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Fundamentals

This first chapter reviews the fundamental principles of fluid mechanics, emphasizing the relationship between the underlying *microscopic description* of the fluid as a swarm of molecules, and the much more useful (but less genuine) *macroscopic description* as a set of continuous fields. Although it is certainly possible to study fluids without recognizing their true particulate nature, such an approach avoids important ideas about averaging that are needed later on, especially in the study of turbulence. It is best to encounter these ideas at the earliest opportunity.

Moreover, even if one adopts a strictly macroscopic viewpoint, as we eventually shall, one still has the choice between *Eulerian* and *Lagrangian* field theories. The Eulerian theory is the more useful and succinct, and most textbooks employ it exclusively. However, the Lagrangian theory, which regards the fluid as a *continuous field of particles*, is the more complete and illuminating, and it represents a natural extension of the ideas associated with the underlying molecular dynamics to the macroscopic level of description.

All fluids are composed of molecules. We shall regard these molecules as *point masses* that exactly obey Newton's laws of motion. This assumption is not precisely correct; the molecular motions are really governed by quantum mechanics. However, quantum effects are frequently unimportant, and the main ideas we want to develop are anyway independent of the precise nature of the underlying molecular dynamics. It only matters that there *be* an exact underlying molecular dynamics, so that one could *in principle* predict the behavior of the whole fluid by solving the equations governing all of its molecules.

It is of course utterly impractical to follow the motion of every molecule, because even the smallest volume of fluid contains an immense number of molecules. We are immediately forced to consider dynamical quantities that represent averages over many molecules. For example, the *velocity* $\mathbf{v}(x,y,z,t)$ at location (x,y,z) and time t is defined as a mass-weighted average,

$$\mathbf{v}(x,y,z,t) = \frac{\sum_i m_i \mathbf{v}_i}{\sum_i m_i}, \tag{0.1}$$

in which the sums run over all the molecules in a small volume δV centered on (x,y,z). Here, m_i is the mass of the i-th molecule, and $\mathbf{v}_i(t)$ is its velocity. However, the definition (0.1) makes sense only if the volume δV is neither too large nor too small. If δV is too small, then it contains too few molecules to give a meaningful average. If, on the other hand, δV is too large, then the average (0.1) smoothes out significant features of the velocity field. In fact, the definition (0.1) makes sense only if $\mathbf{v}(x,y,z,t)$ is independent of the size of δV for a considerable range of sizes, that is, only if the smallest scale L over which the velocity field varies appreciably is much larger than the average separation λ between molecules,

$$\lambda << L. \tag{0.2}$$

In the ocean, L is typically several millimeters or more, while λ is only about 10^{-8} cm. Thus seawater easily satisfies the necessary condition (0.2) for (0.1) to make sense. We shall see that condition (0.2) recurs frequently as we attempt to derive equations for $\mathbf{v}(x,y,z,t)$ and the other macroscopic fields.

There are two general methods for deriving the equations governing macroscopic variables like $\mathbf{v}(x,y,z,t)$. The first, which we shall call the *averaging method,* is by direct averaging of the equations governing the point masses. Unfortunately, this method leads to equations that are exact but mathematically unclosed until further assumptions are invoked. These further assumptions require the methods of kinetic theory and non-equilibrium statistical mechanics.

The second general method is the more traditional. It treats the fluid as if it really were a continuous distribution of mass in space, and it derives the macroscopic equations *by analogy* with the equations for point masses. The success of this second general method can be gauged by the fact that fluid mechanics was a highly developed subject long before the existence of atoms and molecules was generally accepted, at the beginning of the twentieth century. For the most part, we shall follow the traditional method, although the analogy with particle mechanics will be even closer than in the usual presentation. However, we shall also follow the averaging method for a way, in order to appreciate the fundamental difficulties that arise when an exact but complicated dynamics is "simplified" by averaging. We shall encounter these same fundamental difficulties in our later study of turbulence, where they cannot be so easily circumvented.

1. *Eulerian and Lagrangian descriptions*

For the moment, then, we regard our fluid as a *continuum* — a continuous distribution of mass in space. There are two common descriptions of continuum motion. In the *Eulerian description*, the independent variables are the space coordinates $\mathbf{x}=(x,y,z)$ and the time t. The dependent variables include the velocity $\mathbf{v}(x,y,z,t)$, the mass density $\rho(x,y,z,t)$, and the pressure $p(x,y,z,t)$.

In the *Lagrangian description*, the independent variables are a set of *particle labels* $\mathbf{a}=(a,b,c)$, and the time $\tau=t$. The dependent variables are the coordinates

$$x(a,b,c,\tau), \quad y(a,b,c,\tau), \quad z(a,b,c,\tau), \tag{1.1}$$

at time τ, of the fluid particle identified by (a,b,c). The particle labels vary continuously throughout the fluid, but the values of (a,b,c) on each fluid particle remain fixed as the fluid particle moves from place to place. By *fluid particle* we now mean a tiny piece of the imaginary continuum, not a molecule!

The time derivative $\partial/\partial\tau$ is taken with (a,b,c) held fixed. Similarly $\partial/\partial t$ implies that (x,y,z) are held fixed. Thus $\partial F/\partial\tau$ is the rate of change in (arbitrary quantity) F measured by an observer following a fluid particle. In other words,

$$\frac{\partial F}{\partial\tau} \equiv \frac{DF}{Dt} \tag{1.2}$$

is the usual substantial derivative.

We can think of a label space with coordinates (a,b,c), and a location space with coordinates (x,y,z). Then the fluid motion (1.1) is a time-dependent mapping between these two spaces. Alternatively, we can think of the label variables (a,b,c) as curvilinear coordinates in location space. The fluid motion drags these curvilinear coordinates through location space.

The label variables (a,b,c) can be arbitrarily assigned. Commonly, the $\mathbf{a}$ are defined to be the $\mathbf{x}$-location of the corresponding fluid particle at a reference time $\tau=0$. We shall make a different, more convenient definition. But no matter how defined, each fluid particle keeps the same values of (a,b,c) for all time.

The derivatives with respect to Eulerian and Lagrangian coordinates are related by the chain rule. For example,

$$\frac{\partial F}{\partial\tau} = \frac{\partial F}{\partial t}\frac{\partial t}{\partial\tau} + \frac{\partial F}{\partial x}\frac{\partial x}{\partial\tau} + \frac{\partial F}{\partial y}\frac{\partial y}{\partial\tau} + \frac{\partial F}{\partial z}\frac{\partial z}{\partial\tau}, \tag{1.3}$$

for any quantity F that can be regarded as a function of (x,y,z,t) or (a,b,c,τ). But the substantial derivatives of (x,y,z) are, by definition, the components of the velocity,

$$\mathbf{v} \equiv \left(\frac{\partial x}{\partial\tau},\frac{\partial y}{\partial\tau},\frac{\partial z}{\partial\tau}\right) \equiv (u,v,w). \tag{1.4}$$

Thus (1.3) becomes

$$\frac{\partial F}{\partial\tau} = \frac{\partial F}{\partial t} + u\frac{\partial F}{\partial x} + v\frac{\partial F}{\partial y} + w\frac{\partial F}{\partial z} = \frac{\partial F}{\partial t} + \mathbf{v}\cdot\nabla F. \tag{1.5}$$

Eqn. (1.5) is the familiar formula for the substantial derivative.

2. *Mass conservation*

We can assign the labeling coordinates (a,b,c) so that

$$dV_{abc} = d(mass), \tag{2.1}$$

where $dV_{abc} = da\, db\, dc$ is an infinitesimal volume in **a**-space, and *d(mass)* is the enclosed mass.[1] Since the labeling coordinates move with the fluid, (2.1) holds at all subsequent times. By definition,

$$d(mass) = \rho\, dV_{xyz}, \tag{2.2}$$

where ρ is the mass density, and $dV_{xyz} = dx\, dy\, dz$ is the volume in **x**-space corresponding to dV_{abc}. Thus, remembering that

$$\frac{dV_{abc}}{dV_{xyz}} = \frac{\partial(a,b,c)}{\partial(x,y,z)}, \tag{2.3}$$

we find that

$$\rho = \frac{\partial(a,b,c)}{\partial(x,y,z)} \equiv \frac{\partial(\mathbf{a})}{\partial(\mathbf{x})}. \tag{2.4}$$

Eqns. (1.4) and (2.4) define the Eulerian dependent variables $\mathbf{v}(\mathbf{x},t)$ and $\rho(\mathbf{x},t)$ in terms of the Lagrangian dependent variables $\mathbf{x}(\mathbf{a},\tau)$. The corresponding definition of $p(\mathbf{x},t)$ will emerge later on.

Next, define the *specific volume*

$$\alpha \equiv \frac{1}{\rho} = \frac{\partial(x,y,x)}{\partial(a,b,c)} \equiv \frac{\partial(\mathbf{x})}{\partial(\mathbf{a})}. \tag{2.5}$$

The substantial derivative of (2.5) is

$$\begin{aligned}
\frac{\partial\alpha}{\partial\tau} &= \frac{\partial}{\partial\tau}\frac{\partial(x,y,z)}{\partial(a,b,c)} \\
&= \frac{\partial(u,y,z)}{\partial(a,b,c)} + \frac{\partial(x,v,z)}{\partial(a,b,c)} + \frac{\partial(x,y,w)}{\partial(a,b,c)} \\
&= \alpha\left[\frac{\partial(u,y,z)}{\partial(x,y,z)} + \frac{\partial(x,v,z)}{\partial(x,y,z)} + \frac{\partial(x,y,w)}{\partial(x,y,z)}\right] \\
&= \alpha\left[\frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z}\right].
\end{aligned} \tag{2.6}$$

That is,

$$\frac{D\alpha}{Dt} = \alpha\nabla\cdot\mathbf{v}. \tag{2.7}$$

We can rewrite (2.7) in the more familiar form,

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \mathbf{v} = 0. \tag{2.8}$$

Thus the usual equation for mass conservation results from our requirement that fixed volumes in (a,b,c)-space always contain the same mass.

To complete our continuum equations, we need an equation for the conservation of momentum. For this, we adopt the somewhat unusual approach of invoking Hamilton's principle of least action. This approach has several of advantages over the more standard derivation. Here we mention only two. First, the Hamiltonian derivation demonstrates the strength of the analogy between continuum mechanics and particle mechanics. Second, mechanics and thermodynamics enter the Hamiltonian formulation on the same footing: In both cases, we prescribe the dynamics by specifying how energy depends on variables that define the state of the system. The resulting forces — both mechanical and thermodynamic— are then the derivatives of the energy with respect to these variables. Only entropy and the concept of thermodynamic equilibrium separate thermodynamics from mechanics.

The following two sections offer a very brief review of Hamiltonian particle mechanics.[2]

3. *Functionals and variational principles*

A functional is a number that depends on the values taken by a function within some range of its argument. For example, let $x(t)$ be any function defined on $t_1<t<t_2$. Then

$$F[x(t)] = \tfrac{1}{2}\int_{t_1}^{t_2} \left\{ \left(\frac{dx}{dt}\right)^2 - x^2 \right\} dt \tag{3.1}$$

is a functional depending on $x(t)$.

The *calculus of variations* addresses the following question: For what functions $x(t)$ is the functional $F[x(t)]$ stationary? More precisely: For what $x(t)$ is F unchanged by small, arbitrary changes in $x(t)$ that vanish at $t=t_1$ and t_2 ?

Suppose that $x(t)$ is changed to $x(t)+\delta x(t)$, where $\delta x(t)$ is everywhere small, and $\delta x(t_1)=\delta x(t_2)=0$. Then F changes from (3.1) to

$$\begin{aligned} &\tfrac{1}{2}\int_{t_1}^{t_2} \left\{ \left(\frac{dx}{dt} + \frac{d\delta x}{dt}\right)^2 - (x+\delta x)^2 \right\} dt \\ &\approx \tfrac{1}{2}\int_{t_1}^{t_2} \left\{ \left(\frac{dx}{dt}\right)^2 + 2\frac{dx}{dt}\frac{d\delta x}{dt} - x^2 - 2x\delta x \right\} dt \end{aligned} \tag{3.2}$$

where terms of order $(\delta x)^2$ have been neglected. The change in F is therefore

$$\delta F = \int_{t_1}^{t_2} \left\{ \frac{dx}{dt}\frac{d\delta x}{dt} - x\,\delta x \right\} dt = \int_{t_1}^{t_2} \left\{ -\frac{d^2x}{dt^2} - x \right\} \delta x \, dt \,, \tag{3.3}$$

after integration by parts. For F to be stationary, δF must be zero. But since $\delta x(t)$ is arbitrary, its coefficient in the integrand of (3.3) must vanish. Therefore

$$\frac{d^2x}{dt^2} + x = 0 \,, \tag{3.4}$$

and only those $x(t)$ satisfying (3.4) correspond to stationary values of F. The differential equation (3.4) is said to be equivalent to the *variational principle* $\delta F=0$.

4. *Hamilton's principle for point masses*

Now consider a system composed of N point-particles with masses m_i ($i=1$ to N) and locations $\mathbf{x}_i(t)$. Let $V(\mathbf{x}_1, \ldots ,\mathbf{x}_N)$ be the potential energy of the system. If, for example, the N point masses all have equal electric charge q, then

$$V = \sum_{i>j} \frac{q^2}{\left|\mathbf{x}_i - \mathbf{x}_j\right|}. \tag{4.1}$$

Whatever V, Newton's law of motion is

$$m_i \frac{d^2\mathbf{x}_i}{dt^2} = -\frac{\partial V}{\partial \mathbf{x}_i}\,. \tag{4.2}$$

Hamilton's principle is the variational principle equivalent to Newton's law. It states that the *action*

$$A \equiv \int_{t_1}^{t_2} L\,dt, \tag{4.3}$$

is stationary, where the *Lagrangian*

$$L \equiv T - V \,, \tag{4.4}$$

is the difference between the kinetic energy T and the potential energy V of the system. For the collection of point masses,

$$T = \tfrac{1}{2} \sum_i m_i \frac{d\mathbf{x}_i}{dt} \cdot \frac{d\mathbf{x}_i}{dt} \,, \tag{4.5}$$

where the summation runs over all the molecules. Hamilton's principle thus states that

$$0 = \delta\int_{t_1}^{t_2}\left\{\tfrac{1}{2}\sum_i m_i \frac{d\mathbf{x}_i}{dt}\cdot\frac{d\mathbf{x}_i}{dt} - V\right\}dt \tag{4.6}$$

for arbitrary, independent variations $\{\delta x_i(t),\delta y_i(t),\delta z_i(t)\}$ that vanish at t_1 and t_2. Since $\delta\mathbf{x}_i(t_1)=\delta\mathbf{x}_i(t_2)=0$, (4.6) implies that

$$0 = \int_{t_1}^{t_2}\left\{-m_j\frac{d^2\mathbf{x}_j}{dt^2} - \frac{\partial V}{\partial \mathbf{x}_j}\right\}\cdot\delta\mathbf{x}_j\,dt\ , \tag{4.7}$$

for all j. Newton's law (4.2) then follows by the arbitrariness of $\delta\mathbf{x}_j(t)$.

5. *Hamilton's principle for a barotropic fluid*

The only difference between the system of point masses and the fluid continuum is that, in the continuum, the mass is distributed continuously in space. Therefore, we must replace

$$\sum_i m_i \tag{5.1}$$

by

$$\iiint d(mass) = \iiint da\,db\,dc\ , \tag{5.2}$$

and (4.5) becomes

$$T = \tfrac{1}{2}\iiint da\,db\,dc\,\frac{\partial\mathbf{x}}{\partial\tau}\cdot\frac{\partial\mathbf{x}}{\partial\tau}\,. \tag{5.3}$$

In the fluid, the potential energy arises from external and interparticle forces that depend only on the particle locations $\mathbf{x}(a,b,c,\tau)$. The simplest assumption is that these particle locations enter the potential energy V in the special form

$$V = \iiint da\,db\,dc\ \{E(\alpha) + \phi(\mathbf{x})\}, \tag{5.4}$$

where

$$\alpha \equiv \frac{1}{\rho} = \frac{\partial(x,y,z)}{\partial(a,b,c)} \tag{5.5}$$

is the specific volume, and the *specific internal energy* $E(\alpha)$ and *external potential* $\phi(\mathbf{x}(\mathbf{a},\tau))$ are prescribed functions of their respective arguments. That is, the internal energy E depends only on the amount by which the fluid has been compressed (as measured by the Jacobian (5.5)) and the external potential ϕ, typically representing gravity, depends only on the fluid-particle locations $\mathbf{x}(\mathbf{a},\tau)$ (and not, say, on their derivatives). The precise form of $E(\alpha)$ depends on the type of fluid being considered. We shall show that Hamilton's principle and the hypothesis (5.4) with given $E(\alpha)$ and $\phi(\mathbf{x})$, yield the momentum equation for an ideal (barotropic) fluid.

According to Hamilton's principle, the action

$$\begin{aligned}&\int d\tau\,(T-V)=\\&\int d\tau\iiint d\mathbf{a}\left[\tfrac{1}{2}\frac{\partial\mathbf{x}}{\partial\tau}\cdot\frac{\partial\mathbf{x}}{\partial\tau}-E\left(\frac{\partial(\mathbf{x})}{\partial(\mathbf{a})}\right)-\phi(\mathbf{x}(\mathbf{a},\tau))\right]\end{aligned}\tag{5.6}$$

must be stationary with respect to arbitrary variations $\delta\mathbf{x}(a,b,c,\tau)$ in the locations of the fluid particles. The integral in (5.6) is over the whole mass of the fluid, a fixed volume in **a**-space. We suppose that the fluid has two kinds of boundaries: rigid boundaries, with outward unit normal $\mathbf{n}$, at which the fluid velocity in the normal direction must vanish ($\partial\mathbf{x}/\partial\tau\cdot\mathbf{n}=0$), and at which the fluid-particle variations are correspondingly constrained ($\delta\mathbf{x}\cdot\mathbf{n}=0$); and free-surface boundaries, at which $\delta\mathbf{x}$ is wholly unconstrained.

By direct calculation, the change in (5.6) produced by the variation $\delta\mathbf{x}(a,b,c,\tau)$ in the fluid-particle locations, is:

$$\begin{aligned}&\int d\tau\iiint d\mathbf{a}\left\{\frac{\partial\mathbf{x}}{\partial\tau}\cdot\frac{\partial\delta\mathbf{x}}{\partial\tau}-\frac{dE}{d\alpha}\delta\alpha-\frac{\partial\phi}{\partial\mathbf{x}}\cdot\delta\mathbf{x}\right\}\\&=\int d\tau\iiint d\mathbf{a}\left\{-\frac{\partial^2\mathbf{x}}{\partial\tau^2}\cdot\delta\mathbf{x}-\frac{dE}{d\alpha}\delta\frac{\partial(\mathbf{x})}{\partial(\mathbf{a})}-\frac{\partial\phi}{\partial\mathbf{x}}\cdot\delta\mathbf{x}\right\}\end{aligned}\tag{5.7}$$

But for any quantity F,

$$\begin{aligned}&\iiint d\mathbf{a}\ \ F\delta\frac{\partial(x,y,z)}{\partial(a,b,c)}\\&=\iiint d\mathbf{a}\ F\left[\frac{\partial(\delta x,y,z)}{\partial(a,b,c)}+\frac{\partial(x,\delta y,z)}{\partial(a,b,c)}+\frac{\partial(x,y,\delta z)}{\partial(a,b,c)}\right]\\&=\iiint d\mathbf{x}\ F\left[\frac{\partial(\delta x,y,z)}{\partial(x,y,z)}+\frac{\partial(x,\delta y,z)}{\partial(x,y,z)}+\frac{\partial(x,y,\delta z)}{\partial(x,y,z)}\right]\\&=\iiint d\mathbf{x}\ F\ \nabla\cdot\delta\mathbf{x}\end{aligned}\tag{5.8}$$

By the divergence theorem, this is

$$\iiint d\mathbf{x}\ [-\nabla F\cdot\delta\mathbf{x}]+\oiint dA\,[F\,\delta\mathbf{x}\cdot\mathbf{n}], \tag{5.9}$$

where the second term is an integration over the boundary of the fluid. Note, however, that the *rigid* portion of the boundary makes no contribution to this integral, because $\delta\mathbf{x}\cdot\mathbf{n}=0$ at rigid boundaries. Setting $F=-dE/d\alpha$, and using (5.8-9) in (5.7), we see that Hamilton's principle implies that

$$\iiint d\mathbf{x}\ \rho\left[-\frac{\partial^2\mathbf{x}}{\partial\tau^2}-\frac{\partial\phi}{\partial\mathbf{x}}-\frac{1}{\rho}\frac{\partial p}{\partial\mathbf{x}}\right]\cdot\delta\mathbf{x}+\oiint dA\ p\,\delta\mathbf{x}\cdot\mathbf{n}=0, \tag{5.10}$$

where

$$p\equiv-\frac{dE(\alpha)}{d\alpha}. \tag{5.11}$$

Then, remembering that $\delta\mathbf{x}$ is arbitrary, we conclude from (5.10) that

$$\frac{\partial^2\mathbf{x}}{\partial\tau^2}=-\frac{1}{\rho}\frac{\partial p}{\partial\mathbf{x}}-\frac{\partial\phi}{\partial\mathbf{x}}, \tag{5.12}$$

and that $p=0$ at the free-surface boundaries. From (5.12) we see that p must be the pressure. Then (5.11) agrees with a familiar equation from thermodynamics. According to (5.11), the pressure is positive if the fluid resists compression, that is, if energy must be supplied to reduce the volume.

6. *Nonhomentropic flow*

The assumption that the internal energy E increases only through compression is too restrictive. We know that the addition of heat can also increase the internal energy. The simplest conceivable generalization of $E=E(\alpha)$ is

$$E=E(\alpha,\eta) \tag{6.1}$$

where η is an additional parameter, which we call *specific entropy*. The differential of (6.1) is

$$\begin{aligned} dE&=\frac{\partial E(\alpha,\eta)}{\partial\alpha}d\alpha+\frac{\partial E(\alpha,\eta)}{\partial\eta}d\eta\\ &=-p\,d\alpha+T\,d\eta \end{aligned} \tag{6.2}$$

where now

$$p \equiv -\frac{\partial E(\alpha,\eta)}{\partial \alpha}, \tag{6.3}$$

and

$$T \equiv \frac{\partial E(\alpha,\eta)}{\partial \eta} \tag{6.4}$$

is the *temperature*. We recognize the term $-p\,d\alpha$ in (6.2) as the change in energy (per unit mass) caused by mechanical compression. It follows that $T\,d\eta$ must be the change in energy caused by heating. If no heat is added to the fluid or transferred between fluid particles, then $d\eta=0$, and the entropy of each fluid particle does not change. That is,

$$\eta = \eta(a,b,c), \quad \partial\eta/\partial\tau = 0\,. \tag{6.5}$$

We can then regard the entropy $\eta(a,b,c)$ as a *prescribed* function of the fluid-particle identity, determined by the initial conditions.

Since the entropy $\eta(a,b,c)$ is unaffected by changes in the dependence of $\mathbf{x}$ on $(\mathbf{a},\tau)$, Hamilton's principle,

$$0 = \delta \int d\tau \iiint d\mathbf{a} \left[\tfrac{1}{2}\frac{\partial \mathbf{x}}{\partial \tau}\cdot\frac{\partial \mathbf{x}}{\partial \tau} - E\left(\frac{\partial(\mathbf{x})}{\partial(\mathbf{a})}, \eta(\mathbf{a})\right) - \phi(\mathbf{x}(\mathbf{a},\tau)) \right] \tag{6.6}$$

yields the same momentum equation (5.12) as before, but with p defined as the partial derivative (6.3), with entropy held constant. Equations (6.3) and (6.4) agree with the usual thermodynamic definitions of pressure and temperature, respectively. However, it remains to be shown that the temperature defined by (6.4) has the properties associated with temperature.

The *existence* of a *fundamental relation* (6.1), at thermodyamic equilibrium, between E, α, and η is one of the basic postulates in the formulation of thermodynamics developed by Gibbs, Tisza, and Callen.[3] (We shall introduce the other postulates when we discuss molecular transport in Section 12.) Once again, the *form* of the fundamental relation (6.1) depends on the type of fluid under consideration, and cannot be determined from thermodynamics alone. By using the fundamental relation in the Lagrangian for a *moving* fluid, we are assuming *local thermodynamic equilibrium*, that is, that the variables E, α, and η, although changing in space and time, are locally related as they would be in exact thermodynamic equilibrium. This assumption can be true only if the time scale for molecular processes to bring the system into local equilibrium is much shorter than the time scale for macroscopic changes.

7. *Variable composition*

The assumption that E depends only on α and η is true only for a fluid of fixed chemical composition. Seawater is a dilute solution of ionic salts whose composition is specified by the concentrations of its ionic components. Let n_i be the *mass fraction* of component i, defined as the number of grams of i per gram of seawater. Since the n_i are generally different for different seawater particles, the fundamental relation for seawater takes the general form

$$E = E(\alpha,\eta,n_1,..n_N), \tag{7.1}$$

where N is the number of (important) components. The most important components of seawater are Cl^-, Na^{++}, $SO_4^=$ and Mg^{++}.

Measurements show that the mass fractions of the dissolved ions in seawater always have approximately the same ratio to one another. This is because the ionic concentrations change mainly by evaporation and precipitation at the sea surface, and these processes affect all the dissolved ions in the same way. Thus it is possible to specify the composition of seawater by a single parameter, the *salinity*,

$$S = n_1 + n_2 + \cdots + n_N. \tag{7.2}$$

The fundamental relation can therefore be written

$$E = E(\alpha,\eta,S). \tag{7.3}$$

If there is no molecular diffusion of salt,

$$S = S(a,b,c), \quad \partial S/\partial\tau = 0, \tag{7.4}$$

and each fluid particle conserves its salinity. Then, since $S(a,b,c)$, like $\eta(a,b,c)$, is unaffected by variations in the dependence of $\mathbf{x}$ on (a,b,c,τ), Hamilton's principle gives the same momentum equation (5.12) as before, but now with

$$p \equiv -\frac{\partial E(\alpha,\eta,S)}{\partial\alpha}. \tag{7.5}$$

Instead of (6.2) we now have

$$dE = -p\,d\alpha + T\,d\eta + \mu\,dS, \tag{7.6}$$

where

$$T \equiv \frac{\partial E(\alpha,\eta,S)}{\partial\eta} \tag{7.7}$$

is the temperature, and

$$\mu \equiv \frac{\partial E(\alpha,\eta,S)}{\partial S} \tag{7.8}$$

is the *chemical potential* of salt in seawater. In (7.6) the term μdS represents the internal energy change caused by a change dS in salinity, assuming no change in the specific volume or entropy.

Equations (7.5), (7.7) and (7.8) are called *equations of state*. The equation,

$$\rho = \rho(S,T,p), \tag{7.9}$$

obtained by eliminating the entropy η between (7.5) and (7.7), is also often called the *equation of state*. Note that all of (7.5-7.9) follow from the fundamental relation (7.3), which completely defines the thermodynamic equilibrium state of the fluid.

8. *Equations of motion for an ideal fluid*

Now we pause to collect our results. Our equations of motion are, apart from definitions, the result of applying Hamilton's principle to a hypothetical macroscopic continuum, whose internal energy (representing the energy stored in the otherwise ignored microscopic degrees of freedom) is *assumed* to be a prescribed function $E(\alpha,\eta,S)$ of the specific volume, entropy, and salinity. The latter two keep their same value on each moving fluid particle. In conventional notation, our equations are:

$$\begin{aligned} &\frac{D\rho}{Dt} + \rho\nabla\cdot\mathbf{v} = 0 \\ &\frac{D\mathbf{v}}{Dt} = -\alpha\nabla p - \nabla\phi \\ &p = -\frac{\partial E(\alpha,\eta,S)}{\partial\alpha} \\ &\frac{D\eta}{Dt} = 0 \\ &\frac{DS}{Dt} = 0. \end{aligned} \tag{8.1}$$

Eqns. (8.1), in which the molecular transports (*i.e.* diffusion) of momentum, heat, and salt are entirely missing, are the equations for an *ideal fluid*. If the fundamental relation $E=E(\alpha,\eta,S)$ is known (from laboratory measurements, say), then (8.1) form a complete set of seven (scalar) equations in the seven dependent variables $\rho=1/\alpha$, $\mathbf{v}$, p, η, and S. In this section, we rewrite (8.1) in several useful equivalent forms.

We can transform (8.1) into a more convenient form in several ways. By one method, we rearrange (8.1c) into the form

$$\rho = \rho(p,\eta,S)\,. \tag{8.2}$$

Then, taking the substantial derivative of (8.2) and using (8.1d,e), we obtain

$$\begin{aligned}\frac{D\rho}{Dt} &= \frac{\partial\rho}{\partial p}\frac{Dp}{Dt} + \frac{\partial\rho}{\partial\eta}\frac{D\eta}{Dt} + \frac{\partial\rho}{\partial S}\frac{DS}{Dt} \\ &= \frac{1}{c^2}\frac{Dp}{Dt}\end{aligned} \tag{8.3}$$

where

$$c^2 \equiv \frac{\partial p(\rho,\eta,S)}{\partial\rho}\,. \tag{8.4}$$

The quantity c turns out to be the speed of sound. The equations

$$\begin{aligned}&\frac{D\rho}{Dt} + \rho\nabla\cdot\mathbf{v} = 0 \\ &\frac{D\mathbf{v}}{Dt} = -\alpha\nabla p - \nabla\phi \\ &\frac{D\rho}{Dt} = \frac{1}{c^2}\frac{Dp}{Dt} \\ &\frac{DS}{Dt} = 0.\end{aligned} \tag{8.5}$$

form a complete set of equations, with $c(p,\rho,S)$ a prescribed function. Once again, the function $c(p,\rho,S)$ — and all other thermodynamic functions — are uniquely determined by the fundamental relation $E(\alpha,\eta,S)$. The reader should show, by linearizing (8.5), that c is indeed the sound speed.

Another formulation uses the temperature T as one of the dependent variables. This formulation is probably preferable if molecular transports are to be introduced later on. Eliminating the specific volume α between (7.5) and (7.7), we obtain

$$\eta = \eta(S,T,p)\,. \tag{8.6}$$

It follows that

$$0 = \frac{D\eta}{Dt} = \frac{\partial\eta}{\partial p}\frac{Dp}{Dt} + \frac{\partial\eta}{\partial T}\frac{DT}{Dt} + 0\,. \tag{8.7}$$

To put (8.7) in a neater form, we need to express its two thermodynamic partial derivatives in terms of tabulated quantities. Remembering that $Td\eta$ represents the increase in the internal energy per unit mass caused by heating, we see that

$$\frac{\partial\eta(S,T,p)}{\partial T} = \frac{C_p}{T}, \tag{8.8}$$

where C_p is the heat capacity at constant pressure (and salinity).

The other partial derivative in (8.7) can be simplified as follows:

$$\frac{\partial\eta(S,T,p)}{\partial p} = -\frac{\partial\alpha(S,T,p)}{\partial T} \equiv -\alpha\beta, \tag{8.9}$$

where β is the *coefficient of thermal expansion*. The first equality in (8.9) is one of Maxwell's thermodynamic relations. To prove it in the standard way, we rewrite (7.6) as

$$dG(S,T,p) \equiv d(E + p\alpha - T\eta) = \alpha\, dp - \eta\, dT + \mu\, dS \tag{8.10}$$

and require

$$\frac{\partial^2 G}{\partial T \partial p} = \frac{\partial^2 G}{\partial p \partial T}. \tag{8.11}$$

Substituting (8.8) and (8.9) into (8.7), we obtain another complete set of equations,

$$\begin{aligned}
&\frac{D\rho}{Dt} + \rho\nabla\cdot\mathbf{v} = 0 \\
&\frac{D\mathbf{v}}{Dt} = -\alpha\nabla p - \nabla\phi \\
&\rho = \rho(S,T,p) \\
&\frac{DT}{Dt} = \frac{\alpha\beta T}{C_p}\frac{Dp}{Dt} \\
&\frac{DS}{Dt} = 0
\end{aligned} \tag{8.12}$$

where (8.12c) is the equation of state, (7.9).

We often neglect the Dp/Dt-term in (8.12d). Let δT and δp be typical temperature and pressure differences in the flow of interest. Then the right-hand side of (8.12d) is negligible if

$$\delta T >> \frac{\alpha\beta T}{C_p}\delta p. \tag{8.13}$$

For the typical oceanic values,

$$T \approx 275 \text{ deg}, \qquad C_p \approx 1 \text{ cal gm}^{-1} \text{ deg}^{-1},$$
$$\alpha \approx 1 \text{cm}^3 \text{ gm}^{-1}, \qquad \beta \approx 2 \times 10^{-4} \text{ deg}^{-1}$$

this neglect is justified if

$$(\delta T \text{ in deg}) >> 1.3 \times 10^{-3} (\delta p \text{ in atmospheres}). \tag{8.14}$$

However, the condition (8.14) is certainly violated when seawater particles undergo pressure changes of hundreds of atmospheres with small temperature changes, as in the deep ocean. In fact, in the deep ocean, the most significant temperature changes are sometimes *caused* by pressure changes, via (8.12d).

A similar justification sometimes permits the neglect of Dp/Dt in (8.5c). The resulting approximation,

$$D\rho / Dt = 0\,, \tag{8.15}$$

bears a superficial resemblance to the mass conservation equation (8.5a), but it is nevertheless an approximation to (8.5c). Equation (8.15) can *never* be justified as an approximation to (8.5a).

9. *The method of averaging*

Now we start all over again, and re-derive the equations for macroscopic fluid motion by the first of the two general methods described at the beginning of the chapter — by averaging over molecular motions. The resulting equations are *exact* (apart from our assumption that the molecules obey Newton's law) but *mathematically unclosed* without further approximations. However, these exact equations automatically include the molecular transports of momentum, heat and salt omitted above.

Again we regard the fluid molecules as point masses, and let m_i be the mass at location $\mathbf{x}_i(t)$. The governing molecular equations are

$$m_i \frac{d^2\mathbf{x}_i}{dt^2} = -\frac{\partial V(\mathbf{x}_1, \ldots, \mathbf{x}_N)}{\partial \mathbf{x}_i}, \tag{9.1}$$

where V is the potential for intermolecular forces. The mass density at $(\mathbf{x},t)$ can be defined as an average over molecules, in the form

$$\rho(\mathbf{x},t) \equiv \sum_i m_i R(r_i), \qquad r_i \equiv |\mathbf{x}_i(t) - \mathbf{x}|, \tag{9.2}$$

where the summation is an estimate of the mass per unit volume near $\mathbf{x}$ at time t. Here, $R(r)$ is a *sampling function* that counts the molecules near $\mathbf{x}$. The simplest definition of R would be

$$R(r) = \begin{cases} \dfrac{1}{\left(\frac{4}{3}\pi r_0^{\,3}\right)}, & r < r_0 \\ 0 & r > r_0 \end{cases} \tag{9.3}$$

where r_0, the radius of the sampling sphere, is much larger than the average molecular molecular separation λ, but much smaller than the smallest scale L on which $\rho(\mathbf{x},t)$ varies significantly. However, it is more logical and convenient to define *R(r)* to be an infinitely differentiable function with the general shape sketched in Figure 1.1. The only rigid requirement is the normalization condition,

$$\iiint d\mathbf{x}\, R(\mathbf{x}) = 1. \tag{9.4}$$

The time derivative of (9.2) yields

$$\begin{aligned} \frac{\partial \rho(\mathbf{x},t)}{\partial t} &= \sum_i m_i \frac{\partial}{\partial t} R(r_i) \\ &= \sum_i m_i \left[\frac{\partial R(r_i)}{\partial \mathbf{x}_i} \cdot \frac{d\mathbf{x}_i(t)}{dt} \right] \\ &= \sum_i m_i \left[-\frac{\partial R(r_i)}{\partial \mathbf{x}} \cdot \frac{d\mathbf{x}_i(t)}{dt} \right] \\ &= -\frac{\partial}{\partial \mathbf{x}} \cdot \left\{ \sum_i m_i R(r_i) \frac{d\mathbf{x}_i(t)}{dt} \right\}. \end{aligned} \tag{9.5}$$

Defining the macroscopic velocity by

$$\mathbf{v}(\mathbf{x},t) \equiv \frac{\sum_i m_i R(r_i) \dfrac{d\mathbf{x}_i}{dt}}{\sum_i m_i R(r_i)}, \tag{9.6}$$

(*cf*. (0.1)), so that

$$\rho(\mathbf{x},t)\mathbf{v}(\mathbf{x},t) \equiv \sum_i m_i R(r_i) \frac{d\mathbf{x}_i(t)}{dt}, \tag{9.7}$$

we see that (9.5) is equivalent to the continuity equation,

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{v}), \tag{9.8}$$

which is therefore an *exact* consequence of our definitions of ρ and $\mathbf{v}$.

Now suppose that there are two kinds of molecules: water molecules with mass m_W and salt molecules with mass m_S. These two kinds of molecules are separately conserved. In analogy with (9.2), we define the density of salt by

$$\rho_s(\mathbf{x},t) \equiv \sum_s m_s R(r_s), \tag{9.9}$$

where the sum runs over salt molecules only. By the same steps as before, we find that

$$\frac{\partial \rho_s}{\partial t} = -\nabla \cdot (\rho_s \mathbf{v}_s), \tag{9.10}$$

where

$$\rho_s \mathbf{v}_s \equiv \sum_s m_s R(r_s) \frac{d\mathbf{x}_s(t)}{dt} \tag{9.11}$$

defines the velocity $\mathbf{v}_S$ of salt. By our previous definition of salinity,

$$S = \frac{\rho_s}{\rho}. \tag{9.12}$$

Thus (9.10) can also be written

$$\frac{\partial(\rho S)}{\partial t} = -\nabla \cdot (\rho S \mathbf{v}_s). \tag{9.13}$$

Eqn. (9.13) is equivalent to

$$\frac{\partial(\rho S)}{\partial t} = -\nabla \cdot (\rho S \mathbf{v}) - \nabla \cdot \mathbf{F}_s, \tag{9.14}$$

where

$$\mathbf{F}_s \equiv \rho S(\mathbf{v}_s - \mathbf{v}) \tag{9.15}$$

is the molecular flux of salt. Note that a molecular salt flux occurs whenever the average velocity of *salt* molecules differs from the average velocity of *all* molecules. By (9.8), (9.14) can also be written

$$\frac{DS}{Dt} = -\frac{\nabla \cdot \mathbf{F}_s}{\rho}. \tag{9.16}$$

If the molecular salt flux is negligible, (9.16) reduces to the ideal-fluid equation for the salinity, (8.1e).

Unfortunately, the exact derivation of (9.16) has introduced a new dependent variable, $\mathbf{v}_S$ (or $\mathbf{F}_S$), without inceasing the number of equations. As we shall see, the corresponding derivations of the equations for momentum and total energy also introduce new variables. Thus, the method of averaging yields exact expressions for the molecular transports which, however, render the resulting macroscopic equations mathematically unclosed. This *closure problem* is an inevitable consequence of the averaging. To close the equations, we must find approximations for molecular transports like $\mathbf{F}_S$ that involve only the original variables, $\rho,\ S, \mathbf{v}, p$, and T. The most commonly used approximation for the molecular salt flux is

$$\mathbf{F}_s = -\mu_s \nabla S \,, \tag{9.17}$$

for which (neglecting the possible spatial dependence of μ_S) (9.16) becomes

$$\frac{DS}{Dt} = \kappa_s \nabla^2 S \,, \tag{9.18}$$

where $\kappa_S = \mu_S / \rho$ is the diffusion coefficient for salt. The approximation (9.17) can be justified by an appeal to experimental results, or by kinetic-theory arguments similar to those given in Section 11.

Why does the equation (9.16) for *salt* contain a molecular transport term, whereas the corresponding equation (9.8) for *all matter* contains none? Because our definition (9.6) of velocity is an average weighted by the *total* mass. A different convention would lead to differently-placed molecular transport terms, but the closure problem would remain.

10. *Momentum equation by the method of averaging*

We resume our program of re-deriving the macroscopic equations by the method of averaging over the molecular motions.[4] Our next objective is an evolution equation for the macroscopic velocity $\mathbf{v}(\mathbf{x},t)$ defined by (9.7) and (9.2). Taking the time derivative of the x-component of (9.7), we obtain

$$\begin{aligned} \frac{\partial(\rho u)}{\partial t} &= \frac{\partial}{\partial t}\left[\sum_i m_i R_i \frac{dx_i}{dt}\right] \\ &= \sum_i \left[m_i \frac{\partial R_i}{\partial t}\frac{dx_i}{dt} + m_i R_i \frac{d^2 x_i}{dt^2}\right] \end{aligned} \tag{10.1}$$

where $R_i \equiv R(r_i)$. As before,

$$\frac{\partial R_i}{\partial t} = \frac{\partial R_i}{\partial \mathbf{x}_i}\cdot\frac{d\mathbf{x}_i}{dt} = -\frac{\partial R_i}{\partial \mathbf{x}}\cdot\frac{d\mathbf{x}_i}{dt}\,, \tag{10.2}$$

and thus (10.1) becomes

$$\frac{\partial(\rho u)}{\partial t} = -\frac{\partial}{\partial \mathbf{x}}\cdot\left[\sum_i m_i R_i \frac{dx_i}{dt}\frac{d\mathbf{x}_i}{dt}\right] + \sum_i m_i R_i \frac{d^2 x_i}{dt^2}\,. \tag{10.3}$$

We easily obtain the corresponding equations for $\partial(\rho v)/\partial t$ and $\partial(\rho w)/\partial t$.

Now we go to work on the right-hand side of (10.3). We aim to extract the terms that appear in the ideal-fluid momentum equation (8.1b). The remaining terms will represent the previously neglected molecular momentum flux. First, define

$$\mathbf{v}_i'(\mathbf{x},t) \equiv \frac{d\mathbf{x}_i}{dt} - \mathbf{v}(\mathbf{x},t)\,, \tag{10.4}$$

and note that $\mathbf{v}_i'(\mathbf{x},t)$ is the difference between the velocity of the *i*-th molecule and the continuum velocity at $\mathbf{x}$, all at time t. Then the x-component of

$$\sum_i m_i R_i \frac{dx_i}{dt}\frac{d\mathbf{x}_i}{dt} \tag{10.5}$$

is

$$\begin{aligned}\sum_i m_i R_i \frac{dx_i}{dt}\frac{dx_i}{dt} &= \sum_i m_i R_i \left[u(\mathbf{x},t) + u_i'(\mathbf{x},t)\right]^2 \\ &= \rho u^2(\mathbf{x},t) + \sum_i m_i R_i u_i'(\mathbf{x},t) u_i'(\mathbf{x},t)\end{aligned} \tag{10.6}$$

The cross-terms cancel as a matter of definition. Treating the other two components of (10.5) similarly, and substituting the results back into (10.3), we obtain

$$\frac{\partial(\rho u)}{\partial t} = -\nabla\cdot(\rho u \mathbf{v}) - \nabla\cdot\left[\sum_i m_i R_i u_i' \mathbf{v}_i'\right] + \sum_i m_i R_i \frac{d^2 x_i}{dt^2}\,. \tag{10.7}$$

Combining (10.7) with the corresponding equations for the momenta in the y- and z-directions, and using the continuity equation to simplify the result, we finally obtain

$$\rho\frac{D\mathbf{v}}{Dt} = -\nabla\cdot\mathbf{F} + \sum_i m_i R_i \frac{d^2\mathbf{x}_i}{dt^2} \tag{10.8}$$

where $\mathbf{F}(\mathbf{x},t)$ is the symmetric tensor defined by

$$\mathbf{F}(\mathbf{x},t) \equiv \sum_i m_i R_i \mathbf{v}_i' \mathbf{v}_i' \equiv \rho\left\langle \mathbf{v}'_{mol}\mathbf{v}'_{mol}\right\rangle. \tag{10.9}$$

The last equivalence in (10.9) defines the angle-bracket term, the average product of molecular velocity components.

Now, everything so far is a matter of definition. To put in the physics, we need Newton's law for molecules,

$$m_i \frac{d^2\mathbf{x}_i}{dt^2} = -\frac{\partial V}{\partial \mathbf{x}_i}, \tag{10.10}$$

where the potential energy,

$$V(\mathbf{x}_1,\ldots,\mathbf{x}_N) = V_{int} + V_{ext}, \tag{10.11}$$

consists of a part, V_{int}, arising from *intermolecular* forces, and another part, V_{ext}, corresponding to *external* forces. In a uniform gravitational field (pointing in the minus-z direction),

$$V_{ext} = \sum_i m_i\, g\, z_i\ , \tag{10.12}$$

and thus (10.8) becomes

$$\rho\frac{D\mathbf{v}}{Dt} + \rho g\mathbf{k} = -\nabla\cdot\mathbf{F} - \sum_i R_i \frac{\partial V_{int}}{\partial \mathbf{x}_i}. \tag{10.13}$$

where $\mathbf{k}$ is the unit vector in the vertical direction. We show below that

$$-\sum_i R_i \frac{\partial V_{int}}{\partial \mathbf{x}_i} = -\nabla\cdot\mathbf{G} \tag{10.14}$$

for some tensor $\mathbf{G}$, so that (10.13) can be written

$$\rho\frac{D\mathbf{v}}{Dt} + \rho g\mathbf{k} = -\nabla\cdot\mathbf{T}\ , \tag{10.15}$$

where

$$\mathbf{T} = \mathbf{F} + \mathbf{G} \tag{10.16}$$

is the *total* momentum-flux tensor associated with the microscopic flow.

The tensor $\mathbf{G}$ is sometimes negligibly small. In an *ideal gas*, for example, only a tiny fraction of the molecules are interacting (colliding) at any particular instant, and the non-colliding molecules make no contribution to V_{int}. Then $\mathbf{F}$ alone represents the momentum flux associated with the microscopic motion.

To understand $\mathbf{F}$, suppose that $F_{xy}>0$. This means that x-direction momentum flows toward positive y. And this agrees with the definition (10.9), which states that $F_{xy}>0$ if the molecules moving toward positive y (v_{mol}>0) have, on average, a positive x-direction momentum (u_{mol}>0).

Now imagine that the fluid is enclosed by a rigid container, and left undisturbed for a long time. Intuition suggests that the macroscopic flow will eventually die out, and that (away from boundaries) the microscopic, molecular motions will become statistically homogeneous and isotropic. This in turn implies that **T** is diagonal, with all three diagonal components equal. These facts motivate the *general* decomposition

$$\mathbf{T} = p\mathbf{I} - \boldsymbol{\tau}, \tag{10.17}$$

where

$$p \equiv \frac{1}{3}\left(T_{xx} + T_{yy} + T_{zz}\right) \tag{10.18}$$

is the *dynamic pressure* and $\boldsymbol{\tau}$ is the *deviatoric stress tensor*. The momentum equation (10.15) then becomes

$$\rho\frac{D\mathbf{v}}{Dt} + \rho g\mathbf{k} = -\nabla p + \nabla\cdot\boldsymbol{\tau}\ . \tag{10.19}$$

To close (10.19), we need expressions for *both p* and $\boldsymbol{\tau}$ in terms of the macroscopic variables $\mathbf{v}$, ρ, and S.

In the hypothetical, equilibrium situation described above, $\boldsymbol{\tau}$=0. If the deviatoric stress tensor $\boldsymbol{\tau}$ is negligible, then (10.19) *resembles* the ideal-fluid momentum equation (8.1b). However, in the ideal-fluid equations, p is the thermodynamic-equilibrium pressure, determined by the fundamental relation of thermodynamics. The p in (10.19) is, on the other hand, *defined* by (10.18), and, from the standpoint of this section, we should not even mention the fundamental relation unless we can derive it from the exact molecular dynamics. This turns out to be impossible — even in principle — without an additional hypothesis: the basic hypothesis of *equilibrium statistical mechanics*. We shall talk more about equilibrium statistical mechanics in later lectures. But here we note that even if it were somehow possible to equate p to the pressure in (local) thermodynamic equilibrium, we still lack a prescription for the deviatoric stess tensor $\boldsymbol{\tau}$. And since $\boldsymbol{\tau}$ evidently vanishes in thermal equilibrium, the expression for $\boldsymbol{\tau}$ requires ideas from *nonequilibrium* statistical mechanics. We illustrate the general flavor of these ideas in the following section, where we obtain an expression analogous to (9.17) for the molecular flux of momentum.

Now we turn to the proof of (10.14). We assume that the interactions between molecules are pair-wise repulsions. Then

$$V_{int} = \sum\sum_{i>j} \Phi\left(r_{ij}\right), \qquad r_{ij} \equiv \left|\mathbf{x}_i - \mathbf{x}_j\right| \tag{10.20}$$

where

$$\Phi'(r) < 0, \tag{10.21}$$

and the prime denotes differentiation. The inequality (10.21) implies that the molecules repel one another, that is, that energy must be supplied to bring two molecules closer to one another. The x-component of (10.14) is

$$\begin{aligned} &-\sum\sum_{i\neq j} R_i \frac{\partial \Phi(r_{ij})}{\partial x_i} \\ &= -\sum\sum_{i\neq j} R_i \frac{\Phi'(r_{ij})}{r_{ij}}(x_i - x_j) \\ &= -\tfrac{1}{2}\sum\sum_{i\neq j} \frac{\Phi'(r_{ij})}{r_{ij}}(x_i - x_j)(R_i - R_j). \end{aligned} \tag{10.22}$$

Now let $S_{ij}(\mathbf{x})$ be the unique solution to

$$\frac{\partial}{\partial \mathbf{x}} \cdot \left[(\mathbf{x}_i - \mathbf{x}_j) S_{ij} \right] = R_i - R_j \qquad \text{and} \qquad S_{ij} \to 0 \; as \; |\mathbf{x}| \to \infty. \tag{10.23}$$

It is easiest to think about (10.23) in a coordinate system in which the molecules at $\mathbf{x}_i$ and $\mathbf{x}_j$ lie on one of the coordinate axes (the r-axis, say). Refer to Figure 1.2. Then, if r is the distance in the direction of $\mathbf{x}_i$ - $\mathbf{x}_j$, (10.23) is equivalent to

$$\frac{\partial S_{ij}}{\partial r} = \frac{R_i - R_j}{r_{ij}}. \tag{10.24}$$

Thus S_{ij} is nonzero (and negative) only in the cigar-shaped region between molecules i and j. Substituting (10.23) into (10.22), we obtain the x-component of (10.14) in the form

$$-\sum_i R_i \frac{\partial V_{int}}{\partial x_i} = -\frac{\partial G_{xx}}{\partial x} - \frac{\partial G_{xy}}{\partial y} - \frac{\partial G_{xz}}{\partial z}, \tag{10.25}$$

where

$$\mathbf{G} \equiv \tfrac{1}{2}\sum\sum_{i\neq j} \frac{\Phi'(r_{ij})}{r_{ij}}(\mathbf{x}_i - \mathbf{x}_j)(\mathbf{x}_i - \mathbf{x}_j) S_{ij}(\mathbf{x}) \tag{10.26}$$

is a symmetric tensor.

To understand $\mathbf{G}$, consider the contribution of two *particular* molecules, i and j, to (10.26). With no loss in generality, we can assume that these two molecules lie on the x-axis. Then these two molecules contribute only to the G_{xx}-component of $\mathbf{G}$, that is, to the flux of x-direction momentum in the x-direction. Since both $\Phi'(r)$ and S_{ij} are negative, this flux can never be negative, but it is nonzero only within the region of nonvanishing S_{ij} shown in Figure 1.2.

In summary, **F** represents the microscopic momentum flux caused by molecules *moving* from one location to another, while conserving their momentum en route. On the other hand, **G** represents the microscopic flux caused by intermolecular *forces*, and can be nonzero even if the molecules aren't moving.

11. *An example of kinetic theory*

Using the averaging method, we have obtained equations for the salinity and momentum that contain exact expressions for the molecular transports. However, to close the equations, we must find approximate expressions for these molecular transports in terms of the macroscopic variables ρ, $\mathbf{v}$, S, etc. Nonequilibrium statistical mechanics based upon kinetic theory provides the basis for this closure, but the full theory is far beyond our scope.[5] Instead, we examine a very simple-minded version of kinetic theory, which nonetheless illustrates the essential ideas.

Many authors *define* the p in (10.17) to be the pressure $-\partial E/\partial\alpha$ given by equilibrium thermodynamics; then $\boldsymbol{\tau}$ is, by definition, the remainder. If one then *assumes* that the components of $\boldsymbol{\tau}$ depend linearly on the first derivatives $\partial v_i/\partial x_j$ of the velocity components, and that the *relationship* between these two tensors is isotropic, one eventually obtains the Navier-Stokes approximation,

$$\tau_{ij} = (\kappa - \tfrac{2}{3}\mu)\delta_{ij}\nabla\cdot\mathbf{v} + \mu\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right), \quad i = 1,2,3 \tag{11.1}$$

where κ and μ are *undetermined* scalars, and the subscripts denote directional components.[6] Frequently,

$$\nabla\cdot\mathbf{v} \approx 0, \tag{11.2}$$

and hence

$$\frac{D\mathbf{v}}{Dt} = -\alpha\nabla p - g\mathbf{k} + \nu\nabla^2\mathbf{v}, \tag{11.3}$$

where $\nu \equiv \mu/\rho$ is the *kinematic viscosity*.

This conventional derivation of (11.1), while certainly very elegant, is also somewhat empty: *Why*, after all, should the stress depend *linearly* on the strain rate? Furthermore, the conventional derivation leaves the coefficients μ, κ, and hence ν unspecified; like the fundamental relation $E(\alpha,\eta)$, we must then regard them as *given*. In contrast, kinetic theory offers both the physical *motivation* for a relation like (11.1) and a *quantitative* estimate of μ and κ, but accurate numbers often demand impractically difficult computations.

To keep things simple, we suppose that all the molecules have the same mass, and consider the special situation in which the velocity **v**=(*u(y),*0,0) points only in the *x*-direction, and depends only on *y*. We want to estimate the molecular flux of *x*-direction momentum from *y*<0 to *y*>0, that is, through the dashed line in Figure 1.3. We shall also assume that:

(a) The molecules conserve their momentum between collisions.

(b) Before each collision, a molecule's momentum may differ from the average of its neighbors, but after each collision this difference vanishes *on average*.

(c) The molecular mean free path λ is short compared to the scale *L* on which *u(y)* varies.

By assumption (a), only **F** contributes to the total molecular momentum flux **T**. Let *s* be the average speed of a molecule in any particular direction. That is, let

$$s = \tfrac{1}{\sqrt{3}}\left(rms\ molecular\ speed\right). \tag{11.4}$$

Then, by (10.9), the diagonal components of **T** are

$$T_{xx} = \rho\left\langle u_{mol}{}^{2}\right\rangle \approx T_{yy} \approx T_{zz} \approx \rho s^{2}. \tag{11.5}$$

The macroscopic velocity *u*(*y*) has a negligible effect on these diagonal components, because *u* is so much smaller than *s*. By considering the momentum transferred by elastic collisions to a plane surface immersed in the gas, we see that (11.5) is just the dynamic pressure *p*, the normal force per unit area of the gas on the surface.

Now consider the (off-diagonal) flux of *x*-momentum in the *y*-direction,

$$T_{xy} = \rho < u_{mol}\, v_{mol} >, \tag{11.6}$$

at the location *y*=0. If there were no macroscopic velocity, then (11.6) would vanish; thus T_{xy} must depend upon *u*(*y*). To estimate T_{xy}, we divide the molecules crossing *y*=0 into two groups, and suppose that

$$\begin{aligned} < u_{mol} v_{mol} > &= \tfrac{1}{2} < u_{mol} v_{mol} >_{up} + \tfrac{1}{2} < u_{mol} v_{mol} >_{down} \\ &\approx \tfrac{1}{2} < u_{mol} >_{up} < v_{mol} >_{up} + \tfrac{1}{2} < u_{mol} >_{down} < v_{mol} >_{down} \end{aligned} \tag{11.7}$$

where $< >_{up}$ is the average (at *y*=0) over up-going molecules, and $< >_{down}$ is the average over down-going molecules. Now, on average, the down-going molecules crossing *y*=0 experienced their last collision at *y=+λ/2*, and the up-going molecules crossing *y*=0 experienced their last collision at *y=-λ/2*. Therefore, by assumptions (a) and (b),

$$< u_{mol} >_{up} = u(-\lambda / 2,), \qquad < v_{mol} >_{up} = +s \tag{11.8}$$

and

$$< u_{mol} >_{down} = u(+\lambda/2), \quad < v_{mol} >_{down} = -s\,. \tag{11.9}$$

Next we use the Taylor-series expansion

$$u(-\lambda/2) = u(0) + \frac{\partial u}{\partial y}(0)\cdot\left(-\frac{\lambda}{2}\right) + \tfrac{1}{2}\frac{\partial^2 u}{\partial y^2}(0)\cdot\left(-\frac{\lambda}{2}\right)^2 + \cdots \tag{11.10}$$

to relate $u(-\lambda/2)$ to the velocity field at y=0, the level at which we are calculating the flux. The third term in (11.10) is negligible provided that

$$\left|\frac{\partial^2 u}{\partial y^2}(0)\right|\lambda^2 << \left|\frac{\partial u}{\partial y}(0)\right|\lambda\,, \tag{11.11}$$

that is, provided that

$$\lambda << L\,, \tag{11.12}$$

which is true by assumption (c). Similarly,

$$u(+\lambda/2) \approx u(0) + \frac{\partial u}{\partial y}(0)\cdot\left(+\frac{\lambda}{2}\right). \tag{11.13}$$

Substituting these results into (11.7), we obtain

$$T_{xy} \approx -\frac{\rho s\lambda}{2}\frac{\partial u}{\partial y}. \tag{11.14}$$

Thus (11.3) holds, with molecular viscosity

$$\nu \approx \frac{s\lambda}{2}. \tag{11.15}$$

It is interesting to compare this prediction to the measured viscosity of the Earth's atmosphere. At 20° C, s=5.0×10^4 cm/sec and λ=6.5×10^{-6} cm, so (11.15) pedicts that ν≈.165 cm^2/sec. This agrees well with the measured value of .15 cm^2/sec. But don't be *too* impressed. There is no way to define the mean free path precisely. However, for any reasonable definition, (11.15) gives a reasonable estimate for the viscosity of an ideal gas.

Before leaving this subject, we briefly describe the more sophisticated methods actually used by statistical mechanicians to compute transport coefficients like ν. One starts by deriving the Boltzmann equation, an equation describing the evolution of the probability distribution of molecular velocities. The derivation of the Boltzmann equation requires an assumption (*Stosszahlansatz*, or "assumption of molecular disorder") which, like assumption (b) above, imposes a direction of time. The Boltzmann equation has stationary solutions that correspond to thermodynamic equilibrium. To estimate the transport coefficients, one expands the Boltzmann equation about one of these solutions, using a method pioneered by Chapman and Enskog.[7]

Although we have emphasized that calculations of molecular transport coefficients require a *nonequilibrium* theory based upon the underlying molecular dynamics, equilibrium thermodynamics actually places strong constraints on the forms these expressions can take. To explain these constraints, we turn, once again, to the strictly macroscopic point of view. First, however, we must complete the postulational basis of thermodynamics.

12. *Thermodynamic constraints on molecular diffusion*

All of equilibrium thermodynamics can be deduced from four fundamental postulates. They are:

(1.) For any system at thermodynamic equilibrium, there exists a *fundamental relation* $\eta=\eta(E,X_1,X_2,...,X_N)$ between the entropy η, the energy E, and the other macroscopic parameters $X_1, X_2, \ldots, X_N$ that describe the system.

(2.) At equilibrium, the entropy of an *isolated* system is a maximum.

(3.) The entropy of a system is the sum of the entropies of its constituent subsystems.

(4.) The entropy is zero at zero temperature.

Gibbs introduced the first three postulates. Nernst added the fourth, which is important only at temperatures so low that quantum effects become important.[8]

So far, we have used only the first postulate of thermodynamics, with $X_1=\alpha$ and $X_2=S$ as the macroscopic parameters. That is, taking the system to be a gram of seawater, we have assumed the existence of a relation $\eta(E,\alpha, S)$, or, equivalently, $E(\alpha, S, \eta)$. From the standpoint of thermodynamics, these are *given* functions, which must be determined by experiment. However, equilibrium statistical mechanics (which we discuss briefly in Section 18) offers the means of actually calculating $\eta(E,\alpha, S)$, removing (in principle!) the need for any experiments.

In this section, we discuss the constraints imposed by thermodynamics on the exchange of heat and salinity between seawater particles at a fixed pressure. Our discussion will require the first *three* of the fundamental postulates listed above. The system, shown schematically in Figure 1.4, consists of two seawater particles (1 and 2), each of one gram, and an environment (3) of much greater size. The two particles exchange heat and salt with one another, but not with the more distant environment. However, all three systems exchange mechanical work as the two seawater particles adjust their volumes to keep their pressures the same as the pressure of the environment, p_r. We imagine the whole system (1, 2, and 3) to be enclosed by a distant, rigid, adiabatic wall. In this way we fulfill the requirement of postulate 2 that the whole system be "isolated."

By postulates (2) and (3) above, the total entropy

$$\eta = \eta_1 + \eta_2 + \eta_3 \tag{12.1}$$

is a maximum in thermodynamic equilibrium. However,

$$\delta\eta_3 = 0 \tag{12.2}$$

because the environment does not exchange heat with the two seawater particles. Thus postulate (2) reduces to the requirement that

$$\eta_1 + \eta_2 \tag{12.3}$$

be maximum in equilibrium. Now

$$\delta\eta_i = \frac{1}{T_i}\delta E_i + \frac{p_i}{T_i}\delta\alpha_i - \frac{\mu_i}{T_i}\delta S_i\,. \tag{12.4}$$

But, by the conservation of total energy, volume, and salinity,

$$\begin{aligned} &\delta E_1 + \delta E_2 - p_r \delta V_3 = 0 \\ &\delta\alpha_1 + \delta\alpha_2 + \delta V_3 = 0 \\ &\delta S_1 + \delta S_2 + 0 = 0 \end{aligned} \tag{12.5}$$

Here p_r and V_3 are the pressure and volume of the environment, and we have again used the fact that the environment exchanges only mechanical work with the particles. We can treat p_r as a constant because the environment is relatively large. Then, eliminating δV_3 between (12.5a,b), we find that

$$\begin{aligned} &\delta h_1 + \delta h_2 = 0 \\ &\delta S_1 + \delta S_2 = 0 \end{aligned} \tag{12.6}$$

where

$$h \equiv E + p\alpha \tag{12.7}$$

is the *specific enthalpy*. That is, the total enthalpy and salinity *of the two seawater particles alone* are conserved. By (12.4) and (12.6-7) we have

$$\delta(\eta_1 + \eta_2) = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\delta h_1 + \left(\frac{\mu_2}{T_2} - \frac{\mu_1}{T_1}\right)\delta S_1\,. \tag{12.8}$$

Now we can use (12.8) in two ways. At equilibrium (12.8) must be zero for *arbitrary* infinitesimal δh_1 and δS_1. Thus

$$T_1 = T_2 \qquad \text{and} \qquad \mu_1 = \mu_2 \qquad \text{at equilibrium.} \tag{12.9}$$

That is, *for two seawater particles at equilibrium, the temperatures and chemical potentials must be the same.*

Next suppose that our two-particle system is displaced away from equilibrium by a small but *finite* amount. Then δh_1 and δS_1 represent the fluxes (from fluid particle 2 to particle 1) of enthalpy and salt that bring the system back into equilibrium. What do we know about these fluxes? From the macroscopic viewpoint, they can depend only on the states of the two seawater particles. Since the pressure (p_r) is uniform, these states are defined by T_1, μ_1, T_2, μ_2 (two variables for each particle). Furthermore, both fluxes must vanish when $T_1 = T_2$ and $\mu_1 = \mu_2$. If the differences between the temperatures and chemical potentials of the two seawater particles are small, it follows that the fluxes depend *linearly* on their differences. That is,

$$\begin{aligned} \delta h_1 &= k_{TT}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)+k_{T\mu}\left(\frac{\mu_2}{T_2}-\frac{\mu_1}{T_1}\right)+\cdots \\ \delta S_1 &= k_{\mu T}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)+k_{\mu\mu}\left(\frac{\mu_2}{T_2}-\frac{\mu_1}{T_1}\right)+\cdots \end{aligned} \tag{12.10}$$

to leading order in the differences between the temperatures and potentials. The transfer coefficients k_{TT} etc. depend only on T_1 ($\approx T_2$) and μ_1 ($\approx \mu_2$). Furthermore, since (12.3) is a maximum at equilibrium, (12.8) must always be *positive*. This puts a constraint on the transfer coefficients in (12.10).

Now suppose that the two seawater particles can exchange heat and mechanical work, but not salinity (as if separated by a membrane). Then, for (12.8) to be positive, the sign of (T_2-T_1) must be the same as δh_1. That is, heat flows from the particle with the higher temperature. Similarly, if the particles exchange salt but not heat, then salt flows from the particle with the higher μ/T. However, if, as is typically the case, our seawater particles can exchange both heat and salt, then neither of these statements necessarily applies. Thermodynamics demands *only* that the total entropy production (12.8) be positive.

We easily extend these arguments to the fluid continuum. Consider a mass of fluid, at a fixed pressure p_r , that exchanges heat and salt between its constituent fluid particles, but not with the surrounding fluid. The analog of (12.8) is

$$\frac{D}{Dt}\iiint d\mathbf{x}\,\rho\eta = \iiint d\mathbf{x}\,\rho\left[\frac{1}{T}\frac{Dh}{Dt}-\frac{\mu}{T}\frac{DS}{Dt}\right], \tag{12.11}$$

which must be positive. The analog of (12.6) is

$$\frac{Dh}{Dt} = -\frac{\nabla\cdot\mathbf{F}_h}{\rho}, \quad \frac{DS}{Dt} = -\frac{\nabla\cdot\mathbf{F}_S}{\rho}, \tag{12.12}$$

where $\mathbf{F}_h$ and $\mathbf{F}_S$ are the fluxes of enthalpy and salt. Eqn. (12.12) requires that the enthalpy or salt lost by one fluid particle is gained by another. Substituting (12.12) into

(12.11), integrating by parts, and using the fact that the normal components of the fluxes vanish (by hypothesis) at the boundaries of the fluid mass, we obtain the analog of (12.8),

$$\frac{D}{Dt}\iiint d\mathbf{x}\,\rho\eta = \iiint d\mathbf{x}\left[\nabla\left(\frac{1}{T}\right)\cdot\mathbf{F}_h - \nabla\left(\frac{\mu}{T}\right)\cdot\mathbf{F}_S\right]. \tag{12.13}$$

If the departure from thermodynamic equilibrium is slight, then the fluxes must take the general forms

$$\mathbf{F}_h = \kappa_{TT}\nabla\left(\frac{1}{T}\right) - \kappa_{T\mu}\nabla\left(\frac{\mu}{T}\right) \tag{12.14}$$

and

$$\mathbf{F}_S = -\kappa_{\mu\mu}\nabla\left(\frac{\mu}{T}\right) + \kappa_{\mu T}\nabla\left(\frac{1}{T}\right), \tag{12.15}$$

which are the analogs of (12.10). Again, this is true because the fluxes depend on T and μ but must vanish when T and μ are uniform; the flux laws (12.14-15) are the first nonvanishing terms in an expansion about uniform T and μ. Substituting (12.14-15) into (12.13) yields

$$\begin{gathered}\frac{D}{Dt}\iiint d\mathbf{x}\,\rho\eta = \\ \iiint d\mathbf{x}\left[\kappa_{TT}\nabla\left(\frac{1}{T}\right)^2 - \left(\kappa_{T\mu}+\kappa_{\mu T}\right)\nabla\left(\frac{1}{T}\right)\cdot\nabla\left(\frac{\mu}{T}\right) + \kappa_{\mu\mu}\nabla\left(\frac{\mu}{T}\right)^2\right]\end{gathered} \tag{12.16}$$

which again must be positive. Therefore, thermodynamics demands that

$$\kappa_{TT} > 0, \quad \kappa_{\mu\mu} > 0, \quad (\kappa_{T\mu}+\kappa_{\mu T})^2 < 4\kappa_{TT}\kappa_{\mu\mu}. \tag{12.17}$$

That is, even though we require laboratory measurements to determine the values of the diffusion coefficients in (12.14-15), we can be confident beforehand that the results will satisfy (12.17).[9]

It is customary to rewrite (12.12) as equations for DT/Dt and DS/Dt; this requires the thermodynamic expression for $h=h(T, S, p_r)$ (which may be determined from the fundamental relation). Then translating the flux laws (12.14-15) into flux laws for temperature and salinity, the final equations take the forms

$$\frac{DT}{Dt} = \kappa_T\nabla^2 T + \kappa'\,\nabla^2 S \tag{12.18}$$

and

$$\frac{DS}{Dt}=\kappa_S\nabla^2 S+\kappa''\,\nabla^2 T\,. \tag{12.19}$$

Because of the cross-terms in (12.18) and (12.19), a salt gradient generally drives a temperature flux, and vice versa. The κ' term in (12.18) is negligible in the ocean, but the κ'' term in (12.19), called the *Soret effect*, can sometimes be as large as the κ_S term. Nevertheless, both κ' and κ'' are *customarily* neglected.

The discussion given above applies to two seawater particles at the same imposed pressure. Since, the pressures, temperatures, and salinity potentials of the two particles are equal in thermodynamic equilibrium, the two particles also have the same equilibrium salinities. However, one can consider the more general problem of two seawater particles at *different* imposed pressures, or, more generally, the thermodynamic equilibrium attained by an extensive mass of sea water in a gravitational field. The analysis is nearly the same as that given above, but one must be careful to include the gravitational energy per unit mass (gz) as part of the energy. Again one finds that the temperature T and salinity potential μ are uniform in thermodynamic equilibrium. That is,

$$T=uniform, \qquad \mu(S,T,p)=uniform\,. \tag{12.20}$$

But since T is uniform while p is not, it follows that the equilibrium salinity in a gravitational field must be *nonuniform*; the change in S compensates the change in p in (12.20b). Fofonoff (1962) estimated that if the whole ocean were to come to complete thermodynamic equilibrium, then its temperature would be uniform, but its salinity would decrease with depth at the rate of about 3 ppt per kilometer. This is far larger than the observed mid-ocean salinity gradient! Of course this hypothetical equilibrium state has no practical relevance except, perhaps, as a reminder that however close the ocean may be to *local* thermodynamic equilibrium, it is far, far from the state of *global* thermodynamic equilibrium.

13. *Macroscopic averages of the equations of motion*

We have finally completed our derivation of the equations governing the motion of seawater. Subject to the approximations laid out in the preceding sections, these equations are:

$$
\begin{aligned}
&\frac{D\rho}{Dt}+\rho\nabla\cdot\mathbf{v}=0\\
&\frac{D\mathbf{v}}{Dt}=-\frac{1}{\rho}\nabla p-\nabla\phi+\nu\nabla^2\mathbf{v}\\
&\rho=\rho(S,T,p)\\
&\frac{DT}{Dt}=\kappa_T\nabla^2 T\\
&\frac{DS}{Dt}=\kappa_S\nabla^2 S
\end{aligned}
\tag{13.1}
$$

Eqns. (13.1) apply to fields ρ, $\mathbf{v}$, p, T, S in which *only* the molecular fluctuations have been averaged out. However, we often wish to consider fields that represent a much more drastic averaging. Consider, for example, the typical wall map of ocean currents, in which the arrows represent the velocity **v** averaged over a very long time. This time-averaged **v** is the field of interest to oceanographers studying the general circulation, but it is the *unaveraged* **v** that obeys (13.1). We can derive an equation for the time-averaged flow by time-averaging (13.1), but the resulting equations are — like the equations previously obtained by averaging over molecular motions — mathematically unclosed. And, unlike the previous case, there is no really justifiable way of closing them. This *closure problem* is the central problem of oceanography, and of fluid mechanics in general.

To focus the discussion, we consider not the general equations (13.1), but the simpler Navier-Stokes equations for constant-density flow,

$$
\begin{aligned}
&\frac{\partial v_i}{\partial t}+v_j\frac{\partial v_i}{\partial x_j}=-\frac{\partial p}{\partial x_i}+\nu\frac{\partial^2 v_i}{\partial x_j\partial x_j}\\
&\frac{\partial v_i}{\partial x_i}=0.
\end{aligned}
\tag{13.2}
$$

The subscripts in (13.2) stand for vector components, repeated subscripts are summed from 1 to 3, and the constant density has been absorbed into the pressure. Again, (13.2) hold only if the velocity and pressure are defined, as before, as the averages of molecular quantities over sampling volumes between λ^3 and L^3. That is, **v** and p include *all* the space and time scales of the macroscopic flow.

Now let $<F(\mathbf{x},t)>$ denote the *macroscopic* average of an arbitrary flow variable $F(\mathbf{x},t)$. The commonly used types of averages include *spatial averages* ,

$$
<F(\mathbf{x},t)>\equiv\frac{3}{4\pi d^3}\iiint_{|\mathbf{x}-\mathbf{x}'|<d}F(\mathbf{x}',t)\,d\mathbf{x}'\ , \tag{13.3}
$$

time averages,

$$< F(\mathbf{x},t) >\equiv \frac{1}{T}\int_{t-T/2}^{t+T/2} F(\mathbf{x},t')\,dt', \tag{13.4}$$

and *ensemble averages* ,

$$< F(\mathbf{x},t) >\equiv \int F\,P(F;\mathbf{x},t)\,dF, \tag{13.5}$$

where $P(F;\mathbf{x},t)$ is the probability distribution of $F(\mathbf{x},t)$ in an ensemble of flow realizations. Although it is the space- or time-average that is usually computed, it is always much easier to *think* about the ensemble average, because only ensemble averages have all of the following convenient mathematical properties:

(1) $<F+G> = <F> + <G>$
(2) $<c> = c$, c=*any constant*
(3) $<\partial F/\partial s> = \partial<F>/\partial s$, $s=x,y,z$, *or* t
(4) $<<F>G> = <F><G>$.

The ensemble-average of (13.2) is

$$\begin{aligned}&\frac{\partial < v_i >}{\partial t} + < v_j > \frac{\partial < v_i >}{\partial x_j} = -\frac{\partial < p >}{\partial x_i} - \frac{\partial R_{ij}}{\partial x_j} + \nu \frac{\partial^2 < v_i >}{\partial x_j \partial x_j}\\ &\frac{\partial < v_i >}{\partial x_i} = 0\end{aligned} \tag{13.6}$$

where

$$R_{ij}(\mathbf{x},t) \equiv < v_i'\, v_j' >, \quad v_i' \equiv v_i - < v_i > \tag{13.7}$$

is the *Reynolds flux* of *i*-direction average momentum in the *j*-direction. The difficulty with (13.6) is that the averaging has created new dependent variables, the R_{ij}, without adding any new equations. Of course, we can *derive* an equation for $\partial R_{ij}/\partial t$ directly from (13.2), but this equation contains new variables like $<v_i'v_j'v_k'>$, and so on. The tensor $-R_{ij}$ is sometimes called *Reynolds stress*.

The unclosed Reynolds equations (13.6-7) are closely analogous to the equations previously obtained by averaging only over molecular motions. In the case of constant density (and neglecting the momentum flux arising from inter-molecular forces), the latter could be written

$$\begin{aligned}&\frac{Dv_i}{Dt} = -\frac{\partial T_{ij}}{\partial x_j}\\ &T_{ij} \equiv < v_i'\, v_j' >_{mol}, \qquad v_i' \equiv (v_i)_{mol} - v_i.\end{aligned} \tag{13.8}$$

Kinetic-theory assumptions led us to replace

$$-\frac{\partial T_{ij}}{\partial x_j} \quad by \quad -\frac{\partial p}{\partial x_i}+\frac{\partial}{\partial x_j}\left(\nu\frac{\partial v_i}{\partial x_j}\right). \tag{13.9}$$

Analogous arguments, called *mixing-length theory*, are frequently invoked to replace

$$-\frac{\partial R_{ij}}{\partial x_j} \quad by \quad -\frac{\partial\,\delta p}{\partial x_i}+\frac{\partial}{\partial x_j}\left(\nu_e\frac{\partial <v_i>}{\partial x_j}\right) \tag{13.10}$$

where

$$\delta p \equiv \frac{1}{3}\langle v_i'\,v_i'\rangle \tag{13.11}$$

and ν_e is the coefficient of *eddy viscosity*. Then, if ν_e is approximately constant, (13.6) becomes

$$\begin{aligned}&\frac{\partial <v_i>}{\partial t}+<v_j>\frac{\partial <v_i>}{\partial x_j}=-\frac{\partial <p>}{\partial x_i}+\nu_e\frac{\partial^2 <v_i>}{\partial x_j\partial x_j}\\&\frac{\partial <v_i>}{\partial x_i}=0.\end{aligned} \tag{13.12}$$

where δp has been absorbed into $<p>$, and ν into ν_e. (Since δp is much smaller than p, and ν usually much smaller than ν_e, it is also logical to say that δp and ν_e have simply been neglected.) Eqns. (13.12) are formally identical to (13.2), except that the dependent variables now represent *macroscopic averages*, and the molecular-viscosity coefficient ν has been replaced by the eddy-viscosity coefficient ν_e.

Mixing-length theory resembles our simplified kinetic theory but with the *molecules* replaced by turbulent *eddies* that represent the fluctuating velocity field **v**'. According to mixing-length theory, these eddies move an average distance of λ_e, called the *mixing length,* before exchanging momentum with one another. This mixing of momentum between eddies is the macroscopic analogue of molecular collisions, and thus λ_e is analogous to the mean free path λ. If s_e is a speed characteristic of the eddies, then arguments analogous to those leading up to (11.15) predict that ν_e is of size $\lambda_e s_e$. However, none of the three assumptions (11.a-c) about molecular collisions really applies to the interactions between eddies. In particular, there is typically no scale separation between the macroscopically averaged velocity <**v**> and the residual **v**'. Thus while it may be convenient, and sometimes even accurate, to replace the Reynolds stress by an eddy viscosity of type (13.10), the true justification for this step, if it exists, is evidently much more complex than mixing-length theory.

The problem of closure, so successfully addressed by kinetic theory in the case of molecular averages, is the central problem of fluid mechanics. We can avoid it only by considering completely unaveraged macroscopic flow fields that include the full spectrum of space- and time-scales. In most oceanographic applications, this is either impossible or impractically difficult. To make progress, we adopt eddy-viscosity-type closures. This amounts to regarding (13.1) as the equations for the *macroscopically averaged* fields, with *eddy coefficients* ν, κ_T, and κ_S many times larger than their molecular counterparts.

The magnitude of these eddy coefficients depends on the precise definition of the average, *and on the particular flow under consideration*. To appreciate this, consider the eddy diffusion coefficient in the equation for the average salinity $<S>$, namely

$$\kappa_S = -\frac{\langle u' S' \rangle}{\partial \langle S \rangle / \partial x} . \tag{13.13}$$

We can regard (13.13) as the *definition* of κ_S. (This definition really makes sense only if the statistics are isotropic; otherwise κ_S must be a tensor.) The definition (13.13) renders the equation for $<S>$ exact, but that equation is useful only if we can *independently* determine the value of κ_S, which generally depends on location and time. One way to determine κ_S is to *measure* the terms on the right-hand side of (13.13), and then hope that κ_S is sufficiently uniform, in space and time, that the measured value will be useful in other situations for which there are no measurements.

The more inclusive the average, the larger will be the residuals $\mathbf{v}'$ and S', and the larger the expected value of κ_S. Even for a fixed type of average, κ_S also depends on the statistics of $\mathbf{v}$ and S, that is, on the particular flow under consideration. In this respect, it is completely unlike the *molecular* diffusion coefficient which, according to thermodynamics, depends only on the local values of the thermodynamic state variables S, T, and p.

The dependence of the eddy diffusion coefficent on the statistics of the *scalar* being diffused (even when that scalar is, unlike salinity, dynamically passive) has been insufficiently emphasized. There is no *fundamental* reason why the diffusion coefficient obtained, through (13.13), for a blob of scalar of characteristic size (say) 10 km should be the same as that obtained for a blob of size 1000 km, even if the velocity field and the definition of the average are the same.

14. *Stirring and mixing*

So far, we have only managed to *derive* the equations of motion. Now, finally, we begin to study their solutions.[10] Consider the general advection-diffusion equation,

$$\frac{D\theta}{Dt} \equiv \frac{\partial \theta}{\partial t} + \mathbf{v} \cdot \nabla \theta = \kappa \nabla^2 \theta , \tag{14.1}$$

with constant diffusion coefficient κ. Several of the equations (13.1) fit this form. (In fact, if it weren't for the pressure-gradient term in (13.1b), even the velocity components would obey equations like (14.1).) Hence, our conclusions about (14.1) will have general significance. It doesn't even matter whether θ is an average over molecular fluctuations *only* (in which case κ is the molecular diffusion coefficient) or a macroscopic average of the type considered in the previous section (in which case κ is an eddy diffusion coefficient). Our results apply to both cases.

In analyzing (14.1), we shall however assume that the velocity field $\mathbf{v}(x,y,z,t)$ is already known, either from measurements or from the solution of other equations. If the latter, then θ must be considered *passive*, or we would have needed to know $\theta(x,y,z,t)$ to determine $\mathbf{v}$. If $\mathbf{v}(x,y,z,t)$ is given, then (14.1) is a *linear* equation for $\theta(x,y,z,t)$, but the solutions of (14.1) are still surprisingly complicated for all but the simplest choices of $\mathbf{v}(x,y,z,t)$. However, our aim is to state general, qualitative properties of these solutions, and to support our statements with a simple but explicit example.

First consider a two-dimensional flow enclosed by rigid boundaries. For given $\mathbf{v}(x,y,t)$, the scalar field $\theta(x,y,t)$ is determined by (14.1), the initial condition

$$\theta(x,y,0) = \theta_0(x,y), \tag{14.2}$$

and appropriate boundary conditions. The quantity

$$C \equiv \tfrac{1}{2}\iint d\mathbf{x}\ \ \nabla\theta\cdot\nabla\theta \tag{14.3}$$

is a convenient measure of the *spatial variability* in θ at time t. By direct calculation,

$$dC/dt = \iint d\mathbf{x}\ \nabla\theta\cdot\nabla\frac{\partial\theta}{\partial t} = \oint dl(\nabla\theta\cdot\mathbf{n})\frac{\partial\theta}{\partial t} - \iint d\mathbf{x}\ \nabla^2\theta\frac{\partial\theta}{\partial t}, \tag{14.4}$$

where $\mathbf{n}$ is the outward normal at the boundary of the fluid. If there is no flux of θ through the boundary, then $\nabla\theta\cdot\mathbf{n}$ is zero there, and, using (14.1), (14.4) reduces to

$$dC/dt = \iint d\mathbf{x}\left\{(\mathbf{v}\cdot\nabla\theta)\nabla^2\theta - \kappa\left(\nabla^2\theta\right)^2\right\}. \tag{14.5}$$

The last term in (14.5), which represents the effect of *mixing*, is always negative; mixing always reduces the variability C. The first term on the right-hand side of (14.5), which represents *stirring*, can have either sign. In fact, a sudden reversal of the velocity would change the sign of this term. However, this stirring term is *usually* positive, for the same reason that it is easier to stir things up than it is to unstir them. That is, stirring *directly* increases the variability C, on average. However, the eventual, *indirect* effect of stirring is to *decrease* the variability, because the increase in C directly caused by *stirring* makes the *mixing* more efficient. These ideas are summarized in Figure 1.5. Next we consider a simple solution of (14.1) that exhibits these behaviors explicitly.

Consider a spatially unbounded two-dimensional flow in which the velocity field is a simple shear,

$$\mathbf{v} = \left(u(y,t),0\right). \tag{14.6}$$

Then (14.1) becomes

$$\frac{\partial\theta}{\partial t}+u(y,t)\frac{\partial\theta}{\partial x}=\kappa\left(\frac{\partial^2\theta}{\partial x^2}+\frac{\partial^2\theta}{\partial y^2}\right). \tag{14.7}$$

Let (x_0,y_0) be the initial coordinates of the fluid particle located at (x,y) at time t. Then

$$\begin{aligned} x &= x_0+\int_0^t u(y,t')\,dt' \\ y &= y_0 \\ t &= t_0 \end{aligned} \tag{14.8}$$

are the transformation equations from Eulerian coordinates (x,y,t) to Lagrangian coordinates (x_0,y_0,t_0). Thus

$$\begin{aligned} \frac{\partial}{\partial x} &= \frac{\partial}{\partial x_0} \\ \frac{\partial}{\partial y} &= -\int_0^t \frac{\partial u}{\partial y}dt'\cdot\frac{\partial}{\partial x_0}+\frac{\partial}{\partial y_0} \\ \frac{\partial}{\partial t} &= -u\frac{\partial}{\partial x_0}+\frac{\partial}{\partial t_0} \end{aligned} \tag{14.9}$$

and (14.7) transforms to

$$\frac{\partial\theta}{\partial t_0}=\kappa\left[\frac{\partial^2\theta}{\partial x_0{}^2}+\left(-\int_0^t\frac{\partial u}{\partial y}dt'\cdot\frac{\partial}{\partial x_0}+\frac{\partial}{\partial y_0}\right)^2\theta\right], \tag{14.10}$$

with initial condition

$$\theta(x_0,y_0,0)=\theta_0(x_0,y_0). \tag{14.11}$$

If $\kappa=0$, then the solution of (14.10-11) is

$$\theta(x_0,y_0,t_0)=\theta_0(x_0,y_0). \qquad (\kappa=0) \tag{14.12}$$

From (14.10) we see that the transformation to Lagrangian coordinates has simplified the advection terms but made the diffusion terms much more complicated. However, if, as we assume next, the velocity $u(y)$ depends linearly on y, then (14.10) is an equation whose coefficients are independent of location, and we can use a spatial Fourier transform to solve it. Suppose then that

$$u = \alpha y \cos \omega t \tag{14.13}$$

where α is a constant, so that

$$-\int_0^t \frac{\partial u}{\partial y} dt' = -\frac{\alpha}{\omega} \sin \omega t . \tag{14.14}$$

Then (14.10) takes the form

$$\frac{\partial \theta}{\partial t_0} = \kappa \left[\frac{\partial^2 \theta}{\partial {x_0}^2} + \frac{\alpha^2}{\omega^2} \sin^2 \omega t_0 \frac{\partial^2 \theta}{\partial {x_0}^2} - \frac{2\alpha}{\omega} \sin \omega t_0 \frac{\partial^2 \theta}{\partial x_0 \partial y_0} + \frac{\partial^2 \theta}{\partial {y_0}^2} \right], \tag{14.15}$$

in which all the coefficients are independent of (x_0,y_0). The initial value problem (14.11,14.15) can therefore be solved by Fourier analysis and superposition. It suffices to consider solutions of the form

$$\theta(x_0, y_0, t_0) = A(t_0) \exp\{i(kx_0 + ly_0)\}, \tag{14.16}$$

where k and l are constants. The resulting ordinary differential equation

$$\frac{1}{A} \frac{dA}{dt_0} = -\kappa \left\{ k^2 \left(1 + \frac{\alpha^2}{\omega^2} \sin^2 \omega t_0 \right) - \frac{2\alpha k l}{\omega} \sin \omega t_0 + l^2 \right\} \tag{14.17}$$

for $A(t_0)$ can be directly integrated. For simplicity, suppose $l=0$, *i.e.* that θ is initially independent of y. The resulting solution,

$$\begin{aligned} \theta &= A_0 \exp\left\{ ikx_0 - \kappa k^2 t_0 - \frac{\kappa k^2 \alpha^2}{2\omega^2} \left(t_0 - \frac{\sin 2\omega t_0}{2\omega} \right) \right\} \\ &= A_0 \exp\left\{ ikx - ik \left(\frac{\alpha}{\omega} \sin \omega t \right) y \right\} \\ &\qquad \times \exp\left\{ -\kappa k^2 t - \frac{\kappa k^2 \alpha^2}{2\omega^2} \left(t - \frac{\sin 2\omega t}{2\omega} \right) \right\} \end{aligned} \tag{14.18}$$

(where A_0 is an arbitrary constant) is a sinusoid with x-direction wavenumber k, and y-direction wavenumber

$$-\frac{k\alpha}{\omega} \sin \omega t . \tag{14.19}$$

The amplitude of (14.18) is controlled by the final *exp*-factor.

In the limit $\omega \to 0$ we obtain the solution corresponding to a steady shear, $u=\alpha y$, namely

$$\theta = A_0 \exp\left\{ ikx - i(k\alpha t)y - \kappa k^2 t - \frac{\kappa k^2 \alpha^2}{3} t^3 \right\}. \tag{14.20}$$

If α=0 (no shear), then the amplitude of (14.20) decreases like $\exp\{-\kappa k^2 t\}$. If $\alpha \neq 0$, then the initial decrease is similar, but at

$$t \approx \sqrt{3}/\alpha, \tag{14.21}$$

the amplitude begins to decrease at the faster rate corresponding to

$$\exp\left\{ -\frac{\kappa k^2 \alpha^2}{3} t^3 \right\}. \tag{14.22}$$

This faster decrease is caused by the predominance of y-wavenumber as the shear produces the pattern shown in Figure 1.6.

If $\omega \neq 0$, then the shear reverses periodically, and, as anticipated by our general discussion, the mixing is much less enhanced. For large t, the amplitude decreases only like

$$\exp\left\{ -\kappa k^2 t - \kappa \frac{k^2 \alpha^2}{2\omega^2} t \right\} = \exp\left\{ -\kappa k^2 t - \kappa\, l_{rms}{}^2 t \right\} \tag{14.23}$$

where

$$l_{rms}{}^2 = \frac{k^2 \alpha^2}{2\omega^2} \tag{14.24}$$

is the *average*, squared y-wavenumber.

By (14.18), the variability C is proportional to

$$\left[k^2 + \frac{k^2 \alpha^2}{\omega^2} \sin^2 \omega t \right] \exp\left\{ -2\kappa k^2 t - \frac{\kappa k^2 \alpha^2}{\omega^2} \left(t - \frac{\sin 2\omega t}{2\omega} \right) \right\}. \tag{14.25}$$

Thus as $\omega \to 0$

$$C \propto \left(k^2 + k^2 \alpha^2 t^2 \right) \exp\left\{ -2\kappa k^2 t - \frac{2\kappa k^2 \alpha^2}{3} t^3 \right\}. \tag{14.26}$$

For small enough κ, the stirring (α) causes an algebraic *increase* in C at small time, but the exponential *decrease* caused by mixing (κ) eventually dominates. Because of the t^3-term in (14.26), this exponential decrease is ultimately faster with stirring than it would be without it. Thus (14.26) captures all of the behavior shown in Figure 1.5.

15. *Static stability*

The simplest solutions of the equations of motion are states of rest. Suppose then that $\mathbf{v}=0$, and that all the other variables do not change with time. Then (taking $\phi=gz$ and neglecting the diffusion of heat and salt) the equations of motion (13.1) reduce to

$$0=-\frac{1}{\rho}\nabla p-g\mathbf{k}, \tag{15.1}$$

and

$$\rho=\rho(S,T,p). \tag{15.2}$$

The vertical component of (15.1), namely

$$\frac{dp}{dz}=-\rho g\ , \tag{15.3}$$

is called the *hydrostatic relation*.

Equations (15.2-3) are two equations in the four dependent variables $\rho(z)$, $S(z)$, $T(z)$, and $p(z)$; there are thus many possible solutions. We could, for example, choose $S(z)$ and $T(z)$ to be anything we please; then $\rho(z)$ and $p(z)$ are determined by (15.2-3). However, we shall see that only a subset of these solutions are stable with respect to tiny disturbances of the fluid.

Let $\rho(z)$ be a density field satisfying the above equations, and suppose that a particle of fluid is suddenly displaced a small vertical distance δz from its position at z=0 in the state of rest. If the displacement occurs without exchange of heat or salt, then the change in particle density is

$$\delta\rho_{part}=\frac{1}{c^2}\delta p_{part}=-\frac{\rho_0 g}{c^2}\delta z\ , \tag{15.4}$$

where ρ_0 is the density of the fluid at z=0. The displaced particle experiences a buoyancy force per unit volume of[11]

$$-\left(\rho_{part}-\rho\right)g\ . \tag{15.5}$$

Thus, neglecting terms of order δz^2, we obtain the equation of motion

$$\begin{aligned}
\rho_{part}\frac{d^2\,\delta z}{dt^2} &= -[\rho_{part}-\rho]g \\
&\approx -\left[\left(\rho_0+\frac{d\rho_{part}}{dz}\delta z\right)-\left(\rho_0+\frac{\partial\rho}{\partial z}\delta z\right)\right] \\
&= -\left[\left(\rho_0-\frac{\rho_0 g}{c^2}\delta z\right)-\left(\rho_0+\frac{\partial\rho}{\partial z}\delta z\right)\right]g \\
&= g\left[\frac{\rho_0 g}{c^2}+\frac{\partial\rho}{\partial z}\right]\delta z
\end{aligned} \tag{15.6}$$

for the displaced particle. More succinctly,

$$\frac{d^2\,\delta z}{dt^2} = -N^2\;\delta z\,, \tag{15.7}$$

where

$$N^2 \equiv -g\left[\frac{1}{\rho_0}\frac{\partial\rho}{\partial z}+\frac{g}{c^2}\right]. \tag{15.8}$$

N is the *Brunt-Vaisala frequency*. The solution to (15.7) is

$$\delta z\;=e^{\pm iNt}\;. \tag{15.9}$$

Thus the fluid is stable if $N^2>0$, and unstable if $N^2<0$. If $N^2>0$, an upwardly displaced water particle has a density greater than that of its surroundings, and tends to sink. If $N^2<0$, the converse is true. Note that the compressibility of the fluid — the g/c^2-term in (15.8) — is always a destabilizing factor.

16. *Potential density and potential temperature*

The term $\rho_0\, g/c^2$ in (15.6) is the rate at which density changes with depth *solely* on account of the increasing pressure — the so-called *adiabatic lapse rate* — and, as we have shown, stability depends on the *difference* between the actual lapse rate, $-\partial\rho/\partial z$, and the adiabatic lapse rate. As this calculation suggests, it is frequently convenient to remove the pressure effect on density.

Roughly speaking, *potential density* is density with the pressure-dependence removed. More precisely, the potential density ρ_θ of a seawater particle is the density that the particle would have if moved adiabatically (that is, without exchanging heat or salt) to a prescribed reference pressure p_0. Unless otherwise specified, p_0 is the average pressure at sea level. The *potential temperature* θ is similarly defined.

Because the potential temperature and potential density are defined by hypothetical adiabatic displacements, they are closely related to the entropy. Regarding the entropy as a function of salinity, temperature and pressure,

$$\eta = F(S,T,p), \tag{16.1}$$

we have, by definition,

$$\eta = F(S,\theta,p_0)\,. \tag{16.2}$$

Thus, for a given reference pressure p_0, the potential temperature depends only on the entropy and salinity. Since a particle moving adiabatically keeps the same value of η and S, it also conserves its potential temperature (no matter what the reference pressure p_0). For a particle of fixed salinity,

$$d\eta = \frac{\partial F(S,\theta,p_0)}{\partial\theta}d\theta = \frac{C_p}{\theta}d\theta \qquad (dS=0)\,. \tag{16.3}$$

If the equation of state is given in the form

$$\rho = G(S,T,p), \tag{16.4}$$

then the potential density is by definition

$$\rho_\theta = G(S,\theta,p_0)\,. \tag{16.5}$$

Thus η, S, θ, and ρ_θ are all conserved on a particle moving adiabatically. For a seawater particle of fixed salinity,

$$d\rho_\theta = \frac{\partial G(S,\theta,p_0)}{\partial\theta}d\theta = -\rho_\theta\beta\, d\theta \qquad (dS=0) \tag{16.6}$$

where

$$\beta \equiv \frac{1}{\alpha}\frac{\partial\alpha(S,T,p)}{\partial T} \tag{16.7}$$

as before.

As the calculation of Section 15 suggests, the potential density gradient is more simply related to the Vaisala frequency than is the density gradient itself. Again, the critical factor deciding static stability is the difference between the density of the adiabatically displaced fluid particle and the density of its surroundings. Suppose that the reference level for potential density is the level to which the particle is displaced (Figure 1.7). Its density there is, by definition, the potential density at the level it originated, that is, $\rho_\theta(z)$. On the other hand, the ambient density at $z+\delta z$ is $\rho_\theta(z+\delta z)$. Thus the fluid is stable if

$$\rho_\theta(z) > \rho_\theta(z+\delta z), \qquad \text{that is, if} \qquad \frac{\partial \rho_\theta}{\partial z} < 0 \qquad (p = p_0). \tag{16.8}$$

We find that

$$N^2 = -\frac{g}{\rho_\theta}\frac{\partial \rho_\theta}{\partial z}. \qquad (p = p_0) \tag{16.9}$$

However, (16.8-9) are true *only* at the reference pressure, p_0. Far from p_0, they can be grossly inaccurate. For example, in the deep North Atlantic, $\partial\rho_\theta/\partial z$ actually becomes positive if ρ_θ is defined with the reference pressure at the sea surface. We return to this point in the next section.

The potential temperature gradient $\partial\theta/\partial z$ is *not* closely related to static stability. This is because (16.5) implies that

$$\frac{\partial \rho_\theta}{\partial z} = \frac{\partial \rho}{\partial T}\frac{\partial \theta}{\partial z} + \frac{\partial \rho}{\partial S}\frac{\partial S}{\partial z}, \tag{16.10}$$

and the final term in (16.10) is often very important. Thus no particular significance attaches to the sign of $\partial\theta/\partial z$.

17. *The equation of state for seawater*

The equation of state,

$$\rho = \rho(S,T,p) \tag{17.1}$$

is a relation between thermodynamic variables, which, like all other equilibrium thermodynamic functions, is uniquely determined by the fundamental relation $E=E(\alpha,\eta,S)$. The choice of S, T and p as the independent variables is merely conventional. However, the *true salinity,* defined, as in Section 17, as the mass fraction of all dissolved solids, is very difficult to measure. Hence, since about 1978, oceanographers have adopted the *practical salinity,* a precisely defined function of electrical conductivity that agrees as closely as possible with true salinity. The practical salinity is much more easily measured, and, for most purposes, the distinction between practical and true salinity is unimportant. The equation of state (17.1) is a complicated empirical formula involving practical salinity, temperature and pressure. The most recent version was adopted in 1980.[12]

The best way to get a feel for the equation of state is to look at a *T-S* diagram (Figure 1.8), which has axes temperature and salinity and contour lines of constant

$$\sigma = 10^3\left(\rho - 1 gm\ cm^{-3}\right) \tag{17.2}$$

at fixed pressure. Since ρ varies from about 1.02 to 1.07 gm cm^{-3} in the ocean, σ varies from about 20 to 70. There is a different *T-S* diagram for every fixed pressure. If one regards the temperature axis as potential temperature, and the fixed pressure as the reference pressure p_0, then the contours represent potential density. It has become conventional to denote by σ_n the sigma corresponding to potential density at a reference pressure equivalent to a depth of *n* kilometers. Thus

$$\sigma_2 = 10^3\left(\rho(S,\theta_2,2000\,\text{db}) - 1\ gm\ cm^{-3}\right), \tag{17.3}$$

where θ_2 is the potential temperature corresponding to a reference pressure of 2000 decibars.

To assess the relative importance of salinity, temperature, and pressure variations on the density, we write the total differential of specific volume in the form

$$\frac{d\alpha}{\alpha} = \beta\, dT - b\, dS - \kappa\, dp, \tag{17.4}$$

where

$$\begin{aligned} \beta &= \frac{1}{\alpha}\frac{\partial\alpha}{\partial T} \approx 2\times 10^{-4}\ \text{deg}^{-1} \\ b &= -\frac{1}{\alpha}\frac{\partial\alpha}{\partial S} \approx 8\times 10^{-4}\ \text{ppt}^{-1} \\ \kappa &= -\frac{1}{\alpha}\frac{\partial\alpha}{\partial p} \approx 4\times 10^{-6}\ \text{dbar}^{-1} \end{aligned} \tag{17.5}$$

The open-ocean ranges of temperature, salinity and pressure, and the corresponding fractional changes in specific volume (or density) are:

	T	*S*	*p*
typical range	25 deg	6 ppt	10,000 dbar
$d\alpha/\alpha$	.005	.005	.04

We see that the pressure is the most important determinant of the density. However, the pressure effect on density is not as important as the effects of temperature and salinity, because the most significant density differences are those between fluid particles at about the same depth. (This, again, is the motivation for the use of potential density.) Furthermore, the effects of salinity and temperature are partially cancelling, because the warmest waters are also usually the saltiest. Thus the density variation caused by temperature and salinity is nearer .3% than 1%. At the largest scales of motion, the effect of temperature on density is usually more important than that of salinity.

The equation of state for seawater has two interesting peculiarities. The first is the concave-downward shape of isopycnals on the *T-S* diagram. Consider two particles of seawater (A and B) with the same density, but suppose that B has the higher salinity (Figure 1.9). A mixture of equal masses of A and B lies (approximately) at the center of a straight line joining A and B on the *T-S* diagram. That is, the final salinity and temperature are approximately

$$S = \tfrac{1}{2}\left(S_A + S_B\right) \quad \text{and} \quad T = \tfrac{1}{2}\left(T_A + T_B\right). \tag{17.6}$$

However, because of the isopycnal curvature, the mixture at C is denser than that at both A and B. This phenomenon (called *cabbeling*) may contribute to the formation of deep water.[13] Of course, (17.6) are not precisely correct. As shown in Section 12, the correct equations are

$$S = \tfrac{1}{2}\left(S_A + S_B\right) \quad \text{and} \quad h = \tfrac{1}{2}\left(h_A + h_B\right), \tag{17.7}$$

where h is the specific enthalpy.[14]

The second peculiarity of the equation of state is the clockwise turning of isopycnal lines on the *T-S* diagram as the pressure increases. Refer to Figure 1.10. In other words, salty water is less compressible than fresh water. Thus A in Figure 1.10 can be denser than B at sea level, but less dense than B at great depth. Something like this actually occurs: North Atlantic Deep Water is denser than Antarctic Bottom Water at pressures near sea level, but the converse is true when they finally meet at a depth of about 4 km.[15]

18. *Statistical mechanics: the ideal gas*

As already emphasized, the equilibrium thermodynamics of a particular substance is completely determined by its fundamental relation $E=E(\eta, X_1, \ldots, X_N)$, where the X_i are the macroscopic variables (besides the specific entropy η) that determine the state of the substance. For seawater, $N=2$, $X_1=\alpha$, and $X_2=S$. From the standpoint of thermodynamics, the fundamental relation must be *given*, that is, determined by laboratory measurements.

Statistical mechanics offers a means of *calculating* the fundamental relation of thermodynamics, using Boltzmann's famous formula,

$$\eta = k \ln \Omega\left(E, X_1, \ldots, X_N\right), \tag{18.1}$$

and thereby completing the theoretical framework. In (18.1), k is Boltzmann's constant, and Ω is the number of distinct microscopic states of the system that correspond to the macroscopic values $E, X_1, \ldots, X_N$. For a gram of seawater, one would need to count the number of microstates corresponding to energy E, volume α, and salinity S. To determine the fundamental relation, we would then solve (18.1) for E.

Statistical mechanics offers precise rules for counting the number of states. However, the counting rules, though simple in principle, are quite difficult to apply to all but the simplest physical systems (which certainly excludes seawater!). Moreover, even when the counting rules can be applied, they often lead to results that are ambiguous or paradoxical, unless the true quantum nature of the microscopic states is taken into account. There is however one type of system — the ideal gas — in which the counting rules are both easy to apply and relatively free from ambiguity.

Even in the case of an ideal gas, the general counting rule of statistical mechanics requires a rather lengthy explanation. We defer that until Chapter 5, where we shall have further use for statistical mechanics. Here we proceed by means of a shortcut, the so-called *equipartition theorem,* which asserts that in thermodynamic equilibrium each microscopic degree of freedom has the average energy $\frac{1}{2}kT$. Unlike the general counting rule of statistical mechanics, the equipartition theorem applies only to systems in which the energy is a quadratic function; fortunately, the ideal gas is such a system.

Consider a system of ideal gas in which (for simplicity) all the molecules are identical; the results generalize easily. By the equipartition theorem, the total energy of the system is

$$\begin{aligned}&\tfrac{1}{2}kT\cdot d\cdot(number\ of\ molecules)\\&=\tfrac{1}{2}kT\cdot d\cdot N_A\cdot(number\ of\ moles)\end{aligned} \tag{18.2}$$

where d is the number of degrees of freedom *per molecule*, and N_A is Avogadro's number. For a monatomic gas, d=3, corresponding to location in *three*-dimensional space. For a diatomic gas behaving like a rigid dumbell, d=5, with the additional two degrees of freedom needed to specify the orientation of the molecule. From (18.2) it follows that the specific internal energy is

$$E=\tfrac{1}{2}d\,kTN_A/m \tag{18.3}$$

where m is the molecular weight, the number of grams per mole. Let

$$R^*\equiv k\,N_A \tag{18.4}$$

be the *universal gas constant,* and let

$$R\equiv R^*/m \tag{18.5}$$

be the gas constant for the specific gas under consideration. Then (18.3) becomes

$$E=\tfrac{1}{2}d\,RT\,. \tag{18.6}$$

Eqn. (18.6) does not, by itself, determine the fundamental relation. However, we also know that, in an ideal gas, the pressure represents the momentum transferred by collisions. Thus

$$p=\rho<{u_{mol}}^2> \tag{18.7}$$

where u_{mol} is the molecular velocity in (say) the *x*-direction. By the equipartition theorem,

$$\tfrac{1}{2} m_{mol} < u_{mol}{}^2 >= \tfrac{1}{2} \frac{m}{N_A} < u_{mol}{}^2 >= \tfrac{1}{2} kT. \tag{18.8}$$

Thus,

$$p = \frac{\rho k T N_A}{m} = \frac{\rho}{m} R^* T = n R^* T\ , \tag{18.9}$$

where n is the number of moles per unit volume, or,

$$p = \rho R T. \tag{18.10}$$

Eqns. (18.6) and (18.10) are frequently taken as the *definition* of an ideal gas. It can be shown, using (18.6,10) and remembering the definitions $p=-\partial E/\partial \alpha$ and $T=\partial E/\partial \eta$, that

$$E(\alpha, \eta) = const\ \ \alpha^{-2/d} \exp\left[\frac{2\eta}{Rd}\right], \tag{18.11}$$

where *const* is a constant of integration. Thus (18.6,10) determine the fundamental relation up to an undetermined constant factor. This undetermined factor is physically irrelevant (for the same reason that the entropy in *classical* thermodynamics is arbitrary to within a constant).

The choice of *d*, the number of degrees of freedom associated with a single molecule, is somewhat ambiguous. In a diatomic gas (for example), *d*=5 if the two atoms are *rigidly-connected, point* masses, but *d*=6 if the atoms have a finite radius and one takes the rotation about the axis of symmetry into account, and *d*=7 if the distance between atoms can change. If the atoms also have internal degrees of freedom, then *d* must be further increased.

The ambiguity in *d* affects all the formulae in which *d* appears (that is, (18.6) but not the equation of state (18.9) or (18.10)). However, since we can eliminate *d* in favor of the heat capacity, we can also say that the ambiguity affects only the predicted values of heat capacity. At *constant volume*, the change in energy equals the heat added to the system, $\delta E = \delta Q$, so that, by (18.6), the heat capacity $C = \delta Q / \delta T$ is

$$C_V = \frac{d}{2} R, \tag{18.12}$$

and (18.6) becomes

$$E = C_V T. \tag{18.13}$$

At *constant pressure,*

$$\delta E = -\delta(p\alpha) + \delta Q\,, \tag{18.14}$$

which by (18.13) and (18.10) is

$$C_V\,\delta T = -R\,\delta T + \delta Q\,. \tag{18.15}$$

The heat capacity at constant pressure is thus

$$C_P = C_V + R\,, \tag{18.16}$$

and

$$\frac{C_P}{C_V} = \frac{d+2}{d}\,. \tag{18.17}$$

Boltzmann, noting that (18.17) with d=3 and d=5 yields predictions that agree closely with the measurements of monatomic and diatomic gases (respectively) at moderate temperatures, argued that this proved that other degrees of freedom were not excited by the collisions between molecules; Maxwell believed that the theory was seriously flawed. Neither man lived to see quantum mechanics, which resolves the paradox. For air (a predominantly diatomic gas), the measured ratio of heat capacities is so close to (18.17) with d=5 that many textbooks simply state the theoretical result.

To a very good approximation, the Earth's atmosphere behaves like an ideal gas (except at very high altitudes, where the collisions between molecules are too infrequent to maintain statistical equilibrium).

Notes for Chapter 1.

1. Alternatively, one could regard (a,b,c) as the values of (x,y,z) at the initial time. Then the initial density $\rho_0(a,b,c)$ appears on the right-hand side of (2.4).
2. Readers with no previous experience at Hamilton's method should study the first few chapters of Goldstein (1980) or Lanczos (1970).
3. Throughout Chapter 1, I use the postulational basis of thermodynamics developed by Gibbs (1878), Tisza (1966) and Callen (1985). This approach, with its emphasis on energy, nicely parallels Hamilton's approach to mechanics. It is equivalent to, but much handier than, the thermodynamics of Clausius and Kelvin presented in most thermodynamics texts.
4. Section 10 is partly based upon an unpublished manuscript by Carl Eckart (1963).
5. For a thorough introduction to kinetic theory, see, for example, Balescu (1975).
6. For a self-contained derivation of (11.1), see Owczarek (1968, pp. 274-285) .
7. Once again, Balescu (1975) is a good source for details.
8. For a complete development of thermodynamics based upon these four postulates, see Callen (1985).
9. Actually we know even more; using a general argument based upon the time-reversibility of the microscopic dynamics, Onsager (1931) showed that $\kappa_{T\mu} = \kappa_{\mu T}$.
10. Section 14 is based upon the paper by Young, Rhines and Garrett (1982).

11. This is Archimedes principle. The reader should be able to prove it from the momentum equation for a hydrostatic fluid.
12. For a more complete discussion of practical salinity, the equation of state, and other thermodynamic functions, see Fofonoff (1985).
13. See Foster (1972) and McDougall (1987). Talley and Yun (1996) suggest that cabbeling at the confluence of the Kuroshio and Oyashio Currents produces North Pacific Intermediate Water.
14. See Fofonoff (1962) for an estimate of the error in (17.6).
15. See Lynn and Reid (1968).