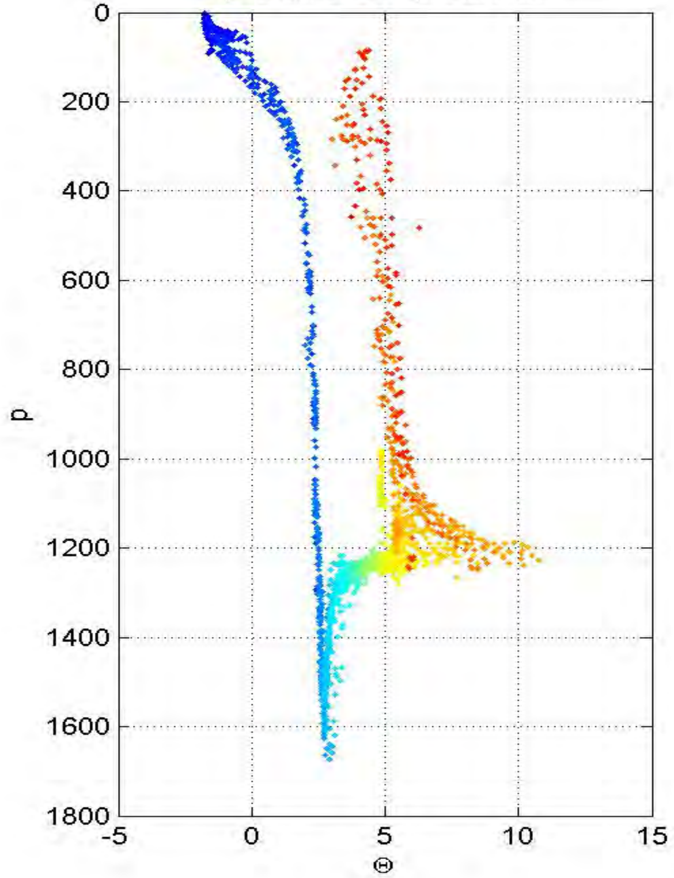
Is this just happenstance?

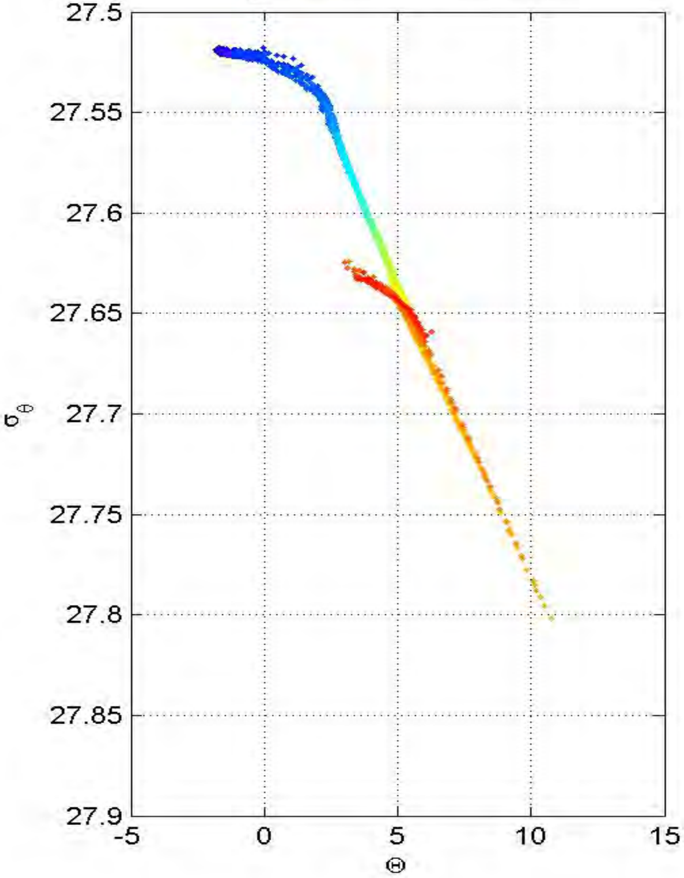
why is the oceanic twiggy so thin?

Why is
$\nabla_n p \times \nabla_n \Theta$
so small?

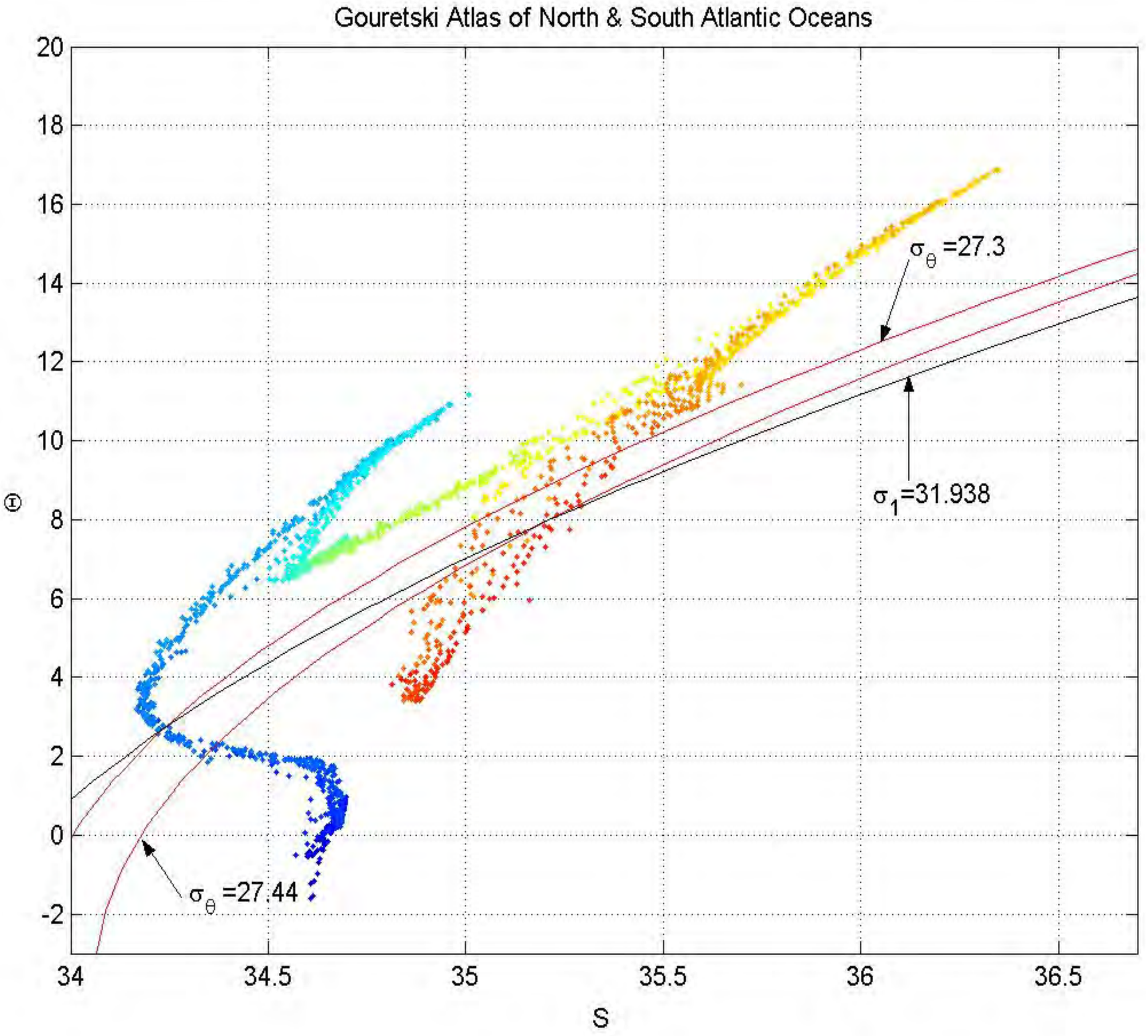

p on 27.77 γ^n surface

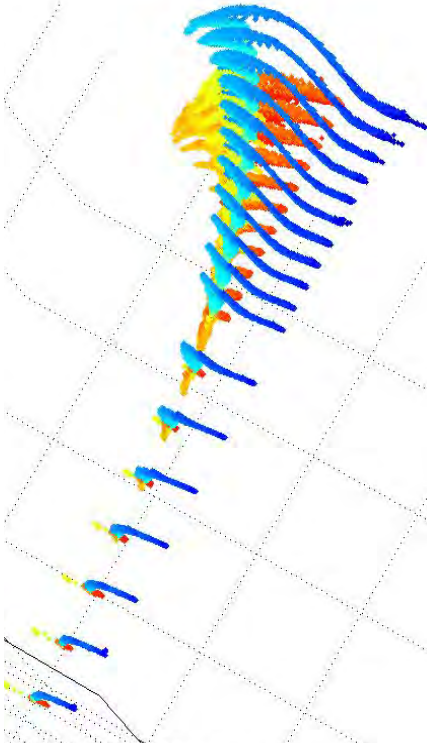

Θ on 27.77 γ^n surface


p-Θ on 27.77 γ^n surface


σ_θ-Θ on 27.77 γ^n surface

An isobaric cut through “Twiggy”





The thermobaric term

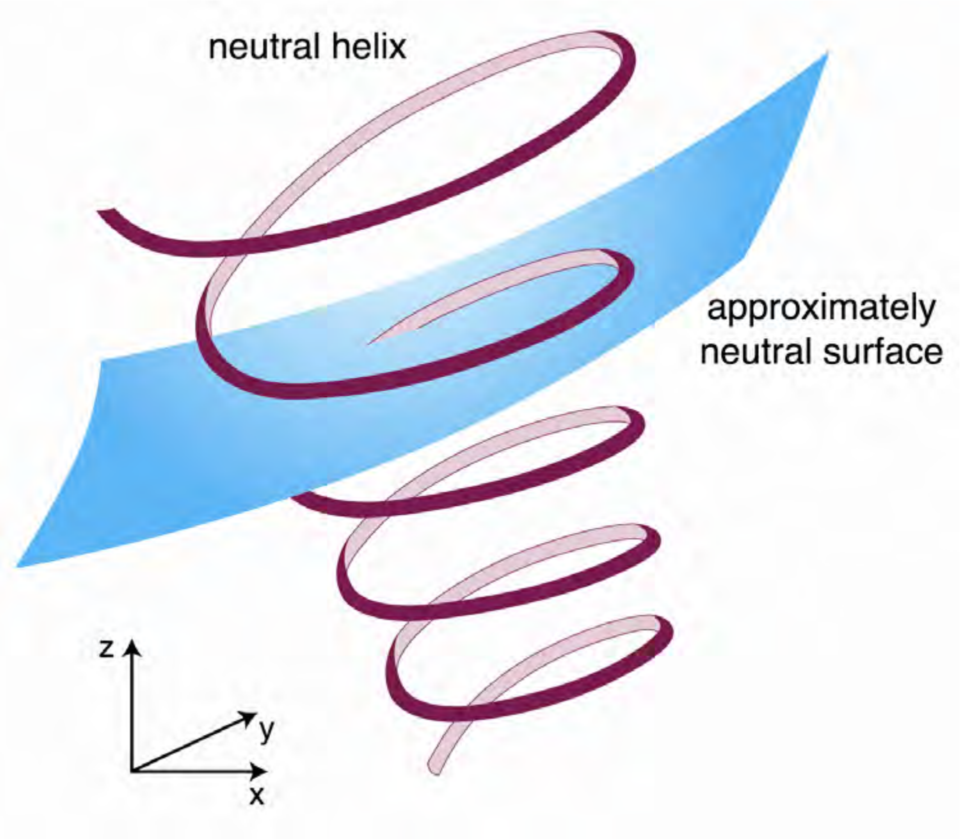
The thermobaric term in the Equation of State causes many weird and wonderful effects.

It confounds the meaning and properties of “isopycnal surfaces”, and it complicates the relationship between vertical mixing, dissipation, and dianeutral advection.

Vertical motion due to the ocean not being 100% “skinny”

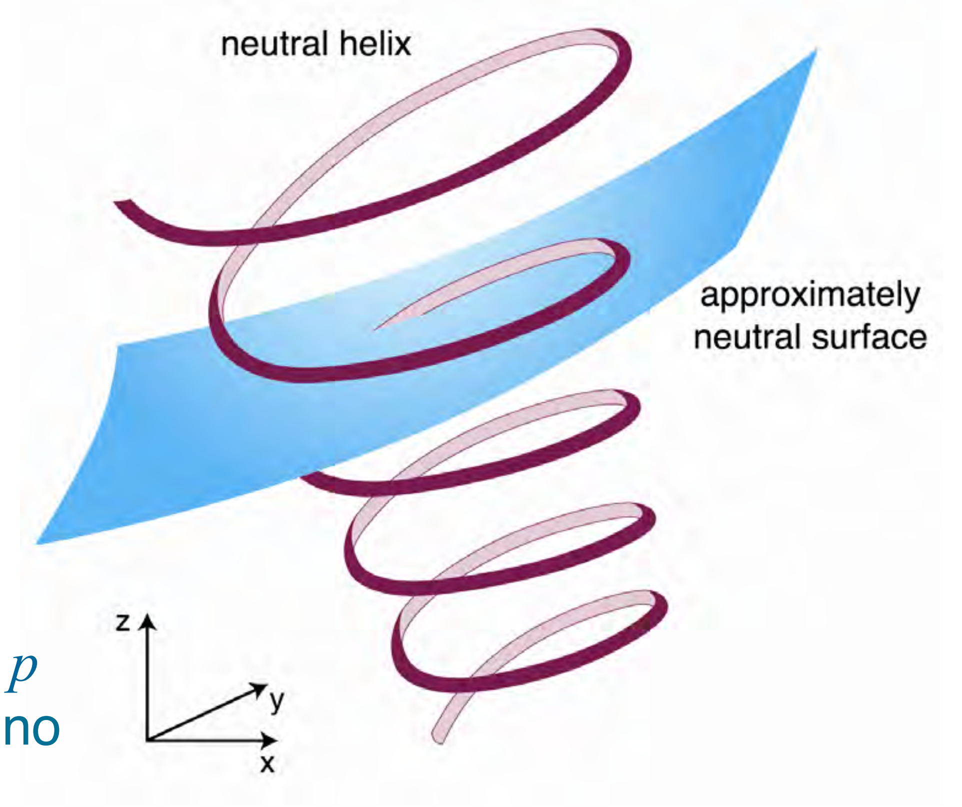
Because the ocean is not totally “empty” in $S_A - \Theta - p$ space, fluid can migrate vertically through any “density” surface simply by cork-screwing its way along helical neutral trajectories without the need for any dissipation of mechanical energy.

That is, “surfaces ain’t surfaces”.



Vertical motion due to the ocean not being 100% “skinny”

Because the ocean is not totally “empty” in $S_\mathrm{A} - \Theta - p$ space, fluid can migrate vertically through any “density” surface simply by cork-screwing its way along helical neutral trajectories without the need for any dissipation of mechanical energy.



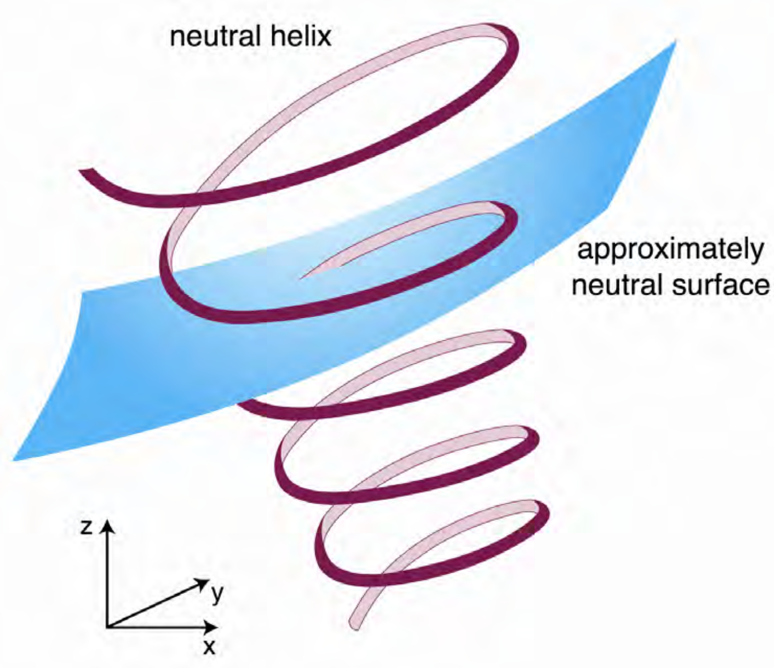
If the global ocean volume in $S_\mathrm{A} - \Theta - p$ space were not so tiny, it would make no sense to study diapycnal mixing, tidal mixing, and diapycnal tracer diffusion.

Why is it important that the World Ocean is ~93% "empty"?

If the concept of a "density" surface through which advection is caused only by dissipative mixing processes is to make sense, all the hydrography from the World Ocean must approximately lie on a single surface in $S_{\mathrm{A}} - \Theta - p$ space.

Otherwise, fluid can migrate through any such "density" surface simply by cork-screwing its way along helical neutral trajectories without the need for any dissipation of energy or any diapycnal mixing.

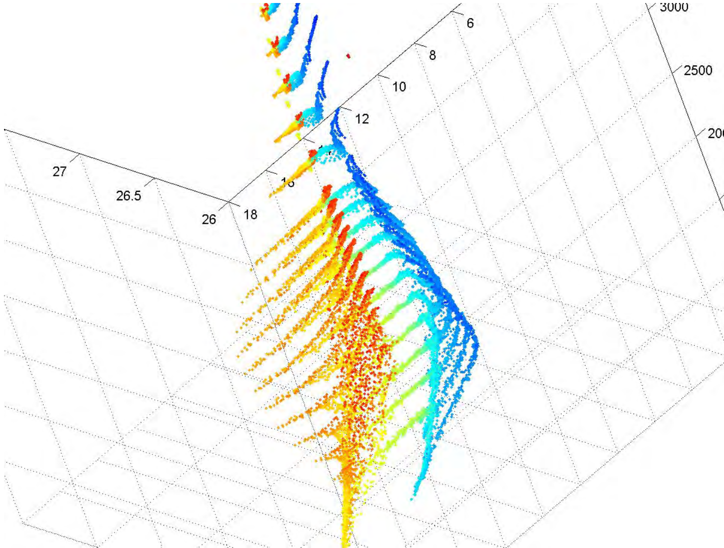
If the global ocean volume in $S_{\mathrm{A}} - \Theta - p$ space were not so tiny, it would make no sense to study diapycnal mixing, tidal mixing, diapycnal tracer diffusion (the WOCE TRE experiment) and breaking internal gravity waves.



Why is it important that the World Ocean is ~93% “empty”?

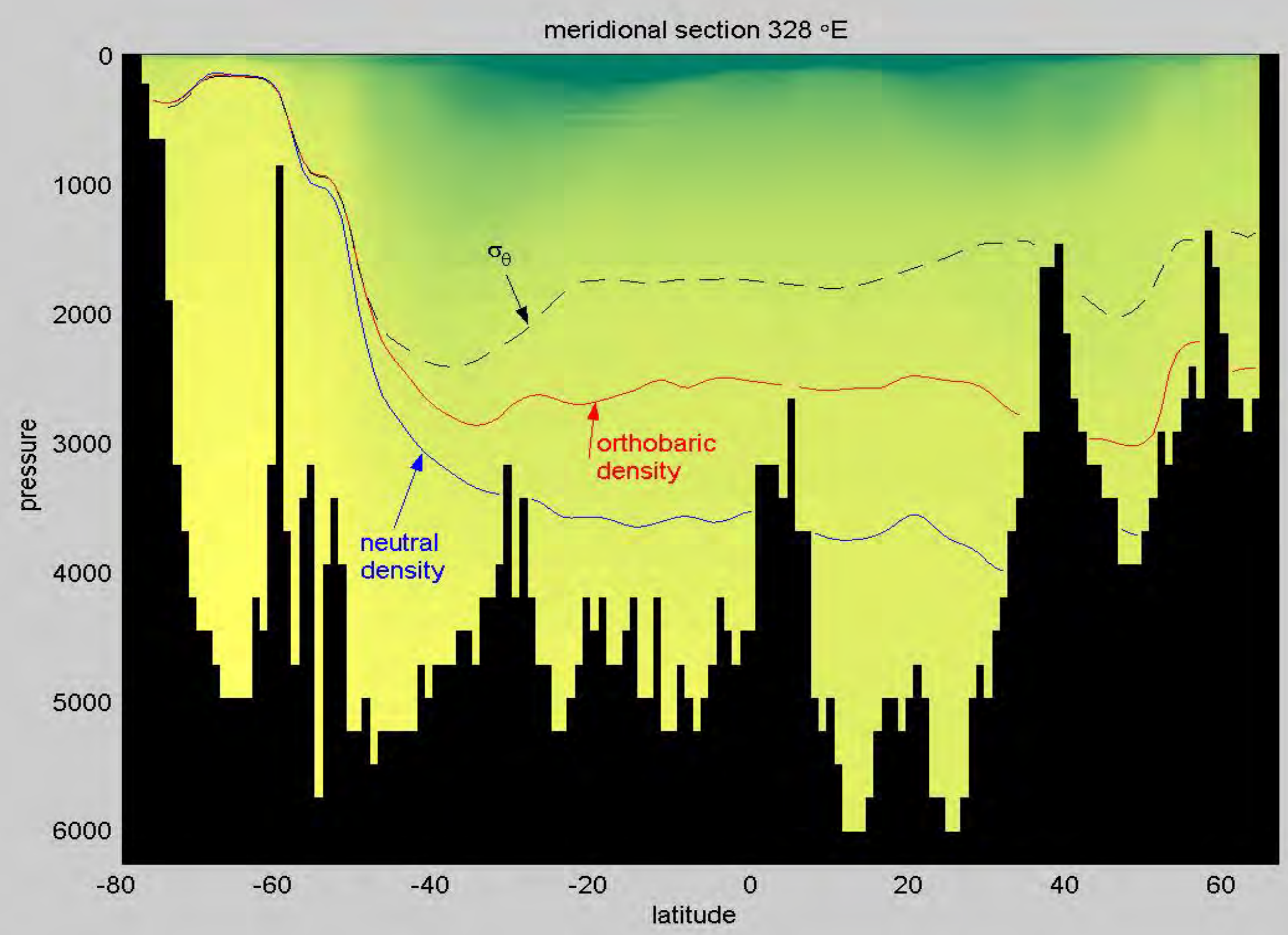
Is the ocean’s skinniness just a fluke? I know of no explanation for the ocean’s emptiness, except that if it were not so, the vertical upwelling achieved by the helical nature of neutral trajectories would be so large as to render the ocean unsteady.

If this hypothesis is correct, it implies that the upwelling caused by helicity is a leading order process, comparable to the Munk upwelling/diffusion balance in the deep ocean.

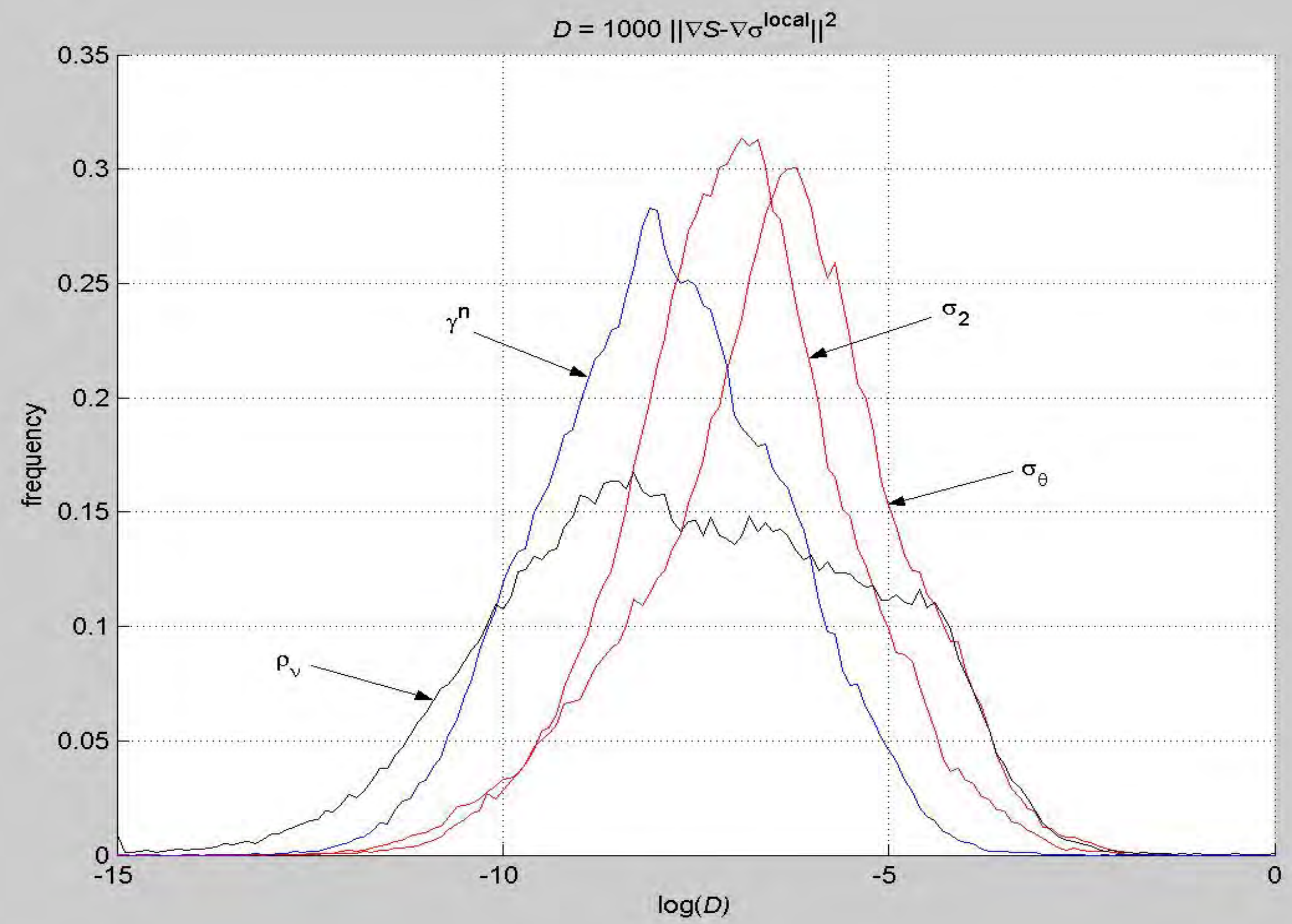


The magnitude of the mean upwelling in the deep ocean achieved by this helicity needs to be quantified. If this is significant, it implies that the zoo of known diapycnal mixing processes of internal waves, double diffusion

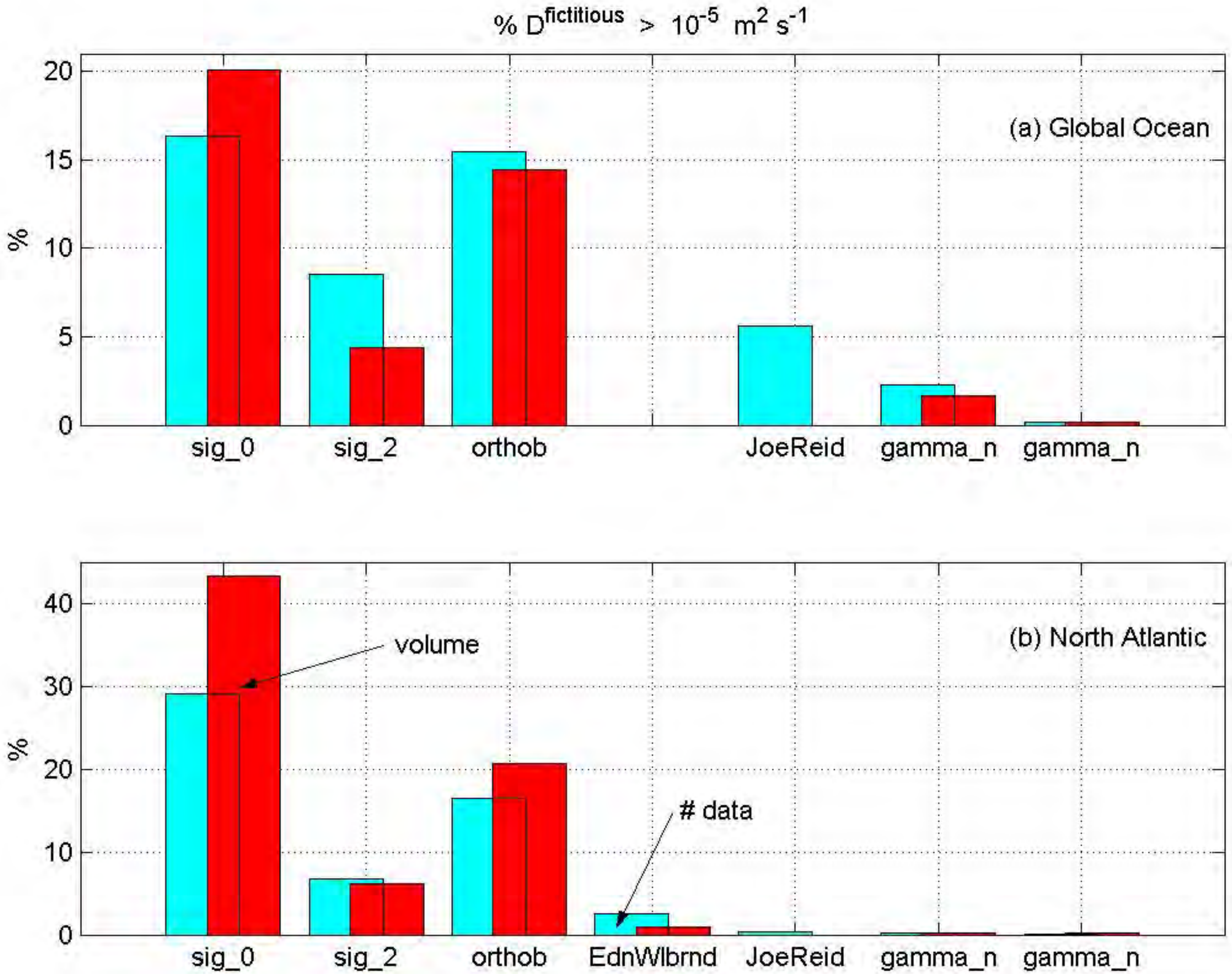
An Atlantic cross- section showing various types of density surface



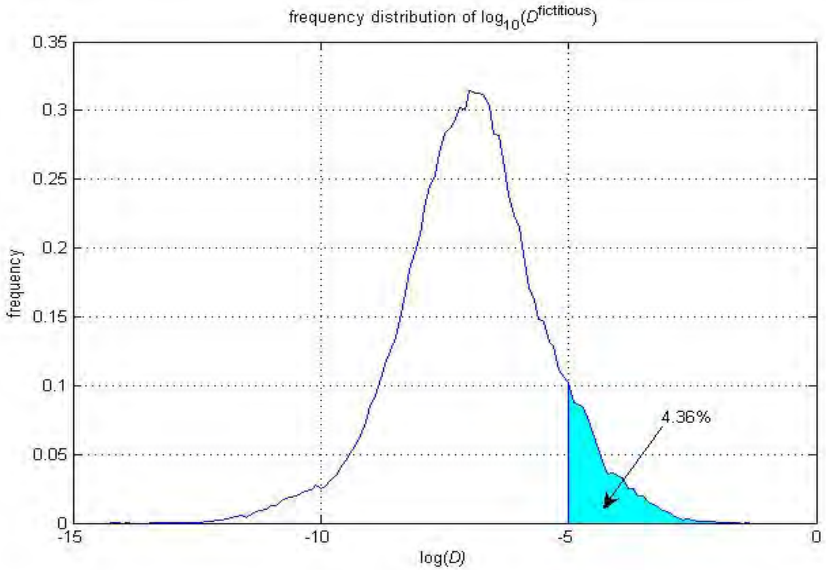
Slope differences between various surfaces & neutral tangent planes

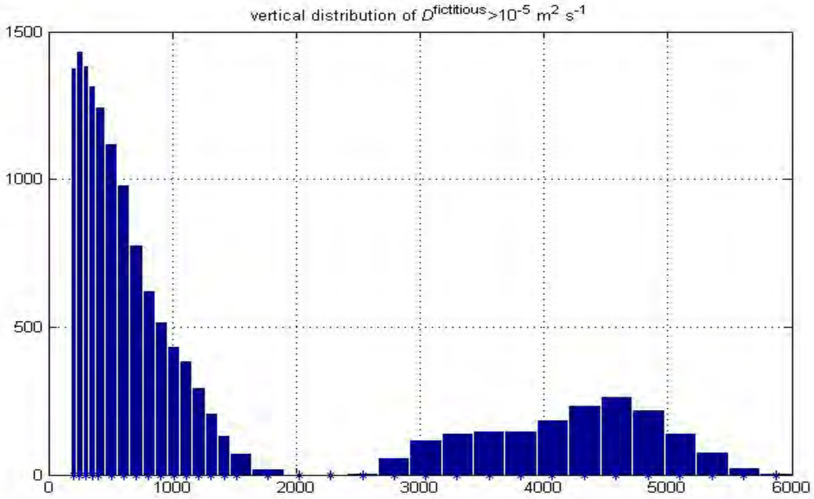


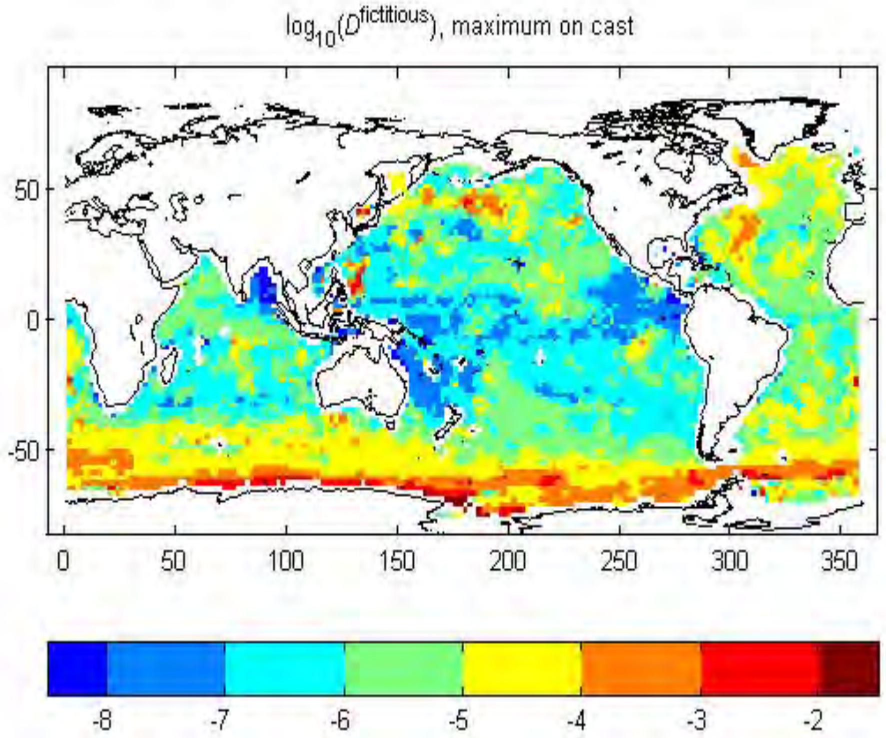
Slope differences between various surfaces & neutral tangent planes



Fictitious Diapycnal Mixing with s_2 as model coordinate







Improvements in forming approximately neutral surfaces

Start with any "density" surface and evaluate

$$\boldsymbol{\varepsilon}^{\text{initial}} = \beta \nabla_a S_{\text{A}} - \alpha \nabla_a \Theta$$

Then find the perturbation field $\Phi'(x, y)$ such that

$$\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}^{\text{initial}} + \nabla_a \Phi'$$

is minimized. $\boldsymbol{\Phi}'$ is the natural logarithm of the locally referenced potential density and its value on the initial surface can be used to find the new height of the new surface.

This process is repeated until the optimized solution is found. This "omega surface" approach was used by Klocker *et al*. (2009) but was hard to justify.

The integrating factor *b*

The integrating factor *b* relates the gradient of locally-referenced potential density to the gradient of Neutral Density.

$$\frac{\nabla\gamma}{\gamma} = b\left(\beta^{\Theta}\nabla S_{\mathrm{A}} - \alpha^{\Theta}\nabla\Theta\right) = b\left(\frac{\nabla\rho}{\rho} - \kappa\nabla P\right)$$

Taking the curl of this expression gives

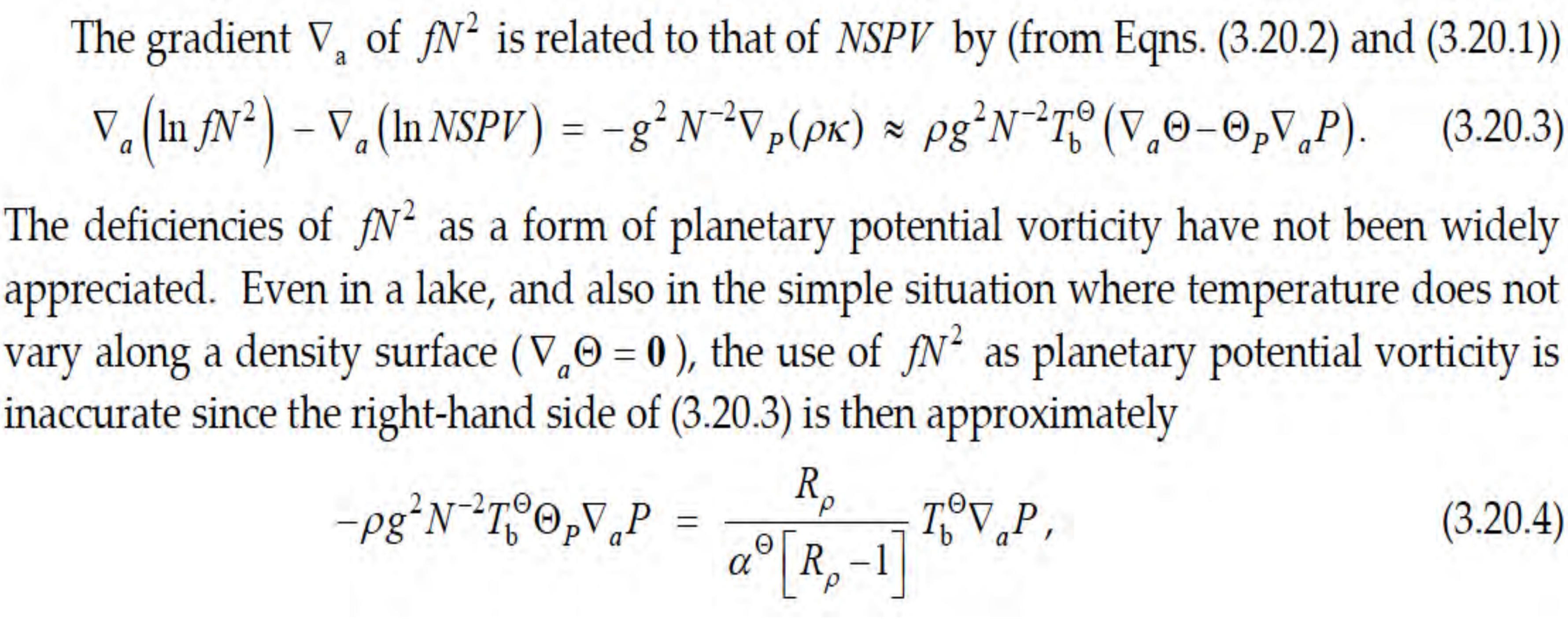
$$\frac{\nabla b}{b}\times\left(\kappa\nabla P - \frac{\nabla\rho}{\rho}\right) = -\nabla\kappa\times\nabla P,$$

and the horizontal component of this equation is

$$\nabla_{n}\ln b = \rho g^{2}N^{-2}\nabla_{p}\kappa = -\rho g^{2}N^{-2}\left(\alpha_{P}^{\Theta}\nabla_{p}\Theta - \beta_{P}^{\Theta}\nabla_{p}S_{\mathrm{A}}\right)$$

The factor *b* and planetary PV

$$\frac{1}{\gamma}\left(\frac{\partial\gamma}{\partial t}+\mathbf{U}\cdot\boldsymbol{\nabla}\gamma\right)\approx\frac{b}{\rho}\left(\frac{\partial\rho}{\partial t}+\mathbf{U}\cdot\boldsymbol{\nabla}\rho\right)$$



The gradient ∇_{a} of fN^2 is related to that of $NSPV$ by (from Eqns. (3.20.2) and (3.20.1))

$$\nabla_a\left(\ln fN^2\right)-\nabla_a\left(\ln NSPV\right)=-g^2N^{-2}\nabla_P(\rho\kappa)\approx\rho g^2N^{-2}T_{\mathrm{b}}^{\Theta}\left(\nabla_a\Theta-\Theta_P\nabla_aP\right).\qquad(3.20.3)$$

The deficiencies of fN^2 as a form of planetary potential vorticity have not been widely appreciated. Even in a lake, and also in the simple situation where temperature does not vary along a density surface ($\nabla_a\Theta=\mathbf{0}$), the use of fN^2 as planetary potential vorticity is inaccurate since the right-hand side of (3.20.3) is then approximately

$$-\rho g^2N^{-2}T_{\mathrm{b}}^{\Theta}\Theta_P\nabla_aP=\frac{R_\rho}{\alpha^{\Theta}\left[R_\rho-1\right]}T_{\mathrm{b}}^{\Theta}\nabla_aP,\qquad(3.20.4)$$

One cause of *b* variation; the epineutral S_A gradient

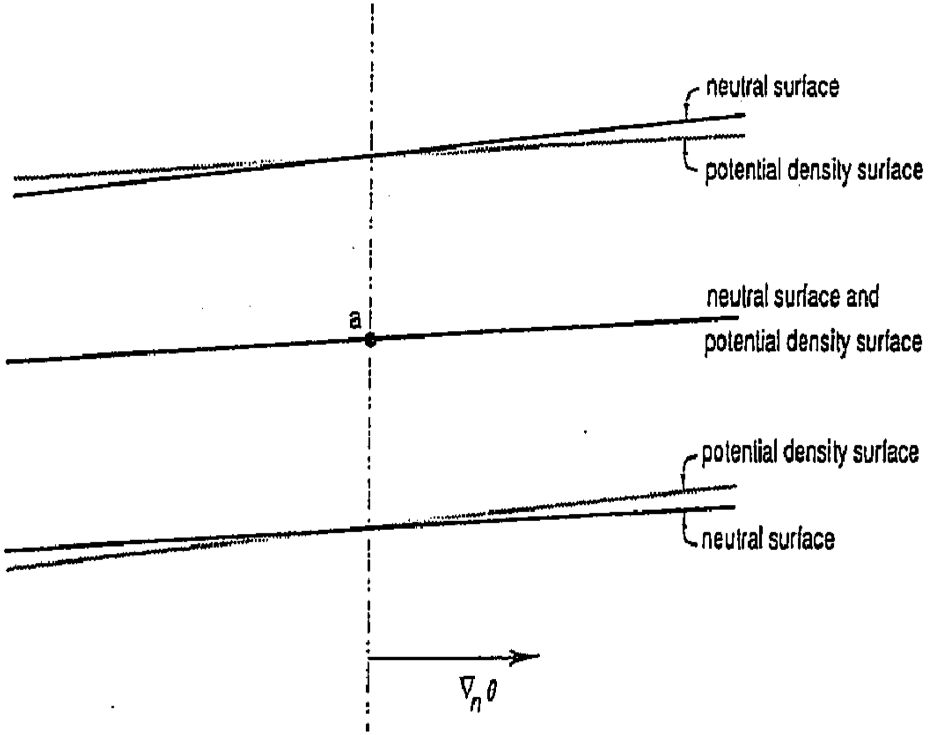
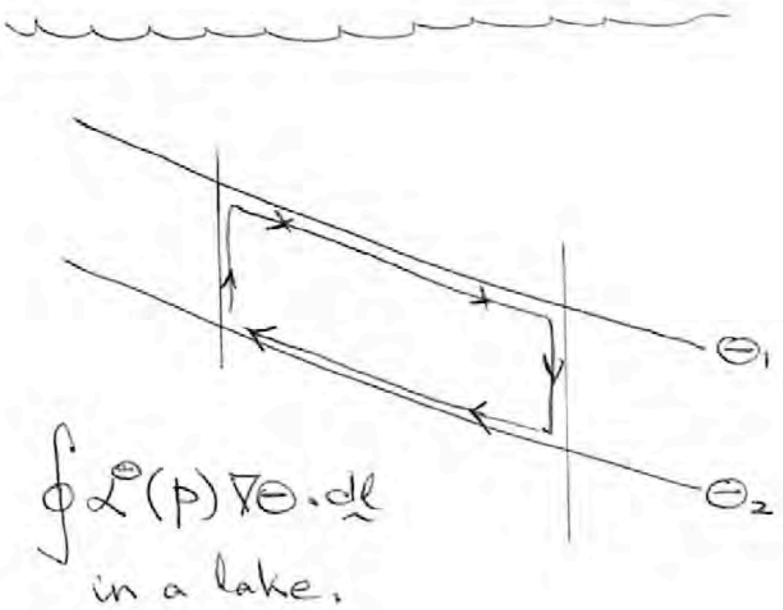
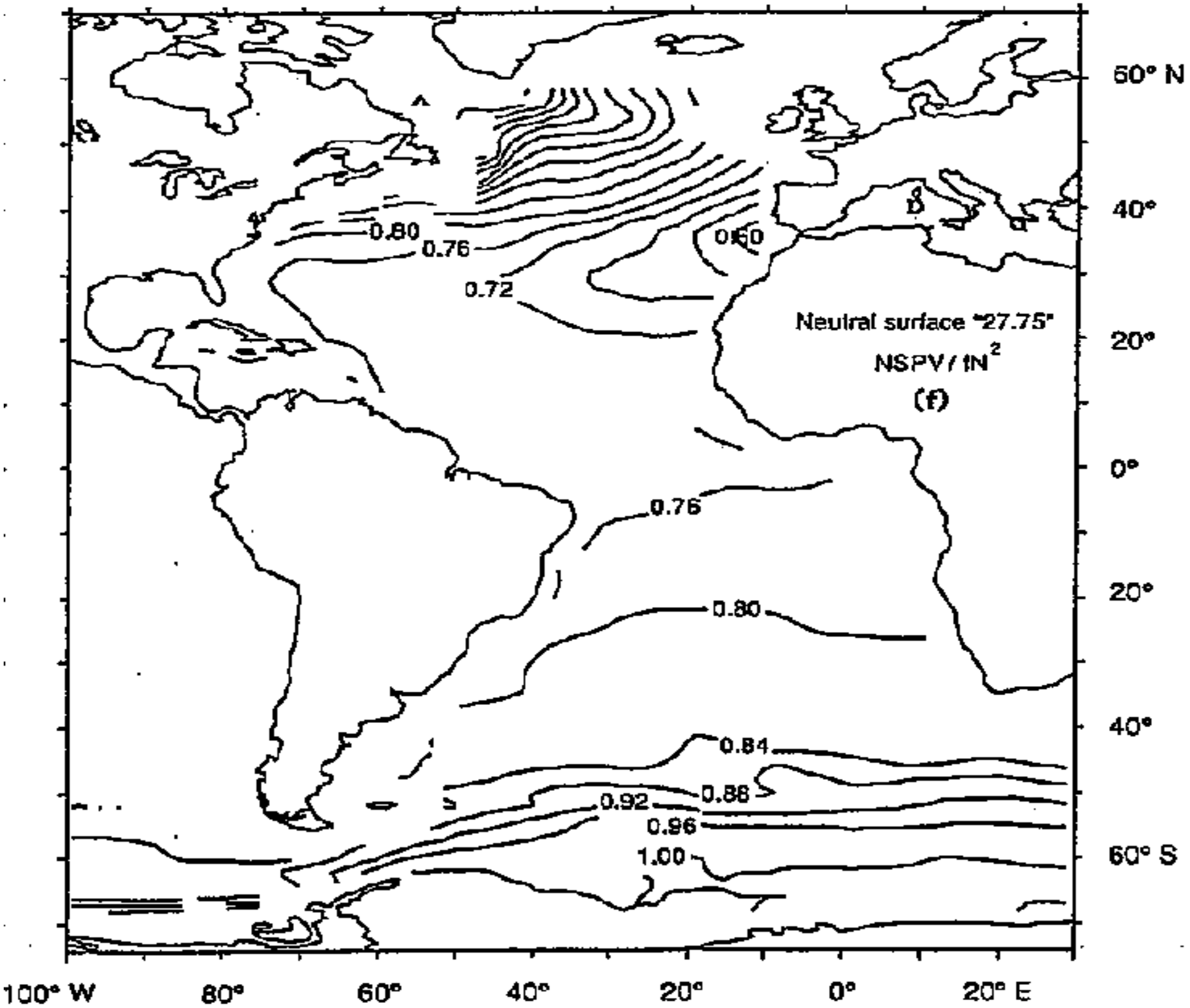


Fig. 14. A vertical cross section through three neutral surfaces and three potential density surfaces. The reference pressure of the potential density is the pressure of the central point, a. The neutral surface and potential density surface that pass though this point are parallel. The slopes of the other pairs of surfaces are different.

Another cause of *b* variation; even in a Lake, *b* varies



The spatial variation of *b* in the Atlantic Ocean



Improvements in forming approximately neutral surfaces

The way we now can justify the vertical step of the “omega surface” approach is to use an estimate of b to form

$$\hat{\varepsilon}^{\text{initial}} = b\beta\nabla_a S_{\text{A}} - b\alpha\nabla_a \Theta$$

Then we find the perturbation field $\Phi''(x, y)$ such that

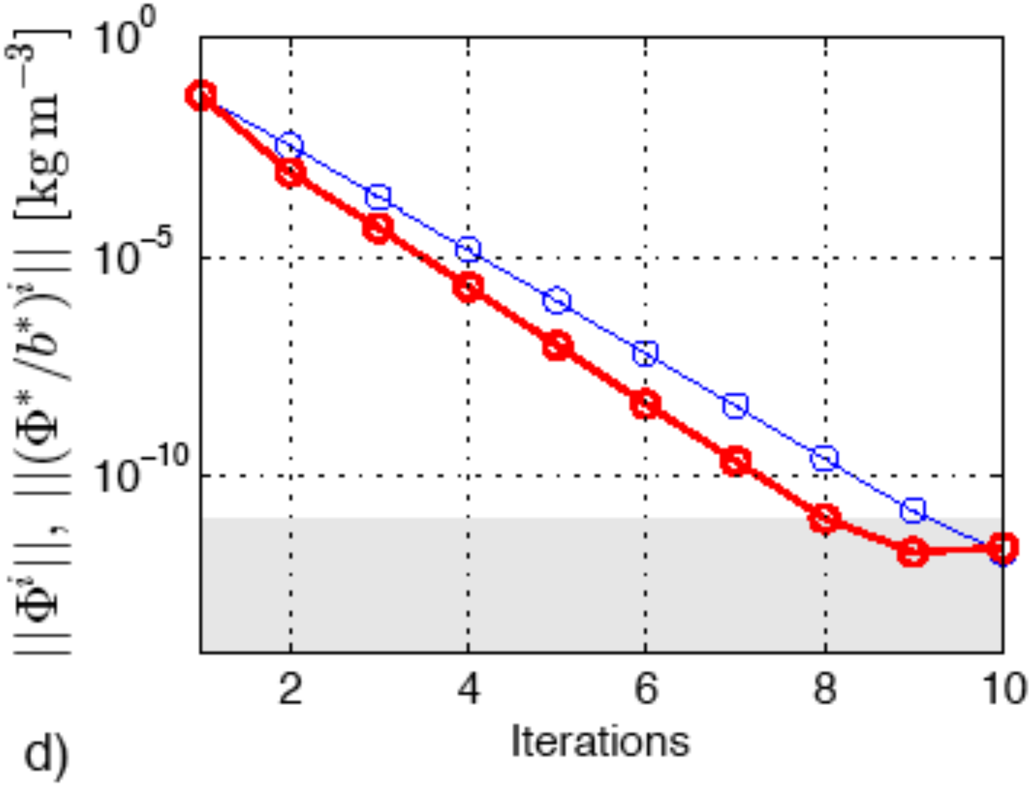
$$\hat{\varepsilon} = \hat{\varepsilon}^{\text{initial}} + \nabla_a \Phi''$$

is minimized. Φ'' is now the natural logarithm of Neutral Density, and its value on the initial surface can be used to find a new height of the new surface.

This process is repeated until the optimized solution is found.

Improvements in forming an approximately neutral surface

This new “omega surface” code is working well, and we plan to implement it in an ocean model at run time so that every grid point in the ocean model gets a Neutral Density label at every time step.



But note the subtle features of Neutral Density surfaces, as illustrated on the following figure.

Non-quasi-material nature of Neutral Density