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.
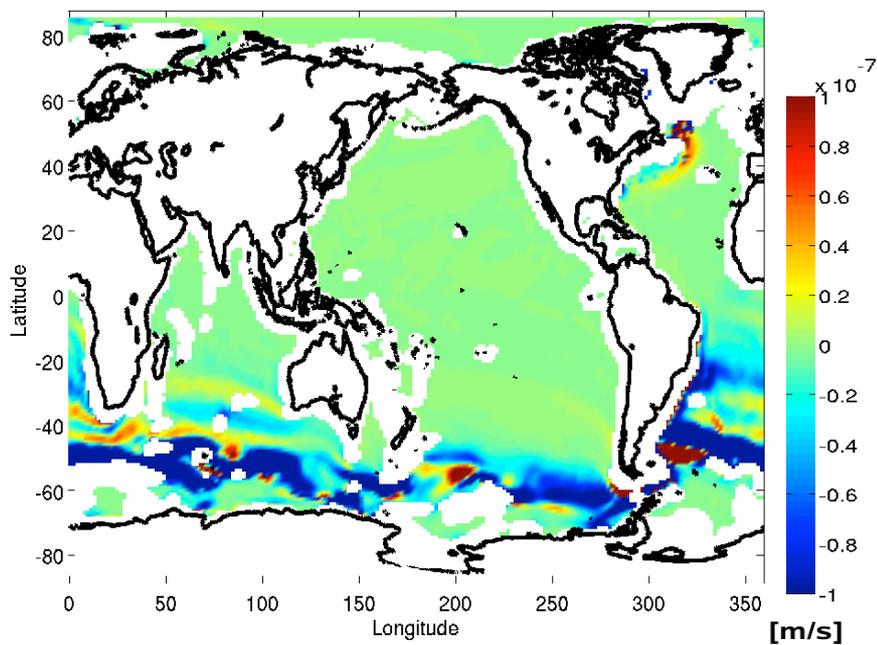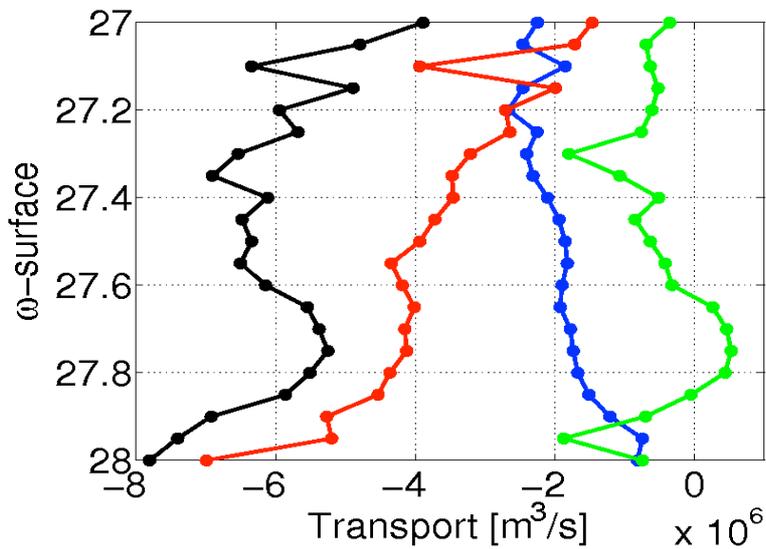
When globally integrated over complete density surfaces, the total transport due to these non-linear processes can be calculated. In green is the mean dianeutral transport from the ill-defined nature of "neutral surfaces", blue is the dianeutral transport due to cabbeling, red due to thermobaricity, 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

$$\mathbf{v} = |\mathbf{v}|(\cos\varphi, \sin\varphi) . \qquad\qquad \text{(V\_rotate\_01)}$$

Vertically differentiate this equation and take the cross product with $\mathbf{v}$ to obtain

$$\mathbf{v} \times \mathbf{v}_z = \mathbf{k}\varphi_z|\mathbf{v}|^2 , \qquad\qquad \text{(V\_rotate\_02)}$$

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

$$\boxed{f\mathbf{v}_z = \left(\tfrac{1}{\rho}\right)_z \mathbf{k}\times\nabla_z P + \tfrac{1}{\rho}\mathbf{k}\times\nabla_z\left(P_z\right) = -\tfrac{g}{\rho}\mathbf{k}\times\nabla_p\rho = \tfrac{N^2}{g\rho}\mathbf{k}\times\nabla_n P,} \qquad \text{(3.12.3)}$$

into Eqn. (V_rotate_03) we find

$$\varphi_z|\mathbf{v}|^2 = -\mathbf{v}\cdot\mathbf{k}\times\mathbf{v}_z = \tfrac{N^2}{fg\rho}\mathbf{v}\cdot\nabla_n P . \qquad\qquad \text{(V\_rotate\_04)}$$

Under the usual Boussinesq approximation $-(g\rho)^{-1}\nabla_n P$ is set equal to the slope of the neutral tangent plane, $\nabla_n z$, so that we have

$$\varphi_z|\mathbf{v}|^2 \approx -\tfrac{N^2}{f}\mathbf{v}\cdot\nabla_n z , \qquad\qquad \text{(V\_rotate\_05)}$$

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),

$$w = z_t\big|_n + \mathbf{v}\cdot\nabla_n z + e , \qquad\qquad \text{(V\_rotate\_06)}$$

we have

$$\boxed{\varphi_z|\mathbf{v}|^2 \approx -\tfrac{N^2}{f}\left(w - e - z_t\big|_n\right),} \qquad\qquad \text{(V\_rotate\_07)}$$

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, $\mathbf{v}\cdot\nabla_n z$.
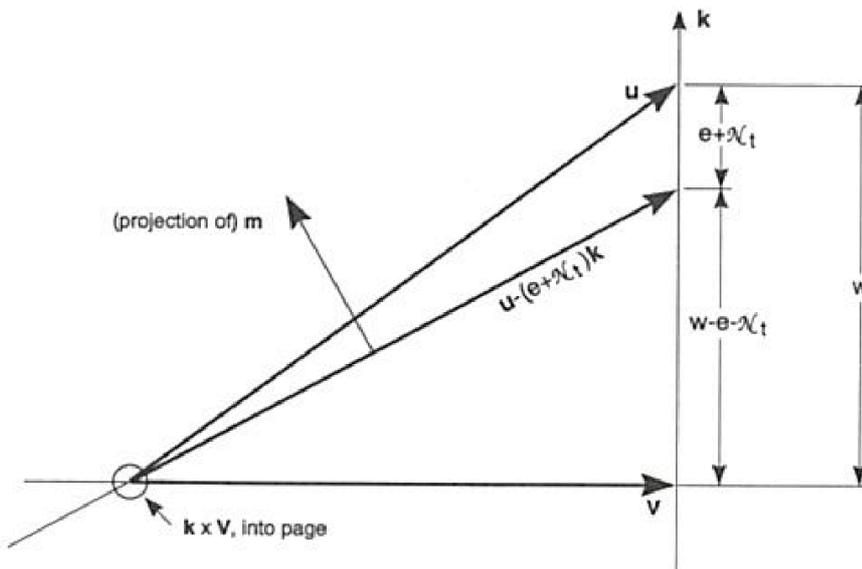
The absolute velocity vector in the ocean

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 $f \mathbf{v}_z = \frac{N^2}{g\rho} \mathbf{k} \times \nabla_n P$, and the third line of (3.13.2), namely $H^n = g^{-1} N^2 T_b^\Theta \left(\nabla_n P \times \nabla_n \Theta \right) \cdot \mathbf{k}$, we find that

$$H^n = \rho T_b^\Theta f \mathbf{v}_z \cdot \nabla_n \Theta. \tag{3.13.4}$$

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

$$
\begin{aligned}
\overline{\mathbf{v}} \cdot \nabla_n \hat{\Theta} \;=\;& \tilde{\gamma}_z \nabla_n \cdot \left(\tilde{\gamma}_z^{-1} K \nabla_n \hat{\Theta} \right) + KgN^{-2} \hat{\Theta}_z \left(C_b^\Theta \nabla_n \hat{\Theta} \cdot \nabla_n \hat{\Theta} + T_b^\Theta \nabla_n \hat{\Theta} \cdot \nabla_n P \right) \\
& + D\beta^\Theta g N^{-2} \hat{\Theta}_z^3 \frac{d^2 \hat{S}_A}{d\hat{\Theta}^2} \;-\; \boldsymbol{\Psi}_z \cdot \nabla_n \hat{\Theta} \;-\; \hat{\Theta}_t \big|_n,
\end{aligned}
\tag{3.13.7}
$$

where the thickness-weighted mean velocity of density-coordinate averaging, $\hat{\mathbf{v}}$, has been written as $\hat{\mathbf{v}} = \overline{\mathbf{v}} + \boldsymbol{\Psi}_z$, that is, as the sum of the Eulerian-mean horizontal velocity $\overline{\mathbf{v}}$ and the quasi-Stokes eddy-induced horizontal velocity $\boldsymbol{\Psi}_z$ (McDougall and McIntosh (2001)). The quasi-Stokes vector streamfunction $\boldsymbol{\Psi}$ 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

$$\overline{\mathbf{v}} \cdot \boldsymbol{\tau} = v^\perp \qquad \text{where} \qquad \boldsymbol{\tau} \equiv \nabla_n \hat{\Theta} \big/ \big| \nabla_n \hat{\Theta} \big|, \tag{3.13.8}$$

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

$$\overline{\mathbf{v}} = v^{\parallel} \boldsymbol{\tau} \times \mathbf{k} + v^\perp \boldsymbol{\tau}, \tag{3.13.9}$$

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

$$\overline{\mathbf{v}} \cdot \boldsymbol{\tau}_z = -\overline{\mathbf{v}}_z \cdot \boldsymbol{\tau} + v_z^\perp = -\frac{N^2}{fg\rho} \mathbf{k} \times \nabla_n P \cdot \boldsymbol{\tau} + v_z^\perp, \tag{3.13.10}$$

where we have used the "thermal wind" equation (3.12.3), $\overline{\mathbf{v}}_z = \frac{N^2}{fg\rho} \mathbf{k} \times \nabla_n P$.

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 $\boldsymbol{\tau} = (\cos\phi, \sin\phi)$, we see that $\boldsymbol{\tau} \times \mathbf{k} = (\sin\phi, -\cos\phi)$, $\boldsymbol{\tau}_z = -\phi_z \boldsymbol{\tau} \times \mathbf{k}$ 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, $\phi_z = -\boldsymbol{\tau} \cdot \nabla \times \boldsymbol{\tau} = -(\boldsymbol{\tau} \times \mathbf{k}) \cdot \nabla \times (\boldsymbol{\tau} \times \mathbf{k})$, 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

$$v^{\parallel} = \frac{N^2}{fg\rho}\frac{\mathbf{k}\cdot\nabla_n P\times\boldsymbol{\tau}}{\phi_z} - \frac{v_z^{\perp}}{\phi_z} \quad\text{or}\quad v^{\parallel} = \frac{H^{\mathrm{n}}}{\phi_z\rho f T_b^{\Theta}\left|\nabla_n\hat{\Theta}\right|} - \frac{v_z^{\perp}}{\phi_z}, \quad (3.13.11)$$

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

$$\boxed{\bar{\mathbf{v}} = \left\{\frac{N^2}{fg\rho}\frac{\mathbf{k}\cdot\nabla_n P\times\boldsymbol{\tau}}{\phi_z} - \frac{v_z^{\perp}}{\phi_z}\right\}\boldsymbol{\tau}\times\mathbf{k} + v^{\perp}\boldsymbol{\tau},} \quad (3.13.12)$$

and the horizontal velocity due to solely the two mixing terms can be expressed as

$$-\frac{v_z^{\perp}}{\phi_z}\boldsymbol{\tau}\times\mathbf{k} + v^{\perp}\boldsymbol{\tau} = \frac{(v^{\perp})^2}{\phi_z}\left(\frac{\boldsymbol{\tau}\times\mathbf{k}}{v^{\perp}}\right)_z, \quad (3.13.13)$$

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), $\nabla_n z - \nabla_p z = \nabla_n P/P_z$)

$$\nabla_n\cdot\mathbf{a} = \nabla_p\cdot\mathbf{a} + \mathbf{a}_z\cdot\nabla_n P/P_z. \quad (3.20.1)$$

Applying this relationship to the two-dimensional vector $f\mathbf{v} = g\mathbf{k}\times\nabla_p z$ we have

$$\nabla_n \cdot (f\mathbf{v}) = g \nabla_p \cdot (\mathbf{k} \times \nabla_p z) + f\mathbf{v}_z \cdot \nabla_n P / P_z = 0. \tag{3.20.2}$$

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 $\nabla_r \cdot (f\mathbf{v}) = 0$ in any surface r which contains the line $\nabla P \times \nabla \rho$.

Eqn. (3.20.2), namely $\nabla_n \cdot (f\mathbf{v}) = 0$, can be interpreted as the divergence form of the evolution equation of <u>planetary potential vorticity</u> since

$$\nabla_n \cdot (f\mathbf{v}) = \nabla_n \cdot \left(\frac{q\mathbf{v}}{\gamma_z} \right) = 0, \tag{3.20.3}$$

where $q = f\gamma_z$ is the <u>planetary potential vorticity</u>, 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

$$\boxed{\nabla_n \cdot \left(\frac{\hat{q}\hat{\mathbf{v}}}{\tilde{\gamma}_z} \right) = -\nabla_n \cdot \overline{\left(\frac{\mathbf{v}''q''}{\gamma_z} \right)} = \nabla_n \cdot \left(\tilde{\gamma}_z^{-1} K \nabla_n \hat{q} \right)}, \tag{3.20.4}$$

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

$$\hat{q} \equiv \tilde{\gamma}_z \left. \left(\frac{q}{\gamma_z} \right) \right|_\gamma = f\tilde{\gamma}_z, \tag{3.20.5}$$

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 $\hat{\mathbf{v}} - \tilde{\mathbf{v}} = K \nabla_n \ln(\hat{q})$, since Eqn. (3.20.4) can be written as $\nabla_n \cdot (f\hat{\mathbf{v}}) = \nabla_n \cdot (\tilde{\gamma}_z^{-1} K \nabla_n \hat{q})$ while the epineutral temporal average of Eqn. (3.20.3) is $\nabla_n \cdot (f\tilde{\mathbf{v}}) = 0$.

The divergence form of the mean <u>planetary potential vorticity</u> evolution equation, Eqn. (3.20.4), is quite different to that of a normal conservative variable such as Absolute Salinity or Conservative Temperature,

$$\left(\left. \frac{\hat{\Theta}}{\tilde{\gamma}_z} \right|_n \right)_t + \nabla_n \cdot \left(\frac{\hat{\Theta}\hat{\mathbf{v}}}{\tilde{\gamma}_z} \right) + \frac{(\tilde{e}\hat{\Theta})_z}{\tilde{\gamma}_z} = \nabla_n \cdot \left(\tilde{\gamma}_z^{-1} K \nabla_n \hat{\Theta} \right) + \frac{(D\hat{\Theta}_z)_z}{\tilde{\gamma}_z}, \qquad (\hat{\Theta}\_\text{Eqn.})$$

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,

$$\left(\left. \frac{1}{\tilde{\gamma}_z} \right|_n \right)_t + \nabla_n \cdot \left(\frac{\hat{\mathbf{v}}}{\tilde{\gamma}_z} \right) + \frac{\tilde{e}_z}{\tilde{\gamma}_z} = 0, \tag{3.20.6}$$

from Eqn. (3.20.4), yielding ($\tilde{\gamma}_z^{-1}$ times)

$$\hat{q}_t \big|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{q} = \tilde{\gamma}_z \nabla_n \cdot \left(\tilde{\gamma}_z^{-1} K \nabla_n \hat{q} \right) + \hat{q}\tilde{e}_z, \tag{3.20.7}$$

or

$$\boxed{\hat{q}_t \big|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{q} + \tilde{e}\hat{q}_z = \frac{d\hat{q}}{dt} = \tilde{\gamma}_z \nabla_n \cdot \left(\tilde{\gamma}_z^{-1} K \nabla_n \hat{q} \right) + (\hat{q}\tilde{e})_z}. \tag{3.20.8}$$

In this form, it is clear that <u>planetary potential vorticity</u> 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,

$$\hat{\Theta}_t\big|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{\Theta} + \tilde{e}\hat{\Theta}_z = \frac{\mathrm{d}\hat{\Theta}}{\mathrm{d}t} = \tilde{\gamma}_z \nabla_n \cdot \left(\tilde{\gamma}_z^{-1} K \nabla_n \hat{\Theta}\right) + \left(D\hat{\Theta}_z\right)_z . \qquad \text{(A.21.15)}$$

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

$$\left(\hat{q}\tilde{e} - D\hat{q}_z\right)_z = f\left(\tilde{e}\tilde{\gamma}_z - D\tilde{\gamma}_{zz}\right)_z \approx f\left(D_z\tilde{\gamma}_z\right)_z = \left(D_z\hat{q}\right)_z \qquad \text{(3.20.9)}$$

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 $\hat{S}_A$ down a vertical water column, so that the $\hat{S}_A - \hat{q}$ and $\hat{S}_A - \hat{\Theta}$ 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 $\hat{S}_A - \hat{\Theta}$ diagram because of the zero $\hat{S}_A - \hat{\Theta}$ 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 $\hat{S}_A - \hat{q}$ 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

$$\frac{\nabla \gamma}{\gamma} = b\left(\beta^{\Theta}\nabla S_A - \alpha^{\Theta}\nabla\Theta\right) = b\left(\frac{\nabla\rho}{\rho} - \kappa\nabla P\right). \tag{3.20.10}$$

Taking the curl of this equation gives

$$\frac{\nabla b}{b}\times\left(\kappa\nabla P - \frac{\nabla\rho}{\rho}\right) = -\nabla\kappa\times\nabla P. \tag{3.20.11}$$

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

$$\begin{aligned}
0 &= \nabla\kappa\times\nabla P\cdot\mathbf{n} = \left(\nabla_n\kappa + \kappa_z\mathbf{n}\right)\times\left(\nabla_n P + P_z\mathbf{n}\right)\cdot\mathbf{n} \\
&= \nabla_n\kappa\times\nabla_n P\cdot\mathbf{n} = \nabla_n\kappa\times\nabla_n P\cdot\mathbf{k} = \left(\kappa_{S_A}\nabla_n S_A + \kappa_{\Theta}\nabla_n\Theta\right)\times\nabla_n P\cdot\mathbf{k} \quad (3.20.12) \\
&= T_b^{\Theta}\nabla_n P\times\nabla_n\Theta\cdot\mathbf{k} = gN^{-2}H^n,
\end{aligned}$$

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 $\kappa_{S_A} = \beta_P^{\Theta}$ 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

$$g^{-1}N^2\,\nabla_n\ln b\times\left(-\nabla_n z + \mathbf{k}\right) = -P_z\nabla_p\kappa\times\left(-\nabla_p z + \mathbf{k}\right), \tag{3.20.13}$$

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

$$\boxed{\nabla_n\ln b = \rho g^2 N^{-2}\nabla_p\kappa = -\rho g^2 N^{-2}\left(\alpha_P^{\Theta}\nabla_p\Theta - \beta_P^{\Theta}\nabla_p S_A\right).} \tag{3.20.14}$$

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 $b\left(\beta^{\Theta}\nabla S_A - \alpha^{\Theta}\nabla\Theta\right) \approx \nabla\ln\gamma$ 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

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

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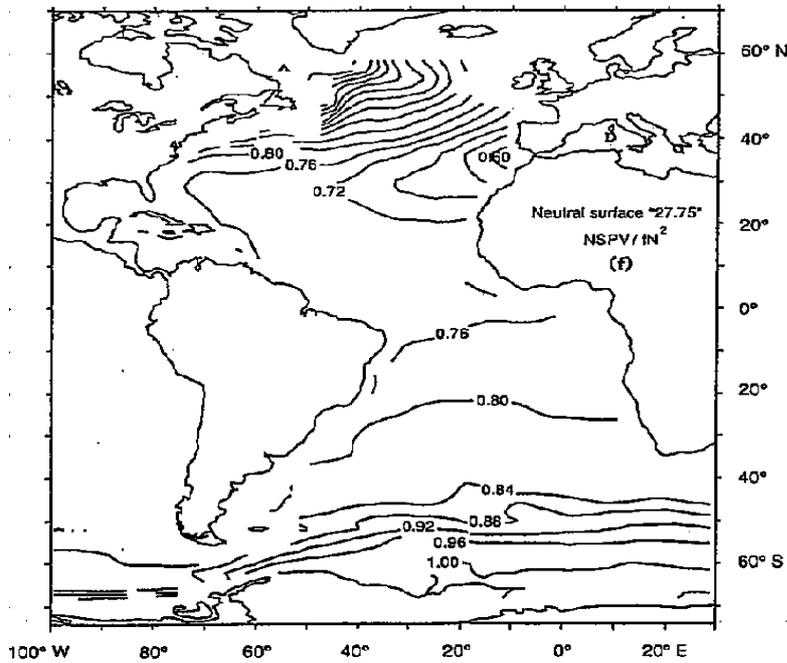
Figure. Map of NSPV versus fN².   Plot of the ratio of NSPV to fN^2 on a Neutral Density surface in the Atlantic.

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.
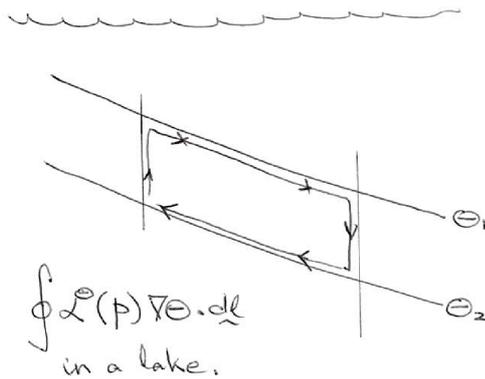

Figure. NSPV versus fN² in a lake.   Because the thermal expansion coefficient is a function of pressure, the vertical integral of N^2 on the two vertical parts of the closed loop are not equal, even in a lake.

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))

$$\frac{IPV}{fN^2} \equiv \frac{-g\rho^{-1}\rho_z^{\Theta}}{N^2} = \frac{\beta^{\Theta}(p_r)}{\beta^{\Theta}(p)}\frac{\left[R_\rho/r-1\right]}{\left[R_\rho-1\right]} = \frac{\beta^{\Theta}(p_r)}{\beta^{\Theta}(p)}\frac{1}{G^{\Theta}} \approx \frac{1}{G^{\Theta}}, \qquad (3.20.17)$$

so that the ratio of $NSPV$ to IPV, evaluated on an approximately neutral surface, is

$$\frac{NSPV}{IPV} = \frac{\beta^{\Theta}(p)}{\beta^{\Theta}(p_r)}\frac{\left[R_\rho-1\right]}{\left[R_\rho/r-1\right]} \exp\left\{\int_{ans} g^2 N^{-2}\nabla_P(\rho\kappa)\cdot d\boldsymbol{l}\right\}. \qquad (3.20.18)$$

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}.
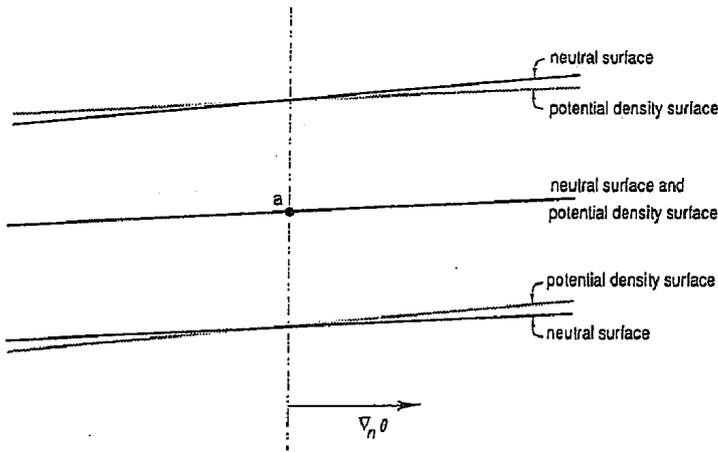

Fig. 14. A vertical cross section through three neutral surfaces and three potential density surfaces. The reference pressure of the potential density is the pressure of the central point, a. The neutral surface and potential density surface that pass though this point are parallel. The slopes of the 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

$$m_{SW}^f = m_{SW}^i + m_{Ih} , \qquad \qquad \text{(Entropy\_1)}$$

$$m_{SW}^f S_A^f = m_{SW}^i S_A^i , \qquad \qquad \text{(Entropy\_2)}$$

$$m_{SW}^f h^f = m_{SW}^i h^i + m_{Ih} h^{Ih} . \qquad \qquad \text{(Entropy\_3)}$$

$$m_{SW}^f \eta^f = m_{SW}^i \eta^i + m_{Ih} \eta^{Ih} + m_{Ih} \delta\eta . \qquad \qquad \text{(Entropy\_4)}$$

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 $m_{SW}^f \delta\eta$, 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 $m_{Ih} \delta\eta$, 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,

$$\left(S_A^f - S_A^i \right) = -\frac{m_{Ih}}{m_{SW}^f} S_A^i = -w^{Ih} S_A^i , \qquad \qquad \text{(Entropy\_5)}$$

$$\left(h^f - h^i \right) = -w^{Ih} \left(h^i - h^{Ih} \right), \qquad \qquad \text{(Entropy\_6)}$$

$$\left(\eta^f - \eta^i \right) = -w^{Ih} \left(\eta^i - \eta^{Ih} \right) + w^{Ih} \delta\eta , \qquad \qquad \text{(Entropy\_7)}$$

where we have defined the mass fraction of melted ice Ih m_{Ih}/m_{SW}^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, $\delta\eta$,

$$\boxed{\delta\eta \;=\; \frac{\left(\eta^{\mathrm{f}} - \eta^{\mathrm{i}}\right)}{w^{\mathrm{Ih}}} \;+\; \left(\eta^{\mathrm{i}} - \eta^{\mathrm{Ih}}\right)}. \qquad\qquad \text{(Entropy\_8)}$$

Another way of expressing this uses Eqn. (Entropy_6) to arrive at

$$\boxed{\delta\eta = -\left(\eta^{\mathrm{f}} - \eta^{\mathrm{i}}\right)\frac{\left(h^{\mathrm{i}} - h^{\mathrm{Ih}}\right)}{\left(h^{\mathrm{f}} - h^{\mathrm{i}}\right)} + \left(\eta^{\mathrm{i}} - \eta^{\mathrm{Ih}}\right)}. \qquad\qquad \text{(Entropy\_9)}$$

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

$$\begin{aligned}
\eta^{\mathrm{f}} - \eta^{\mathrm{i}} \;=\;& \breve{\eta}_{S_{\mathrm{A}}}\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right) + \breve{\eta}_{h}\left(h^{\mathrm{f}} - h^{\mathrm{i}}\right) \\
& + \tfrac{1}{2}\breve{\eta}_{S_{\mathrm{A}}S_{\mathrm{A}}}\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right)^{2} + \breve{\eta}_{hS_{\mathrm{A}}}\left(S_{\mathrm{A}}^{\mathrm{f}} - S_{\mathrm{A}}^{\mathrm{i}}\right)\left(h^{\mathrm{f}} - h^{\mathrm{i}}\right) + \tfrac{1}{2}\breve{\eta}_{hh}\left(h^{\mathrm{f}} - h^{\mathrm{i}}\right)^{2} + \text{h.o.t.,}
\end{aligned}$$

$$\text{(Entropy\_10)}$$

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))

$$\delta \eta = -\breve{\eta}_{S_A} S_A^i - \breve{\eta}_h \left(h^i - h^{Ih} \right) + \left(\eta^i - \eta^{Ih} \right)$$
$$+ w^{Ih} \left[\tfrac{1}{2} \breve{\eta}_{S_A S_A} \left(S_A^i \right)^2 + \breve{\eta}_{h S_A} S_A^i \left(h^i - h^{Ih} \right) + \tfrac{1}{2} \breve{\eta}_{hh} \left(h^i - h^{Ih} \right)^2 \right] + \text{h.o.t.}$$

(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 $\left(S_A^i, h^i, p \right)$.

From the Fundamental Thermodynamic Relation, $dh - v dP = (T_0 + t) d\eta + \mu dS_A$, we note that the partial derivatives of specific entropy that appear in Eqn. (Entropy_11) are given by

$$\breve{\eta}_{S_A} = -\mu/T \quad \text{and} \quad \breve{\eta}_h = 1/T, \quad\quad\quad \text{(Entropy\_12a,b)}$$

where $T = T_0 + t$ is the Absolute Temperature and μ is the relative chemical potential of seawater. Substituting these expressions for $\breve{\eta}_{S_A}$ and $\breve{\eta}_h$ into Eqn. (Entropy_11) gives

$$\delta \eta = \frac{\mu^i}{T^i} S_A^i - \frac{1}{T^i} \left(h^i - h^{Ih} \right) + \left(\eta^i - \eta^{Ih} \right)$$
$$+ w^{Ih} \left[\tfrac{1}{2} \breve{\eta}_{S_A S_A} \left(S_A^i \right)^2 + \breve{\eta}_{h S_A} S_A^i \left(h^i - h^{Ih} \right) + \tfrac{1}{2} \breve{\eta}_{hh} \left(h^i - h^{Ih} \right)^2 \right] + \text{h.o.t.}$$

(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 $h = g - T g_T$, and the enthalpy of ice Ih is given in term of the Gibbs function of ice Ih by $h^{Ih} = g^{Ih} - T^{Ih} g_T^{Ih}$. Correspondingly, the entropies of seawater and of ice Ih are the negatives of their respective temperature derivatives, that is, $\eta = -g_T$ and $\eta^{Ih} = -g_T^{Ih}$. Also, the relative chemical potential of seawater μ is the derivative of the Gibbs function of seawater with respect to Absolute Salinity, $\mu = g_{S_A}$, the chemical potential of ice Ih is $\mu^{Ih} = g^{Ih}$ and the chemical potential of water in seawater is $\mu^W = g - S_A g_{S_A} = g - S_A \mu$. Considering the case where the mass fraction of ice tends to zero, the right-hand side of Eqn. (Entropy_13) becomes

$$\left. \delta \eta \right|_{w^{Ih} \to 0} = \frac{\mu^i}{T^i} S_A^i - \frac{1}{T^i} \left(h^i - h^{Ih} \right) + \left(\eta^i - \eta^{Ih} \right)$$
$$= \frac{1}{T^i} \left(g^{Ih} - g^i + \mu^i S_A^i \right) - \eta^{Ih} \left(1 - \frac{T^{Ih}}{T^i} \right)$$
$$= \frac{1}{T^i} \left(\mu^{Ih} - \mu^{Wi} - \eta^{Ih} \left[T^i - T^{Ih} \right] \right).$$

(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 $w^{Ih} \to 0$ 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 $g^{\text{Ih}} - g^{\text{i}} + \mu^{\text{i}} S_{\text{A}}^{\text{i}}$ 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 $\left[T^{\text{i}} - T^{\text{Ih}} \right] \to 0$, and since both $\left(\mu^{\text{Ih}} - \mu^{\text{Wi}} \right) \to 0$ and $w^{\text{Ih}} \to 0$ in this limit, we see by combing Eqns. (Entropy_13) and (Entropy_14) that $\delta\eta \to 0$.

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 $S_{\text{A}} = S_{\text{SO}} = 35.16504 \text{ g kg}^{-1}$ at $p = 0 \text{ dbar}$ in both Figures Ice_16 and Ice_17. As noted above, as $w^{\text{Ih}} \to 0$, Eqn. (Entropy_9) and Eqn. (Entropy_14) give the same results for $\delta\eta$.

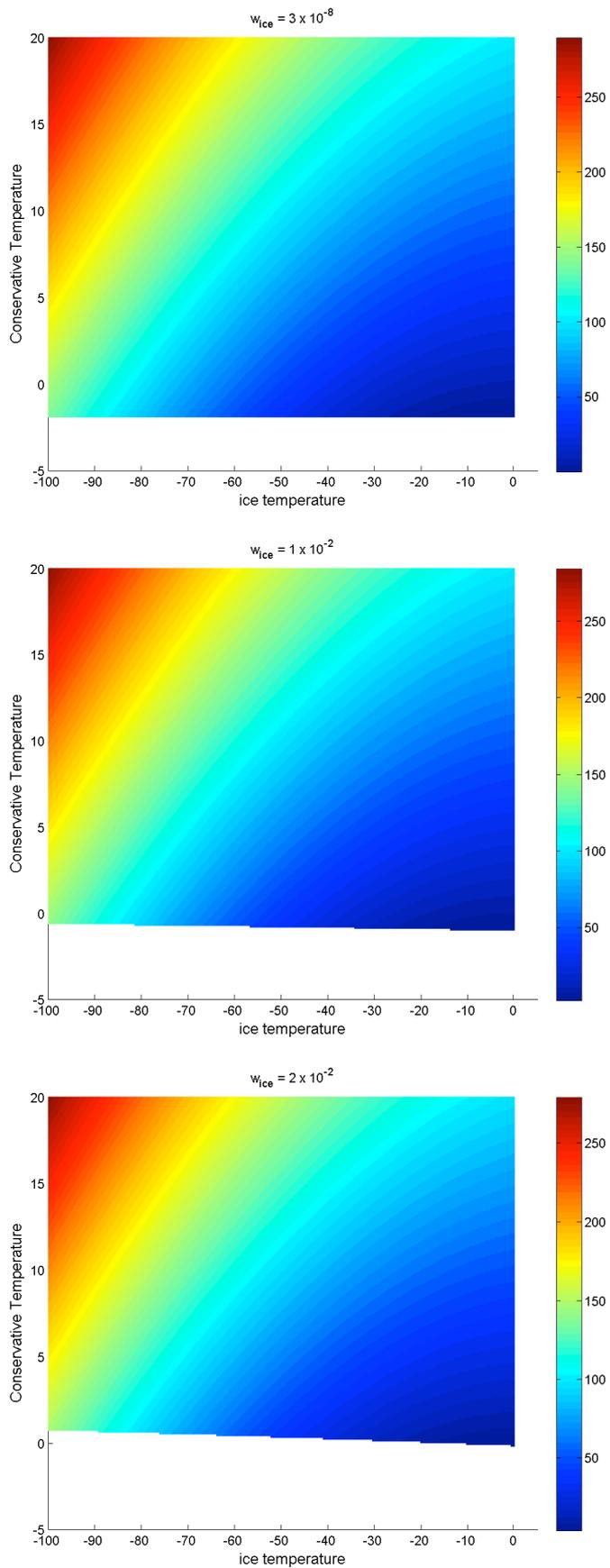**Figure Ice_16.**   The production of entropy ($J\ K^{-1}\left(kg\ ice\ Ih\right)^{-1}$) from Eqn. (Entropy_9) for three different values of w^{Ih} and for $S_A = S_{SO} = 35.16504\ g\ kg^{-1}$ at $p = 0\ dbar$.
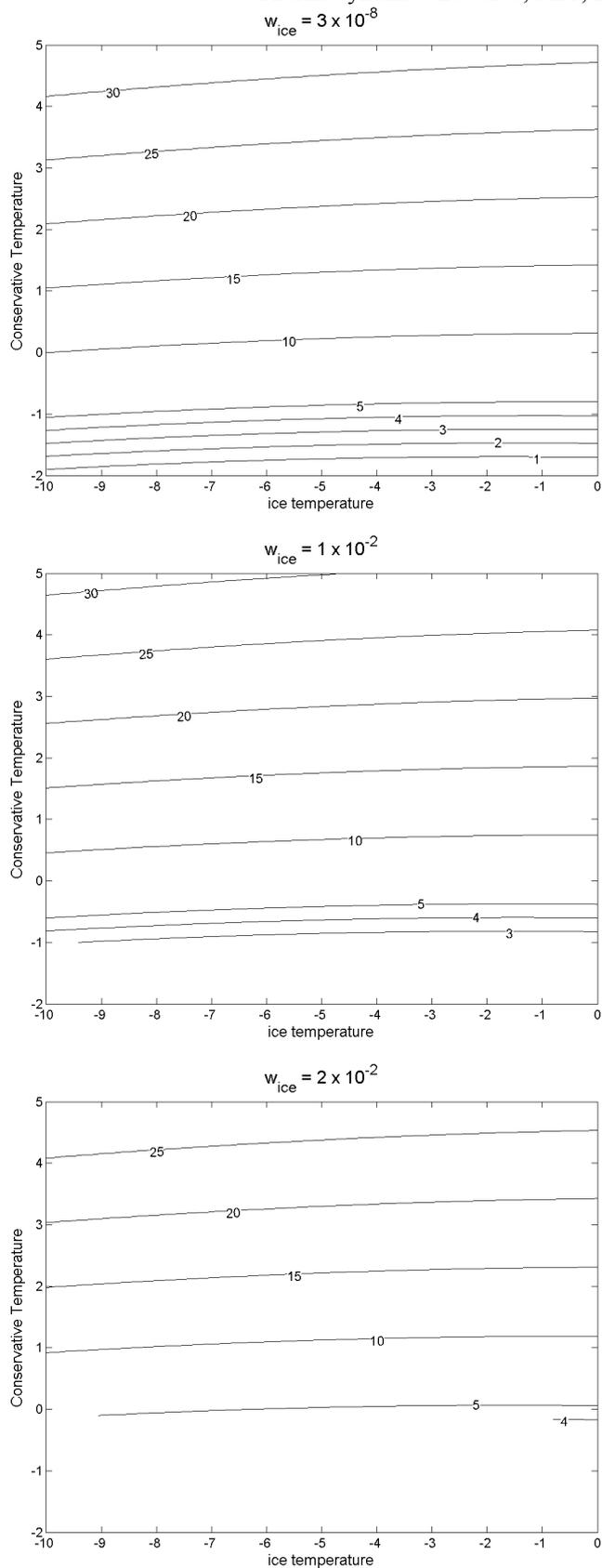
Figure Ice_17.   The production of entropy $\left(\mathrm{J\ K^{-1}\left(kg\ ice\ Ih\right)^{-1}}\right)$ from Eqn. (Entropy_9) for three different values of w^{Ih} and for $S_{\mathrm{A}} = S_{\mathrm{SO}} = 35.16504\ \mathrm{g\ kg^{-1}}$ at $p = 0\ \mathrm{dbar}$. This is the same as Figure Ice_16, 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 <u>linearly</u> 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,

$$\delta \eta \;=\; -\tfrac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \breve{\eta}_{hh} \left(\Delta h \right)^2 + 2 \breve{\eta}_{hS_A} \, \Delta h \, \Delta S_A + \breve{\eta}_{S_A S_A} \left(\Delta S_A \right)^2 \right\}, \qquad (\text{A.16.6})$$

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,

$$\rho \frac{\mathrm{d}\eta}{\mathrm{d}t} = \left(\rho\eta \right)_t + \nabla\cdot\left(\rho\mathbf{u}\eta \right) \;=\; -\nabla\cdot\left(\frac{1}{T}\mathbf{F}^Q - \frac{\mu}{T}\mathbf{F}^S \right)$$
$$+ \, \mathbf{F}^Q \cdot \nabla\left(\frac{1}{T} \right) + \mathbf{F}^S \cdot \nabla\left(\frac{-\mu}{T} \right). \qquad (\text{B.24})$$

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

$$\left[\frac{\left(h^{\mathrm{i}} - h^{\mathrm{Ih}} \right)}{\left(T^{\mathrm{i}} \right)^2} + \left(\frac{\mu^{\mathrm{i}}}{T^{\mathrm{i}}} \right)_T S_A^{\mathrm{i}} \right] \left[T^{\mathrm{i}} - T_{\mathrm{freeze}} \right] + ...$$

$$= \; \left[h^{\mathrm{i}} - h^{\mathrm{Ih}} - S_A^{\mathrm{i}} h_{S_A}^{\mathrm{i}} \right] \frac{\left[T^{\mathrm{i}} - T_{\mathrm{freeze}} \right]}{\left(T^{\mathrm{i}} \right)^2} + ... \qquad (\text{Entropy\_15})$$

The enthalpy flux $\left[h^{\mathrm{i}} - h^{\mathrm{Ih}} - S_A^{\mathrm{i}} h_{S_A}^{\mathrm{i}} \right]$, 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.