6

Irreversible processes: macroscopic theory

In the preceding chapters, we have limited our analysis to equilibrium situations. This is rather restrictive since non-equilibrium phenomena, such as heat conduction or diffusion, are of great interest and cannot be ignored. To remedy this, we focus in this chapter on an introduction to non-equilibrium phenomena. Further developments of the subject will be found in Chapters 8 and 9.

We have seen that equilibrium statistical mechanics is built on a general and systematic approach, namely the Boltzmann–Gibbs distribution. No such general approach is available for non-equilibrium situations; instead, we find a large variety of methods suited to particular cases and situations. What we are able to control well are cases close to equilibrium where we can rely on rather general methods like linear response theory, which will be described in Sections 9.1 and 9.2. In the present chapter, we shall consider a macroscopic approach, that of transport coefficients, which is the non-equilibrium analogue of equilibrium thermodynamics. At this stage, we shall not attempt a calculation of these transport coefficients from a microscopic theory. We shall only show that these coefficients satisfy a number of general properties, their actual values being taken from experiments. This parallels equilibrium thermodynamics where we uncovered a number of general relations between thermodynamic quantities while we did not attempt to calculate, for example, the specific heat from a microscopic theory but took its value from experiments. In Chapters 8 and 9 we shall demonstrate, for some simple cases, how to calculate transport coefficients starting with a microscopic theory (kinetic theory in Chapter 8 and linear response in Chapter 9) just as we calculated the specific heats in some simple cases by using equilibrium statistical mechanics.

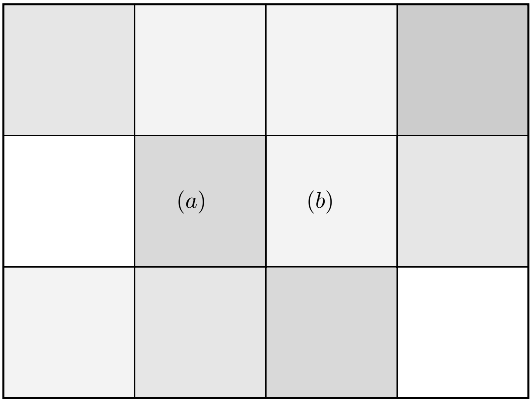

Figure 6.1 Dividing a system into cells.

6.1 Flux, affinities, transport coefficients

6.1.1 Conservation laws

A physical system can be so far out of equilibrium that quantities like the temperature or pressure cannot even be defined. We shall not consider such extreme cases and concentrate, instead, on cases where we can define locally thermodynamic variables. We start with an idealized case where we assume the system to be composed of homogeneous cells, small on the macroscopic scale but large on the microscopic one, and labelled $(a, b, \dots)$ (Figure 6.1).[1] We also assume that cells interact weakly with their neighbours so that each cell independently attains a local equilibrium with a microscopic relaxation time, τ_{micro}, which is very small compared to the macroscopic relaxation time, τ_{macro}, needed to achieve global equilibrium:[2] $\tau_{\text{micro}} \ll \tau_{\text{macro}}$. We say we have a situation of *local equilibrium* when

(i) each subsystem is at equilibrium independently of the other subsystems,
(ii) interactions between neighbouring subsystems are weak.

Let $A_i(a, t)$ be an extensive quantity (e.g. energy, number of particles, momentum etc.) labelled by the index i and contained in cell a at time t. We call *flux* $\Phi_i(a \to b)$ the amount of A_i transferred from cell a to cell b per unit time. Note that $\Phi_i(a \to b)$ is the net flux between a and b and therefore

$$\Phi_i(a \to b) = -\Phi_i(b \to a) \tag{6.1}$$

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[1] In some cases (see Problem 6.5.4) these cells are not spatial.

[2] Key to the existence of these two time scales are conservation laws that forbid certain physical quantities (called slow variables) to return to global equilibrium on short time (and space) scales. As will be explained in Section 9.3, non-equilibrium statistical mechanics distinguishes fast variables, characterized by microscopic time and space scales, from slow variables characterized by macroscopic time and space scales. In Section 9.3 and in Section 2.6.3, τ_{micro} is denoted by τ^* and τ_{macro} by τ.

Cell a may have a source of quantity A_i. For example, if our system is a nuclear reactor and $A_i(a, t)$ the number of neutrons in cell a, neutrons are produced when uranium or plutonium atoms fission and therefore act as sources. On the other hand, the moderator absorbs neutrons, and therefore acts as a sink. The change per unit time of $A_i(a, t)$, $\mathrm{d}A_i(a, t)/\mathrm{d}t$, is then the sum of the contributions of the other cells and those of the sources. This leads to the equation

$$\boxed{\frac{\mathrm{d}A_i(a,t)}{\mathrm{d}t} = -\sum_{b \neq a} \Phi_i(a \to b) + \Phi_i(\text{sources} \to a)} \tag{6.2}$$

This is a *conservation equation* for the quantity A_i.

Clearly, this decomposition of the system into independent cells is an idealization. We can obtain a more realistic formulation if we express Equation (6.2) in local form. We assume that in the neighbourhood of each point in space reigns a local equilibrium, so that we can locally define thermodynamic quantities, for example a local temperature $T(\vec{r}, t)$ or a local chemical potential $\mu(\vec{r}, t)$. For such a local equilibrium to be possible, we need, in addition to $\tau_{\text{micro}} \ll \tau_{\text{macro}}$, a condition on length scales. If l_{micro} is a characteristic length scale over which is established a local equilibrium, and l_{macro} a length characteristic of the variations of thermodynamic quantities like the temperature, then we must have $l_{\text{micro}} \ll l_{\text{macro}}$. A regime of local equilibrium is also called a *hydrodynamic regime*: the hydrodynamic description of a fluid relies crucially on the condition of local equilibrium. So, from this construction, we see that the hydrodynamic regime, i.e. local equilibrium, describes the dynamics of a system subject to perturbations of *long wavelength* λ (long compared to microscopic lengths, $\lambda \gg l_{\text{micro}}$) and *low frequencies* ω (low compared to microscopic frequencies $\omega \ll 1/\tau_{\text{micro}}$). A local equilibrium regime will often be obtained by imposing external constraints on the system, for example a temperature gradient. If these constraints are time-independent, the system will reach a *stationary (*i.e. *time independent) non-equilibrium regime*.

Let $\rho_i(\vec{r}, t)$ be the density of quantity A_i, e.g. density of energy, of particles of momentum etc. $A_i(a, t)$ is then the integral of the density over the volume $V(a)$ of the cell[3]

$$A_i(a,t) = \int_{V(a)} \mathrm{d}^3r \, \rho_i(\vec{r}, t) \tag{6.3}$$

We can therefore define a corresponding current density, or more briefly a current, $\vec{j}_i(\vec{r}, t)$. If $\overrightarrow{\Delta S}$ is the small oriented surface separating cells a and b (Figure 6.2(a)),

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[3] The definition of densities supposes a process of ‘coarse graining’: the cell size needs to be large enough for the concepts of local temperature etc. to have a meaning. We also note that we are using the so-called Eulerian description: the cells are fixed in space and do not follow the movement of a given mass of fluid, which would correspond to the Lagrangian description.

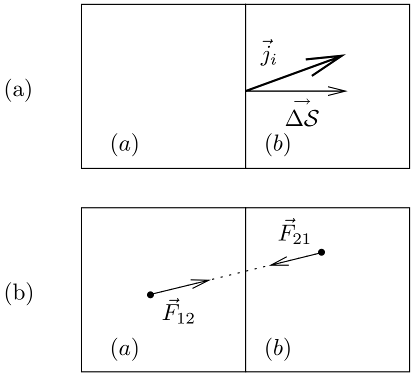

Figure 6.2 (a) Current and flux, (b) momentum exchange between two cells.

the flux $\Phi_i(a \to b)$ may be written as

$$\Phi_i(a \to b) \simeq \overrightarrow{\Delta\mathcal{S}} \cdot \vec{j}_i$$

Now let $\mathcal{S}(a)$ be the surface surrounding cell (a): the total flux crossing $\mathcal{S}(a)$ is given by the surface integral of the current

$$\Phi_i^{\mathcal{S}}(t) = \sum_b \Phi_i(a \to b) = \int_{\mathcal{S}(a)} \overrightarrow{\mathrm{d}\mathcal{S}} \cdot \vec{j}_i(\vec{r}, t) \tag{6.4}$$

The current $\vec{j}_i$ characterizes the flow of quantity i across a surface. Let us consider a simple example. If $\rho_N(\vec{r}, t) \equiv n(\vec{r}, t)$ is the particle density and $\vec{u}(\vec{r}, t)$ the average particle velocity, the current $\vec{j}_N$ is of course given by (a microscopic demonstration is proposed in Exercise 6.4.1)

$$\vec{j}_N(\vec{r}, t) = n(\vec{r}, t)\vec{u}(\vec{r}, t) \tag{6.5}$$

One should be careful, however, since currents are not always the product of a density and an average velocity. In fact, (6.5) implies that, in the absence of sources, the number of particles in cell a can change only because particles enter and leave this cell by crossing the surface $\mathcal{S}(a)$ and that the only contributions to the current are of the form (6.5). In the case of energy or momentum, there can also be exchanges between two cells even if no particles cross the surface separating them. Figure 6.2(b) illustrates that two cells can exchange momentum due to the principle of action and reaction. If we focus on the forces between the two particles, the momenta $\vec{p}_1$ and $\vec{p}_2$ of the two particles belonging to two different cells satisfy

$$\frac{\mathrm{d}\vec{p}_1(t)}{\mathrm{d}t} + \frac{\mathrm{d}\vec{p}_2(t)}{\mathrm{d}t} = 0$$

In general, the momentum current cannot be put in the form (6.5) and the right hand side of (6.2) will have three contributions from

(*i*) particles entering and leaving the volume $V(a)$ of the cell surrounded by the surface $\mathcal{S}(a)$,
(*ii*) forces applied by the other particles of the fluid outside the cell in question,[4]
(*iii*) external forces, such as gravity, which play in this case the rôle of sources.

The local version of the conservation equation (6.2) is obtained by using the Green theorem. The flux $\Phi_i^{\mathcal{S}}$ is written as a volume integral

$$\Phi_i^{\mathcal{S}} = \int_{\mathcal{S}} \overrightarrow{\mathrm{d}\mathcal{S}} \cdot \vec{j}_i = \int_V \mathrm{d}^3 r \, \vec{\nabla} \cdot \vec{j}_i$$

whereas the source term becomes the integral of a density σ_i

$$\Phi_i(\text{sources} \to \text{a}) = \int_V \mathrm{d}^3 r \, \sigma_i$$

The conservation equation (6.2) becomes

$$\int_V \mathrm{d}^3 r \, \frac{\partial \rho_i}{\partial t} = -\int_V \mathrm{d}^3 r \, \vec{\nabla} \cdot \vec{j}_i + \int_V \mathrm{d}^3 r \, \sigma_i$$

Since this equation is valid for all volumes V, we obtain from it the *local conservation equation* (or the continuity equation)

$$\boxed{\frac{\partial \rho_i}{\partial t} + \vec{\nabla} \cdot \vec{j}_i = \sigma_i} \tag{6.6}$$

Physical quantities obeying Equation (6.6) are called *conserved quantities* and will play a fundamental rôle in what follows.

6.1.2 Local equation of state

Returning to the cell picture, we can attribute an entropy $S(a)$ to each of these cells since each is at local equilibrium. Since the interactions among the cells are assumed weak, the total entropy S_{tot} is obtained as a simple sum of the individual entropies[5]

$$S_{\text{tot}} = \sum_a S(a) \tag{6.7}$$

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[4] We assume that all forces have short range. Ambiguities may appear for long range forces. A remark along those lines has already been made in Chapter 1.

[5] The reader should have noted the special rôle played by the entropy compared to the other extensive variables. This special rôle will be confirmed throughout this chapter.

Let $\gamma_i(a)$ be the intensive conjugate variable of $A_i(a)$ defined by

$$\gamma_i(a) = \frac{\partial S_{\text{tot}}}{\partial A_i(a)} = \frac{\partial S(a)}{\partial A_i(a)} \tag{6.8}$$

For the five extensive quantities we consider in this chapter, namely the particle number N, the energy E, the three components of the momentum[6] $\vec{P}$ (with components $P_\alpha, \alpha = (x, y, z)$) the intensive conjugate variables are

$$A_i = N \qquad \gamma_N = -\frac{\mu}{T} \tag{6.9}$$

$$A_i = E \qquad \gamma_E = \frac{1}{T} \tag{6.10}$$

$$A_i = P_\alpha \qquad \gamma_{P_\alpha} = -\frac{u_\alpha}{T} \tag{6.11}$$

The first two equations are the classic thermodynamic relations (1.9) and (1.11); the third involves the average local velocity $\vec{u}$, or the *flow velocity* of the fluid in the considered cell. To demonstrate the third equation, we note that collective motion does not change the entropy of a fluid:[7] a glass of water on a plane in uniform motion has the same entropy as the same glass of water back on the ground. Let E' be the energy of the fluid at rest and S_0 its entropy,

$$S_0(E') = S(E, \vec{P} = 0)$$

To go from E' to E, we need to add the kinetic energy of the mass M of the fluid which is in motion

$$E = E' + \frac{\vec{P}^{\,2}}{2M}$$

and

$$S(E, \vec{P}) = S_0\left(E - \frac{\vec{P}^{\,2}}{2M}\right)$$

This yields

$$\gamma_{P\alpha} = \frac{\partial S}{\partial P_\alpha} = -\frac{P_\alpha}{M}\frac{\partial S_0}{\partial E'} = -\frac{u_\alpha}{T}$$

Let us consider all the extensive variables and use a reasoning based on the extensivity of the entropy which we already encountered in Section 1.3.3:

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[6] To avoid all confusion between the momentum and the pressure, the pressure will be noted by $\mathcal{P}$ in Chapters 6 and 8. The lower case letter $\vec{p}$ will denote the momentum of a single particle while $\vec{P}$ that of a collection of particles.

[7] We can show this rigorously in statistical mechanics (Exercise 2.7.7).

$S(\lambda A_i) = \lambda S(A_i)$, where λ is a scale factor. Differentiating this equation with respect to λ and putting $\lambda = 1$, we find

$$\sum_i A_i(a)\,\frac{\partial S(a)}{\partial A_i(a)} = \sum_i \gamma_i(a) A_i(a) = S(a)$$

which gives

$$\boxed{\sum_{i,a} \gamma_i(a) A_i(a) = S_{\text{tot}}} \tag{6.12}$$

The local version of (6.12) is

$$\boxed{\sum_i \int \mathrm{d}^3 r\; \gamma_i(\vec{r}, t) \rho_i(\vec{r}, t) = S_{\text{tot}}(t)} \tag{6.13}$$

which we can also write in the form of functional derivatives (Section A.6)

$$\gamma_i(\vec{r}, t) = \frac{\delta S_{\text{tot}}(t)}{\delta \rho_i(\vec{r}, t)} \tag{6.14}$$

6.1.3 Affinities and transport coefficients

When two neighbouring cells a and b have different intensive variables γ_i, an exchange of A_i will take place between them. For example, a difference in temperature engenders an exchange of heat. The difference $\gamma_i(b) - \gamma_i(a)$, which measures the deviation from equilibrium, is called the *affinity* $\Gamma_i(a, b)$

$$\boxed{\Gamma_i(a, b) = \gamma_i(b) - \gamma_i(a)} \tag{6.15}$$

Let us consider the example of the temperature and suppose $\gamma_E(a) < \gamma_E(b)$ or $T(a) > T(b)$. In order to re-establish equality of temperatures, i.e. thermal equilibrium, a heat flux is established from a to b. In general, a system responds to differences in affinities between cells by attempting to establish an equilibrium state via the exchange of A_i between them. For sufficiently small affinities, we may use a linear approximation that expresses the flux in terms of the affinities

$$\boxed{\Phi_i(a \to b) = \sum_j L_{ij}(a, b) \Gamma_j(a, b)} \tag{6.16}$$

Note (i) the coupled character of these equations: an affinity Γ_j can produce a flux of the quantity A_i, and (ii) the equality $L_{ij}(a, b) = L_{ij}(b, a)$. The proportionality coefficients which relate the flux and the affinities are called response coefficients.

Let us now examine the local version of (6.16). If the centre of cell a is at point $\vec{r}$ and that of cell b at point $\vec{r} + \mathrm{d}\vec{r}$, the differences $\gamma_i(b) - \gamma_i(a)$ can be written as gradients

$$\gamma_i(b) - \gamma_i(a) \simeq \mathrm{d}\vec{r} \cdot \vec{\nabla}\gamma_i$$

However, care must be taken because, in general, currents also contain contributions from equilibrium currents which do not lead to any net exchange of A_i: only the difference $\vec{j}_i - \vec{j}_i^{\,\mathrm{eq}}$ is affected by the gradients of γ_i. For the current components j_α^i,[8] the local version of (6.16) then becomes,

$$\boxed{j_\alpha^i(\vec{r}, t) - j_\alpha^{i,\mathrm{eq}} = \sum_{j,\beta} L_{ij}^{\alpha\beta}\, \partial_\beta \gamma_j(\vec{r}, t)} \tag{6.17}$$

Equation (6.17) is called a *transport equation* and the coefficients $L_{ij}^{\alpha\beta}$ are called *transport coefficients*.

6.1.4 Examples

We illustrate the preceding formal definition with a few simple examples of transport equations.

Heat diffusion in an insulating solid (or a simple fluid)

Heat transport in an insulating solid is accomplished entirely by lattice vibrations, there is no net transport of particles. We thus write a transport equation for the heat (or energy) current $\vec{j}_E$[9]

$$\boxed{\vec{j}_E = -\kappa \vec{\nabla} T} \tag{6.18}$$

where κ is the *coefficient of thermal conductivity*. Since κ is positive, the heat current flows in a direction opposite to that of the temperature gradient. To make the connection between (6.18) and the general transport equation (6.17), we remark that, with $\gamma_E = 1/T$, the latter becomes

$$j_\alpha^E = \sum_\beta L_{EE}^{\alpha\beta}\, \partial_\beta \left(\frac{1}{T}\right) = \sum_\beta L_{EE} \delta_{\alpha\beta}\, \partial_\beta \left(\frac{1}{T}\right) = -L_{EE} \frac{1}{T^2}\, \partial_\alpha T$$

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[8] There is no difference between upper and lower indexes. Our convention is to write $\vec{j}_i$ for the current and j_α^i for a component. Also, as in A.4, we write ∂_x for the partial derivative $\partial/\partial x$.

[9] For a conductor, however, conduction electrons play the dominant rôle in heat transfer. For reasons to be explained in Section 6.3.3, Equation (6.18) is also valid for a simple fluid at rest.

Since the only available vector is the temperature gradient $\vec{\nabla} T$, $\vec{j}_E$ is necessarily parallel to it which results in the Kronecker $\delta_{\alpha\beta}$.[10] Comparing with (6.18) yields

$$L_{EE}^{\alpha\beta} = \kappa T^2 \delta_{\alpha\beta} \tag{6.19}$$

We now use the exact continuity equation (6.6). In the absence of heat sources, and using $\epsilon = \rho_E$ for the energy density, we have

$$\frac{\partial \epsilon}{\partial t} = -\vec{\nabla} \cdot \vec{j}_E = \kappa \vec{\nabla} \cdot (\vec{\nabla} T) = \kappa \nabla^2 T$$

By assuming that the specific heat per unit volume,[11] C, is independent of T, i.e. $\epsilon = CT$, we obtain the diffusion equation for T

$$\boxed{\frac{\partial T}{\partial t} = \frac{\kappa}{C} \nabla^2 T} \tag{6.20}$$

Equation (6.20) is also called a heat equation. The general form of a diffusion equation for a quantity $A(\vec{r}, t)$ is

$$\boxed{\frac{\partial A}{\partial t} = D \nabla^2 A} \tag{6.21}$$

where D is the *diffusion coefficient*. From the heat equation (6.20) we therefore have $D = \kappa/C$. This equation plays a very important rôle in physics and it is worthwhile to discuss briefly its solution. By taking the spatial Fourier transform of $A(\vec{r}, t)$

$$\tilde{A}(\vec{k}, t) = \int \mathrm{d}^3 r \, \mathrm{e}^{-\mathrm{i}\vec{k}\cdot\vec{r}} A(\vec{r}, t) \tag{6.22}$$

we obtain

$$\frac{\partial}{\partial t} \tilde{A}(\vec{k}, t) = -Dk^2 \tilde{A}(\vec{k}, t)$$

whose solution is

$$\tilde{A}(\vec{k}, t) = \mathrm{e}^{-Dk^2 t} \tilde{A}(\vec{k}, 0)$$

We obtain $A(\vec{r}, t)$ by performing the inverse Fourier transform

$$A(\vec{r}, t) = \int \frac{\mathrm{d}^3 k}{(2\pi)^3} \, \mathrm{e}^{\mathrm{i}\vec{k}\cdot\vec{r}} \, \mathrm{e}^{-Dk^2 t} \, \tilde{A}(\vec{k}, 0) \tag{6.23}$$

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[10] In general terms, the proportionality to the gradient is due to rotation invariance, see Section A.

[11] For a solid, the specific heats at constant volume and pressure are almost the same. It is therefore not necessary to specify which we are using.

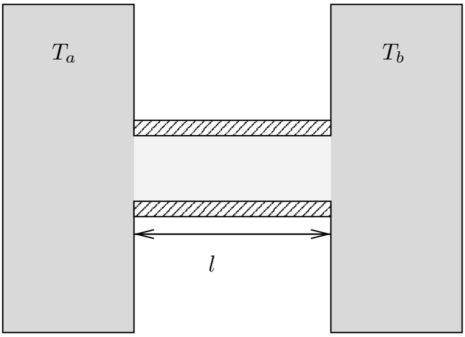

Figure 6.3 A heat conductor of length l connecting two heat reservoirs.

If the initial condition is $A(\vec{r}, 0) = \delta(\vec{r})$, that is we introduce a certain amount of A at time $t = 0$ at point $\vec{r} = 0$, then $\tilde{A}(\vec{k}, 0) = 1$ and the Fourier transform in (6.23) is that of a Gaussian

$$A(\vec{r}, t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left(-\frac{\vec{r}^{\,2}}{4Dt}\right) \tag{6.24}$$

It is easy to obtain from (6.24) the solution of the diffusion equation for an arbitrary initial condition. This is done in Exercise 6.4.2, which also shows the remarkable connection between a random walk and diffusion: Equation (6.24) shows that $\langle \vec{r}^{\,2} \rangle = 6Dt$. The property $\langle \vec{r}^{\,2} \rangle \propto t$ is a common characteristic of random walks and diffusion.[12]

As another example illustrating a simple solution of the diffusion equation, we take the case of a heat conducting bar of length l connecting two heat reservoirs at temperatures T_a and T_b with $T_a > T_b$. The entire system is thermally insulated from the outside world (Figure 6.3). We assume the heat flux to be small enough for the reservoirs to remain at constant temperatures and we consider the stationary (but not equilibrium!) situation $\partial T/\partial t = 0$. The heat equation (6.20) is thus reduced to $\partial^2 T/\partial x^2 = 0$. Applying the correct boundary conditions, we obtain the temperature of the bar as a function of position

$$T(x) = T_a + \frac{x}{l}(T_b - T_a) \tag{6.25}$$

Particle diffusion

We now examine the non-equilibrium case of a solute with inhomogeneous concentration $n(\vec{r}, t)$ in a solvent, where the temperature of the whole system is uniform. To return to equilibrium, the system will homogenize the concentration by establishing a particle current $\vec{j}_N$, thus transporting particles from higher to lower

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[12] In the case of so-called anomalous diffusion, the exponent of t is different from unity.

concentration regions. To leading approximation, the current is proportional to the concentration gradient (Fick's law)

$$\boxed{\vec{j}_N(\vec{r},t) = -D\vec{\nabla}n(\vec{r},t)} \tag{6.26}$$

The positive proportionality coefficient D is the diffusion constant. Equation (6.26) shows that the current is in the opposite direction to the concentration gradient, as is expected. Let us relate Fick's law to the general formulation in (6.17). By using (1.42) that relates $(\partial\mu/\partial n)_T$ to the coefficient of isothermal compressibility, κ_T,

$$\left(\frac{\partial\mu}{\partial n}\right)_T = \frac{1}{\kappa_T n^2}$$

we obtain

$$\vec{\nabla}\gamma_N = \vec{\nabla}\left(-\frac{\mu}{T}\right) = -\frac{1}{T}\left(\frac{\partial\mu}{\partial n}\right)_T \vec{\nabla}n = -\frac{1}{T}\frac{1}{\kappa_T n^2}\vec{\nabla}n$$

Comparing the two expressions for the current

$$\vec{j}_N = -D\vec{\nabla}n = L_{NN}\vec{\nabla}\gamma_N$$

allows us to identify the transport coefficients $L_{NN}^{\alpha\beta}$

$$L_{NN}^{\alpha\beta} = \delta_{\alpha\beta}DT\kappa_T n^2 \tag{6.27}$$

6.1.5 Dissipation and entropy production

Let us examine the rate of change of the entropy $S(a)$ in cell (a). In the absence of sources, (6.2) gives together with (6.8)

$$\frac{\mathrm{d}S(a)}{\mathrm{d}t} = \sum_i \frac{\partial S(a)}{\partial A_i(a)}\frac{\mathrm{d}A_i(a)}{\mathrm{d}t} = \sum_i \gamma_i(a)\frac{\mathrm{d}A_i(a)}{\mathrm{d}t} = -\sum_{i,b\neq a}\gamma_i(a)\Phi_i(a\to b) \tag{6.28}$$

We then have, using the definition (6.15) of the affinity $\Gamma_i(a,b)$,

$$\begin{aligned}\gamma_i(a) &= \frac{1}{2}(\gamma_i(a)+\gamma_i(b)) + \frac{1}{2}(\gamma_i(a)-\gamma_i(b))\\ &= \frac{1}{2}(\gamma_i(a)+\gamma_i(b)) - \frac{1}{2}\Gamma_i(a,b)\end{aligned}$$

The evolution equation of $S(a)$ becomes

$$\frac{\mathrm{d}S(a)}{\mathrm{d}t} + \sum_{b\neq a}\Phi_S(a\to b) = \frac{1}{2}\sum_{i,b\neq a}\Gamma_i(a,b)\Phi_i(a\to b) \tag{6.29}$$

with

$$\Phi_S(a \to b) = \frac{1}{2}\sum_i (\gamma_i(a) + \gamma_i(b))\Phi_i(a \to b) = -\Phi_S(b \to a) \quad (6.30)$$

If we calculate the evolution of the total entropy, $(\mathrm{d}S_{\mathrm{tot}}/\mathrm{d}t)$, the sum over a will cause the Φ_S to cancel in pairs due to their antisymmetry (6.30) under the exchange of a and b. The Φ_S part in (6.29) does not contribute to $(\mathrm{d}S_{\mathrm{tot}}/\mathrm{d}t)$ and, therefore, corresponds to reversible exchanges. Only the right hand side of (6.29), which vanishes for reversible processes, contributes to total entropy production. This production takes place at the interfaces between cells and corresponds to dissipation. *In general, entropy production is called dissipation: all physical phenomena which are accompanied by entropy production will be called* dissipative.

At this point, it is appropriate to mention two fundamental properties of the response coefficients L_{ij} defined in (6.16). If the system is isolated, we know that the total entropy can only increase, and therefore

$$\sum_{i,a,b\neq a} \Gamma_i(a,b)\Phi_i(a \to b) \geq 0 \quad (6.31)$$

Using techniques of advanced non-equilibrium statistical mechanics, one can prove the more detailed property[13]

$$\sum_i \Gamma_i(a,b)\Phi_i(a \to b) \geq 0 \quad (6.32)$$

and from (6.16), this becomes

$$\boxed{\sum_{i,j} \Gamma_i(a,b)L_{ij}(a,b)\Gamma_j(a,b) \geq 0} \quad (6.33)$$

This equation shows that the symmetric matrix $[L_{ij}(a,b) + L_{ji}(a,b)]$ is positive.[14] The rate of change of total entropy is

$$\frac{\mathrm{d}S_{\mathrm{tot}}}{\mathrm{d}t} = \frac{1}{2}\sum_{i,j,a,b} \Gamma_i(a,b)L_{ij}(a,b)\Gamma_j(a,b) \geq 0 \quad (6.34)$$

The second essential property of L_{ij} is the Onsager symmetry relation

$$L_{ij}(a,b) = L_{ji}(b,a) \; (= L_{ji}(a,b)) \quad (6.35)$$

This symmetry property is the result of time reversal invariance, or microreversibility. The proof of (6.35) is similar to that given in (9.67) for the dynamical

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[13] However, the principle of maximum entropy is, in a sense, stronger than (6.32) because it applies even if the intermediate states, between the initial and final states, are not at local equilibrium.

[14] See Section 1.4.2 for the definition and properties of positive matrices.

susceptibility. The most precise form of (6.35) is as follows. Suppose that A_i has definite parity, $\varepsilon_i = \pm 1$, under time reversal as discussed in Sections 2.6 and 9.2.4

$$A_i^\theta(t) = \varepsilon_i A_i(-t) \tag{6.36}$$

where $A_i^\theta(t)$ is the time reversed $A_i(t)$. For example, position, particle number and energy all have parity $+1$ while velocity and momentum have parity -1. If, in addition, the system is in a magnetic field $\vec{B}$, the precise version of (6.35) is

$$L_{ij}(a, b; \{\gamma_k\}; \vec{B}) = \varepsilon_i \varepsilon_j L_{ji}(b, a; \{\varepsilon_k \gamma_k\}; -\vec{B}) \tag{6.37}$$

because time reversal implies inversion of the electrical currents that create the magnetic field. In the local formulation, the transport coefficients $L_{ij}^{\alpha\beta}$ (6.17) will therefore satisfy

$$\boxed{L_{ij}^{\alpha\beta}(\{\gamma_k\}; \vec{B}) = \varepsilon_i \varepsilon_j L_{ji}^{\beta\alpha}(\{\varepsilon_k \gamma_k\}; -\vec{B})} \tag{6.38}$$

In this local formulation, we define the entropy density s as the entropy per unit volume and, from (6.7) and (6.8) in the absence of external sources for A_i, we can write $\mathrm{d}S_{\mathrm{tot}} = \sum_{i,a} \gamma_i \, \mathrm{d}A_i(a)$ and thus $\mathrm{d}s = \sum_i \gamma_i \, \mathrm{d}\rho_i$. The local version of (6.28) is then

$$\frac{\partial s}{\partial t} = \sum_i \gamma_i \frac{\partial \rho_i}{\partial t} = -\sum_i \gamma_i (\vec{\nabla} \cdot \vec{j}_i) \tag{6.39}$$

where the sum runs over all conserved quantities of the system. To obtain the analog of (6.29) we rewrite (6.39) in the form

$$\frac{\partial s}{\partial t} + \vec{\nabla} \cdot \left(\sum_i \gamma_i \vec{j}_i \right) = \sum_i \vec{j}_i \cdot \vec{\nabla} \gamma_i \tag{6.40}$$

If we integrate over the volume of the system to calculate $\mathrm{d}S_{\mathrm{tot}}/\mathrm{d}t$, the second term on the left hand side of (6.40) does not contribute. In fact, using the Green theorem

$$\int \mathrm{d}^3 r \, \vec{\nabla} \cdot \left(\sum_i \gamma_i \vec{j}_i \right) = \sum_i \int \left(\mathrm{d}\vec{S} \cdot \vec{j}_i \right) \gamma_i = 0$$

because the currents vanish at the surface of the system. Only the term $\sum_i \vec{j}_i \cdot \vec{\nabla} \gamma_i$ contributes to the creation of total entropy: in other words, it acts as an entropy source.

We have seen in (6.17) that we should distinguish between total currents and equilibrium currents: equilibrium currents do not contribute to entropy production because at equilibrium the entropy remains constant. Then the quantity

$$\sum_i \vec{j}_i^{\,\mathrm{eq}} \cdot \vec{\nabla}\gamma_i$$

must be written as a divergence. We can show (Problem 6.5.1) for a simple fluid, i.e. a fluid with one type of molecule, that

$$\sum_{i=1}^{5} \vec{j}_i^{\,\mathrm{eq}} \cdot \vec{\nabla}\gamma_i = -\vec{\nabla} \cdot \left(\frac{\mathcal{P}}{T}\,\vec{u}\right) \tag{6.41}$$

where $\mathcal{P}$ is the pressure. The index i goes from 1 to 5: particle number, energy and the three components of the momentum. Define the entropy current as

$$\boxed{\vec{j}_S = \sum_i \gamma_i \vec{j}_i + \frac{\mathcal{P}}{T}\,\vec{u}} \tag{6.42}$$

Then, (6.40) gives

$$\frac{\partial s}{\partial t} + \vec{\nabla} \cdot \vec{j}_S = \sum_i \left[(\vec{j}_i - \vec{j}_i^{\,\mathrm{eq}}) \cdot \vec{\nabla}\gamma_i\right]$$

which, upon using (6.17), becomes

$$\boxed{\frac{\partial s}{\partial t} + \vec{\nabla} \cdot \vec{j}_S = \sum_{i,j,\alpha,\beta} (\partial_\alpha \gamma_i)\, L_{ij}^{\alpha\beta}\, (\partial_\beta \gamma_j)} \tag{6.43}$$

The right hand side of this equation describes entropy production at point $\vec{r}$.

We illustrate entropy production with the simple example of the heat conducting bar (Figure 6.3) in a stationary regime. Let Q be the heat transferred per unit time from a to b and $\mathcal{S}$ the cross-sectional area of the bar. The only current is the energy current flowing along the x axis and which is equal to $j_E = Q/\mathcal{S}$. Therefore, (6.42) gives the entropy current as

$$j_S(x) = \frac{1}{T(x)}\, j_E = \frac{1}{T(x)}\, \frac{Q}{\mathcal{S}} \tag{6.44}$$

where the temperature, $T(x)$, is given by (6.25). Now consider a section of the bar $[x, x + \mathrm{d}x]$, and the entropy current entering and leaving it. The position dependence of the entropy current leads to a negative entropy balance

$$j_S(x) - j_S(x + \mathrm{d}x) = \frac{Q}{\mathcal{S}}\left(\frac{1}{T(x)} - \frac{1}{T(x + \mathrm{d}x)}\right) = \frac{1}{T^2}\,\frac{Q}{\mathcal{S}}\,\frac{\mathrm{d}T}{\mathrm{d}x}\,\mathrm{d}x < 0 \tag{6.45}$$

In this stationary situation, the entropy of the slice must remain constant, which cannot happen unless entropy is produced at every point of the bar. The entropy production is given by

$$-\frac{1}{T^2}\,\frac{Q}{\mathcal{S}}\,\frac{\mathrm{d}T}{\mathrm{d}x}\,\mathrm{d}x > 0 \tag{6.46}$$

This term corresponds to the entropy source in the continuity equation (6.43). It is instructive to obtain the above result using this equation. For the present case, the right hand side of (6.43) is given by

$$L_{EE}\left(\frac{\partial \gamma_E}{\partial x}\right)^2 = \kappa T^2 \frac{1}{T^4}\left(\frac{\mathrm{d}T}{\mathrm{d}x}\right)^2 = -\frac{\kappa}{T^2}\,\frac{\mathrm{d}T}{\mathrm{d}x}\,\frac{Q}{\kappa \mathcal{S}} = -\frac{1}{T^2}\,\frac{Q}{\mathcal{S}}\,\frac{\mathrm{d}T}{\mathrm{d}x}$$

where we have used (6.19) for L_{EE} and (6.18) in the form $Q/\mathcal{S} = -\kappa\,\mathrm{d}T/\mathrm{d}x$, which indeed gives (6.46). We also verify that the rate of total entropy production per unit time corresponds to that obtained from the entropy change of the reservoirs

$$\frac{\mathrm{d}S_{\text{tot}}}{\mathrm{d}t} = -Q\int_0^l \mathrm{d}x\,\frac{1}{T^2}\,\frac{\mathrm{d}T}{\mathrm{d}x} = Q\left(\frac{1}{T_b} - \frac{1}{T_a}\right) \tag{6.47}$$

This example illustrates clearly that entropy is produced at every point of the bar.

6.2 Examples

6.2.1 Coupling between thermal and particle diffusion

A simple but instructive model for transport is that of a gas of light particles in motion, scattering elastically off randomly located scattering centres. This model, which we will identify as the Boltzmann–Lorentz model in Chapter 8, applies, for example, in the following situations:

- neutrons in a nuclear reactor,
- electrons in a semiconductor or conductor,
- light solute molecules in a solvent with very heavy molecules,
- impurities in a solid at high temperature.

In general, we also use the ideal gas approximation, classical or quantum, for the light particles, which often have a very small density. In this model, energy is conserved since the collisions are elastic, but momentum is not conserved because it is absorbed in collisions with scattering centres. We therefore only consider the conserved particle and energy densities, n and ϵ, as well as the associated currents $\vec{j}_N$ and $\vec{j}_E$. This gives equations which couple the diffusion of heat and particles: a temperature gradient can produce a particle flux and, conversely, a density gradient can cause heat flow. Assuming the medium is isotropic, which means

$L_{ij}^{\alpha\beta} = \delta_{\alpha\beta} L_{ij}$ (see Section A.4.2), we can write Equation (6.17) as

$$\vec{j}_E = L_{EE} \vec{\nabla} \frac{1}{T} + L_{EN} \vec{\nabla} \left(\frac{-\mu}{T} \right) \tag{6.48}$$

$$\vec{j}_N = L_{NE} \vec{\nabla} \frac{1}{T} + L_{NN} \vec{\nabla} \left(\frac{-\mu}{T} \right) \tag{6.49}$$

The Onsager relations (6.35) imply $L_{EN} = L_{NE}$. The thermal conductivity is defined in the absence of particle current: $\vec{j}_N = 0$,

$$L_{NE} \vec{\nabla} \frac{1}{T} + L_{NN} \vec{\nabla} \left(\frac{-\mu}{T} \right) = 0$$

Expressing $\vec{\nabla}(-\mu/T)$ in terms of $\vec{\nabla}(1/T)$, we find

$$\vec{j}_E = L_{EE} \vec{\nabla} \frac{1}{T} - \frac{L_{NE}}{L_{NN}} L_{EN} \vec{\nabla} \left(\frac{1}{T} \right)$$

Comparing with Equation (6.18) we obtain the coefficient of thermal conductivity κ

$$\kappa = \frac{1}{T^2 L_{NN}} \left(L_{EE} L_{NN} - L_{EN}^2 \right) \tag{6.50}$$

We note that the positivity of the 2×2 matrix of transport coefficients implies that κ is positive. It is instructive to emphasize the differences between (6.50) and (6.19). In an insulating solid, heat transport is effected by the vibrations of the lattice and it is tempting to interpret it as the result of particle transport where the particles are phonons. However, unlike for molecules, the phonon density does not obey a continuity equation since phonons can be destroyed and created with no constraints. Therefore, heat transport in an insulating solid cannot be interpreted as being due to particle transport. The diffusion coefficient is defined at constant temperature and results of Section 6.1.4 remain unchanged.

6.2.2 Electrodynamics

As another example, we examine the case where the gas of light particles is a gas of charge carriers to which correspond an electric charge density, $\rho_{\rm el}$, and an electric current density, $\vec{j}_{\rm el}$,

$$\rho_{\rm el} = qn \qquad \vec{j}_{\rm el} = q\vec{j}_N \tag{6.51}$$

where q is the charge of the carriers. We assume that these charges are placed in an average electric potential $\Phi(\vec{r})$, and thus an average electric field $\vec{E} = -\vec{\nabla}\Phi$. We ignore magnetic and polarization effects of the medium. The electric current is given by the local Ohm's law

$$\vec{j}_{\mathrm{el}} = \sigma_{\mathrm{el}} \vec{E} = -\sigma_{\mathrm{el}} \vec{\nabla} \Phi \tag{6.52}$$

The *electrical conductivity* σ_{el} is a transport coefficient, in fact one of the most familiar transport coefficients, which gives rise to dissipation via the Joule effect. We shall show that electrical conductivity and diffusion are intimately connected. To this end, we study the effect of the potential Φ on the entropy. Placing the system in a macroscopic force field that changes very slowly at the microscopic scale does not change its entropy because each energy level of a particle is simply shifted by $q\Phi$. The densities of charge carriers and energy in the absence of the potential, n' and ϵ', are related to those in the presence of the potential, n and ϵ, by

$$n' = n \qquad \epsilon' = \epsilon - nq\Phi$$

and the entropy density satisfies

$$s(\epsilon, n; \Phi) = s(\epsilon - nq\Phi, n; \Phi = 0) = s'(\epsilon', n') \tag{6.53}$$

where s' is the entropy density in the absence of the potential. This yields the chemical potential[15]

$$\mu = -T \frac{\partial}{\partial n} s(\epsilon, n; \Phi) = -T \frac{\partial}{\partial n} s'(\epsilon - nq\Phi, n) = \mu' + q\Phi \tag{6.54}$$

where μ' is the chemical potential in the absence of the electric potential

$$\mu' = \mu(\epsilon - nq\Phi, n; \Phi = 0) \tag{6.55}$$

For uniform temperature, we deduce from (6.54) the particle current density

$$\vec{j}_N = L_{NN} \vec{\nabla} \left(-\frac{\mu}{T} \right) = -\frac{1}{T} L_{NN} \left. \frac{\partial \mu'}{\partial n} \right|_T \vec{\nabla} n + \frac{q}{T} L_{NN} \vec{E} \tag{6.56}$$

The current density $\vec{j}_N$ has a component due to diffusion which tends to make the system uniform, and an electric component produced by the externally applied electric field. Both components are governed by the same microscopic mechanism and controlled by the transport coefficient L_{NN}. For a uniform density we have

$$\vec{j}_{\mathrm{el}} = \sigma_{\mathrm{el}} \vec{E} \qquad \sigma_{\mathrm{el}} = \frac{q^2}{T} L_{NN} \tag{6.57}$$

Anticipating results in Chapter 8, we now follow a simple argument from kinetic theory. If τ^* is the time between two successive collisions of a charge carrier, which we call collision time, and if collisions are not correlated (no memory), a

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[15] The transformation rule for μ is obvious in the grand canonical ensemble where nothing changes if we shift all energy levels and μ by $q\Phi$.

particle of mass m will be accelerated while between collisions and its velocity will increase by[16]

$$\vec{u} = \frac{q\vec{E}}{m}\tau^* = \mu_{\rm el}(q\vec{E}) = \mu_{\rm el}\vec{F} \tag{6.58}$$

The quantity $\mu_{\rm el}$ is called electric mobility. We see in Equation (6.58) that it is the velocity, not the acceleration, that is proportional to the force! Of course this is due to the fact that the particle has to restart its motion from zero after each collision since it has no memory of its previous condition. The concept of mobility also appears in problems involving viscous forces. For example, an object falling in a viscous fluid will attain a limiting speed $v_L = g/\gamma$, where g is the gravitational acceleration, and the viscous force is given by $-\gamma m v$ (Exercise 6.4.3). The velocity v_L is proportional to the force mg.

In general, the electric current is given as a function of the mobility by

$$\vec{j}_{\rm el} = qn\vec{u} = q^2 n\mu_{\rm el}\vec{E}$$

Comparing this with (6.57) we find

$$\sigma_{\rm el} = q^2 n\mu_{\rm el} \qquad L_{NN} = Tn\mu_{\rm el} \tag{6.59}$$

For a classical ideal gas, we have $\kappa_T = 1/\mathcal{P}$ and $\mathcal{P} = nkT$ and, therefore, Equation (6.27) becomes

$$\boxed{D = \mu_{\rm el}kT} \tag{6.60}$$

This is an Einstein relation. Another Einstein relation, relating the diffusion coefficient D of a spherical particle of radius R and the viscosity (defined in Section 6.3.3), is the object of Exercise 6.4.3 where we show

$$\boxed{D = \frac{kT}{6\pi\eta R}} \tag{6.61}$$

It is instructive to obtain (6.60) using an argument from equilibrium statistical mechanics. We suppose that the potential Φ depends only on the position x. Clearly, this position dependence of the potential creates an electric current

$$\vec{j}_{\rm el} = -\sigma_{\rm el}\vec{\nabla}\Phi$$

corresponding to a particle current

$$\frac{1}{q}\vec{j}_{\rm el} = -qn\mu_{\rm el}\frac{\partial\Phi}{\partial x}\hat{x}$$

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[16] The velocity is written $\vec{u}$ because it is a collective velocity on top of the velocities due to thermal fluctuations.

When the particles are at equilibrium in an external force field, $q\Phi(x)$, the density $n(x)$ follows a Boltzmann law

$$n(x) \propto \exp(-\beta q \Phi(x))$$

The non-uniform density entails a diffusion current

$$\vec{j}_D = -D\frac{\partial n}{\partial x}\hat{x} = D\beta q \frac{\partial \Phi}{\partial x}\, n\hat{x}$$

However, at equilibrium the total particle current must vanish

$$\vec{j}_N = \frac{1}{q}\vec{j}_{\mathrm{el}} + \vec{j}_D = \vec{0}$$

This condition of vanishing total current gives Equation (6.60). A similar argument is applied in Exercise 6.4.3 to obtain (6.61).

6.3 Hydrodynamics of simple fluids

6.3.1 Conservation laws in a simple fluid

Our aim in this section is not to study hydrodynamic flow, for which the interested reader is referred to the appropriate references. Instead, our goal is to illustrate with an important example the concepts defined in Section 6.1. A *simple fluid* is a fluid made of one type of structureless molecule, the archetypal example being argon in liquid form (dense fluid) or gaseous form (dilute fluid). In such a case there are only five conserved densities: particle density, energy density and the three components of the momentum density. Instead of using the particle density, we shall use the mass density, $\rho = mn$, where m is the mass of the molecule. The momentum density is $\vec{g}$ and the energy density is ϵ as before. To these densities correspond currents and conservation laws in the form of continuity equations like (6.6). We shall see that the mass current, $\vec{j}_M$, is nothing more than the momentum density, $\vec{g}$. The momentum current is a tensor of components $T_{\alpha\beta}$ since the momentum density itself is a vector. The energy current is a vector $\vec{j}_E$. We shall use in this section the convention that repeated indexes are summed (see Section 10.4). With this convention, the divergence of a vector $\vec{A}$ is written

$$\vec{\nabla} \cdot \vec{A} = \partial_\alpha A_\alpha \qquad (6.62)$$

We now examine the conservation of mass and momentum.[17]

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[17] We recommend that the reader who has no previous experience with hydrodynamics solves Problem 6.5.2 before continuing.

Mass conservation

Let the flow velocity $\vec{u}(\vec{r}, t)$ be the velocity of a fluid element (also called 'fluid particle' in hydrodynamics) at point $\vec{r}$ and time t. Recall that the hydrodynamic approximation assumes that at each point reigns a local equilibrium corresponding to a local temperature $T(\vec{r}, t)$, a local entropy density $s(\vec{r}, t)$ etc. According to (6.6), the mass current is given by (Exercise 6.4.1 provides a microscopic demonstration)

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{u}) = 0 \tag{6.63}$$

With our convention on repeated indexes, we write this as

$$\boxed{\frac{\partial \rho}{\partial t} + \partial_\beta (\rho u_\beta) = 0} \tag{6.64}$$

We can rewrite this mass conservation equation by expanding the second term

$$\frac{\partial \rho}{\partial t} + u_\beta \, \partial_\beta \rho + \rho \, \partial_\beta u_\beta = \frac{D\rho}{Dt} + \rho(\vec{\nabla} \cdot \vec{u}) = 0$$

where we have introduced the *material* (*or convective*) *derivative* D/Dt

$$\boxed{\frac{D}{Dt} = \frac{\partial}{\partial t} + u_\beta \, \partial_\beta = \frac{\partial}{\partial t} + \vec{u} \cdot \vec{\nabla}} \tag{6.65}$$

The physical interpretation of this material derivative is very important. Suppose we follow the motion of a fluid element between t and $t + \mathrm{d}t$ and where $\vec{r}$ is a fixed point in space. During the time interval $\mathrm{d}t$, the fluid element moves a distance $\mathrm{d}\vec{r} = \vec{u}\,\mathrm{d}t$, and the change in the α component of its velocity is (see Figure 6.4)

$$\begin{aligned} u_\alpha(\vec{r} + \mathrm{d}\vec{r}, t + \mathrm{d}t) - u_\alpha(\vec{r}, t) &= \frac{\partial u_\alpha}{\partial t}\mathrm{d}t + \mathrm{d}\vec{r} \cdot \vec{\nabla} u_\alpha \\ &= \left(\frac{\partial u_\alpha}{\partial t} + (\vec{u} \cdot \vec{\nabla}) u_\alpha \right) \mathrm{d}t = \frac{D u_\alpha}{Dt}\,\mathrm{d}t \end{aligned}$$

$D\vec{u}/Dt$ is then the acceleration of the element of fluid. The term $(\vec{u} \cdot \vec{\nabla})$ is called the *advection* or *convection* term.

Conservation of momentum

We assume that the fluid element is in the form a parallelepiped whose faces are parallel to the coordinate axes. Consider the face with the normal vector (pointing toward the outside of the parallelepiped) parallel to the β axis, and let $\mathcal{S}_\beta$ be the oriented surface labelled by its normal vector. Let us introduce the stress tensor $\mathcal{P}_{\alpha\beta}$ where $-\mathcal{P}_{\alpha\beta}$ is the α component of the force per unit area applied by the fluid outside the parallelepiped on the surface $\mathcal{S}_\beta$ (see Figure 6.5). Clearly we may have $\alpha = \beta$. To obtain the total force applied by the rest of the fluid on the fluid enclosed

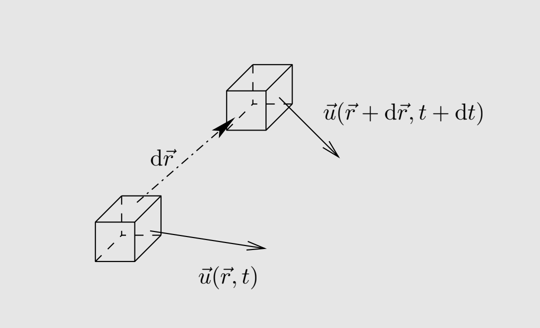

Figure 6.4 Motion of an element of fluid.

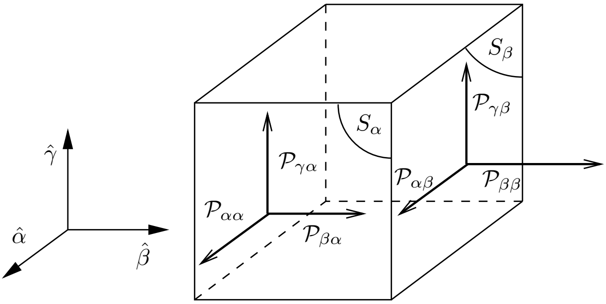

Figure 6.5 Definition of $\mathcal{P}_{\alpha\beta}$.

in the parallelepiped, we need to integrate over all the faces. Since the mass of the enclosed fluid is ρV, where V is the volume of the parallelepiped, Newton's law is given by

$$\rho V\,\frac{Du_\alpha}{Dt} = -\int_{\mathcal{S}} \mathrm{d}^2\mathcal{S}_\beta \mathcal{P}_{\alpha\beta} = -\int_V \mathrm{d}^3r\ \partial_\beta \mathcal{P}_{\alpha\beta} \tag{6.66}$$

Green's theorem allows us to express the surface integral giving the flux of $\mathcal{P}_{\alpha\beta}$ across the parallelepiped as a volume integral. The above equation becomes

$$\boxed{\rho\,\frac{Du_\alpha}{Dt} = -\partial_\beta \mathcal{P}_{\alpha\beta}} \tag{6.67}$$

The α component of the force exerted by the rest of the fluid on a unit volume element is given by $-\partial_\beta\mathcal{P}_{\alpha\beta}$. This result leads to the momentum conservation law. If at time t we use a Galilean reference frame moving at a constant uniform velocity $\vec{u}$ with respect to the laboratory frame, the fluid element is instantaneously at rest in this frame. We say 'instantaneously' because, whereas the velocity of the reference frame does not change, the velocity of the fluid element itself will, in general, change. Furthermore, while this frame was chosen such that at time t the fluid element under consideration is at rest, its neighbours will not be at rest, unless the fluid flow velocity is uniform. This Galilean frame will be called the *rest frame of the fluid*, at point $\vec{r}$ and time t. In this frame the advection term vanishes, and by using (6.65), the fundamental dynamic equation (6.67) at $\vec{r}$ and t becomes

$$\rho \frac{\partial u_\alpha}{\partial t} = -\partial_\beta \mathcal{P}_{\alpha\beta} \tag{6.68}$$

Recalling that $\vec{g}$ is the momentum density, let us calculate $\partial g_\alpha / \partial t$ in this same frame where $\vec{u} = 0$

$$\frac{\partial g_\alpha}{\partial t} = \frac{\partial(\rho u_\alpha)}{\partial t} = \rho\,\frac{\partial u_\alpha}{\partial t} = -\partial_\beta \mathcal{P}_{\alpha\beta}$$

Since the above equation may be written as a continuity equation

$$\frac{\partial g_\alpha}{\partial t} + \partial_\beta \mathcal{P}_{\alpha\beta} = 0 \tag{6.69}$$

we conclude that $\mathcal{P}_{\alpha\beta}$ is the current associated with g_α in the frame where the fluid is instantaneously at rest. If we use primes for quantities measured in the rest frame, this equation allows the identification of the tensor $T_{\alpha\beta}$ in this frame: $T'_{\alpha\beta} = \mathcal{P}_{\alpha\beta}$. When the fluid is incompressible and the tensor $\mathcal{P}_{\alpha\beta} = \delta_{\alpha\beta}\mathcal{P}$ (i.e. diagonal), the equation of motion (6.67) takes a familiar form (see Problem 6.5.2). In fact, it is reduced to the Euler equation for perfect fluids

$$\boxed{\rho\,\frac{D\vec{u}}{Dt} = -\vec{\nabla}\mathcal{P}} \tag{6.70}$$

which confirms that $\mathcal{P}$ should be interpreted as the pressure.

Viscous effects, which are ignored in the Euler equations, make the tensor $\mathcal{P}_{\alpha\beta}$ non-diagonal. This can be illustrated by the following simple example. A horizontal plate moves at a height $z = L$ with a velocity $\vec{u} = u_0\hat{x}$ in the x direction (see Figure 6.6). The fluid between $z = 0$ and $z = L$ acquires a horizontal velocity $u_x(z)$, which depends on the height z. In the laminar regime, the relative velocity of the fluid with respect to the walls vanishes at the walls, $u_x(0) = 0$, $u_x(L) = u_0$, and varies linearly in between. The fluid above a plane of constant z applies on

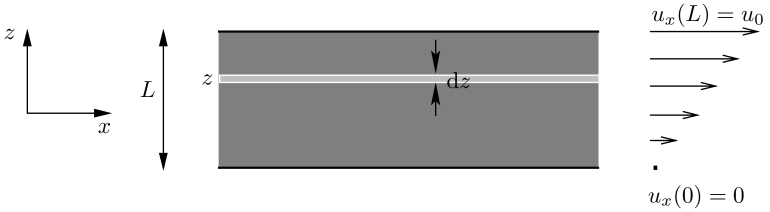

Figure 6.6 A fluid in simple shear motion.

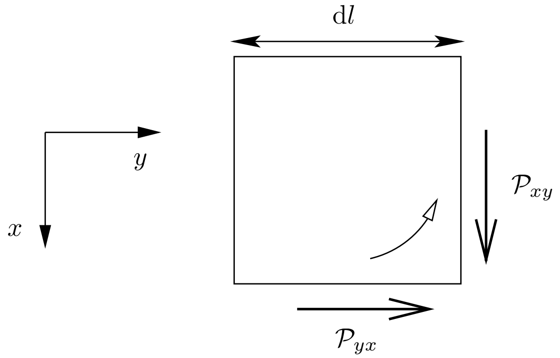

Figure 6.7 Symmetry of $\mathcal{P}_{\alpha\beta}$: if $\mathcal{P}_{yx} \neq \mathcal{P}_{xy}$, the cube will start rotating. The curved arrow shows the rotation direction when $\mathcal{P}_{yx} > \mathcal{P}_{xy}$.

the fluid below it a force per unit area equal to $-\mathcal{P}_{xz}$ where, from (6.66), x is the direction of the force and z that of the normal to the surface of separation. The *shear viscosity* η is defined by the transport equation

$$-\mathcal{P}_{xz} = \eta \, \frac{\mathrm{d}u_x(z)}{\mathrm{d}z} \tag{6.71}$$

We easily show an important symmetry property of $\mathcal{P}_{\alpha\beta}$. Consider the z component of the torque $\vec{\Gamma}$ applied on an infinitesimal cube of fluid of side dl (Figure 6.7)

$$\Gamma_z \propto (\mathrm{d}l)^3(\mathcal{P}_{yx} - \mathcal{P}_{xy})$$

The z component of the angular velocity $\vec{\omega}$ satisfies

$$I \, \frac{\mathrm{d}\omega_z}{\mathrm{d}t} = \Gamma_z \tag{6.72}$$

where I is the moment of inertia. Writing I as a function of dl and the mass M of the cube, we obtain

$$I \propto M(\mathrm{d}l)^2 = \rho(\mathrm{d}l)^3(\mathrm{d}l)^2$$

We see from (6.72) that if d$l \to 0$, we have

$$\mathrm{d}\omega_z/\mathrm{d}t = \Gamma_z/I \propto (\mathrm{d}l)^{-2} \to \infty$$

unless $\mathcal{P}_{yx} = \mathcal{P}_{xy}$, in other words $\mathcal{P}_{\alpha\beta}$ is a symmetric tensor

$$\boxed{\mathcal{P}_{\alpha\beta} = \mathcal{P}_{\beta\alpha}} \tag{6.73}$$

Finally, we may introduce external sources to the continuity equation. If the fluid is subjected to external forces, like gravity, with the external force density $\vec{f}$ (=

$-\rho g\hat{z}$ in the case of gravity), we have to add this force density to the equation of motion (6.67), which becomes

$$\rho\,\frac{Du_\alpha}{Dt} = -\partial_\beta \mathcal{P}_{\alpha\beta} + f_\alpha \tag{6.74}$$

The new term acts as a source of momentum in the continuity equation (6.69).

6.3.2 Derivation of current densities

We now use Galilean invariance to express the currents in terms of their values in the reference frame where the fluid is locally at rest. In the reference frame of the laboratory, a fluid element moves with a velocity $\vec{u}$. Equivalently, in the rest frame of the fluid element, the laboratory moves with a velocity $-\vec{u}$. More generally, we use a Galilean frame $R(-\vec{v})$ moving at some velocity $-\vec{v}$ relative to the rest frame of the fluid. In the frame $R(-\vec{v})$, the densities are given in terms of the (primed) densities in the rest frame by

$$\text{mass density}\qquad \rho = \rho' \tag{6.75}$$

$$\text{momentum density}\qquad \vec{g} = \rho\vec{v} \tag{6.76}$$

$$\text{energy density}\qquad \epsilon = \epsilon' + \frac{1}{2}\,\rho\vec{v}^{\,2} \tag{6.77}$$

To derive the current conservation law, consider a density χ and its associated current $\vec{j}_\chi$. Going from a frame at velocity $-\vec{v}$ to one at $-(\vec{v}+\mathrm{d}\vec{v})$ has two effects on the current.

(*i*) A first effect comes from the change $\mathrm{d}\chi$ in the density χ when we go from $-\vec{v}$ to $-(\vec{v}+\mathrm{d}\vec{v})$

$$\mathrm{d}\chi = \chi(\vec{v}+\mathrm{d}\vec{v}) - \chi(\vec{v}) = \zeta_\alpha(\vec{v})\,\mathrm{d}v_\alpha \tag{6.78}$$

which defines $\zeta_\alpha(\vec{v})$. If $\vec{j}_{\zeta_\alpha}$ is the current associated with ζ_α, the change in the density (6.78) causes a change in the β component of the current

$$\mathrm{d}^{(1)} j^\chi_\beta = j^{\zeta_\alpha}_\beta \mathrm{d}v_\alpha \tag{6.79}$$

(*ii*) The second effect comes from the fact that a flux is calculated relative to a fixed surface $\mathcal{S}$ in a given reference frame. But a fixed surface in the frame $R(-(\vec{v}+\mathrm{d}\vec{v}))$ moves with a velocity $-\mathrm{d}\vec{v}$ in the frame $R(-\vec{v})$, which induces an additional flux

$$\mathrm{d}\Phi_\chi = \chi(\vec{v})\vec{\mathcal{S}}\cdot\mathrm{d}\vec{v} = \chi(\vec{v})\mathcal{S}_\beta\,\mathrm{d}v_\beta$$

and a contribution to the current

$$\mathrm{d}^{(2)} j^\chi_\beta = \chi(\vec{v})\,\mathrm{d}v_\beta \tag{6.80}$$

In the case of mass current, only the second effect is present since the mass is a Galilean invariant: $\mathrm{d}\vec{j}_M = \rho\,\mathrm{d}\vec{v}$, or $\vec{j}_M = \rho\vec{v} = \vec{g}$ as expected. We now choose χ as the α component of the momentum density, $\chi = g_\alpha = \rho v_\alpha$. For an infinitesimal Galilean transformation we have $\mathrm{d}g_\alpha = \rho\,\mathrm{d}v_\alpha$. The β component of the mass density current is ρv_β, and if $T_{\alpha\beta}$ is the β component of the current associated with g_α, we have

$$\mathrm{d}^{(1)}T_{\alpha\beta} = \rho v_\beta\,\mathrm{d}v_\alpha$$

whereas the second contribution is

$$\mathrm{d}^{(2)}T_{\alpha\beta} = \rho v_\alpha\,\mathrm{d}v_\beta$$

Adding the two effects we obtain

$$\mathrm{d}T_{\alpha\beta} = \rho v_\beta\,\mathrm{d}v_\alpha + \rho v_\alpha\,\mathrm{d}v_\beta$$

This can be integrated from $\vec{v} = 0$ to $\vec{v} = \vec{u}$

$$\boxed{T_{\alpha\beta} = \mathcal{P}_{\alpha\beta} + \rho u_\alpha u_\beta} \tag{6.81}$$

subject to the boundary conditions

$$T_{\alpha\beta}(\vec{v} = 0) = T'_{\alpha\beta} = \mathcal{P}_{\alpha\beta}$$

The term $\rho u_\alpha u_\beta = g_\alpha u_\beta$ is a convection term: all currents $\vec{j}_\chi$ include a convection term $\chi\vec{u}$ due to the transport of the density χ with a velocity $\vec{u}$.

We now consider the energy density $\chi = \epsilon$. The infinitesimal transformation law for ϵ is

$$\mathrm{d}\epsilon = \rho v_\alpha\,\mathrm{d}v_\alpha = g_\alpha\,\mathrm{d}v_\alpha$$

The β component of the current associated with g_α is $T_{\alpha\beta}$. This gives

$$\mathrm{d}^{(1)}j^E_\beta = T_{\alpha\beta}\,\mathrm{d}v_\alpha$$

whereas

$$\mathrm{d}^{(2)}j^E_\beta = \epsilon\,\mathrm{d}v_\beta = \left(\epsilon' + \frac{1}{2}\rho\vec{v}^{\,2}\right)\mathrm{d}v_\beta$$

Adding the two effects and using (6.81) we obtain

$$\mathrm{d}j^E_\beta = (\rho v_\alpha v_\beta + \mathcal{P}_{\alpha\beta})\mathrm{d}v_\alpha + \left(\epsilon' + \frac{1}{2}\rho\vec{v}^{\,2}\right)\mathrm{d}v_\beta$$

which we can write in the form of a differential equation

$$\frac{\partial j^E_\beta}{\partial v_\alpha} = \left[\mathcal{P}_{\alpha\beta} + \epsilon'\delta_{\alpha\beta}\right] + \left[\rho v_\alpha v_\beta + \frac{1}{2}\rho\vec{v}^{\,2}\delta_{\alpha\beta}\right] \tag{6.82}$$

The term in the first bracket in (6.82) is measured in the rest frame and is independent of $\vec{v}$. The integration of (6.82) in the general case is left for Exercise 6.4.4. Here we consider only the one-dimensional case

$$\frac{\partial j^E}{\partial v} = (\mathcal{P} + \epsilon') + \frac{3}{2}\rho v^2$$

which, when integrated from $v = 0$ to $v = u$, gives

$$j^E = j^{E'} + (\mathcal{P} + \epsilon')u + \frac{1}{2}\rho u^3 = j^{E'} + \mathcal{P}u + \epsilon u$$

In the general case (Exercise 6.4.4) we obtain

$$\boxed{j^E_\beta = j^{E'}_\beta + \mathcal{P}_{\alpha\beta}u_\alpha + \epsilon u_\beta} \tag{6.83}$$

The term ϵu_β is a convection term whereas $\mathcal{P}_{\alpha\beta}u_\alpha$ is the work done by the pressure. The current $\vec{j}^{\,\prime}_E$ in the rest frame is the heat current. In addition to the mass conservation equation (6.64), we have, in the absence of external sources, the momentum conservation equations

$$\boxed{\frac{\partial g_\alpha}{\partial t} + \partial_\beta T_{\alpha\beta} = 0} \tag{6.84}$$

as well as energy conservation

$$\boxed{\frac{\partial \epsilon}{\partial t} + \partial_\beta j^E_\beta = 0} \tag{6.85}$$

The expressions for the momentum current $T_{\alpha\beta}$ and energy current $\vec{j}_E$ are given in (6.81) and (6.83) respectively. Adding to these equations the transport equations, (6.87) and (6.88), and the local equations of state one obtains a closed set of equations as shown in Table 6.1.

6.3.3 Transport coefficients and the Navier–Stokes equation

We conclude this brief discussion of hydrodynamics by writing down the corresponding transport equations (6.17). In principle, we expect a 5×5 matrix of transport coefficients, in other words a total of 15 coefficients after taking into

Table 6.1 *Densities and currents for a simple fluid.*

Density	Current	Equilibrium current	Continuity equation
ρ	$\vec{j}_M = m\vec{j}_N = \vec{g} = \rho\vec{u}$	$\vec{j}_M^{\,\mathrm{eq}} = \vec{j}_M$	$\dfrac{\partial\rho}{\partial t} + \vec{\nabla}\cdot\vec{g} = 0$
g_α	$T_{\alpha\beta} = \mathcal{P}_{\alpha\beta} + \rho u_\alpha u_\beta$	$T_{\alpha\beta}^{\mathrm{eq}} = \mathcal{P}\delta_{\alpha\beta} + \rho u_\alpha u_\beta$	$\dfrac{\partial g_\alpha}{\partial t} + \partial_\beta T_{\alpha\beta} = 0$
ϵ	$j_\beta^E = j_\beta^{E'} + \mathcal{P}_{\alpha\beta}u_\alpha + \epsilon u_\beta$	$\vec{j}_E^{\,\mathrm{eq}} = (\epsilon + \mathcal{P})\vec{u}$	$\dfrac{\partial\epsilon}{\partial t} + \partial_\beta j_\beta^E = 0$

account the Onsager symmetry relations (6.38). Fortunately, there are further simplifications that reduce this number to only three transport coefficients. A first crucial simplification comes from the fact that the mass current $\vec{j}_M$ is always equal to the equilibrium current $\rho\vec{u}$ regardless of whether or not the system is at equilibrium. Consequently, $L_{Mi} = L_{iM} = 0$ for all i; a spatial variation of the chemical potential does not cause a particle flux (nor an energy one), at least not directly. There is no diffusion coefficient in a simple fluid; return to equilibrium is accomplished by a complex mechanism. The number of possible affinities remains twelve: $\partial_\beta(1/T)$ and $\partial_\beta(u_\alpha/T)$. However, we can always choose to write the transport equations in a frame where the fluid is locally at rest and use the Galilean transformations (6.81) and (6.83) to obtain the currents in an arbitrary frame. Since in the rest frame we have $\vec{u} = 0$, $\partial_\beta(u_\alpha/T)$ reduces to $(1/T)\partial_\beta u_\alpha$.[18] It remains to exploit rotation and parity invariance. The energy current $\vec{j}_E'$ must be proportional to a vector and the only candidate at hand is the affinity $\vec{\nabla}(1/T)$. In fact another possible candidate would be the other affinity $\vec{\nabla} \times \vec{u}$, but this is a pseudo-vector and parity invariance does not allow a vector to be proportional to a pseudo-vector. The difference $\mathcal{P}_{\alpha\beta} - \delta_{\alpha\beta}\mathcal{P}$ is a two-dimensional symmetric tensor. The two possible constructions, using the affinities, that give such a quantity are

$$\partial_\alpha u_\beta + \partial_\beta u_\alpha \quad \text{and} \quad \delta_{\alpha\beta}(\partial_\gamma u_\gamma) = \delta_{\alpha\beta}(\vec{\nabla}\cdot\vec{u})$$

Instead of these combinations, it is convenient to introduce the traceless symmetric tensor $\Delta_{\alpha\beta}$ $(\Delta_{\alpha\alpha} = 0)$

$$\Delta_{\alpha\beta} = \frac{1}{2}\left(\partial_\alpha u_\beta + \partial_\beta u_\alpha\right) - \frac{1}{3}\,\delta_{\alpha\beta}(\partial_\gamma u_\gamma) \tag{6.86}$$

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[18] It is important to keep in mind the local nature of the rest frame: $\vec{u} = 0$ only at one point and $\partial_\beta u_\alpha \neq 0$ at this point.

Then, the transport equations can be written in terms of the three independent coefficients L_{EE}, η and ζ

$$\boxed{\begin{aligned} \vec{j}_E^{\,\prime} &= L_{EE}\vec{\nabla}\frac{1}{T} \\ \mathcal{P}_{\alpha\beta} - \delta_{\alpha\beta}\mathcal{P} &= -\zeta\, \delta_{\alpha\beta}(\partial_\gamma u_\gamma) - 2\eta\, \Delta_{\alpha\beta} \end{aligned}} \qquad \begin{aligned} (6.87) \\ (6.88) \end{aligned}$$

The coefficient of thermal conductivity κ is defined for a fluid uniformly at rest ($\vec{u} = 0\ \forall\vec{r}$) where there is a temperature gradient. In a fluid (uniformly) at rest, there are no shear forces and $\mathcal{P}_{\alpha\beta} = \delta_{\alpha\beta}\mathcal{P}$. The equation of motion (6.68) then gives $\partial_\beta\mathcal{P}_{\alpha\beta} = \partial_\alpha\mathcal{P} = 0$; thus the pressure is uniform. This implies that the density variations are such that the pressure gradient remains zero. For example, for a dilute gas we have $\mathcal{P} \simeq nkT$ and so the product nT must remain constant. As we have seen above, a density gradient does not cause a particle current: in a simple fluid, it is the pressure gradient that produces fluid motion. According to (6.19), the coefficient L_{EE} is related to the coefficient of thermal conductivity by $L_{EE} = \kappa T^2$.

In order to identify the coefficient η, consider the definition of shear viscosity and Figure 6.6. Since only the velocity component u_x is non-zero and since it depends only on z, we have $\vec{\nabla}\cdot\vec{u} = 0$. Consequently, the tensor $\Delta_{\alpha\beta}$ simplifies to

$$\Delta_{xz} = \frac{1}{2}\left(\frac{\partial u_z}{\partial x} + \frac{\partial u_x}{\partial z}\right) = \frac{1}{2}\,\frac{\mathrm{d}u_x}{\mathrm{d}z} \tag{6.89}$$

and Equation (6.88) becomes

$$\mathcal{P}_{xz} = -\eta\,\frac{\mathrm{d}u_x}{\mathrm{d}z} \tag{6.90}$$

The transport coefficient ζ is called bulk viscosity and in general plays a rather minor rôle. In fact it is absent for an incompressible fluid ($\vec{\nabla}\cdot\vec{u} = 0$) and we will see in Section 8.3.2 that it vanishes for a dilute mono-atomic gas.

The combination of the equations of motion with the transport equations allows us to write the fundamental equation for the dynamics of a simple fluid, the Navier–Stokes equation. The pressure tensor is written in terms of the viscosities η and ζ as

$$\mathcal{P}_{\alpha\beta} = \delta_{\alpha\beta}\mathcal{P} - \zeta\,\delta_{\alpha\beta}(\vec{\nabla}\cdot\vec{u}) - \eta(\partial_\alpha u_\beta + \partial_\beta u_\alpha) + \frac{2}{3}\,\eta\,\delta_{\alpha\beta}(\vec{\nabla}\cdot\vec{u})$$

and its divergence is

$$\partial_\beta\mathcal{P}_{\alpha\beta} = \partial_\alpha\mathcal{P} - \zeta\,\partial_\alpha(\vec{\nabla}\cdot\vec{u}) - \eta(\partial_\beta^2 u_\alpha) - \eta\partial_\alpha(\vec{\nabla}\cdot\vec{u}) + \frac{2}{3}\,\eta\partial_\alpha(\vec{\nabla}\cdot\vec{u})$$

The right hand side is the α component of the vector

$$\vec{\nabla}\mathcal{P} - \zeta\vec{\nabla}(\vec{\nabla}\cdot\vec{u}) - \eta\nabla^2\vec{u} - \frac{1}{3}\,\eta\vec{\nabla}(\vec{\nabla}\cdot\vec{u})$$

which then leads to the Navier–Stokes equation[19]

$$\boxed{\frac{\partial\vec{u}}{\partial t} + (\vec{u}\cdot\vec{\nabla})\vec{u} + \frac{1}{\rho}\,\vec{\nabla}\mathcal{P} = \frac{\eta}{\rho}\,\nabla^2\vec{u} + \frac{1}{\rho}\left(\frac{\eta}{3}+\zeta\right)\vec{\nabla}(\vec{\nabla}\cdot\vec{u})} \tag{6.91}$$

In the absence of dissipation, when the transport coefficients vanish, we regain the Euler equation

$$\frac{\partial\vec{u}}{\partial t} + (\vec{u}\cdot\vec{\nabla})\vec{u} + \frac{1}{\rho}\,\vec{\nabla}\mathcal{P} = 0 \tag{6.92}$$

To achieve the construction of Section 6.1 in this particular case, we need to establish the form of the entropy current. We start in the rest frame where, according to the general construction (6.42), we have

$$\vec{j}_S^{\,\prime} = \sum_i \gamma_i^{\prime}\vec{j}_i^{\,\prime} = \frac{1}{T}\,\vec{j}_E^{\,\prime} \tag{6.93}$$

Since the entropy density is a Galilean invariant, the entropy current is given in general by (Problem 6.5.1)

$$\vec{j}_S = \vec{j}_S^{\,\prime} + s\vec{u} = \frac{1}{T}\,\vec{j}_E^{\,\prime} + s\vec{u} \tag{6.94}$$

According to (6.43), we have

$$\begin{aligned}\frac{\partial s}{\partial t} + \vec{\nabla}\cdot\vec{j}_S &= \vec{\nabla}\left(\frac{1}{T}\right)\cdot\vec{j}_E^{\,\prime} + \sum_{\alpha,\beta}\left(-\frac{1}{T}\partial_\alpha u_\beta\right)\left(\mathcal{P}_{\alpha\beta} - \delta_{\alpha\beta}\mathcal{P}\right)\\ &= \kappa T^2\left(\vec{\nabla}\frac{1}{T}\right)^2 + \frac{\zeta}{T}\left(\vec{\nabla}\cdot\vec{u}\right)^2 + \frac{2\eta}{T}\sum_{\alpha,\beta}\left(\Delta_{\alpha\beta}\right)^2 \geq 0\end{aligned} \tag{6.95}$$

which implies the positivity of the coefficients κ, η and ζ.

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[19] The reader will remark that $(\eta/\rho)\,\nabla^2\vec{u}$ in Equation (6.91) is a diffusion term. In the absence of advection, and if $\vec{\nabla}\mathcal{P} = 0$ and $\vec{\nabla}\cdot\vec{u} = 0$, the Navier–Stokes equation becomes a diffusion equation for the velocity. This equation allows us to justify the linear dependence of $u_x(z)$ on z in Figure 6.6.

6.4 Exercises

6.4.1 Continuity equation for the density of particles

The distribution function $f(\vec{r}, \vec{p}, t)$ of a collection of particles is the ensemble average

$$f(\vec{r}, \vec{p}, t) = \Big\langle \sum_{j=1}^{N} \delta(\vec{r} - \vec{r}_j(t))\delta(\vec{p} - \vec{p}_j(t)) \Big\rangle \tag{6.96}$$

$f(\vec{r}, \vec{p}, t)\mathrm{d}^3r\,\mathrm{d}^3p$ is the number of particles in the phase space volume element $\mathrm{d}^3r\,\mathrm{d}^3p$. Show that the density n and the current $\vec{j}_N$ are given by

$$n(\vec{r}, t) = \int \mathrm{d}^3p\, f(\vec{r}, \vec{p}, t) \qquad \vec{j}_N(\vec{r}, t) = \int \mathrm{d}^3p\, \vec{v} f(\vec{r}, \vec{p}, t) \tag{6.97}$$

Use this result to obtain Equation (6.6). Also demonstrate the continuity equation.

6.4.2 Diffusion equation and random walk

1. Let $A(\vec{r}, t)$ be a quantity obeying the diffusion equation (6.21) with the initial condition

$$A(\vec{r}, t = 0) = A_0(\vec{r}) \tag{6.98}$$

Give the expression for $A(\vec{r}, t)$ $\forall t > 0$.

2. During a random walk (in one dimension for simplicity), a walker takes a step at regular time intervals of ε. With a 50% probability, the walker jumps a distance a left or right on the x axis. Each step is independent of preceding steps and one says the random walk is a Markovian process. The walker leaves point $x = 0$ at time $t = 0$. Calculate the average distance $\langle x \rangle$ travelled in N steps as well as $\langle x^2 \rangle$. Show that $\langle x^2 \rangle$ is proportional to N, or in other words to $t = N\varepsilon$. Show that for $N \to \infty$, the probability $P(x, t)$ of finding the walker at point x at time t is a Gaussian.[20] Identify the diffusion coefficient.

6.4.3 Relation between viscosity and diffusion

Consider very small particles (but macroscopic compared to atomic scales) suspended in a fluid in thermal equilibrium at temperature T. The particle density as a function of height z is $n(z)$, m is the particle mass, k the Boltzmann constant and g the gravitational acceleration.

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[20] $P(x, t)$ is in fact the conditional probability of finding the walker at x at time t knowing that at $t = 0$ it was at $x = 0$.

1. Show that $n(z)$ has the form

$$n(z) = n_0 \mathrm{e}^{-\lambda z}$$

Determine λ as a function of m, g, k and T. If we want to have observable effects over distances of the order of a centimetre, what should be the order of magnitude of the mass m at $T = 300\,\mathrm{K}$?

2. The particles are now under the influence both of gravity and a viscous force proportional to velocity

$$\vec{F} = -\alpha \vec{v}$$

where $\alpha = 6\pi\eta R$, η is the fluid viscosity and R is the radius of the particles, which are assumed spherical.[21] What is the limiting velocity v_L of the particles in the gravitational field?

3. The particles are subjected to two mutually opposing influences: on the one hand, they move down with a velocity v_L and on the other hand, diffusion tries to re-establish a uniform density. Let D be the coefficient of diffusion of the particles in the fluid. What is the diffusion current j_z^N? Why is it directed toward $z > 0$?

4. By considering that at equilibrium the gravitational and diffusion effects balance each other, establish the Einstein relation (6.61) between the viscosity and the diffusion coefficient.

6.4.4 Derivation of the energy current

Derive Equation (6.83) for the energy current. Hint: Treat the cases $\alpha = \beta$ and $\alpha \neq \beta$ separately.

6.4.5 Lord Kelvin's model of Earth cooling

Lord Kelvin's assumptions to compute the age of the Earth were the following.

- (*i*) Earth was formed initially with a uniform temperature equal to the fusion temperature θ_0. In this exercise, temperatures will be measured in degrees Celsius and denoted by θ.
- (*ii*) Cooling is due to diffusion, heat being transported by thermal diffusion to the Earth surface at a temperature $\theta = 0\,^\circ\mathrm{C}$, and then dissipated in the atmosphere and in outer space. Being unaware of radioactivity, Lord Kelvin could not include in his assumptions the heat generated by radioactivity in the centre of the Earth.

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[21] This law was demonstrated by Stokes. Its proof can be found in many volumes on fluid mechanics. See for example [37] or [53].

(*iii*) He also approximated Earth by a semi-infinite medium limited by the plane $x = 0$, the interior of the Earth corresponding to $x \le 0$. Thus one is led to a one-dimensional model with a single coordinate, x.

1. Show that the following form of the temperature for $x \le 0$

$$\theta(x,t) = \frac{\theta_0}{\sqrt{\pi D t}} \int_{-\infty}^{0} \mathrm{d}x' \exp\left(-\frac{(x-x')^2}{4Dt}\right)$$

obeys the heat equation (6.20) with the correct boundary conditions. $D = \kappa/C$ is the thermal diffusivity.

2. Compute the temperature gradient at point x inside the Earth, and at the Earth surface $x = 0$

$$\left.\frac{\partial \theta}{\partial x}\right|_{x=0} = -\frac{\theta_0}{\sqrt{\pi D t}}$$

Hint: Use the change of variables $u = x - x'$.

3. From the following value of the temperature gradient at the Earth surface as measured today

$$\left.\frac{\partial \theta}{\partial x}\right|_{x=0} = -3 \times 10^{-2}\,{}^\circ\mathrm{C\,m^{-1}}$$

and the values $4D = 1.2 \times 10^6\,\mathrm{m^2\,s^{-1}}$, $\theta_0 = 3800\,{}^\circ\mathrm{C}$, estimate the age of the Earth. Given your numerical result and the estimate of 4.5 billion years for the age of the Earth, what do you think is wrong with Lord Kelvin's assumptions? Hint: The answer is *not* in radioactivity!

4. Write an expression for $\theta(r,t)$ assuming spherical symmetry in terms of the Earth radius R. The integral that you will obtain cannot be computed analytically, but you should be able to show that the previous one-dimensional approximation is valid provided $R \gg \sqrt{Dt}$.

6.5 Problems

6.5.1 Entropy current in hydrodynamics

Consider a simple fluid characterized by the following five densities and conjugate intensive variables

$$\begin{array}{lllll} \rho_1 = \epsilon & \rho_2 = n & \rho_3 = g_x & \rho_4 = g_y & \rho_5 = g_z \\ \gamma_1 = \dfrac{1}{T} & \gamma_2 = -\dfrac{\mu}{T} & \gamma_3 = -\dfrac{u_x}{T} & \gamma_4 = -\dfrac{u_y}{T} & \gamma_5 = -\dfrac{u_z}{T} \end{array}$$

where $\vec{g} = mn\vec{u} = \rho\vec{u}$ is the momentum density. Each fluid element has a flow velocity $\vec{u}(\vec{r})$ measured in the laboratory reference frame R. We define a local Galilean frame, $R'(\vec{u}(\vec{r}))$, in which the element d^3r is at rest. All quantities in this frame are primed.

1. Starting with the Galilean invariance of the entropy density,

$$s(\epsilon, n, \vec{g}) = s'(\epsilon - \vec{g}^{\,2}/2mn, n, 0)$$

which you should justify briefly, show that the transformation law for the chemical potential is

$$\mu = \mu' - \frac{1}{2}m\vec{u}^{\,2}$$

2. Derive the following relation

$$\sum_i \gamma_i \rho_i = \sum_i \gamma_i' \rho_i' = s - \frac{\mathcal{P}}{T} \tag{6.99}$$

3. We recall that the rate of entropy dissipation is given by (6.40) and that Table 6.1 gives the definitions of the currents and equilibrium currents. At equilibrium, the total entropy of the system remains constant. This implies that the contribution of the equilibrium currents to the local entropy balance

$$\sum_i \vec{j}_i^{\,\mathrm{eq}} \cdot \vec{\nabla}\gamma_i$$

may be written in the form of a divergence of a vector. Show that

$$\sum_i \vec{j}_i^{\,\mathrm{eq}} \cdot \vec{\nabla}\gamma_i = (\vec{u} \cdot \vec{\nabla}) \sum_i \gamma_i \rho_i - \sum_i \gamma_i (\vec{u} \cdot \vec{\nabla})\rho_i - \frac{\mathcal{P}}{T}\vec{\nabla} \cdot \vec{u} \tag{6.100}$$

Justify the following expression for the gradient of the entropy density

$$\vec{\nabla}s = \sum_i \gamma_i \vec{\nabla}\rho_i$$

and use this result as well as (6.99) to show that (6.100) can be written as

$$\sum_i \vec{j}_i^{\,\mathrm{eq}} \cdot \vec{\nabla}\gamma_i = -\vec{\nabla} \cdot \left(\frac{\mathcal{P}}{T}\vec{u}\right) \tag{6.101}$$

4. The contributions of equilibrium currents are taken into account in the definition of the entropy current

$$\vec{j}_S = \sum_i \gamma_i \vec{j}_i + \frac{\mathcal{P}}{T}\vec{u}$$

Show that

$$\sum_i \gamma_i(\vec{j}_i - \rho_i\vec{u}) = \sum_i \gamma_i' \vec{j}_i{}' = \frac{\vec{j}_E{}'}{T} \tag{6.102}$$

and establish the transformation law of the entropy density current

$$\vec{j}_S = \vec{j}_S{}' + s\vec{u} = \frac{\vec{j}_E{}'}{T} + s\vec{u}$$

Interpret these two expressions.

6.5.2 Hydrodynamics of the perfect fluid

Consider a fluid where the only internal force is the pressure; the tensor $\mathcal{P}_{\alpha\beta}$ has the form $\mathcal{P}\delta_{\alpha\beta}$. We also assume that there is no thermal conduction. In such a fluid, dissipation is absent and the fluid is called a 'perfect fluid': the right hand side of the transport equations (6.87) and (6.88) vanishes.

1. Show that the force acting on a fluid volume element $\mathrm{d}V$ is $-\vec{\nabla}\mathcal{P}\,\mathrm{d}V$. Hint: Study first the case of pressure changing only along the z axis, and take the volume element to be a parallelepiped with faces parallel to the axes. Obtain the Euler equation (6.92).

2. For what is to follow, we need a thermodynamic identity. We will derive this by considering a volume V that follows the current locally and is thus at rest in the fluid's frame. Let $s = S/V$ and $h' = \overline{H}/V$ be the entropy and enthalpy per unit volume in this reference frame (since the entropy is a Galilean invariant, there is no need to distinguish between s and s'). The entropy and enthalpy per particle are given by $\check{s} = S/N$ and $\check{h}' = \overline{H}/N$ (see Section 3.5.1). Using (3.95), show that

$$\mathrm{d}\epsilon' = T\,\mathrm{d}s + \left(\frac{h' - Ts}{\rho}\right)\mathrm{d}\rho \tag{6.103}$$

3. Define the kinetic energy density $k = \frac{1}{2}\rho\vec{u}^{\,2}$ and the corresponding current $\vec{j}_K = \frac{1}{2}\rho\vec{u}^{\,2}\vec{u}$. By using (6.92) and the equation for mass conservation, (6.64), show that

$$\frac{\partial k}{\partial t} + \partial_\beta\left[j_\beta^K + \mathcal{P}u_\beta\right] = \mathcal{P}(\partial_\beta u_\beta) \tag{6.104}$$

4. The absence of dissipation in an ideal fluid is expressed by the entropy conservation law

$$\frac{\partial s}{\partial t} + \partial_\beta(su_\beta) = 0 \tag{6.105}$$

Use this equation and (6.103) to put the time derivative of the total energy density

$$\epsilon = k + \epsilon' = \frac{1}{2}\rho\vec{u}^{\,2} + \epsilon'$$

in the form

$$\frac{\partial\epsilon}{\partial t} + \partial_\beta\left[j_\beta^K + \mathcal{P}u_\beta\right] = \mathcal{P}(\partial_\beta u_\beta) - T\,\partial_\beta(su_\beta) - \left(\frac{h' - Ts}{\rho}\right)\partial_\beta(\rho u_\beta) \quad (6.106)$$

Again use (6.103) to obtain the final result

$$\frac{\partial\epsilon}{\partial t} + \partial_\beta\left(\left[\frac{1}{2}\rho\vec{u}^{\,2} + h'\right]u_\beta\right) = 0 \quad (6.107)$$

Give the physical interpretation of this result.

6.5.3 Thermoelectric effects

A metal is a binary system made of a lattice of fixed positive ions and mobile electrons. We can observe a charge current in response to a temperature gradient and, conversely, heat is produced when current is flowing. The metal is put at a uniform potential Φ (cf. Section 6.2.2). Primed quantities correspond to the case $\Phi = 0$ and the unprimed quantities to the case $\Phi \neq 0$. We recall that in this situation $T' = T$, $n' = n$ and (6.54) $\mu = \mu' + q\Phi$.

1. *Transformation laws of* L_{ij}. We consider a non-equilibrium situation where the linear response model is relevant. We know, for the isolated system, the coefficients of linear response

$$\vec{j}_E^{\,\prime} = L'_{EE}\vec{\nabla}\left(\frac{1}{T}\right) + L'_{EN}\vec{\nabla}\left(-\frac{\mu'}{T}\right) \quad (6.108a)$$

$$\vec{j}_N^{\,\prime} = L'_{NE}\vec{\nabla}\left(\frac{1}{T}\right) + L'_{NN}\vec{\nabla}\left(-\frac{\mu'}{T}\right) \quad (6.108b)$$

The metal is now put at the potential $\Phi(\vec{r})$, which depends on space but *varies very slowly at the microscopic scale*. The transformation laws established for the uniform case are still valid locally. Establish the following transformation laws for the particle and energy current densities

$$\vec{j}_N = \vec{j}_N^{\,\prime} \qquad \vec{j}_E = \vec{j}_E^{\,\prime} + q\Phi\vec{j}_N$$

Use this result to show that in the presence of the potential $\Phi(r)$, the linear response coefficients transform as

$$L_{NN} = L'_{NN} \tag{6.109a}$$

$$L_{EE} = L'_{EE} + 2q\Phi\, L'_{NE} + q^2\Phi^2\, L'_{NN} \tag{6.109b}$$

$$L_{NE} = L_{EN} = L'_{NE} + q\Phi\, L'_{NN} \tag{6.109c}$$

Verify, with the help of these results, that the thermal conductivity coefficient of the metal κ (6.50) is the same in the presence or absence of the external potential.

2. *Seebeck effect.* The first thermoelectric effect to be studied was the Seebeck effect: in an open circuit, a temperature gradient produces an electromotive force (i.e. a gradient of the electrochemical potential μ/q). We define the 'Seebeck coefficient' (or coefficient of thermoelectric power) $\bar{\varepsilon}$ of a material as the electromotive force created in an open circuit by a unit temperature gradient

$$\vec{\nabla}\left(\frac{\mu}{q}\right) = -\bar{\varepsilon}\vec{\nabla}T \qquad \vec{j}_N = \vec{0}$$

Express the Seebeck coefficient in terms of the linear response coefficients.

We construct a thermocouple with two metallic wires A and B of different Seebeck coefficients (Figure 6.8). The junctions are maintained at two different temperatures T_1 and T_2. A capacitor is introduced in the metal B and maintained at temperature T. Calculate the potential difference across the capacitor in terms of T_1, T_2 and the Seebeck coefficients $\bar{\varepsilon}_A$ and $\bar{\varepsilon}_B$ of metals A and B respectively.

3. *Joule effect.* In an electrically neutral metal where the temperature, electric field, density of charge carriers and current densities are uniform, an electric current produces the well-known thermoelectric phenomenon, the Joule effect. Verify

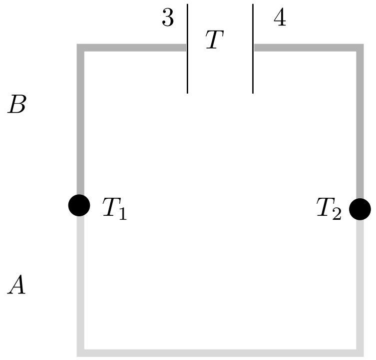

Figure 6.8 Schematic representation of a thermocouple.

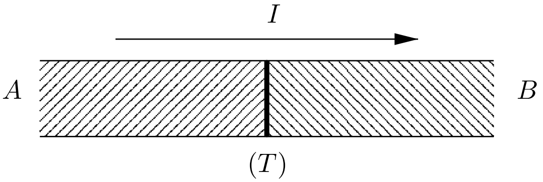

Figure 6.9 A junction between two different metals.

that the particle (charge carriers) flux is accompanied by an energy flux

$$\vec{j}_E = -\frac{q}{T} L_{EN} \vec{\nabla} \Phi = \frac{L_{EN}}{q L_{NN}} \vec{j}_{\mathrm{el}} \tag{6.110}$$

where $\vec{j}_{\mathrm{el}} = -\sigma_{\mathrm{el}} \vec{\nabla} \Phi$. Find expression (6.57) for the coefficient of electrical conductivity σ_{el}.

Calculate the electric power density $\partial \epsilon / \partial t$ and the entropy current density $\vec{j}_S$. What is the value of $\vec{\nabla} \cdot \vec{j}_S$? Verify that the rate of entropy dissipation is given by

$$\frac{\partial s}{\partial t} = \frac{1}{T} \frac{\vec{j}_{\mathrm{el}}^{\,2}}{\sigma_{\mathrm{el}}} \tag{6.111}$$

The above equation shows that the 'Joule power', $\vec{j}_{\mathrm{el}}^{\,2}/\sigma_{\mathrm{el}}$, is directly related to the rate of entropy dissipation. In the model considered here, the charge carriers do not exchange energy with the medium, which, therefore, in turn cannot exchange heat with the outside world. In a realistic situation, what is the mechanism that permits energy to be transferred to the outside thus allowing the Joule effect to be observed?

4. *Peltier effect.* Consider a junction between two different metals A and B through which flows a uniform current of intensity I (Figure 6.9).

The system is maintained at temperature T. Show that at the junction a thermoelectric effect, heating or cooling depending on the direction of the current, will be observed. What power W must we supply to the junction to keep its temperature at T?

If the current I flows from A to B, we define the 'Peltier coefficient', Π_{AB}, as the power per unit current absorbed by the circuit, $\Pi_{AB} = W/I$. Relate this coefficient to the Seebeck coefficients of the two materials.

6.5.4 Isomerization reactions

A chemical exists in three isomeric forms A, B and C related by the triangle of isomerization reactions schematically shown in Figure 6.10.

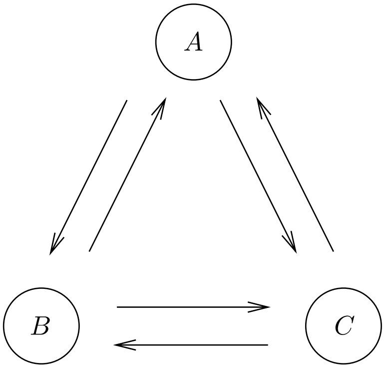

Figure 6.10 Possible exchange directions between three isomeric forms.

Designate by $N_A(t)$, $N_B(t)$ and $N_C(t)$ the numbers of A, B, and C molecules present at time t.

1. If k_{ij} is the spontaneous transformation rate between isomers i and j, write the three equations which govern the kinetics of the reactions. We assume that a stationary situation can be established, i.e. that equilibrium currents ensure that the numbers of molecules N_A^0, N_B^0 and N_C^0 remain constant. Verify that for any isomer i we have

$$\sum_{j \neq i} (k_{ij} N_j^0 - k_{ji} N_i^0) = 0$$

Applying detailed balance (see Section 7.1), which is based on time reversal invariance of microscopic processes, we can demonstrate the sufficient but not necessary relation

$$k_{ij} N_j^0 = k_{ji} N_i^0$$

2. We now move a little away from the stationary situation and designate the deviations by $x_i = N_i - N_i^0$ ($|x_i| \ll N_i^0$). The isomers are assumed to be ideal solutions (or ideal gases). Show that the mixing entropy may be written as

$$S - S_0 = -k \sum_i \left(N_i \ln N_i - N_i^0 \ln N_i^0 \right) \tag{6.112}$$

where S_0 is the entropy at equilibrium. It is sufficient to calculate the mixing entropy of two ideal gases at fixed pressure.

3. This problem cannot be analyzed using weakly coupled spatial cells (Section 6.1) and we therefore have to define the affinities (6.15) differently. Since the affinities are a measure of departure from equilibrium, it is natural to write

$$\Gamma_i = \frac{\partial(S - S_0)}{\partial x_i}$$

We want to re-express the kinetic equations of the first question in the form of linear relations between the fluxes $j_i = \dot{x}_i$ and the affinities Γ_i. Express the entropy change in terms of the deviations from equilibrium by expanding $S - S_0$ to leading order in x_i. Verify that the entropy is indeed maximum at equilibrium. Calculate the affinities and show that the kinetic equations can be written in the form

$$j_i = L_{ii}\Gamma_i + \sum_{j \neq i} L_{ij}\Gamma_j$$

Identify the phenomenological coefficients L_{ij} and verify that detailed balance implies the Onsager symmetry relations $L_{ij} = L_{ji}$.

6.6 Further reading

Sections 6.1 and 6.2 follow closely (including notation) Chapter 14 in Balian [5], which the reader should consult for further reading. Other useful references are Reif [109] (Chapter 15), Landau and Lifshitz [70] (Chapter XII), Kubo [68] (Chapter 6) and Kreuzer [67] (Chapters 1 to 3). At a more advanced level, the book by Foerster [43] is indispensable: in particular, one finds there an extensive discussion of the relation between time scales and conservation laws. A discussion of hydrodynamics geared for physicists can be found in Guyon *et al.* [53] and Faber [37].