

Chapter 2. Linear Irreversible Thermodynamics

- 2.1 The Conservation Equations
- 2.2 Entropy production
- 2.3 Curie's theorem
- 2.4 Non-Markovian Constitutive Relations: Viscoelasticity

2.1 The Conservation Equations

At the hydrodynamic level we are interested in the macroscopic evolution of densities of conserved extensive variables such as mass, energy and momentum. Because these quantities are conserved, their respective densities can only change by a process of **redistribution**. As we shall see, this means that the relaxation of these densities is slow, and therefore the relaxation plays a macroscopic role. If this relaxation were fast (i.e. if it occurred on a molecular time scale for instance) it would be unobservable at a macroscopic level. The macroscopic equations of motion for the densities of conserved quantities are called the Navier-Stokes equations. We will now give a brief description of how these equations are derived. It is important to understand this derivation because one of the objects of statistical mechanics is to provide a microscopic or molecular justification for the Navier-Stokes equations. In the process, statistical mechanics sheds light on the limits of applicability of these equations. Similar treatments can be found in de Groot and Mazur (1962) and Kreuzer (1981).

Let $M(t)$ be the total mass contained in an arbitrary volume V , then

$$M = \int_V d\mathbf{r} \rho(\mathbf{r}, t) \quad (2.1.1)$$

where $\rho(\mathbf{r}, t)$ is the mass density at position \mathbf{r} and time t . Since mass is conserved, the only way that the mass in the volume V can change is by flowing through the enclosing surface, S (see Figure 2.1).

$$\begin{aligned} \frac{dM}{dt} &= - \int_S d\mathbf{S} \cdot \rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t) \\ &= - \int_V d\mathbf{r} \nabla \cdot [\rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t)] \end{aligned} \quad (2.1.2)$$

Here $\mathbf{u}(\mathbf{r}, t)$ is the fluid streaming velocity at position \mathbf{r} and time t . $d\mathbf{S}$ denotes an area element of the enclosing surface S , and ∇ is the spatial gradient vector operator, $(\partial/\partial x, \partial/\partial y, \partial/\partial z)$. It is clear that the rate of change of the enclosed mass can also be written in terms of the change in mass density $\rho(\mathbf{r}, t)$, as

$$\frac{dM}{dt} = \int_V d\mathbf{r} \frac{\partial \rho(\mathbf{r}, t)}{\partial t} \quad (2.1.3)$$

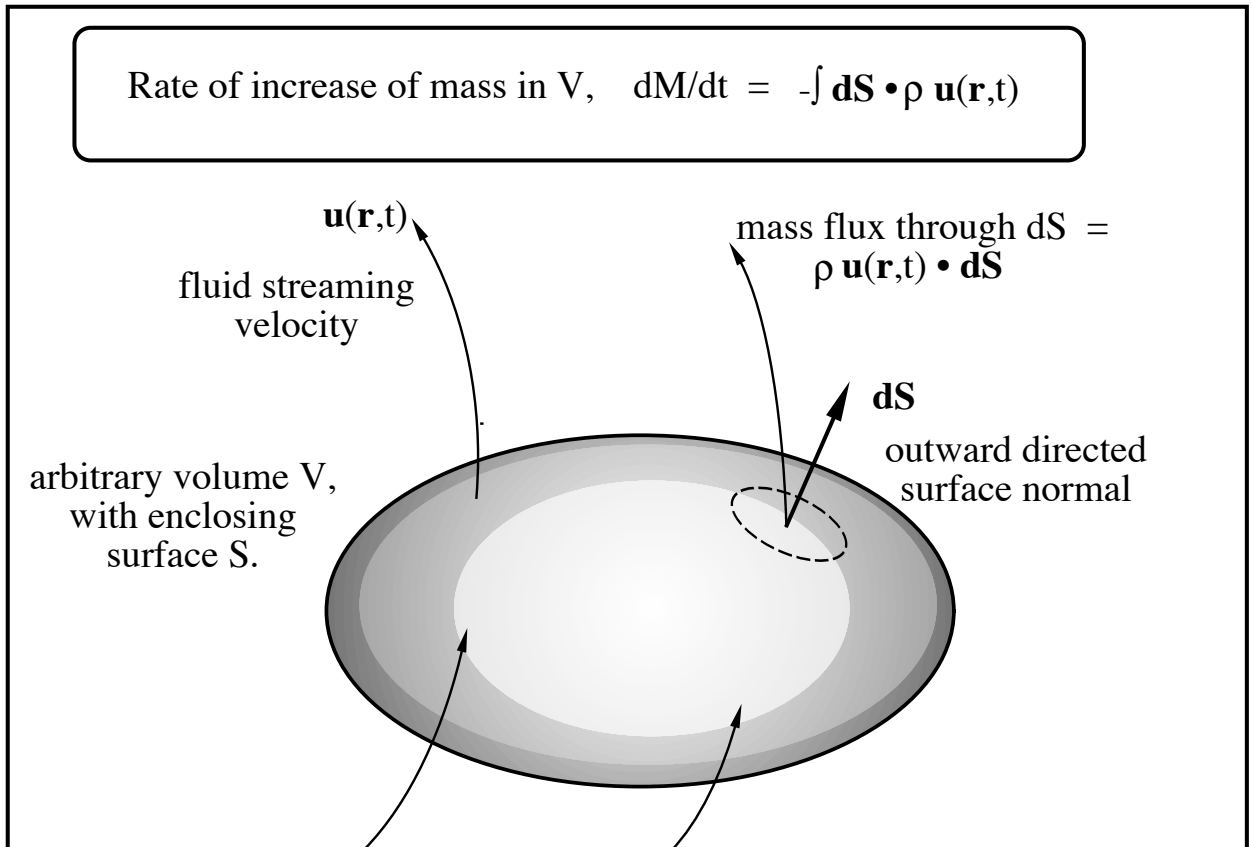


Figure 2.1. The change in the mass contained in an arbitrary closed volume V can be calculated by integrating the mass flux through the enclosing surface S .

If we equate these two expressions for the rate of change of the total mass we find that since the volume V was arbitrary,

$$\frac{\partial \rho(\mathbf{r}, t)}{\partial t} = -\nabla \cdot [\rho(\mathbf{r}, t) \mathbf{u}(\mathbf{r}, t)]. \quad (2.1.4)$$

This is called the mass continuity equation and is essentially a statement that mass is conserved. We can write the mass continuity equation in an alternative form if we use the relation between the total or streaming derivative, and the various partial derivatives. For an arbitrary function of position \mathbf{r} and time t , for example $a(\mathbf{r}, t)$, we have

$$\frac{d}{dt} a(\mathbf{r}, t) = \frac{\partial}{\partial t} a(\mathbf{r}, t) + \mathbf{u} \cdot \nabla a(\mathbf{r}, t) \quad (2.1.5)$$

If we let $a(\mathbf{r}, t) \equiv \rho(\mathbf{r}, t)$ in equation (2.1.5), and combine this with equation (2.1.4) then the mass continuity equation can be written as

$$\frac{d \rho(\mathbf{r}, t)}{dt} = -\rho(\mathbf{r}, t) \nabla \cdot \mathbf{u}(\mathbf{r}, t). \quad (2.1.6)$$

In an entirely analogous fashion we can derive an equation of continuity for momentum. Let $\mathbf{G}(t)$ be the total momentum of the arbitrary volume V , then the rate of change of momentum is given by

$$\frac{d\mathbf{G}}{dt} = \int_V d\mathbf{r} \frac{\partial [\rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t)]}{\partial t} . \quad (2.1.7)$$

The total momentum of volume V can change in two ways. Firstly it can change by convection. Momentum can flow through the enclosing surface. This convective term can be written as,

$$\frac{d\mathbf{G}_c}{dt} = - \int_S d\mathbf{S} \cdot \rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) \quad (2.1.8)$$

The second way that the momentum could change is by the pressure exerted on V by the surrounding fluid. We call this contribution the stress contribution. The force $d\mathbf{F}$, exerted by the fluid across an elementary area $d\mathbf{S}$, which is moving with the streaming velocity of the fluid, must be proportional to the magnitude of the area $d\mathbf{S}$. The most general such linear relation is,

$$d\mathbf{F} \equiv - d\mathbf{S} \cdot \mathbf{P} . \quad (2.1.9)$$

This is in fact the definition of the pressure tensor \mathbf{P} . It is also the negative of the stress tensor. That the pressure tensor is a second rank tensor rather than a simple scalar, is a reflection of the fact that the force $d\mathbf{F}$, and the area vector $d\mathbf{S}$, need not be parallel. In fact for molecular fluids the pressure tensor is not symmetric in general.

As \mathbf{P} is the first tensorial quantity that we have introduced it is appropriate to define the notational conventions that we will use. \mathbf{P} is a second rank tensor and thus requires two subscripts to specify the element. In Einstein notation equation (2.1.9) reads $dF_\alpha = - dS_\beta P_{\beta\alpha}$, where the repeated index β implies a summation. Notice that the contraction (or dot product) involves the first index of \mathbf{P} and that the vector character of the force $d\mathbf{F}$ is determined by the second index of \mathbf{P} . We will use bold san serif characters to denote tensors of rank two or greater. Figure 2.2 gives a diagrammatic representation of the tensorial relations in the definition of the pressure tensor.

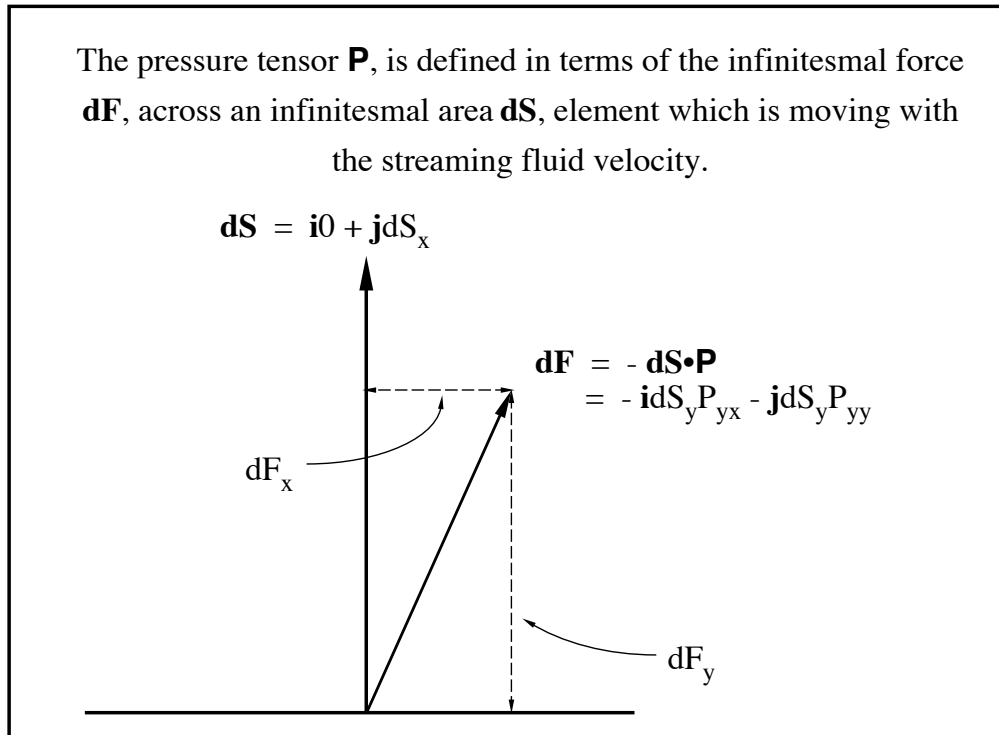


Figure 2.2. Definition of the pressure tensor.

Using this definition the stress contribution to the momentum change can be seen to be,

$$\frac{d\mathbf{G}_s}{dt} = - \int_S d\mathbf{S} \cdot \mathbf{P} \quad (2.1.10)$$

Combining (2.1.8, 2.1.10) and using the divergence theorem to convert surface integrals to volume integrals gives,

$$\frac{d\mathbf{G}}{dt} = \int_V d\mathbf{r} \frac{\partial [\rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t)]}{\partial t} = - \int_V d\mathbf{r} \nabla \cdot [\rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) + \mathbf{P}] \quad (2.1.11)$$

Since this equation is true for arbitrary V we conclude that,

$$\frac{\partial [\rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t)]}{\partial t} = - \nabla \cdot [\rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) + \mathbf{P}] \quad (2.1.12)$$

This is one form of the momentum continuity equation. A simpler form can be obtained using streaming derivatives of the velocity rather than partial derivatives. Using the chain rule the left hand side of (2.1.12) can be expanded as,

$$\rho(\mathbf{r},t) \frac{\partial \mathbf{u}(\mathbf{r},t)}{\partial t} + \mathbf{u}(\mathbf{r},t) \frac{\partial \rho(\mathbf{r},t)}{\partial t} = - \nabla \cdot [\rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) + \mathbf{P}] \quad (2.1.13)$$

Using the vector identity

$$\nabla \cdot (\rho \mathbf{u} \mathbf{u}) = \mathbf{u} (\nabla \cdot \rho \mathbf{u}) + \rho \mathbf{u} \cdot \nabla \mathbf{u} ,$$

and the mass continuity equation (2.1.4), this becomes

$$\begin{aligned} \rho(\mathbf{r},t) \frac{\partial \mathbf{u}(\mathbf{r},t)}{\partial t} &= - \nabla \cdot [\rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) \mathbf{u}(\mathbf{r},t)] + \mathbf{u}(\mathbf{r},t) \nabla \cdot [\rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t)] - \nabla \cdot \mathbf{P} \\ &= - \rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) \cdot \nabla \mathbf{u}(\mathbf{r},t) - \nabla \cdot \mathbf{P} \end{aligned} \quad (2.1.14)$$

Now,

$$\rho(\mathbf{r},t) \frac{d \mathbf{u}(\mathbf{r},t)}{dt} = \rho(\mathbf{r},t) \frac{\partial \mathbf{u}(\mathbf{r},t)}{\partial t} + \rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) \cdot \nabla \mathbf{u}(\mathbf{r},t), \quad (2.1.15)$$

so that (2.1.14) can be written as,

$$\rho(\mathbf{r},t) \frac{d \mathbf{u}(\mathbf{r},t)}{dt} = - \nabla \cdot \mathbf{P} \quad (2.1.16)$$

The final conservation equation we will derive is the energy equation. If we denote the total energy per unit mass or the specific total energy as $e(\mathbf{r},t)$, then the total energy density is $\rho(\mathbf{r},t) e(\mathbf{r},t)$. If the fluid is convecting there is obviously a simple convective kinetic energy component in $e(\mathbf{r},t)$. If this is removed from the energy density then what remains should be a thermodynamic internal energy density, $\rho(\mathbf{r},t) U(\mathbf{r},t)$.

$$\rho(\mathbf{r},t) e(\mathbf{r},t) = \rho(\mathbf{r},t) \frac{\mathbf{u}(\mathbf{r},t)^2}{2} + \rho(\mathbf{r},t) U(\mathbf{r},t) \quad (2.1.17)$$

Here we have identified the first term on the right hand side as the convective kinetic energy. The rate of change of this term is given by

$$\begin{aligned} \rho(\mathbf{r},t) \frac{d}{dt} \frac{\mathbf{u}(\mathbf{r},t)^2}{2} &= \rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) \cdot \frac{d \mathbf{u}(\mathbf{r},t)}{dt} \\ &= - \mathbf{u}(\mathbf{r},t) \cdot [\nabla \cdot \mathbf{P}] = - \mathbf{u} \nabla : \mathbf{P} . \end{aligned} \quad (2.1.18)$$

The second equality is a consequence of the momentum conservation equation (2.1.16). In this equation we use the dyadic product of two first rank tensors (or ordinary vectors) \mathbf{u} and ∇ to obtain a second rank tensor $\mathbf{u}\nabla$. In Einstein notation $(\mathbf{u}\nabla)_{\alpha\beta} \equiv \mathbf{u}_\alpha \nabla_\beta$. In the first form given in equation (2.1.18) ∇ is contracted into the first index of \mathbf{P} , and then \mathbf{u} is contracted into the second remaining index. This defines the meaning of the double contraction notation after the second equals sign in equation (2.1.18) - inner indices are contracted first, then outer indices - that is $\mathbf{u}\nabla:\mathbf{P} \equiv (\mathbf{u}\nabla)_{\alpha\beta} \mathbf{P}_{\beta\alpha} \equiv \mathbf{u}_\alpha \nabla_\beta \mathbf{P}_{\beta\alpha}$.

For any variable a , using equation (2.1.5) we have

$$\begin{aligned} \rho(\mathbf{r},t) \frac{d a(\mathbf{r},t)}{dt} &= \rho(\mathbf{r},t) \frac{\partial a(\mathbf{r},t)}{\partial t} + \rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) \cdot \nabla a(\mathbf{r},t) \\ &= \frac{\partial [\rho(\mathbf{r},t) a(\mathbf{r},t)]}{\partial t} + \rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) \cdot \nabla a(\mathbf{r},t) - a(\mathbf{r},t) \frac{\partial \rho(\mathbf{r},t)}{\partial t} \end{aligned} \quad (2.1.19)$$

Using the mass continuity equation (2.1.4)

$$\begin{aligned} \rho(\mathbf{r},t) \frac{d a(\mathbf{r},t)}{dt} &= \frac{\partial [\rho(\mathbf{r},t) a(\mathbf{r},t)]}{\partial t} + \rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) \cdot \nabla a(\mathbf{r},t) + a(\mathbf{r},t) \nabla \cdot [\rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t)] \\ &= \frac{\partial [\rho(\mathbf{r},t) a(\mathbf{r},t)]}{\partial t} + \nabla \cdot [\rho(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) a(\mathbf{r},t)] \end{aligned} \quad (2.1.20)$$

If we let the total energy inside a volume V be E , then clearly,

$$\frac{dE}{dt} = \int_V d\mathbf{r} \frac{\partial [\rho(\mathbf{r},t) \epsilon(\mathbf{r},t)]}{\partial t} . \quad (2.1.21)$$

Because the energy is conserved we can make a detailed account of the energy balance in the volume V . The energy can simply convect through the containing surface, it could diffuse through the surface and the surface stresses could do work on the volume V . In order these terms can be written,

$$\frac{dE}{dt} = - \int_S d\mathbf{S} \cdot [\rho(\mathbf{r},t) \epsilon(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) + \mathbf{J}_Q] + \int_S (d\mathbf{S} \cdot \mathbf{P}(\mathbf{r},t)) \cdot \mathbf{u}(\mathbf{r},t) \quad (2.1.22)$$

In equation (2.1.22) \mathbf{J}_Q , is called the heat flux vector. It gives the energy flux across a surface which is moving with the local fluid streaming velocity. Using the divergence theorem, (2.1.22) can be written as,

$$\frac{dE}{dt} = - \int_V d\mathbf{r} \nabla \cdot [\rho(\mathbf{r},t) e(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) + \mathbf{J}_Q(\mathbf{r},t) + \mathbf{P}(\mathbf{r},t) \cdot \mathbf{u}(\mathbf{r},t)] \quad (2.1.23)$$

Comparing equations (2.1.21) and (2.1.23) we derive the continuity equation for total energy,

$$\frac{\partial [\rho(\mathbf{r},t) e(\mathbf{r},t)]}{\partial t} = -\nabla \cdot [\rho(\mathbf{r},t) e(\mathbf{r},t) \mathbf{u}(\mathbf{r},t) + \mathbf{J}_Q(\mathbf{r},t) + \mathbf{P}(\mathbf{r},t) \cdot \mathbf{u}(\mathbf{r},t)] \quad (2.1.24)$$

We can use (2.1.20) to express this equation in terms of streaming derivatives of the total specific energy

$$\rho(\mathbf{r},t) \frac{d e(\mathbf{r},t)}{dt} = -\nabla \cdot [\mathbf{J}_Q(\mathbf{r},t) + \mathbf{P}(\mathbf{r},t) \cdot \mathbf{u}(\mathbf{r},t)] \quad (2.1.25)$$

Finally equations (2.1.17) and (2.1.18) can be used to derive a continuity equation for the specific internal energy

$$\rho(\mathbf{r},t) \frac{d U(\mathbf{r},t)}{dt} = -\nabla \cdot \mathbf{J}_Q(\mathbf{r},t) - \mathbf{P}(\mathbf{r},t)^T : \nabla \mathbf{u}(\mathbf{r},t) . \quad (2.1.26)$$

where the superscript T denotes transpose. The transpose of the pressure tensor appears as a result of our double contraction notation because in equation (2.1.25) ∇ is contracted into the first index of \mathbf{P} .

The three continuity equations (2.1.6), (2.1.16) and (2.1.26) are continuum expressions of the fact that mass, momentum and energy are conserved. These equations are exact.

2.2 Entropy Production

Thus far our description of the equations of hydrodynamics has been exact. We will now derive an equation for the rate at which entropy is produced spontaneously in a nonequilibrium system. The second law of thermodynamics states that entropy is not a conserved quantity. In order to complete this derivation we must assume that we can apply the laws of equilibrium thermodynamics, at least on a local scale, in nonequilibrium systems. This assumption is called the **local thermodynamic equilibrium postulate**. We expect that this postulate should be valid for systems that are sufficiently close to equilibrium (de Groot and Mazur, 1962). This macroscopic theory provides no information on how *small* these deviations from equilibrium should be in order for local thermodynamic equilibrium to hold. It turns out however, that the local thermodynamic equilibrium postulate is satisfied for a wide variety of systems over a wide range of conditions. One obvious condition that must be met is that the characteristic distances over which inhomogeneities in the nonequilibrium system occur must be large in terms molecular dimensions. If this is not the case then the thermodynamic state variables will change so rapidly in space that a local thermodynamic state cannot be defined. Similarly the time scale for nonequilibrium change in the system must be large compared to the time scales required for the attainment of local equilibrium.

We let the entropy per unit mass be denoted as, $s(\mathbf{r},t)$ and the entropy of an arbitrary volume V , be denoted by S . Clearly,

$$\frac{dS}{dt} = \int_V d\mathbf{r} \frac{\partial [\rho(\mathbf{r},t) s(\mathbf{r},t)]}{\partial t} \quad (2.2.1)$$

In contrast to the derivations of the conservation laws we do not expect that by taking account of convection and diffusion, we can totally account for the entropy of the system. The *excess* change of entropy is what we are seeking to calculate. We shall call the entropy produced per unit time per unit volume, the entropy source strength, $\sigma(\mathbf{r},t)$.

$$\frac{dS}{dt} = \int_V d\mathbf{r} \sigma(\mathbf{r},t) - \int_S d\mathbf{S} \cdot \mathbf{J}_{ST}(\mathbf{r},t) \quad (2.2.2)$$

In this equation $\mathbf{J}_{ST}(\mathbf{r},t)$ is the total entropy flux. As before we use the divergence theorem and the arbitrariness of V to calculate,

$$\frac{\partial [\rho(\mathbf{r},t) s(\mathbf{r},t)]}{\partial t} = \sigma(\mathbf{r},t) - \nabla \cdot \mathbf{J}_{ST}(\mathbf{r},t) \quad (2.2.3)$$

We can decompose $\mathbf{J}_{ST}(\mathbf{r},t)$ into a streaming or convective term $\rho(\mathbf{r},t)s(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)$ in analogy with

equation (2.1.8), and a diffusive term $\mathbf{J}_S(\mathbf{r},t)$. Using these terms (2.2.3) can be written as,

$$\frac{\partial [\rho(\mathbf{r},t) s(\mathbf{r},t)]}{\partial t} = \sigma(\mathbf{r},t) - \nabla \cdot [\mathbf{J}_S(\mathbf{r},t) + \rho(\mathbf{r},t) s(\mathbf{r},t) \mathbf{u}(\mathbf{r},t)] \quad (2.2.4)$$

Using (2.1.5) to convert to total time derivatives we have,

$$\rho(\mathbf{r},t) \frac{d s(\mathbf{r},t)}{dt} = \sigma(\mathbf{r},t) - \nabla \cdot \mathbf{J}_S(\mathbf{r},t) \quad (2.2.5)$$

At this stage we introduce the assumption of local thermodynamic equilibrium. We **postulate** a local version of the Gibbs relation $TdS = dU + pdV$. Converting this relation to a local version with extensive quantities replaced by the specific entropy energy and volume respectively and noting that the specific volume V/M is simply $\rho(\mathbf{r},t)^{-1}$, we find that,

$$\begin{aligned} T(\mathbf{r},t) \frac{d s(\mathbf{r},t)}{dt} &= \frac{d U(\mathbf{r},t)}{dt} + p(\mathbf{r},t) \frac{d}{dt} \rho(\mathbf{r},t)^{-1} \\ &= \frac{d U(\mathbf{r},t)}{dt} - \frac{p(\mathbf{r},t)}{\rho(\mathbf{r},t)^2} \frac{d \rho(\mathbf{r},t)}{dt} \end{aligned} \quad (2.2.6)$$

We can now use the mass continuity equation to eliminate the density derivative,

$$T(\mathbf{r},t) \frac{d s(\mathbf{r},t)}{dt} = \frac{d U(\mathbf{r},t)}{dt} + \frac{p(\mathbf{r},t)}{\rho(\mathbf{r},t)} \nabla \cdot \mathbf{u}(\mathbf{r},t) \quad (2.2.7)$$

Multiplying (2.2.7) by $\rho(\mathbf{r},t)$ and dividing by $T(\mathbf{r},t)$ gives

$$\rho(\mathbf{r},t) \frac{d s(\mathbf{r},t)}{dt} = \frac{\rho(\mathbf{r},t)}{T(\mathbf{r},t)} \frac{d U(\mathbf{r},t)}{dt} + \frac{p(\mathbf{r},t)}{T(\mathbf{r},t)} \nabla \cdot \mathbf{u}(\mathbf{r},t) \quad (2.2.8)$$

We can substitute the energy continuity expression (2.1.26) for dU/dt into (2.2.8) giving,

$$\rho(\mathbf{r},t) \frac{d s(\mathbf{r},t)}{dt} = \frac{-1}{T(\mathbf{r},t)} \left[\nabla \cdot \mathbf{J}_Q(\mathbf{r},t) + \mathbf{P}(\mathbf{r},t) : \nabla \mathbf{u}(\mathbf{r},t) - p(\mathbf{r},t) \nabla \cdot \mathbf{u}(\mathbf{r},t) \right] \quad (2.2.9)$$

We now have two expressions for the streaming derivative of the specific entropy, $\rho(\mathbf{r},t) ds(\mathbf{r},t)/dt$, equation (2.2.5) and (2.2.9). The diffusive entropy flux $\mathbf{J}_S(\mathbf{r},t)$, using the time derivative of the local equilibrium postulate $dQ = TdS$, is equal to the heat flux divided by the absolute temperature and therefore,

$$\nabla \cdot \mathbf{J}_S(\mathbf{r},t) = \nabla \cdot \left[\frac{\mathbf{J}_Q(\mathbf{r},t)}{T(\mathbf{r},t)} \right] = \frac{\nabla \cdot \mathbf{J}_Q(\mathbf{r},t)}{T(\mathbf{r},t)} - \frac{\mathbf{J}_Q(\mathbf{r},t) \cdot \nabla T(\mathbf{r},t)}{T(\mathbf{r},t)^2} \quad (2.2.10)$$

Equating (2.2.5) and (2.2.9) using (2.2.10) gives,

$$\begin{aligned} \sigma(\mathbf{r},t) &= \frac{-1}{T(\mathbf{r},t)} \left[\mathbf{P}(\mathbf{r},t)^T : \nabla \mathbf{u}(\mathbf{r},t) - p(\mathbf{r},t) \nabla \cdot \mathbf{u}(\mathbf{r},t) + \frac{\mathbf{J}_Q(\mathbf{r},t) \cdot \nabla T(\mathbf{r},t)}{T(\mathbf{r},t)} \right] \\ &= - \frac{\mathbf{J}_Q(\mathbf{r},t) \cdot \nabla T(\mathbf{r},t)}{T(\mathbf{r},t)^2} - \frac{\left[\mathbf{P}(\mathbf{r},t)^T : \nabla \mathbf{u}(\mathbf{r},t) - p(\mathbf{r},t) \nabla \cdot \mathbf{u}(\mathbf{r},t) \right]}{T(\mathbf{r},t)} \end{aligned} \quad (2.2.11)$$

We define the viscous pressure tensor $\mathbf{\Pi}^{(2)}$, as the nonequilibrium part of the pressure tensor.

$$\mathbf{\Pi}(\mathbf{r},t) = \mathbf{P}(\mathbf{r},t) - p(\mathbf{r},t) \mathbf{I} \quad (2.2.12)$$

Using this definition the entropy source strength can be written as,

$$\sigma(\mathbf{r},t) = - \frac{1}{T(\mathbf{r},t)^2} \mathbf{J}_Q(\mathbf{r},t) \cdot \nabla T(\mathbf{r},t) - \frac{1}{T(\mathbf{r},t)} \mathbf{\Pi}(\mathbf{r},t)^T : \nabla \mathbf{u}(\mathbf{r},t) \quad (2.2.13)$$

A second postulate of nonlinear irreversible thermodynamics is that the entropy source strength always takes the canonical form (de Groot and Mazur, 1962),

$$\sigma = \sum_i J_i X_i \quad (2.2.14)$$

This canonical form defines what are known as thermodynamic fluxes, J_i , and their conjugate thermodynamic forces, X_i . We can see immediately that our equation (2.2.13) takes this canonical form provided we make the identifications that: the thermodynamic fluxes are the various Cartesian elements of the heat flux vector, $\mathbf{J}_Q(\mathbf{r},t)$, and the viscous pressure tensor, $\mathbf{\Pi}(\mathbf{r},t)$. The thermodynamic forces conjugate to these fluxes are the **corresponding** Cartesian components of the temperature gradient divided by the square of the absolute temperature, $T(\mathbf{r},t)^{-2} \nabla T(\mathbf{r},t)$, and the strain rate tensor divided by the absolute temperature, $T(\mathbf{r},t)^{-1} \nabla \mathbf{u}(\mathbf{r},t)$, respectively. We use the term *corresponding* quite deliberately; the α^{th} element of the heat flux is conjugate to the α^{th} element of the temperature gradient. There are no cross couplings. Similarly the α, β element of the pressure viscous pressure tensor is conjugate to the α, β element of the strain rate tensor.

There is clearly some ambiguity in defining the thermodynamic fluxes and forces. There is no fundamental thermodynamic reason why we included the temperature factors, $T(\mathbf{r},t)^{-2}$ and $T(\mathbf{r},t)^{-1}$, into the forces rather than into the fluxes. Either choice is possible. Ours is simply one of

convention. More importantly there is no thermodynamic way of distinguishing between the fluxes and the forces. At a macroscopic level it is simply a convention to identify the temperature gradient as a thermodynamic force rather than a flux. The canonical form for the entropy source strength and the associated postulates of irreversible thermodynamics do not permit a distinction to be made between what we should identify as fluxes and what should be identified as a force. Microscopically it is clear that the heat flux is a *flux*. It is the diffusive energy flow across a comoving surface. At a macroscopic level however, no such distinction can be made.

Perhaps the simplest example of this macroscopic duality is the Norton constant current electrical circuit, and the Thévenin constant voltage equivalent circuit. We can talk of the resistance of a circuit element or of a conductance. At a macroscopic level the choice is simply one of practical convenience or convention.

2.3 Curie's Theorem

Consistent with our use of the local thermodynamic equilibrium postulate, which is assumed to be valid sufficiently close to equilibrium, a linear relation should hold between the conjugate thermodynamic fluxes and forces. We therefore postulate the existence of a set of linear phenomenological transport coefficients $\{L_{ij}\}$ which relate the set forces $\{X_j\}$ to the set of fluxes $\{J_i\}$. We use the term *phenomenological* to indicate that these transport coefficients are to be defined within the framework of linear irreversible thermodynamics and as we shall see there may be slight differences between the phenomenological transport coefficients L_{ij} and practical transport coefficients such as the viscosity coefficients or the usual thermal conductivity.

We postulate that **all** the thermodynamic forces appearing in the equation for the entropy source strength (2.2.14), are related to the various fluxes by a linear equation of the form

$$J_i = \sum_j L_{ij} X_j \quad (2.3.1)$$

This equation could be thought of as arising from a Taylor series expansion of the fluxes in terms of the forces. Such a Taylor series will only exist if the flux is an analytic function of the force at $\mathbf{X}=\mathbf{0}$.

$$J_i(\mathbf{X}) = J_i(\mathbf{0}) + \sum_j \left. \frac{\partial J_i}{\partial X_j} \right|_{\mathbf{X}=\mathbf{0}} \cdot X_j + \sum_{j,k} \frac{1}{2!} \left. \frac{\partial^2 J_i}{\partial X_j \partial X_k} \right|_{\mathbf{X}=\mathbf{0}} : X_j X_k + O(\mathbf{X}^3) \quad (2.3.2)$$

Clearly the first term is zero as the fluxes vanish when the thermodynamic forces are zero. The term which is linear in the forces is evidently derivable, at least formally, from the equilibrium properties of the system as the functional derivative of the fluxes with respect to the forces computed at equilibrium, $\mathbf{X}=\mathbf{0}$. The quadratic term is related to what are known as the nonlinear Burnett coefficients (see §9.5). They represent nonlinear contributions to the linear theory of irreversible thermodynamics.

If we substitute the linear phenomenological relations into the equation for the entropy source strength (2.2.14), we find that,

$$\sigma = \sum_{ij} X_i L_{ij} X_j \quad (2.3.3)$$

A postulate of linear irreversible thermodynamics is that the entropy source strength is always positive. There is always an increase in the entropy of a system so the transport coefficients are positive. Since this is also true for the mirror image of any system, we conclude that the entropy

source strength is a positive polar scalar quantity. (A polar scalar is invariant under a mirror inversion of the coordinate axes. A pseudo scalar, on the other hand, changes its sign under a mirror inversion. The same distinction between polar and scalar quantities also applies to vectors and tensors.)

Suppose that we are studying the transport processes taking place in a fluid. In the absence of any external non-dissipative fields (such as gravitational or magnetic fields), the fluid is at equilibrium and assumed to be isotropic. Clearly since the linear transport coefficients can be formally calculated as a zero-field functional derivative they should have the symmetry characteristic of an isotropic system. Furthermore they should be invariant under a mirror reflection of the coordinate axes.

Suppose that all the fluxes and forces are scalars. The most general linear relation between the forces and fluxes is given by equation (2.3.1). Since the transport coefficients must be polar scalars there cannot be any coupling between a pseudo scalar flux and a polar force or between a polar flux and a pseudo scalar force. This is a simple application of the quotient rule in tensor analysis. Scalars of like parity only, can be coupled by the transport matrix L_{ij} .

If the forces and fluxes are vectors, the most general linear relation between the forces and fluxes which is consistent with isotropy is,

$$\mathbf{J}_i = \sum_j \mathbf{L}_{ij} \cdot \mathbf{X}_j = \sum_j L_{ij} \mathbf{I} \cdot \mathbf{X}_j = \sum_j L_{ij} \mathbf{X}_j. \quad (2.3.4)$$

In this equation \mathbf{L}_{ij} is a second rank polar tensor because the transport coefficients must be invariant under mirror inversion just like the equilibrium system itself. If the equilibrium system is isotropic then \mathbf{L}_{ij} must be expressible as a scalar L_{ij} times the only isotropic second rank tensor \mathbf{I} , (the Kronecker delta tensor $\mathbf{I} = \delta_{\alpha\beta}$). The thermodynamic forces and fluxes which couple together must either all be pseudo vectors or polar vectors. Otherwise since the transport coefficients are polar quantities, the entropy source strength could be pseudo scalar. By comparing the trace of \mathbf{L}_{ij} with the trace of $L_{ij} \mathbf{I}$, we see that the polar scalar transport coefficients are given as,

$$L_{ij} = \frac{1}{3} \text{tr}(\mathbf{L}_{ij}) = \frac{1}{3} \mathbf{L}_{ij} : \mathbf{I} \quad (2.3.5)$$

If the thermodynamic forces and fluxes are all symmetric traceless second rank tensors $\mathbb{J}_i, \mathbb{X}_i$, where $\mathbb{J}_i = 1/2 (\mathbf{J}_i + \mathbf{J}_i^T) - 1/3 \text{Tr}(\mathbf{J}_i) \mathbf{I}$, (we denote symmetric traceless tensors as outline sans serif characters), then

$$\mathbb{J}_i^{(2)} = \sum_j \mathbf{L}_{ij}^{(4)} : \mathbb{X}_j^{(2)} \quad (2.3.6)$$

is the most linear general linear relation between the forces and fluxes. $\mathbf{L}_{ij}^{(4)}$ is a symmetric fourth rank transport tensor. Unlike second rank tensors there are three linearly independent isotropic fourth rank polar tensors. (There are no isotropic pseudo tensors of the fourth rank.) These tensors can be related to the Kronecker delta tensor, and we depict these tensors by the forms,

$$\mathbb{U}\mathbb{U}_{\alpha\beta\gamma\eta} = \delta_{\alpha\beta} \delta_{\gamma\eta} \quad (2.3.7a)$$

$$\mathbb{W}_{\alpha\beta\gamma\eta} = \delta_{\alpha\gamma} \delta_{\beta\eta} \quad (2.3.7b)$$

$$\mathbb{U}_{\alpha\beta\gamma\eta} = \delta_{\alpha\eta} \delta_{\beta\gamma} \quad (2.3.7c)$$

Since $\mathbf{L}_{ij}^{(4)}$ is an isotropic tensor it must be representable as a linear combination of isotropic fourth rank tensors. It is convenient to write,

$$\mathbf{L}_{ij}^{(4)} = L_{ij}^s \left[\frac{1}{2} (\mathbb{U} + \mathbb{W}) - \frac{1}{3} \mathbb{U}\mathbb{U} \right] + L_{ij}^a \frac{1}{2} (\mathbb{U} - \mathbb{W}) + L_{ij}^{tr} \frac{1}{3} \mathbb{U}\mathbb{U} \quad (2.3.8)$$

It is easy to show that for any second rank tensor \mathbf{A} ,

$$\mathbf{L}_{ij} : \mathbf{A}^{(2)} = L_{ij}^s \mathbb{A} + L_{ij}^a \mathbb{A} + L_{ij}^{tr} \mathbf{A} \mathbf{I}, \quad (2.3.9)$$

where \mathbb{A} is the symmetric traceless part of $\mathbf{A}^{(2)}$, $\mathbb{A} = 1/2(\mathbf{A} - \mathbf{A}^T)$ is the antisymmetric part of $\mathbf{A}^{(2)}$ (we denote antisymmetric tensors as shadowed sans serif characters), and $A = 1/3 \text{Tr}(\mathbf{A})$. This means that the three isotropic fourth rank tensors decouple the linear force flux relations into three separate sets of equations which relate respectively, the symmetric second rank forces and fluxes, the antisymmetric second rank forces and fluxes, and the traces of the forces and fluxes. These equations can be written as

$$\mathbb{J}_i = \sum_j L_{ij}^s \mathbb{X}_j \quad (2.3.10a)$$

$$\mathbb{J}_i = \sum_j L_{ij}^a \mathbb{X}_j \quad (2.3.10b)$$

$$\mathbf{J}_i = \sum_j L_{ij}^{tr} \mathbf{X}_j \quad (2.3.10c)$$

where \mathbb{J}_i is the antisymmetric part of \mathbf{J} , and $J = 1/3 \text{Tr}(\mathbf{J})$. As \mathbb{J}_i has only three independent

elements it turns out that \mathbb{J}_i can be related to a pseudo vector. This relationship is conveniently expressed in terms of the Levi-Civita isotropic third rank tensor $\boldsymbol{\epsilon}^{(3)}$. (Note: $\boldsymbol{\epsilon}_{\alpha\beta\gamma} = +1$ if $\alpha\beta\gamma$ is an even permutation, -1 if $\alpha\beta\gamma$ is an odd permutation and is zero otherwise.) If we denote the pseudo vector dual of \mathbb{J}_i as \mathbf{J}_i^{ps} then,

$$\mathbf{J}_i^{\text{ps}} = -\frac{1}{2}\boldsymbol{\epsilon}^{(3)}:\mathbb{J}_i^{(2)} \quad \text{and} \quad \mathbb{J}_i^{(2)} = \mathbf{J}_i^{\text{ps}} \bullet \boldsymbol{\epsilon}^{(3)} \quad (2.3.11)$$

This means that the second equation in the set (2.3.10b) can be rewritten as,

$$\mathbf{J}_i^{\text{ps}} = \sum_j L_{ij}^a \mathbf{X}_j^{\text{ps}}. \quad (2.3.12)$$

Looking at (2.3.10) and (2.3.12) we see that we have decomposed the 81 elements of the (3-dimensional) fourth rank transport tensor $\mathbf{L}_{ij}^{(4)}$, into three scalar quantities, L_{ij}^s , L_{ij}^a and L^{tr}_{ij} . Furthermore we have found that there are three *irreducible* sets of forces and fluxes. Couplings only exist within the sets. There are no couplings of forces of one set with fluxes of another set. The sets naturally represent the symmetric traceless parts, the antisymmetric part and the trace of the second rank tensors. The three irreducible components can be identified with irreducible second rank polar tensor component an irreducible pseudo vector and an irreducible polar scalar. Curie's principle states that linear transport couples can only occur between irreducible tensors of the same rank and parity.

If we return to our basic equation for the entropy source strength (2.2.14) we see that our irreducible decomposition of Cartesian tensors allows us to make the following decomposition for second rank fields and fluxes,

$$\begin{aligned} \sigma &= \sum_i \left(\mathbf{J}_i \cdot \mathbf{X}_i + \mathbb{J}_i : \mathbb{X}_i + \mathbb{J}_i : \mathbb{X}_i \right) \\ &= \sum_i \left(3 \mathbf{J}_i \cdot \mathbf{X}_i - 2 \mathbf{J}_i^{\text{ps}} \bullet \mathbf{X}_i^{\text{ps}} + \mathbb{J}_i : \mathbb{X}_i \right) \end{aligned} \quad (2.3.13)$$

The conjugate forces and fluxes appearing in the entropy source equation separate into irreducible sets. This is easily seen when we realise that all cross couplings between irreducible tensors of different rank and parity vanish; $\mathbf{I} : \mathbb{J}_i = \mathbf{I} : \mathbb{X}_i = \mathbb{J}_i : \mathbb{X}_i = 0$, etc. Conjugate thermodynamic forces and fluxes must have the same irreducible rank and parity.

We can now apply Curie's principle to the entropy source equation (2.2.13),

$$\sigma(\mathbf{r},t) = \frac{-1}{T(\mathbf{r},t)} \left[\frac{\mathbf{J}_Q(\mathbf{r},t) \cdot \nabla T(\mathbf{r},t)}{T(\mathbf{r},t)} - \mathbb{P}(\mathbf{r},t) : \nabla \mathbf{u}(\mathbf{r},t) - \Pi^{ps}(\mathbf{r},t) \cdot \nabla \mathbf{xu}(\mathbf{r},t) - \Pi(\mathbf{r},t) \nabla \cdot \mathbf{u}(\mathbf{r},t) \right] \quad (2.3.14)$$

In writing this equation we have used the fact that the transpose of \mathbb{P} is equal to \mathbb{P} , and we have used equation (2.3.11) and the definition of the cross product $\nabla \mathbf{xu} = -\boldsymbol{\epsilon}^{(3)} : \nabla \mathbf{u}$ to transform the antisymmetric part of \mathbb{P}^T . Note that the transpose of \mathbb{P} is equal to $-\mathbb{P}$. There is no conjugacy between the vector $\mathbf{J}_Q(\mathbf{r},t)$ and the pseudo vector $\nabla \mathbf{xu}(\mathbf{r},t)$ because they differ in parity. It can be easily shown that for atomic fluids the antisymmetric part of the pressure tensor is zero so that the terms in (2.3.14) involving the vorticity $\nabla \mathbf{xu}(\mathbf{r},t)$ are identically zero. For molecular fluids, terms involving the vorticity do appear but we also have to consider another conservation equation - the conservation of angular momentum. In our description of the conservation equations we have ignored angular momentum conservation. The complete description of the hydrodynamics of molecular fluids must include this additional conservation law.

For single component atomic fluids we can now use Curie's principle to define the phenomenological transport coefficients.

$$\mathbf{J}_Q = L_Q \mathbf{X}_Q = -L_Q \frac{\nabla T}{T^2} \quad (2.3.15a)$$

$$\mathbb{P} = L_{\mathbb{P}} \mathbb{X}_{\mathbb{P}} = -L_{\mathbb{P}} \frac{\nabla \mathbf{u}}{T} \quad (2.3.15b)$$

$$\Pi = L_{\Pi} X_{\Pi} = -L_{\Pi} \frac{3 \nabla \cdot \mathbf{u}}{T} \quad (2.3.15c)$$

The positive sign of the entropy production implies that each of the phenomenological transport coefficients must be positive. As mentioned before these phenomenological definitions differ slightly from the usual definitions of the Navier-Stokes transport coefficients.

$$\mathbf{J}_Q = -\lambda \nabla T \quad (2.3.16a)$$

$$\mathbb{P} = -2\eta \nabla \mathbf{u} \quad (2.3.16b)$$

$$\Pi = -\eta_v \nabla \cdot \mathbf{u} \quad (2.3.16c)$$

These equations were postulated long before the development of linear irreversible thermodynamics. The first equation is known as Fourier's law of heat conduction. It gives the definition of the thermal conductivity λ . The second equation is known as Newton's law of

viscosity (illustrated in Figure 2.3). It gives a definition of the shear viscosity coefficient η . The third equation is a more recent development. It defines the bulk viscosity coefficient η_V . These equations are known collectively as linear constitutive equations. When they are substituted into the conservation equations they yield the Navier-Stokes equations of hydrodynamics. The conservation equations relate thermodynamic fluxes and forces. They form a system of equations in two unknown fields - the force fields and the flux fields. The constitutive equations relate the forces and the fluxes. By combining the two systems of equations we can derive the Navier-Stokes equations which in their usual form give us a closed system of equations for the thermodynamic forces. Once the boundary conditions are supplied the Navier-Stokes equations can be solved to give a complete macroscopic description of the nonequilibrium flows expected in a fluid close to equilibrium in the sense required by linear irreversible thermodynamics. It is worth restating the expected conditions for the linearity to be observed:

- 1.) The thermodynamic forces should be sufficiently small so that linear constitutive relations are accurate.
- 2.) The system should likewise be sufficiently close to equilibrium for the local thermodynamic equilibrium condition to hold. For example the nonequilibrium equation of state must be the same function of the local position and time dependent thermodynamic state variables (such as the temperature and density), that it is at equilibrium.
- 3.) The characteristic distances over which the thermodynamic forces vary should be sufficiently large so that these forces can be viewed as being constant over the microscopic length scale required to properly define a local thermodynamic state.
- 4.) The characteristic times over which the thermodynamic forces vary should be sufficiently long that these forces can be viewed as being constant over the microscopic times required to properly define a local thermodynamic state.

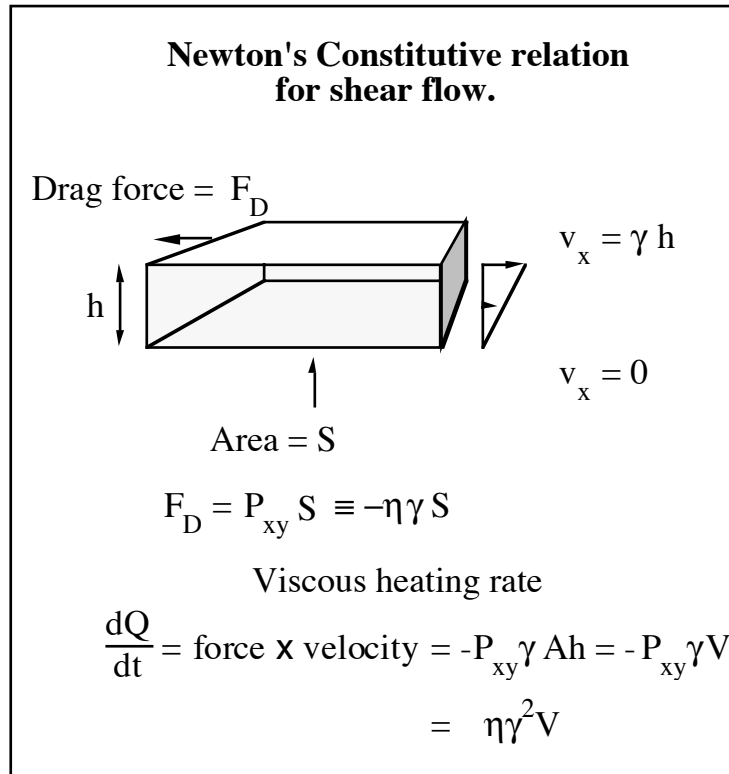


Figure 2.3. Newton's Constitutive relation for shear viscosity.

After some tedious but quite straightforward algebra (de Groot and Mazur, 1962), the Navier-Stokes equations for a single component atomic fluid are obtained. The first of these is simply the mass conservation equation (2.1.4).

$$\frac{\partial \rho}{\partial t} = -\nabla \cdot (\rho \mathbf{u}) \quad (2.3.17)$$

To obtain the second equation we combine equation (2.1.16) with the definition of the stress tensor from equation (2.2.12) which gives

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla \cdot \mathbf{P} = -\nabla \cdot \{ (p + \Pi) \mathbf{I} + \mathbb{II} \} \quad (2.3.18)$$

We have assumed that the fluid is atomic and the pressure tensor contains no antisymmetric part. Substituting in the constitutive relations, equations (2.3.16b) and (2.3.16c) gives

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla p + \eta_V \nabla (\nabla \cdot \mathbf{u}) + 2\eta \nabla \cdot (\nabla \mathbf{u}) \quad (2.3.19)$$

Here we explicitly assume that the transport coefficients η_V and η are simple constants, independent of position \mathbf{r} , time and flow rate \mathbf{u} . The $\alpha\beta$ component of the symmetric traceless tensor $\nabla \mathbf{u}$ is given by

$$(\nabla \mathbf{u})_{\alpha\beta} = \frac{1}{2} \left(\frac{\partial u_\beta}{\partial x_\alpha} + \frac{\partial u_\alpha}{\partial x_\beta} \right) - \delta_{\alpha\beta} \frac{1}{3} \frac{\partial u_\gamma}{\partial x_\gamma} \quad (2.3.20)$$

where as usual the repeated index γ implies a summation with respect to γ . It is then straightforward to see that

$$\nabla \cdot (\nabla \mathbf{u}) = \frac{1}{2} \nabla^2 \mathbf{u} + \frac{1}{6} \nabla (\nabla \cdot \mathbf{u}) \quad (2.3.21)$$

and it follows that the momentum flow Navier-Stokes equation is

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla p + \eta \nabla^2 \mathbf{u} + \left(\frac{\eta}{3} + \eta_V \right) \nabla (\nabla \cdot \mathbf{u}) \quad (2.3.22)$$

The Navier-Stokes equation for energy flow can be obtained from equation (2.1.26) and the constitutive relations, equation (2.3.16). Again we assume that the pressure tensor is symmetric, and the second term on the right hand side of equation (2.1.26) becomes

$$\begin{aligned} \mathbf{P}^T : \nabla \mathbf{u} &= \left\{ (p + \Pi) \mathbf{I} + \mathbb{II} \right\} : \left(\frac{1}{3} (\nabla \cdot \mathbf{u}) \mathbf{I} + \nabla \mathbf{u} \right) \\ &= \left\{ (p - \eta_V (\nabla \cdot \mathbf{u})) \mathbf{I} - 2\eta \nabla \mathbf{u} \right\} : \left(\frac{1}{3} (\nabla \cdot \mathbf{u}) \mathbf{I} + \nabla \mathbf{u} \right) \\ &= p (\nabla \cdot \mathbf{u}) - \eta_V (\nabla \cdot \mathbf{u})^2 - 2\eta \nabla \mathbf{u} : \nabla \mathbf{u} \end{aligned} \quad (2.3.23)$$

It is then straightforward to see that

$$\rho \frac{dU}{dt} = \lambda \nabla^2 T - p (\nabla \cdot \mathbf{u}) + \eta_V (\nabla \cdot \mathbf{u})^2 + 2\eta \nabla \mathbf{u} : \nabla \mathbf{u}. \quad (2.3.24)$$

2.4 Non-Markovian Constitutive Relations: Viscoelasticity

Consider a fluid undergoing planar Couette flow. This flow is defined by the streaming velocity,

$$\mathbf{u}(\mathbf{r},t) = (u_x, u_y, u_z) = (\gamma y, 0, 0) \quad (2.4.1)$$

According to Curie's principle the only nonequilibrium flux that will be excited by such a flow is the pressure tensor. According to the constitutive relation equation (2.3.16) the pressure tensor is,

$$\mathbf{P} = \begin{bmatrix} p & -\eta\gamma & 0 \\ -\eta\gamma & p & 0 \\ 0 & 0 & p \end{bmatrix} \quad (2.4.2)$$

where η is the shear viscosity and γ is the strain rate. If the strain rate is time dependent then the shear stress, $-\mathbf{P}_{xy} = -\mathbf{P}_{yx} = \eta\gamma(t)$. It is known that many fluids do not satisfy this relation regardless of how small the strain rate is. There must therefore be a **linear** but time dependent constitutive relation for shear flow which is more general than the Navier-Stokes constitutive relation.

Poisson (1829) pointed out that there is a deep correspondence between the shear stress induced by a strain rate in a fluid, and the shear stress induced by a strain in an elastic solid. The strain tensor is, $\nabla\boldsymbol{\varepsilon}$ where $\boldsymbol{\varepsilon}(\mathbf{r},t)$ gives the displacement of atoms at \mathbf{r} from their equilibrium lattice sites. It is clear that,

$$\frac{d\nabla\boldsymbol{\varepsilon}}{dt} = \nabla\mathbf{u} \quad (2.4.3)$$

Maxwell (1873) realised that if a displacement were applied to a liquid then for a short time the liquid must behave as if it were an elastic solid. After a *Maxwell relaxation time* the liquid would relax to equilibrium since **by definition** a liquid cannot support a strain (Frenkel, 1955).

It is easier to analyse this matter by transforming to the frequency domain. Maxwell said that at low frequencies the shear stress of a liquid is generated by the Navier-Stokes constitutive relation for a Newtonian fluid (2.4.2). In the frequency domain this states that,

$$\tilde{\mathbf{P}}_{xy}(\omega) = -\eta \tilde{\gamma}(\omega) \quad (2.4.4)$$

where,

$$\tilde{A}(\omega) = \int_0^{\infty} dt e^{-i\omega t} A(t) \quad (2.4.5)$$

denotes the Fourier-Laplace transform of $A(t)$.

At very high frequencies we should have,

$$\tilde{P}_{xy}(\omega) = -G \frac{\partial \tilde{\epsilon}_x}{\partial y}, \quad (2.4.6)$$

where G is the infinite frequency shear modulus. From equation (2.4.3) we can transform the terms involving the strain into terms involving the strain rate (we assume that at $t=0$, the strain $\epsilon(0)=0$). At high frequencies therefore,

$$\tilde{P}_{xy}(\omega) = -\frac{G}{i\omega} \frac{\partial \tilde{u}_x}{\partial y} = -\frac{G}{i\omega} \tilde{\gamma}(\omega). \quad (2.4.7)$$

The Maxwell model of viscoelasticity is obtained by simply summing the high and low frequency expressions for the compliances $i\omega/G$ and η^{-1} ,

$$\tilde{\gamma}(\omega) = -\left(\frac{i\omega}{G} + \frac{1}{\eta}\right) \tilde{P}_{xy}(\omega) = -\frac{\tilde{P}_{xy}(\omega)}{\tilde{\eta}_M(\omega)}. \quad (2.4.8)$$

The expression for the frequency dependent Maxwell viscosity is,

$$\tilde{\eta}_M(\omega) = \frac{\eta}{1 + i\omega\tau_M}. \quad (2.4.9)$$

It is easily seen that this expression smoothly interpolates between the high and low frequency limits. The Maxwell relaxation time $\tau_M = \eta/G$ controls the transition frequency between low frequency viscous behaviour and high frequency elastic behaviour.

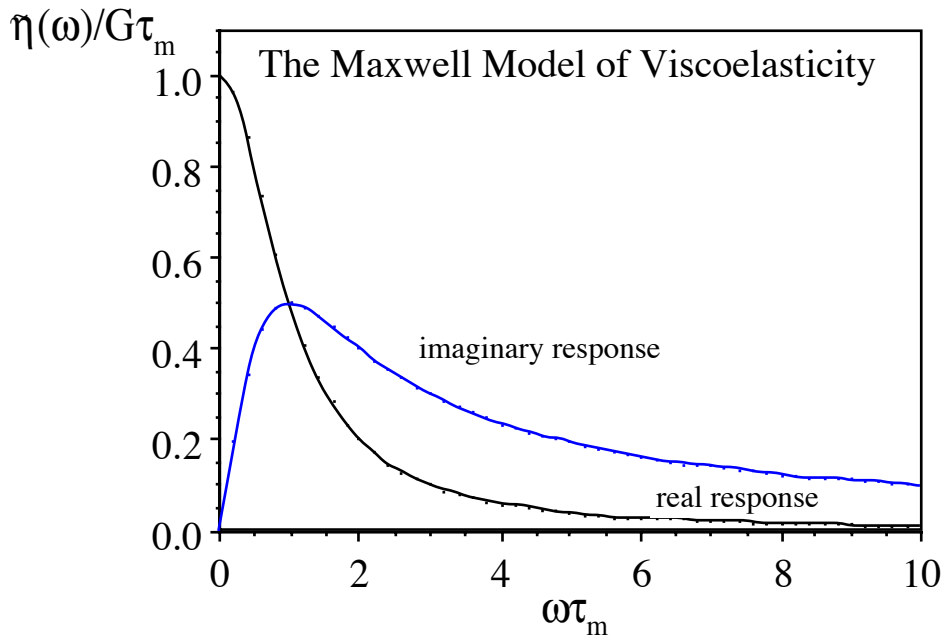


Figure 2.4. Frequency Dependent Viscosity of the Maxwell Model.

The Maxwell model provides a rough approximation to the viscoelastic behaviour of so-called viscoelastic fluids such as polymer melts or colloidal suspensions. It is important to remember that viscoelasticity is a linear phenomenon. The resulting shear stress is a linear function of the strain rate. It is also important to point out that Maxwell believed that all fluids are viscoelastic. The reason why polymer melts are observed to exhibit viscoelasticity is that their Maxwell relaxation times are macroscopic, of the order of seconds. On the other hand the Maxwell relaxation time for argon at its triple point is approximately 10^{-12} seconds! Using standard viscometric techniques elastic effects are completely unobservable in argon.

If we rewrite the Maxwell constitutive relation in the time domain using an inverse Fourier-Laplace transform we see that,

$$P_{xy}(t) = - \int_0^t ds \eta_M(t-s) \dot{\gamma}(s) \quad (2.4.10)$$

In this equation $\eta_M(t)$ is called the Maxwell memory function. It is called a memory function because the shear stress at time t is not simply linearly proportional to the strain rate at the current time t , but to the entire strain rate **history**, over times s where $0 \leq s \leq t$. Constitutive relations which are history dependent are called non-Markovian. A Markovian process is one in which the present state of the system is all that is required to determine its future. The Maxwell model of viscoelasticity describes non-Markovian behaviour. The Maxwell memory function is easily identified as an exponential,

$$\eta_M(t) = G e^{-t/\tau_M} \quad (2.4.11)$$

Maxwell Response to a Step

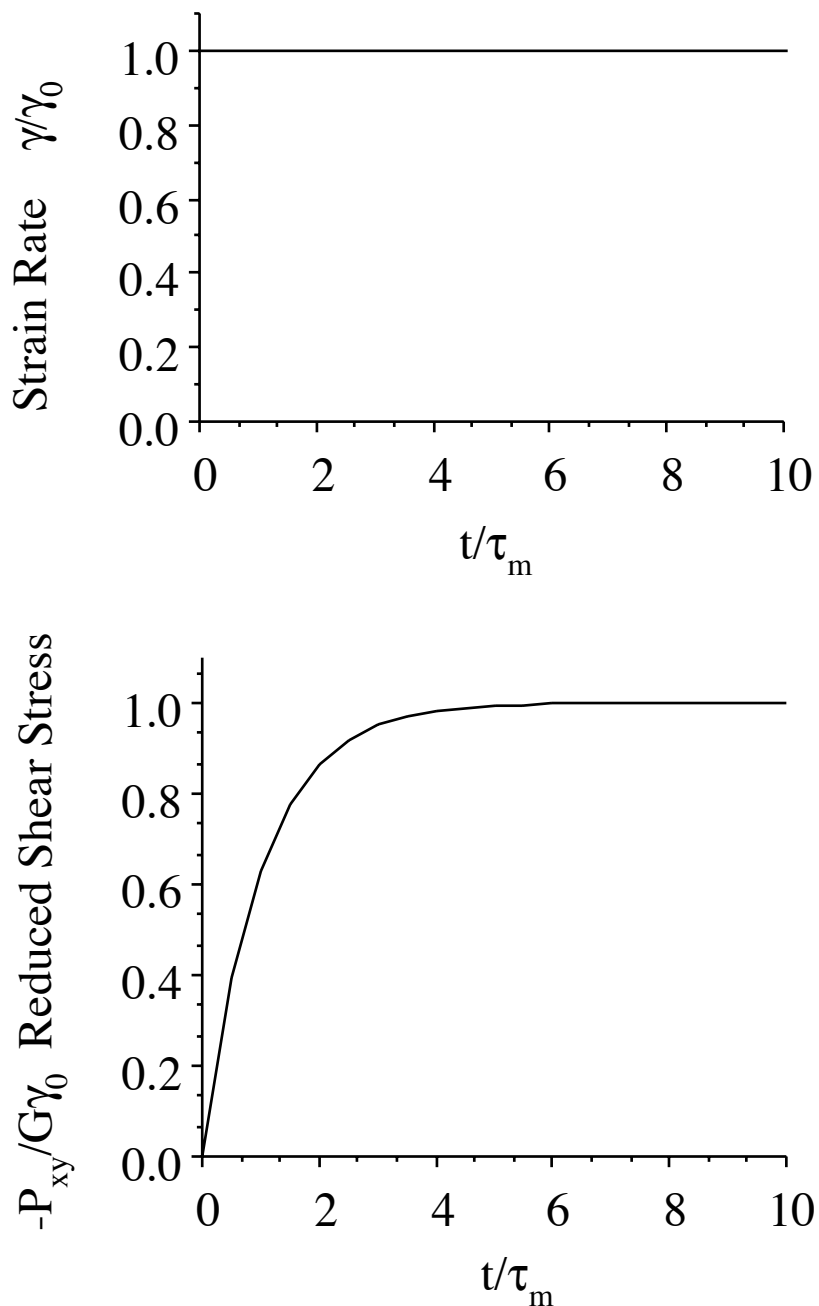


Figure 2.5. The transient response of the Maxwell fluid to a step-function strain rate is the integral of the memory function for the model, $\eta_M(t)$.

Impulse Response of the Maxwell Fluid

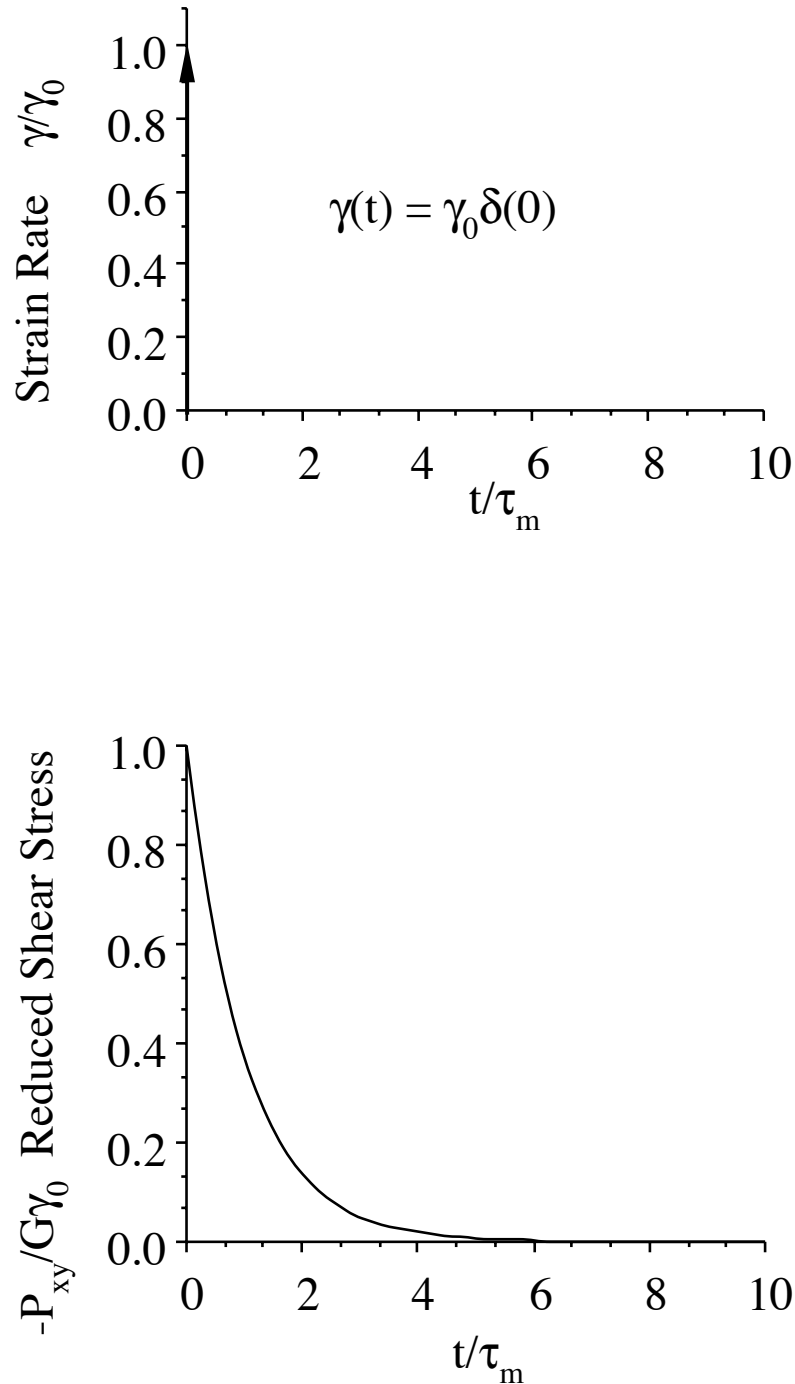


Figure 2.6. The transient response of the Maxwell model to a zero time delta function in the strain rate is the memory function itself, $\eta_M(t)$.

Although the Maxwell model of viscoelasticity is approximate the basic idea that liquids take a finite time to respond to changes in strain rate, or equivalently that liquids remember their

strain rate histories, is correct. The most general linear relation between the strain rate and the shear stress for a homogeneous fluid can be written in the time domain as,

$$P_{xy}(t) = - \int_0^t ds \eta(t-s) \gamma(s). \quad (2.4.12)$$

There is an even more general linear relation between stress and strain rate which is appropriate in fluids where the strain rate varies in space as well as in time,

$$P_{xy}(\mathbf{r},t) = - \int_0^t ds \int d\mathbf{r}' \eta(\mathbf{r}-\mathbf{r}', t-s) \gamma(\mathbf{r}', s). \quad (2.4.13)$$

We reiterate that the differences between these constitutive relations and the Newtonian constitutive relation, equations (2.3.16), are only observable if the strain rate varies significantly over either the time or length scales characteristic of the molecular relaxation for the fluid. The surprise is not so much the validity of the Newtonian constitutive relation is limited. The more remarkable thing is that for example in argon, the strain rates can vary in time from essentially zero frequency to 10^{12}Hz , or in space from zero wavevector to 10^{-9}m^{-1} , before non-Newtonian effects are observable. It is clear from this discussion that analogous corrections will be needed for all the other Navier-Stokes transport coefficients if their corresponding thermodynamic fluxes vary on molecular time or distance scales.