

Introduction to Non-equilibrium Thermodynamics

J. M. Adams

These notes are still a work in progress

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Chapter 1

Introduction

1.1 Example: Heat diffusion in an insulating solid

The central problem of equilibrium thermodynamics is to determine the equilibrium state that a system reaches after removal of constraints. An example of this is illustrated in Fig. 1.1 where we have two regions of different temperature, coupled by a diathermal wall. We can use law of maximum entropy

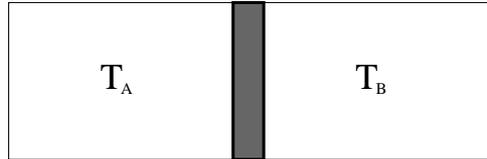


Figure 1.1: Two regions of different temperature coupled by a diathermal wall.

at equilibrium to calculate what happens to the system subsequently. The entropy is given by

$$dS = \frac{1}{T}dU + \frac{p}{T}dV - \frac{\mu_i}{T}dN_i + F_j dX_j, \quad (1.1)$$

where temperature, T , pressure p , chemical potential, μ_i , and in general a force F_j are intensive variables, and the internal energy U , volume V , particle number N_i , and X_j are extensive variables. For the closed system illustrated we must have $dU_A = -dU_B$, so the total change in entropy is

$$dS_T = \left(\frac{1}{T_A} - \frac{1}{T_B} \right) dU_A. \quad (1.2)$$

If the two temperatures in the different compartments are not equal then the system is not in equilibrium, and entropy will be produced. In non-

equilibrium thermodynamics the production of entropy is give by

$$\frac{dS_T}{dt} = \underbrace{\Delta \left(\frac{1}{T} \right)}_{\text{Force}} \underbrace{\frac{dU_A}{dt}}_{\text{Flux}} = F_i J_i. \quad (1.3)$$

Generically the entropy production is given by a sum of thermodynamic forces and their associated fluxes.

To introduce the basic purpose of non-equilibrium thermodynamics, we start with a simple example of heat diffusion in an insulating solid (heat transport occurs by lattice vibration, not via net transport of particles) [1]. We extend the above equilibrium example to a continuum system. Consider an insulating solid connecting two heat reservoirs. In this case there is a heat current flowing through the material between the two baths, \mathbf{j}_E . In

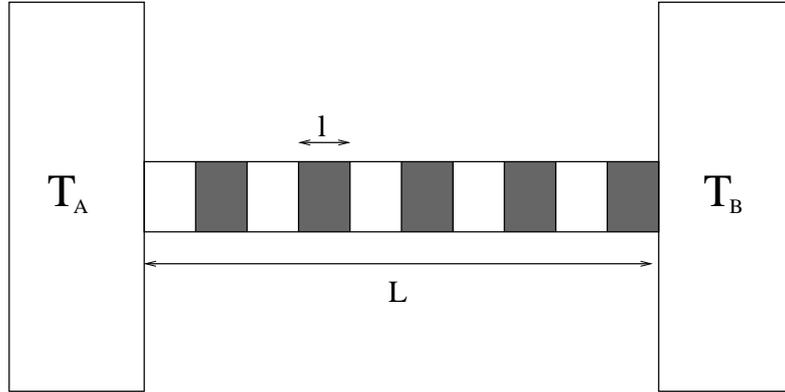


Figure 1.2: An insulating solid divided up into small regions, with heat reservoirs at either end.

linear irreversible thermodynamics the heat current is assumed to be proportional to the thermodynamic force: here the temperature gradient

$$\mathbf{j}_E = L_{EE} \nabla \left(\frac{1}{T} \right). \quad (1.4)$$

The *transport* coefficient relating the two must obey various symmetry considerations (Curie principle and Onsager relations). From Fourier's law we know that $\mathbf{j}_E = -\kappa \nabla T$, so the transport coefficient is $L_{EE} = \kappa T^2$.

The conservation equations (mass, energy, momentum etc.) enable us to write down the energy flow in the system. In this case we have

$$\frac{\partial \epsilon}{\partial t} + \nabla \cdot \mathbf{j}_E = 0. \quad (1.5)$$

Substituting in the constitutive equation for the relation of internal energy and temperature ($\epsilon = CT$) produces

$$\frac{\partial T}{\partial t} = \frac{\kappa}{C} \nabla^2 T. \quad (1.6)$$

This equation can be solved in the steady state giving

$$T(x) = T_A + \frac{x}{L}(T_B - T_A). \quad (1.7)$$

We also have a balance equation for the entropy of the system. Although this equation is redundant as far as solving the dynamics of the system, it is important to ensure to identify the forces and fluxes, and to make sure that the second law is not violated locally. Substituting the linear constitutive equation into that for entropy production produces

$$\frac{dS}{dt} = JF = L_{EE} \left(\nabla \frac{1}{T} \right)^2. \quad (1.8)$$

Since the entropy production must be positive we have more symmetry properties that must be obeyed by the transport coefficients. The balance equation for entropy is given by

$$\frac{\partial s}{\partial t} + \nabla \cdot \mathbf{j}_s = \sigma \quad (1.9)$$

where σ denotes the entropy production. We shall see that the entropy flux here is given by $\mathbf{j}_s = \mathbf{j}_q/T$ i.e. the heat flux divided by the temperature. It is straightforward to show that the entropy production exactly cancels out with the divergence of the entropy current, that is

$$-\frac{\partial}{\partial x} \frac{1}{T} \frac{Q}{A} = L_{EE} \left(\nabla \frac{1}{T} \right)^2, \quad (1.10)$$

where A is the cross sectional area, and Q is the heat transported. In steady state we can also find the total entropy produced as follows

$$\frac{dS_T}{dt} = \int_0^L \sigma dx = -\frac{Q}{A} \int_0^L \frac{Q}{A} \frac{1}{T^2} \frac{dT}{dx} dx = \frac{Q}{A} \left(\frac{1}{T_A} - \frac{1}{T_B} \right) \quad (1.11)$$

This result is consistent with the equilibrium result obtained earlier, and shows that the entropy change arises purely from heat transported along the bar once steady state has been reached. In this simple example we have illustrated the main points of non-equilibrium thermodynamics that will be covered in this course.

1.2 Equilibrium thermodynamics

Macroscopic objects have a huge number of degrees of freedom – typically of the order 10^{23} . Their characterization can be vastly simplified by choosing the relevant set of macroscopic variables that coarse grain the 10^{23} microscopic degrees of freedom. Mechanics enables us to describe the behaviour of these macroscopic variables, whereas thermodynamics treats the consequences of ignoring the vast majority of the degrees of freedom, in particular the transfer of energy to and from them.

The equilibrium state is characterised by the macroscopic variables such as internal energy U , the volume V , and the mole numbers of the chemical components, N_i . Thermodynamics can be framed in two equivalent ways: the energy and the entropy representations [2]. Although the energy representation is typically used as the basis for thermodynamic potentials, the entropy representation lends itself to the calculation of fluctuations in the system and to non-equilibrium where entropy production plays a central role.

1.2.1 Energy Representation

In this representation the fundamental equation is $U = U(S, V, \{N_i\}, \{X_j\})$, where S is the entropy, V the volume, $\{N_i\}$ denotes the mole numbers of the chemical components, and $\{X_j\}$ denotes the remaining extensive variables. From this equation we can obtain all the information we require about the system by taking derivatives:

$$dU = \left(\frac{\partial U}{\partial S}\right) dS + \left(\frac{\partial U}{\partial V}\right) dV + \left(\frac{\partial U}{\partial N_i}\right) dN_i + \left(\frac{\partial U}{\partial X_j}\right) dX_j \quad (1.12)$$

$$dU = TdS - pdV + \mu_i dN_i + P_j dX_j, \quad (1.13)$$

where T is the temperature, p the pressure, μ_i the chemical potential of component i , and P_j denotes the general intensive parameter derived from the extensive variable X_j . The *equations of state* can then be calculated from the fundamental equation

$$T = T(S, V, \{N_i\}, \{X_j\}) \quad (1.14)$$

$$p = p(S, V, \{N\}, \{X_j\}) \quad (1.15)$$

$$\mu_i = \mu_i(S, V, \{N_i\}, \{X_j\}) \quad (1.16)$$

$$P_j = P_j(S, V, \{N\}, \{X_j\}). \quad (1.17)$$

Since these are intensive quantities it is possible to eliminate the extensive variables between these equations and obtain a relation between the intensive parameters known as the Gibbs-Duhem relation

$$SdT - pdV + \mu_i dN_i + X_j dP_j = 0. \quad (1.18)$$

This relation can be used to calculate one of the equations of state if we know all of the others.

To find the equilibrium state of the system we use the energy minimum principle: The equilibrium state is such that the energy is minimized for a given value of the total entropy. However, practically it is often more useful to work in terms of intensive variables, and perform a Legendre transformation. For example the Helmholtz free energy is obtained by performing a partial Legendre transformation that replaces entropy with temperature:

$$F[T] = U - TS. \quad (1.19)$$

The square bracket notation here is used to denote the new variable resulting from the Legendre transformation. Similarly the enthalpy, $H[p]$ is obtained by performing a partial Legendre transformation that replaces volume by pressure, and the Gibbs free energy, $G[p, T]$ is a partial Legendre transformation replacing entropy with temperature and volume with pressure. These Legendre transformations of the energy are known as thermodynamic potentials. They are useful because there is a minimum principle that can be used to find the values of the internal parameters of a system in equilibrium. For example the Helmholtz free energy is a minimum with respect to the internal parameters for a system in contact with a heat reservoir at a temperature $T = T^r$.

1.2.2 Entropy Representation

In the entropy representation $S = S(U, V, \{N_i\}, \{X_j\})$ is the fundamental equation. The equations of state of the system can be calculated as discussed in the previous section:

$$dS = \left(\frac{\partial S}{\partial U}\right) dU + \left(\frac{\partial S}{\partial V}\right) dV + \left(\frac{\partial S}{\partial N}\right) dN + \left(\frac{\partial S}{\partial X_j}\right) dX_j \quad (1.20)$$

$$dS = \frac{1}{T} dU + \frac{p}{T} dV - \frac{\mu_i}{T} dN_i + F_j dX_j. \quad (1.21)$$

The quantity F_j is now the generalised force associated with X_j , and is related to the generalised force P_j in the energy representation by

$$F_j = \frac{\partial S}{\partial X_j} = -\frac{\partial U / \partial X_j}{\partial U / \partial S} = -\frac{P_j}{T}. \quad (1.22)$$

In the approach to equilibrium these generalised forces drive changes in the extensive variables to equilibrate a system. For example consider a box divided into two by a wall. The wall may be only permeable to heat (allowing energy to flow), only move mechanically (allowing the volumes to change), or in general allow any combination of extensive variables to change. The total entropy of the system is $S^T = S^{(1)} + S^{(2)}$. Since the system is closed we

have $dX_j^{(1)} = -dX_j^{(2)}$, e.g. if (1) has a volume increase then (2) must have an equal and opposite volume decrease. Consequently using Eq. (1.21) we have

$$dS^T = \Delta F_j dX_j^{(1)} \quad (1.23)$$

where $\Delta F_j = F_j^{(1)} - F_j^{(2)}$ i.e. any difference in the generalized force F_j drives a flux of the corresponding extensive quantity X_j .

The entropy representation is also useful in non-equilibrium thermodynamics because it enables calculation of the entropy production (the derivative of entropy with respect to time):

$$\frac{dS}{dt} = \frac{\partial S}{\partial X_k} \frac{dX_k}{dt}. \quad (1.24)$$

The first term in this equation is the analog of the force, and the second is the current created by the force. We will see these flux force pairs arise in the calculation of the general entropy balance equation.

Analogs of the thermodynamic potentials can be calculated, and are called Massieu functions. These Legendre transformed quantities are maximised at constant values of the transformed variables. They are useful in the calculation of the size of fluctuations which we will now discuss.

1.2.3 Fluctuations

The Boltzmann equation provides the route to the calculation of the probability that the system occupies a particular macroscopic state:

$$S = k_B \ln W \Rightarrow W = e^{S/k_B} \quad (1.25)$$

For a system in contact with a heat reservoir, the fluctuations in the internal energy can be calculated from the canonical probability distribution

$$P(\hat{U}) = \frac{e^{-\beta\hat{U}}}{Z} = e^{\beta F - \beta\hat{U}} \quad (1.26)$$

where \hat{U} denotes the instantaneous value of the quantity U . The variance of the internal energy is then

$$\langle(\hat{U} - U)^2\rangle = \sum_{\hat{U}} (\hat{U} - U)^2 e^{\beta(F - \hat{U})} \quad (1.27)$$

Using $\frac{\partial(\beta F)}{\partial\beta} = U$, it can be shown that this average is:

$$\langle(\hat{U} - U)^2\rangle = -\frac{\partial U}{\partial\beta} = k_B T^2 N c_V \quad (1.28)$$

where c_V is the specific heat capacity per molecule. Note that as is typical here the relative amplitude $\langle(\hat{U} - U)^2\rangle^{1/2}/U$ is proportional to $N^{-1/2}$.

A similar analysis can be performed for a system in contact with reservoirs corresponding to the extensive parameters $\{X_i\}$. When the system is in a microstate corresponding to extensive parameters $\{\hat{X}_i\}$ the probability distribution is

$$P(\{\hat{X}_i\}) = \exp\{-k_B^{-1}S[\{F_j\}] - k_B^{-1}F_k\hat{X}_k\}. \quad (1.29)$$

If we again ask about the fluctuations of a pair of extensive variables X_j and X_k , then we have to calculate

$$\langle\Delta\hat{X}_j\Delta\hat{X}_k\rangle = \sum(\hat{X}_j - X_j)(\hat{X}_k - X_k)P(\{\hat{X}_i\}) \quad (1.30)$$

It can be shown that the fluctuations here are given by

$$\langle\Delta\hat{X}_j\Delta\hat{X}_k\rangle = -k_B \frac{\partial X_j}{\partial F_k} \quad (1.31)$$

As an example consider a system where both the internal energy, and the volume can fluctuate. In this case we have:

$$\langle(\delta\hat{U})^2\rangle = -k_B \left. \frac{\partial U}{\partial(1/T)} \right|_{p/T} = k_B (T^2 N c_p - T^2 p V \alpha + T p^2 V \kappa_T) \quad (1.32)$$

$$\langle\delta\hat{U}\delta\hat{V}\rangle = -k_B \left. \frac{\partial V}{\partial(1/T)} \right|_{p/T} = k_B T^2 V \alpha - k_B T p V \kappa_T \quad (1.33)$$

$$\langle(\delta\hat{V})^2\rangle = -k_B \left. \frac{\partial V}{\partial(p/T)} \right|_{1/T} = k_B T V \kappa_T \quad (1.34)$$

To make sure that the system is in local equilibrium it is necessary to calculate the fluctuations in the temperature and the pressure. If we imagine trying to measure the temperature of a system locally with a small thermometer then it can be seen that the reading will fluctuate as the local value of the energy fluctuates. We can therefore obtain estimates for the fluctuations in intensive parameters (such as the temperature) by using the fluctuations in the extensive parameters given here.

$$\frac{\delta U}{U} = \left(\frac{k_B}{N c_V} \right)^{1/2}; \quad \Delta U = N c_V \Delta T \Rightarrow \frac{\delta T}{T} = \left(\frac{k_B}{N c_V} \right)^{1/2} \quad (1.35)$$

$$\frac{\delta V}{V} = \left(\frac{k_B T \kappa_T}{V} \right)^{1/2}; \quad \Delta V = \kappa_T \Delta p \Rightarrow \frac{\delta p}{p} = \left(\frac{k_B T}{p^2 V \kappa_T} \right)^{1/2} \quad (1.36)$$

Estimating the size of these fluctuations is crucial in determining the region of validity of non-equilibrium thermodynamics.

1.3 Aims of non-equilibrium thermodynamics

The purpose of non-equilibrium thermodynamics (NEQTD) is to answer questions about systems out of equilibrium. Here we consider linear irreversible thermodynamics that is based on the balance equations (conservation of mass, momentum etc.) and the linear relation between forces and fluxes from symmetry and phenomenological considerations, following [3]. NEQTD provides a prescription for determining the dynamics of a system that is out of equilibrium, with a few assumptions. Essentially the recipe is as follows:

1. Choose the relevant slow variables of the system, typically conserved quantities and broken symmetry variables.
2. Write down the balance equations for the conserved variables.
3. Write down the (redundant) entropy balance equation and identify the entropy production (sources of dissipation).
4. Identify the force (\mathbf{F}) - current (\mathbf{j}) pairs in the entropy production.
5. Write down the phenomenological constitutive equations, ensuring they obey the relevant symmetries e.g. Onsager relations.
6. Use the constitutive equations to substitute for the unknown fluxes in the equations of motion.

In looking for the steady state of the system there are some analogies with equilibrium thermodynamics. In equilibrium thermodynamics the maximum entropy principle can be used to find equilibrium (this is a postulate in some formulations of thermodynamics). In NEQTD the steady state can be characterized, in some systems, by a *minimum in the dissipation*, or entropy production of the system.

An alternative framework for non-equilibrium thermodynamics has also been constructed: the "GENERIC" formalism by Öttinger and co-workers [4]. Additional structural variables are introduced here that characterize the state of the system, leading to more general dynamics, however due to the generality of linear irreversible thermodynamics it must be contained within the GENERIC formalism in the correct limits.

1.3.1 Identifying hydrodynamic variables

1. Due to the assumption of local equilibrium the variables of equilibrium thermodynamics U, S, V, N, \dots and T, p, μ, \dots vary slowly (both spatially and in time).
2. Conserved variables, e.g. mass, particle number, etc. are slow because it takes a finite time to transport them.

3. Systems with broken symmetries have extra variables, such as the lattice distortion in crystals or the nematic director in liquid crystals, which exhibit slow dynamics (Goldstone's theorem \rightarrow broken symmetry variables are slow in the limit of large wavelength).

1.3.2 Equations of motion

The equation of motion for the system is typically one of force balance between reversible (reactive) and irreversible (dissipative) forces.

$$\mathbf{F}_{rev} + \mathbf{F}_{irrev} = 0$$

Dissipation occurs because of the coarse-grained nature of the description of the system. We transfer energy from the macroscopic variables with which we describe the system, into some of the microscopic variables that were thrown away in the coarse graining process. Time reversal symmetry, which is the basis of the Onsager relations, can be used to classify the terms in the equations of motion and identify them as either reversible or irreversible and gain insight into the equation of motion.

1.3.3 Reversible

If under time reversal the relation between the two terms retains the same sign, then the dynamics they describe is reactive for example propagating waves $\partial_t^2 \theta = \nabla^2 \theta$.

1.3.4 Irreversible

If under time reversal the relation between the two terms changes sign then the dynamics described are dissipative (producing entropy). For example

$$m \frac{\partial^2 x}{\partial t^2} = -b \frac{\partial x}{\partial t} + \mathbf{f}_{ext} \quad (1.37)$$

Note that quantum mechanically it can be difficult to insert a dissipative term because the Schrödinger equation is reversible.

An example of the typical sort of equation we wish to derive is the Navier-Stokes equation describing fluid flow

$$\underbrace{\rho(\partial_t + \mathbf{v} \cdot \nabla) \mathbf{v}}_{\text{reversible}} = \underbrace{\eta \nabla^2 \mathbf{v}}_{\text{dissipative}} - \underbrace{\nabla p}_{\text{reversible}} \quad (1.38)$$

1.4 Local equilibrium

In non-equilibrium thermodynamics we are interested in the *hydrodynamic regime*, that is where the system is locally in equilibrium. The theory is only

valid if we are at long wavelength, and low frequency. We now discuss in detail what limits are placed on the length scales and field strengths in this regime.

As we have seen fluctuations in an extensive quantity of a thermodynamic system are typically $\sim N^{-1/2}$, where N is the number of particles in the system. Thus small changes of system parameters of order $N^{-1/2}$ do not disturb the equilibrium of the system and are reversible. Equilibrium thermodynamics discusses infinitely large systems and so fluctuations are infinitesimally small. Consequently reversible processes proceed infinitely slowly.

1.4.1 Spatial resolution

In a non-equilibrium system we wish to describe spatially inhomogeneous states, so must divide up the system into small cells of side λ . If the j^{th} cell has N_j particles then we must ensure that this number is large enough to perform statistical mechanics. However we must also ensure that it is small enough so that we can capture the variation of the fields ($T(\mathbf{r}, t), \rho(\mathbf{r}, t), \dots$) smoothly. The cell size is bounded by these two constraints

$$(N_j \gg 1) < \lambda < \text{Smooth field variation} \quad (1.39)$$

1.4.2 Time Evolution

In equilibrium thermodynamics a process that passes through a dense succession of equilibrium states forms a curve in the space spanned by the thermodynamic variables. This series of equilibrium states can be used to approximate a real process (providing that the entropy is monotonically non-decreasing function). At each step it must be ensured that the system has reached its equilibrium state i.e. the process must be slow relative to an internal relaxation time τ_{rel} . In non-equilibrium systems there is a characteristic time scale for the evolution of the whole system, τ_{ev} , and a timescale for the relaxation of the system back to equilibrium. So for a time scale Δt equilibrium will be maintained in a particular cell provided

$$\tau_{rel} \ll \Delta t \ll \tau_{ev} \quad (1.40)$$

i.e. there must be a separation of time scales.

1.4.3 Field strengths

It must also be ensured that the variation in the fields over each cell is not so large that it destroys the equilibrium of the system (i.e. consistent with the fluctuation in the system). This provides a constraint on the maximum field

gradients that may be applied ∇P

$$\frac{\lambda|\nabla P|}{P} < \frac{\delta P}{P} \ll 1, \quad (1.41)$$

where δP is the size of the fluctuations of the thermodynamic property P in the cell of side λ . This criterion together with those outlined above should ensure that the system is in local equilibrium.

1.4.4 Examples

Gas

For gas at STP we can estimate the bounds on the various time scales in the system to ensure local equilibrium. For a typical gas the relaxation time is $\sim \nu_{coll}^{-1}$, where ν_{coll} is the collision frequency of the gas particles.

$$\tau_{rel} \sim 10^{-10}\text{s} \quad (1.42)$$

The length scale of the cells must be of order the mean free path

$$\lambda \sim 10^{-7}\text{m} \quad (1.43)$$

The number of particles in each cell is then $N_j \sim (10^{-7})^3 \times 10^{25} = 10^4$ which is enough for good statistics. The maximum temperature gradients in the system must be less than:

$$\frac{\delta T}{T} \sim \left(\frac{2}{3N_j}\right)^{1/2} \sim 5 \times 10^{-3} \rightarrow \nabla T \sim 10^7 \text{K m}^{-1}. \quad (1.44)$$

Liquid

For a liquid where there is no obvious length scale (interparticle spacing and correlation length are of the same order, and far too small) we can use fluctuations in the particle number in the cell to calculate the appropriate length scale. For water at STP then $\kappa_t \sim 0.5 \text{ GPa}^{-1}$

$$\frac{\delta n}{n} = \left(\frac{k_B T \kappa_T}{V}\right)^{1/2} \sim 10^{-2} \Rightarrow V^{1/3} \sim 2 \text{ nm}. \quad (1.45)$$

Correspondingly $N_j \sim 300$. Using $C_V \sim 75 \text{ J mol}^{-1} \text{ K}^{-1}$ the maximum temperature gradient must be less than

$$\frac{\delta T}{T} \sim 10^{-5} \Rightarrow \nabla T \sim 10^5 \text{K m}^{-1} \quad (1.46)$$

Thus the approximation of local equilibrium can be maintained quite accurately for both liquids and gases in very large temperature gradients. However, it should be noted that near phase transitions, the box size λ can diverge as κ_T diverges. The maximum temperature gradient then falls to zero because fluctuations in extensive variables grow too large. It is then impossible to maintain the local equilibrium and the theory breaks down.

Chapter 2

Balance Equations

Having discussed the main approximations in the theory we now start by formulating the appropriate balance equations in the system following [3], [5] and [6]. The aim is to formulate the two fundamental laws of thermodynamics (conservation of energy, and entropy production) for a non-equilibrium system containing a mixture of different fluids. However, to formulate these laws it will be necessary to first discuss the local conservation of momentum and mass which form the basis for the other laws (and arise from the microscopic laws of mechanics governing particles in the gas).

2.1 First Law

An extensive variable can be written in terms of its density as follows

$$F(t) = \int_V \rho(\mathbf{r}, t) f(\mathbf{r}, t) dV \quad (2.1)$$

where ρ is the mass density, and f is the amount of F per unit mass (mass is always conserved here, whereas volume may not be e.g. expansion of a gas). The general form of a balance equation is then

$$\frac{dF}{dt} = \int_V \sigma_F dV - \int \mathbf{J}_F \cdot d\mathbf{S} \quad (2.2)$$

where the first term is the production of F and the second term is the flux of F out of the system. Using the divergence theorem this relation can be written as a relation between local quantities

$$\partial_t(\rho f) + \nabla \cdot \mathbf{J}_F = \sigma_F. \quad (2.3)$$

We can now apply this balance equation to mass, momentum, energy and entropy.

Mass conservation

Total mass is conserved and so has no source term. Consequently for a one component system

$$\partial_t \rho + \nabla \cdot (\rho \mathbf{v}) = 0 \quad (2.4)$$

where the mass flux is $\mathbf{J}_\rho = \rho \mathbf{v}$. The Eulerian formulation here is used where we take the reference frame to be the lab coordinate system. The convected derivative may be defined here as follows

$$D_t = \partial_t + \mathbf{v} \cdot \nabla. \quad (2.5)$$

This derivative can be thought of as giving the rate of change in the center of mass frame. An example of this is an incompressible fluid, $\partial_t \rho + \mathbf{v} \cdot \nabla \rho = -\rho \nabla \cdot \mathbf{v}$. Since the rate of change of the density in the center of mass frame is zero we have $D_t \rho = 0$, hence $\nabla \cdot \mathbf{v} = 0$. Using this notation, the following useful relation can be derived

$$\rho D_t f = \partial_t(\rho f) + \nabla \cdot (f \rho \mathbf{v}) \quad (2.6)$$

where we have used conservation of mass (Eq. (2.4)). We can then write the balance equation as

$$\rho D_t f = \partial_t(\rho f) + \nabla \cdot (f \rho \mathbf{v}) = \sigma_F - \nabla \cdot (\mathbf{j}_F - \rho f \mathbf{v}) \quad (2.7)$$

Thus for an observer in the center of mass frame the current seen is reduced by an amount $\rho f \mathbf{v}$.

For a multicomponent system composed of different species of density ρ_α , the center of mass is defined by

$$\mathbf{v} = \frac{1}{\rho} \sum_{\alpha} \rho_{\alpha} \mathbf{v}_{\alpha} \quad \text{where} \quad \rho = \sum_{\alpha} \rho_{\alpha} \quad (2.8)$$

We then have mass conservation for each species: $D_t \rho_{\alpha} + \rho_{\alpha} \nabla \cdot \mathbf{v}_{\alpha} = 0$. In principle we could insert chemical processes that transform one species into another. Such processes would lead to a source term in the above equation from chemical processes that create or destroy the appropriate species. We will ignore such processes here for clarity. The diffusion current is defined as

$$\mathbf{j}_{\alpha}^{\text{diff}} = \rho_{\alpha} (\mathbf{v}_{\alpha} - \mathbf{v}). \quad (2.9)$$

This is one of several unknown currents that will be introduced during the formulation of NEQTD. We will then have to find out what these currents are by formulating a constitutive equation. The mass conservation for each species may then be written as

$$D_t \rho_{\alpha} + \rho_{\alpha} (\nabla \cdot \mathbf{v}_{\alpha}) + \rho_{\alpha} \nabla \cdot \mathbf{v} - \rho_{\alpha} \nabla \cdot \mathbf{v} = 0 \quad (2.10)$$

$$D_t \rho_{\alpha} + \rho_{\alpha} \nabla \cdot \mathbf{v} + \nabla \cdot \mathbf{j}_{\alpha}^{\text{diff}} = 0 \quad (2.11)$$

Momentum balance

Applying Newton's 2nd law to the system in the center of mass frame gives

$$\rho D_t \mathbf{v} = -\nabla \cdot \underline{\underline{P}} + \sum_{\alpha} \rho_{\alpha} \mathbf{F}_{\alpha} \quad (2.12)$$

where \mathbf{F}_{α} is the sum of the body forces per unit mass on species α , and $\underline{\underline{P}}$ is the local pressure tensor (or negative stress tensor) arising from short range interactions. Deriving this expression from an integral formulation, with the pressure tensor acting on the surfaces, then using the divergence theorem gives a clear idea of where the divergence of the pressure comes from. It can be assumed that the pressure tensor is symmetric provided that the constituent particles carry no angular momentum.

The momentum balance can also be written in the following form

$$\partial_t(\rho \mathbf{v}) = -\nabla \cdot (\underline{\underline{P}} + \rho \mathbf{v} \mathbf{v}) + \sum_{\alpha} \rho_{\alpha} \mathbf{F}_{\alpha}. \quad (2.13)$$

So the current is made up of a convected part of momentum density $\rho \mathbf{v} \mathbf{v}$ (not present in the center of mass frame in Eq. (2.12)) plus a term from short range interactions, $\underline{\underline{P}}$ with a source $\sum_k \rho_k \mathbf{F}_k$ due to external and long range forces.

Energy balance

To work out the balance equation we start with the kinetic energy

$$\partial_t \frac{1}{2} \rho v^2 = \rho \partial_t \frac{1}{2} v^2 + \frac{1}{2} v^2 \partial_t \rho \quad (2.14)$$

$$= \rho \partial_t \frac{1}{2} v^2 - \frac{1}{2} v^2 \nabla \cdot \rho \mathbf{v} \quad (2.15)$$

$$= \rho D_t \frac{1}{2} v^2 - \frac{1}{2} \nabla \cdot (\rho \mathbf{v} v^2) \quad (2.16)$$

$$= \rho \mathbf{v} \cdot D_t \mathbf{v} - \frac{1}{2} \nabla \cdot (\rho \mathbf{v} v^2) \quad (2.17)$$

$$= -\mathbf{v} \cdot (\nabla \cdot \underline{\underline{P}}) + \sum_{\alpha} \rho_{\alpha} \mathbf{v} \cdot \mathbf{F}_{\alpha} - \frac{1}{2} \nabla \cdot (\rho \mathbf{v} v^2) \quad (2.18)$$

If we reorganise this into the usual form of a balance equation the we obtain the following

$$\partial_t \frac{1}{2} \rho v^2 + \nabla \cdot \left[\frac{1}{2} \rho v^2 \mathbf{v} + \underline{\underline{P}} \cdot \mathbf{v} \right] = \sum_{\alpha} \rho_{\alpha} \mathbf{v} \cdot \mathbf{F}_{\alpha} + \underline{\underline{P}} : \nabla \mathbf{v} \quad (2.19)$$

The second term on the left is the flux of kinetic energy, made up of a convected term, and a conduction term. The two terms on the right are sources of kinetic energy, the first is the work done by external forces and the second is the power from compression.

We need a similar equation for the potential energy. Assuming the body forces can be derived from a time independent potential ψ_{α} then $\mathbf{F}_{\alpha} = -\nabla \psi_{\alpha}$.

The total potential energy can be defined by

$$\rho\psi = \sum_{\alpha} \rho_{\alpha}\psi_{\alpha} \quad (2.20)$$

The balance equation for the local potential can then be derived

$$\partial_t(\rho\psi) = \sum_{\alpha} \psi_{\alpha}\partial_t\rho_{\alpha} = - \sum_{\alpha} \psi_{\alpha}\nabla \cdot (\rho_{\alpha}\mathbf{v}_{\alpha}) = - \sum_{\alpha} \psi_{\alpha}\nabla \cdot (\mathbf{j}_{\alpha}^{\text{diff}} + \rho_{\alpha}\mathbf{v}) \quad (2.21)$$

$$\partial_t(\rho\psi) + \nabla \cdot \left[\sum_{\alpha} \psi_{\alpha}(\mathbf{j}_{\alpha}^{\text{diff}} + \rho_{\alpha}\mathbf{v}) \right] = \sum_{\alpha} (\mathbf{j}_{\alpha}^{\text{diff}} + \rho_{\alpha}\mathbf{v})\nabla\psi_{\alpha} \quad (2.22)$$

$$\partial_t(\rho\psi) + \nabla \cdot \left[\rho\psi\mathbf{v} + \sum_{\alpha} \psi_{\alpha}\mathbf{j}_{\alpha}^{\text{diff}} \right] = - \sum_{\alpha} [\mathbf{j}_{\alpha}^{\text{diff}} \cdot \mathbf{F}_{\alpha} + \rho_{\alpha}\mathbf{v} \cdot \mathbf{F}_{\alpha}] \quad (2.23)$$

Here we can see a convected part of the potential energy in the current, and transport due to diffusion. The source has contributions from the conversion of potential energy into kinetic energy, and conversion to internal energy by diffusion. The sum of kinetic and potential energy is not conserved, we must include the internal energy, u which is increased by compressing the material for example. From a microscopic point of view the internal energy u represents the energy of thermal agitation, and short range molecular interactions. The total energy can now be formed as follows

$$\rho e = \frac{1}{2}\rho v^2 + \rho\psi + \rho u. \quad (2.24)$$

Energy conservation can be expressed as

$$\partial_t(\rho e) + \nabla \cdot \mathbf{j}_e = 0 \quad (2.25)$$

An internal energy balance equation has the following form

$$\partial_t(\rho u) + \nabla \cdot \mathbf{j}_u = \sigma_u \quad (2.26)$$

$$\sigma_u = -\underline{P} : \nabla\mathbf{v} + \sum_{\alpha} \mathbf{j}_{\alpha}^{\text{diff}} \cdot \mathbf{F}_{\alpha} \quad (2.27)$$

$$\mathbf{j}_u = \mathbf{j}_q + \rho u\mathbf{v} \quad (2.28)$$

where the heat current is associated with the internal energy, and σ_u is the source term. The source term can be derived by forcing conservation of energy as outline above. By using the following equations we can rearrange the internal energy balance

$$\rho D_t q + \nabla \cdot \mathbf{j}_q = 0 \quad (2.29)$$

$$D_t \rho^{-1} = \rho^{-1} \nabla \cdot \mathbf{v} \quad (2.30)$$

The internal energy equation can then be put in the form

$$D_t u = D_t q - p D_t \rho^{-1} - \rho^{-1} \underline{\Pi} : \nabla\mathbf{v} + \rho^{-1} \sum_{\alpha} \mathbf{j}_{\alpha}^{\text{diff}} \cdot \mathbf{F}_{\alpha} \quad (2.31)$$

where $\underline{\underline{\Pi}} = \underline{\underline{P}} - p\underline{\underline{\delta}}$ (the traceless part of the pressure tensor). This is the expression we have been aiming for; an expression of the first law of thermodynamics.

2.2 Entropy Law

Main equilibrium properties of the entropy: additive, positive in the absence of external sources and $dS_e = dQ/T$ for a system in contact with a heat reservoir. Here we will split up the entropy into two sources

$$dS = dS_e + dS_i \quad (2.32)$$

where dS_e is the external source of entropy from the surroundings of the system (can be positive, negative or zero) and dS_i is the internal source of entropy which must be nonnegative. The balance equation for the entropy is then

$$\partial_t(\rho s) + \nabla \cdot \mathbf{j}_s = \sigma_s, \quad (2.33)$$

where we must ensure that $\sigma_s \geq 0$. We now require the following expression from equilibrium thermodynamics

$$Tds = du + pdv - \sum_{\alpha} \mu_{\alpha} dc_{\alpha} \quad (2.34)$$

where $c_{\alpha} = \rho_{\alpha}/\rho$, and μ_{α} denotes the chemical potential. From this expression we obtain

$$TD_t s = D_t u + pD_t \rho^{-1} - \sum_{\alpha} \mu_{\alpha} D_t c_{\alpha} \quad (2.35)$$

by assuming local equilibrium in the centre of mass frame (that is the system relaxes locally much faster than the global evolution of the system, and the field gradients are not too large etc.) and substituted ρ^{-1} for the specific volume. Now we assemble the necessary pieces as follows:

$$D_t \rho^{-1} = -\frac{1}{\rho^2} D_t \rho = \frac{1}{\rho} \nabla \cdot \mathbf{v} \quad (2.36)$$

$$\rho D_t u = \partial_t(\rho u) + \nabla \cdot (\rho u \mathbf{v}) \quad (2.37)$$

$$\rho D_t s = \partial_t(\rho s) + \nabla \cdot (\rho s \mathbf{v}) \quad (2.38)$$

$$\rho D_t c_{\alpha} = \partial_t \rho_{\alpha} + \nabla \cdot (\rho_{\alpha}(\mathbf{v} - \mathbf{v}_{\alpha} + \mathbf{v}_{\alpha})) = -\nabla \cdot \mathbf{j}_{\alpha}^{\text{diff}}. \quad (2.39)$$

Using these equations we can obtain the following expression for the entropy

$$\rho D_t s = -\frac{1}{T} \nabla \cdot \mathbf{j}_q - \frac{1}{T} \underline{\underline{\Pi}} : \nabla \mathbf{v} + \frac{1}{T} \sum_{\alpha} \mathbf{j}_{\alpha}^{\text{diff}} \cdot \mathbf{F}_{\alpha} + \frac{1}{T} \sum_{\alpha} \mu_{\alpha} \nabla \cdot \mathbf{j}_{\alpha}^{\text{diff}} \quad (2.40)$$

From this we can identify the entropy current, and the entropy source by some rather careful rearrangements.

$$\mathbf{j}_s = \rho s \mathbf{v} + \frac{\mathbf{j}_q}{T} - \sum_{\alpha} \mu_{\alpha} \frac{\mathbf{j}_{\alpha}^{\text{diff}}}{T} \quad (2.41)$$

$$\sigma_s = \mathbf{j}_q \cdot \nabla \frac{1}{T} + \sum_{\alpha} \mathbf{j}_{\alpha}^{\text{diff}} \cdot \left[\frac{1}{T} \mathbf{F}_{\alpha} - \nabla \frac{\mu_{\alpha}}{T} \right] + \frac{1}{T} \underline{\underline{\Pi}} : \nabla \mathbf{v} \quad (2.42)$$

Note whilst it seems like a slightly arbitrary separation, there are a few properties that we must satisfy. The entropy production σ_s must be zero in equilibrium, there must be no divergence of a vector field in σ_s that could lead to violation of $\sigma_s \geq 0$. Thus we see contributions to the entropy current from a transport term $\rho s \mathbf{v}$, from the heat flow and from the diffusion of matter. Also note that only the viscous part ($\underline{\underline{\Pi}}$) of the pressure tensor contributes to the entropy production (the isotropic part is cancelled out in Eq. (2.35) by an equivalent term in the internal energy). The contributions to the entropy production is from the sum over source of dissipation (converting macroscopically measurable quantities into microscopic motions that are coarse grained out). Each term is made up of force flux pairs:

$$\sigma_s = \sum_i J_i F_i \quad (2.43)$$

where the forces are typically identified by $F = \frac{\partial S}{\partial X_i}$ where X_i is an extensive variable, and the current is $J = \frac{\partial X_i}{\partial t}$. Since F and J have different parity under time reversal the entropy production is odd on reversing the time.

Chapter 3

Constitutive equations

In the previous chapter we saw that the entropy production was constructed from pairs of forces, such as ∇T and currents such as \mathbf{j}_q . If we want to solve for the temperature distribution in the system then we must know how the current depends on ∇T . In this chapter we look at some constraints on the phenomenological relation between the currents and the forces.

3.1 Phenomenological constitutive equations

The simplest constitutive equation that can be constructed is known as the *Onsager expansion*, and is a linear relation between the currents, and the thermodynamic forces that drive them:

$$J_i = \sum_j L_{ij} F_j. \quad (3.1)$$

We have met some of these forces and fluxes:

| J_i | F_i |
|-----------------------------------|---|
| \mathbf{j}_q | $\nabla \left(\frac{1}{T} \right)$ |
| $\mathbf{j}_\alpha^{\text{diff}}$ | $\frac{1}{T} \mathbf{F}_\alpha - \nabla \frac{\mu_\alpha}{T}$ |
| $\underline{\underline{\Pi}}$ | $\frac{1}{T} (\nabla \mathbf{v})_{\text{tr}=0}^{(s)}$ |

There are several examples of phenomenological laws that have turned out to be linear. Examples of this include Fourier's law of heat conduction ($\mathbf{j}_q = -\lambda \nabla T$), Fick's law of diffusion ($\mathbf{j}^{\text{diff}} = -D \nabla c$), Newton's law of friction ($\underline{\underline{\sigma}} = \eta [\nabla \mathbf{v} + (\nabla \mathbf{v})^T]$) and Ohm's law ($\mathbf{J} = \sigma \mathbf{E}$). There are other examples

in which the current is dependent on several forces such as thermoelectric effects. It should also be noted that the currents only depend on the instantaneous values of the intensive variables, i.e. the system has no memory. Consequently these types of system are referred to as purely resistive linear systems. The Onsager coefficients are local and are linear functions of the intensive parameters, F_j .

We can put some constraints on the Onsager coefficients by using the non-negative definite nature of the entropy production:

$$\sigma_s = \sum_i F_i J_i = \sum_{ij} F_i L_{ij} F_j \geq 0 \quad (3.2)$$

Consequently we must have that $L_{ii} \geq 0$ (each diagonal element must be nonnegative). The off diagonal elements must also satisfy $L_{ii}L_{kk} \geq \frac{1}{4}(L_{ik} + L_{ki})^2$. We should also note at this stage that the antisymmetric part of the matrix of Onsager coefficients does not contribute to the entropy production because the Onsager coefficients are contracted with a symmetric matrix.

3.2 Curie Principle

The number of couplings between the different types of fluxes can be reduced slightly by use of the Curie principle. Roughly speaking the Curie principle states that *in an isotropic system the currents and thermodynamic forces of different tensorial character do not couple* (isotropic system being invariant under rotations). To show that this is true we first need to carefully identify the tensorial objects of different symmetry within a rank two tensor:

$$\underline{T} = \frac{1}{3}\delta \text{tr}\underline{T} + \underline{T}^{(a)} + \underline{\overset{\circ}{T}}^{(s)} \quad (3.3)$$

where $\underline{T}^{(a)}$ is the antisymmetric part of the tensor and $\underline{\overset{\circ}{T}}^{(s)}$ is the traceless symmetric part of the tensor. The double contraction of two tensors can be written as

$$\underline{T} : \underline{R} = \frac{1}{3}(\text{tr}\underline{T})(\text{tr}\underline{R}) + \underline{T}^{(a)} : \underline{R}^{(a)} + \underline{\overset{\circ}{T}}^{(s)} : \underline{\overset{\circ}{R}}^{(s)}. \quad (3.4)$$

Thus in the entropy production we expect four types of term

$$\sigma_s = J^s F^s + \mathbf{J}^v \cdot \mathbf{F}^v + \mathbf{J}^a \cdot \mathbf{F}^a + \underline{J}^t : \underline{F}^t, \quad (3.5)$$

where s indicates a scalar, v indicates a vector, a indicates an axial, or pseudo vector, and t indicates a traceless symmetric tensor. Using the Onsager expansion we can replace the currents here with a linear combination of the forces, remembering to put in coupling to the forces of different character

$$J^s = L^{ss} F^s + \mathbf{L}^{sv} \cdot \mathbf{F}^v + \mathbf{L}^{sa} \cdot \mathbf{F}^a + \underline{L}^{st} : \underline{F}^t \quad (3.6)$$

$$\mathbf{J}^v = \mathbf{L}^{vs} F^s + \underline{\underline{L}}^{vv} \cdot \mathbf{F}^v + \underline{\underline{L}}^{va} \cdot \mathbf{F}^a + \underline{\underline{L}}^{vt} : \underline{\underline{F}}^t \quad (3.7)$$

$$\mathbf{J}^a = \mathbf{L}^{as} F^s + \underline{\underline{L}}^{av} \cdot \mathbf{F}^v + \underline{\underline{L}}^{aa} \cdot \mathbf{F}^a + \underline{\underline{L}}^{at} : \underline{\underline{F}}^t \quad (3.8)$$

$$\mathbf{J}^t = \underline{\underline{L}}^{ts} F^s + \underline{\underline{L}}^{tv} \cdot \mathbf{F}^v + \underline{\underline{L}}^{ta} \cdot \mathbf{F}^a + \underline{\underline{L}}^{tt} : \underline{\underline{F}}^t. \quad (3.9)$$

Under an orthogonal transformation $\underline{\underline{A}}$ a tensorial quantity $\underline{\underline{T}}$ must transform as follows

$$T'_{ij\dots} = (\det \underline{\underline{A}})^\epsilon A_{ip} A_{jq} \dots T_{pq\dots} \quad (3.10)$$

where $\epsilon = 0, 1$ for polar and pseudo (axial) vectors respectively. Now if the system has a symmetry property under which the Onsager coefficients are invariant, then $\underline{\underline{L}} = \underline{\underline{L}}'$ under the transformation. For example if $\underline{\underline{A}}$ is an inversion then we have (schematically)

$$(\det \underline{\underline{A}})^\epsilon \underline{\underline{A}}^n \underline{\underline{L}} = \underline{\underline{L}} \Rightarrow (-1)^{\epsilon+n} \underline{\underline{L}} = \underline{\underline{L}} \quad (3.11)$$

Thus L must be zero if $\epsilon + n$ is odd, which eliminates sv and vs , vt and tv , and av and va couplings. If we consider an arbitrary rotation $\underline{\underline{R}}$ then we can deduce

$$\underline{\underline{R}} \cdot \mathbf{L}^{as} = \mathbf{L}^{as} \quad \text{and} \quad \underline{\underline{R}} \cdot \mathbf{L}^{sa} = \mathbf{L}^{sa}. \quad (3.12)$$

Consequently there are no as and sa couplings. Now since the couplings aa , vv , st , ts must be proportional to the identity (only isotropic rank two tensor) we can deduce that the last two are zero since they must have zero trace (since they couple a traceless tensor to a scalar, and a scalar to a traceless tensor). Since $\underline{\underline{F}}^t$ is symmetric then only the symmetric part of $\underline{\underline{L}}^{st}$ and $\underline{\underline{L}}^{ts}$ is relevant. However, these third rank tensors must be isotropic, and so proportional to ϵ_{ijk} (the Levi-Civita symbol). Since this is antisymmetric, then both the at and ta coefficients must be zero. Thus we have eliminated all the couplings between currents and forces of different tensorial character by using the transformational properties of an isotropic system. For systems with lower symmetry than the isotropic system, a similar analysis can be performed.

3.3 Onsager relations

As a consequence of microscopic reversibility we can also derive another relation between the coefficients of the Onsager expansion, known as the Onsager relations. We first consider a set of extensive variables, A_i , with equilibrium values of A_i^{eq} . Their deviation from equilibrium is given by $\alpha_i = A_i - A_i^{eq}$. If we are close to equilibrium then the entropy can be expanded in terms of α

$$S(\alpha) = S(0) + \frac{\partial S}{\partial \alpha_i} \alpha_i + \frac{1}{2} \frac{\partial^2 S}{\partial \alpha_i \partial \alpha_j} \alpha_i \alpha_j + \dots \quad (3.13)$$

where the second term is zero since we are expanding about the equilibrium state. The change in the entropy can then be written

$$\Delta S = S(\alpha) - S(0) = -\frac{1}{2}S_{ij}\alpha_i\alpha_j. \quad (3.14)$$

The driving forces can be identified as

$$F_i = \frac{\partial S}{\partial \alpha_i} = -S_{ij}\alpha_j \quad (3.15)$$

and the fluctuations in α calculated from the usual probability density

$$W(\alpha)d\alpha = \frac{e^{\Delta S/k_B}d\alpha}{\int e^{\Delta S/k_B}d\alpha'}. \quad (3.16)$$

From this it can be shown that $\langle \alpha_i \alpha_j \rangle_{av} = k_B S_{ij}^{-1}$, and consequently that $\langle \alpha_i F_j \rangle_{av} = -k_B \delta_{ij}$. These averages can be calculated from an ensemble of systems, or via the ergodic hypothesis as a long-time average over a single system. This second method is useful in non-equilibrium thermodynamics as a way to introduce the variable time. Time reversal symmetry (arising because of the symmetry of Hamilton's equations under time reversal) for every microscopic motion means that the average of α_i must be the same for equal positive and negative times from an arbitrary origin

$$\langle \alpha_i(t + \tau) \rangle_{av}^{\alpha(t)} = \langle \alpha_i(t - \tau) \rangle_{av}^{\alpha(t)}. \quad (3.17)$$

From this relation we can obtain

$$\langle \alpha_j(t) \alpha_i(t + \tau) \rangle = \langle \alpha_j(t) \alpha_i(t - \tau) \rangle \quad (3.18)$$

which are both independent of t in equilibrium. We now apply this to non-equilibrium thermodynamics, via the assumption of local equilibrium (through the usual assumption of time scales etc.). To evaluate the required we require the thermodynamic currents

$$\dot{\alpha}_i = L_{ij}F_j + \kappa_i(t) \quad (3.19)$$

where $\kappa_i(t)$ is a random driving force with zero averages. This equation can be solved via an integrating factor

$$\alpha(t) = e^{-tL \cdot S} \alpha(0) + e^{-tL \cdot S} \int_0^t e^{t' L \cdot S} \kappa(t') dt'. \quad (3.20)$$

This solution can be used to calculate the averages and correlations

$$\begin{aligned} \langle \alpha(t + \tau) - \alpha(t) \rangle_{av}^{\alpha(t)} &= [e^{-\tau L \cdot S} - 1] \langle \alpha(t) \rangle_{av}^{\alpha(t)} \approx -\tau L \cdot S \langle \alpha(t) \rangle_{av}^{\alpha(t)} = \tau L \langle F \rangle_{av} \\ \langle \alpha_l(t) [\alpha_k(t + \tau) - \alpha_k(t)] \rangle_{av}^{\alpha(t)} &= \tau L_{kj} \langle \alpha_l F_j \rangle = k_B \tau L_{kl} \\ \langle \alpha_k(t) [\alpha_l(t + \tau) - \alpha_l(t)] \rangle_{av}^{\alpha(t)} &= k_B \tau L_{lk} \end{aligned}$$

and the Onsager relations follow here we have that $L_{ij} = L_{ji}$. Note that it was assumed here that α was even under time reversal. If we have variables β that are odd under time reversal then we have

$$\langle \beta_i(t)\beta_j(t+\tau) \rangle = \langle \beta_i(t)\beta_j(t-\tau) \rangle \quad (3.21)$$

$$\langle \alpha_i(t)\beta_j(t+\tau) \rangle = -\langle \alpha_i(t)\beta_j(t-\tau) \rangle. \quad (3.22)$$

The entropy is even under time reversal, so only contains $\alpha\alpha$ and $\beta\beta$ terms. The derivation outlined above can then be followed through, resulting in

$$\alpha\alpha : \quad L_{ij}(\mathbf{B}, \omega) = L_{ji}(-\mathbf{B}, -\omega) \quad (3.23)$$

$$\alpha\beta : \quad L_{ij}(\mathbf{B}, \omega) = -L_{ji}(-\mathbf{B}, -\omega) \quad (3.24)$$

$$\beta\beta : \quad L_{ij}(\mathbf{B}, \omega) = L_{ji}(-\mathbf{B}, -\omega). \quad (3.25)$$

3.4 Examples

3.4.1 Thermoelectricity

As a first example of the Onsager relations we examine a thermocouple, consisting of two metal wires connected together. Experimentally it is known that a temperature difference between the two junctions produces both a heat and an electrical current. The latter establishes a potential difference across the system. We can write down the relation between the forces and the currents as follows

$$\mathbf{j}_e = L_{ee}\mathbf{F}_e + L_{eq}\mathbf{F}_q \quad (3.26)$$

$$\mathbf{j}_q = L_{qe}\mathbf{F}_e + L_{qq}\mathbf{F}_q \quad (3.27)$$

where the thermodynamic forces are given by $F_q = \nabla \frac{1}{T}$ and $F_e = -\frac{1}{T}\nabla\mu$, where the electrostatic forces have been included in the chemical potential and assumed to be the only spatially varying part of the potential. Substituting these into the constitutive equations produces

$$\mathbf{j}_e = L_{ee} \left(-\frac{1}{T}\nabla\mu \right) + L_{eq} \nabla \frac{1}{T} \quad (3.28)$$

$$\mathbf{j}_q = L_{qe} \left(-\frac{1}{T}\nabla\mu \right) + L_{qq} \nabla \frac{1}{T} \quad (3.29)$$

The Onsager relations imply that $L_{eq} = L_{qe}$. For a system with conductivity σ we can identify L_{ee} by setting the temperature gradients to zero, then $\sigma = -\left(\frac{eL_{ee}}{T}\right)$. The thermal conductivity ($\mathbf{j}_q = -\lambda\nabla T$) can be calculated by setting the electrical current to zero. This produces

$$T^2\lambda = \frac{L_{qq}L_{ee} - L_{qe}L_{eq}}{L_{ee}} \quad (3.30)$$

We need one more relation to fix all of the Onsager coefficients, and another to test the theory. The first we might use is the Seebeck effect, in which an EMF is measured (with a fixed temperature difference) under zero current flow. If we set $\mathbf{j}_e = 0$ then we find that

$$V = \frac{1}{e} (\mu_r - \mu_l) = \int_1^2 \left(\frac{L_{eq}^A}{eTL_{ee}^A} - \frac{L_{eq}^B}{eTL_{ee}^B} \right) dT \quad (3.31)$$

so that the thermoelectric power (the change in voltage per unit change in temperature difference) is

$$\epsilon_{AB} = \frac{\partial V}{\partial T} = \epsilon_B - \epsilon_A \quad \text{where} \quad \epsilon_A = \frac{-L_{eq}^A}{eTL_{ee}^A}. \quad (3.32)$$

The thermoelectric power enables the determination of all the Onsager coefficients. The Peltier effect (evolution of heat due to electric current flow across a junction) can be used as a further test of the theory. The Peltier coefficient is defined as the heat required when unit electric current flows across the junction.

$$\pi_{AB} = \frac{(j_q^B - j_q^A)}{j_e} = T(\epsilon_B - \epsilon_A) \quad (3.33)$$

since the system is isothermal, and the flux of particles is continuous. Note there is a further effect of the evolution of heat as a result of current traversing a temperature gradient (the Thomson effect).

3.4.2 Single component fluid

If we consider a single component fluid, then the Onsager relations are not required as there is no coupling between the vector heat and the tensor pressure. The constitutive equations are then

$$\mathbf{j}_q = -\lambda \nabla T \quad (3.34)$$

$$\Pi_0 = -\zeta \nabla \cdot \mathbf{v} \quad (3.35)$$

$$\underline{\underline{\Pi}}_{\text{tr}=0}^{(s)} = -\eta(\nabla \mathbf{v} + (\nabla \mathbf{v})^T) \quad (3.36)$$

where we have decomposed the viscous tensor as follows

$$\underline{\underline{P}} = p\underline{\underline{\delta}} + \underline{\underline{\Pi}} = p\underline{\underline{\delta}} + \Pi_0\underline{\underline{\delta}} + \underline{\underline{\Pi}}_{\text{tr}=0}^{(s)} + \underline{\underline{\Pi}}^{(a)} \quad (3.37)$$

These constitutive equations can be substituted into the equations of motion for the system

$$\partial_t \rho = -\nabla \cdot \rho \mathbf{v} \quad (3.38)$$

$$\rho D_t \mathbf{v} = -\nabla p + \eta \nabla^2 \mathbf{v} + \left(\frac{1}{3}\eta + \zeta\right) \nabla \nabla \cdot \mathbf{v} \quad (3.39)$$

$$\rho D_t u = \lambda \nabla^2 T - p \nabla \cdot \mathbf{v} + 2\eta(\overset{\circ}{\nabla} \mathbf{v}^{(s)}) : (\overset{\circ}{\nabla} \mathbf{v}^{(s)}) + \zeta(\nabla \cdot \mathbf{v})^2 \quad (3.40)$$

The first equation gives conservation of mass, the second is the equation of motion, and the third is conservation of energy. We also require equations of state to determine the system

$$p = p(\rho, T) \quad (3.41)$$

$$u = u(\rho, T) \quad (3.42)$$

for a medium with zero velocity these equations reduce to the heat conduction equation.

3.4.3 Multicomponent fluid

Returning to the multicomponent fluid, for which we can now write down the general Onsager expansion, ignoring body forces:

$$\mathbf{j}_q = L_{qq} \nabla \frac{1}{T} - L_{q\alpha} \sum_{\alpha} \nabla \frac{\mu_{\alpha}}{T} \quad (3.43)$$

$$\mathbf{j}_{\alpha}^{\text{diff}} = -L_{\alpha\alpha} \nabla \frac{\mu_{\alpha}}{T} - \sum_{\substack{\beta \\ \alpha \neq \beta}} L_{\alpha\beta} \nabla \frac{\mu_{\beta}}{T} + L_{\alpha q} \nabla \frac{1}{T} \quad (3.44)$$

for the vectorial fluxes (which can only couple to each other). We also have the relations $L_{\alpha q} = L_{q\alpha}$ and $L_{\alpha\beta} = L_{\beta\alpha}$. For the viscous pressure, we have the same as the single component fluid, as it is a tensor so cannot couple to the other components. These constitutive equations can again be substituted into the equations of motion to remove the undetermined currents.

3.4.4 Heat diffusion

We will use the final example to illustrate the principle of minimum entropy in a one-component isotropic system (this follows from a single component system with zero velocity). The local entropy production is then:

$$\sigma_s = \mathbf{j}_q \cdot \nabla \frac{1}{T} \quad (3.45)$$

The phenomenological constitutive equation is then

$$\mathbf{j}_q = L_{qq} \nabla \frac{1}{T} \quad (3.46)$$

Note that the heat conductivity coefficient is given by $L_{qq} = \lambda T^2$. The energy equation is then given by

$$\rho \partial_t u = \rho c_v \partial_t T = -\nabla \cdot \mathbf{j}_q \quad (3.47)$$

3.5 Minimum Entropy production

The total entropy production is given by

$$P = \int \sigma dV = \int L_{qq} \left(\nabla \frac{1}{T} \right)^2 dV \quad (3.48)$$

If we solve $\delta P = 0$ for the minimum entropy production, then the Euler equations produce

$$\nabla^2 \frac{1}{T} = 0 \quad (3.49)$$

which is the steady state of the system. The steady state of the system in can thus be obtained directly from the entropy production. It can be shown that these minimum dissipation states are stable with respect to perturbations.

Chapter 4

Liquid Crystals

Liquid crystals are classified as complex fluids because, like polymer melts and wormlike micelles, they have extra internal degrees of freedom that have to be taken into account when calculating their hydrodynamics. In the nematic phase they are anisotropic liquids, so their constitutive equations do not obey the Curie principle discussed in the previous chapter. In this section we formulate the hydrodynamics for nematic liquid crystals in the non-inertial limit, and examine the Onsager relations for the new degrees of freedom.

4.1 Order parameter and elasticity

Liquid crystals are composed of rod like molecules that disordered (isotropic) in the high temperature phase, but on cooling form a nematic phase in which the rods start to align with a particular direction \mathbf{n} . After this transition the rotational symmetry of the original isotropic system is broken. An order parameter associated with this transition can be calculated from the distribution of the directions in which the rods point ν . Due to the symmetry of the rods the first moment of the rod orientation is zero (e.g. see [7]). The second moment must be used to obtain an orientational order parameter. It is typically forced to be traceless

$$\underline{Q} = \langle \nu\nu - \frac{1}{3}\delta \rangle \quad (4.1)$$

In its principal frame this tensor can be written in terms of two parameters as it is traceless. One of the parameters quantifies the degree of biaxial ordering in the system so will be ignored here, and the other defines the degree of uniaxial ordering. The order parameter for the system can thus be written in terms of the degree of uniaxial order S , and the direction of the order \mathbf{n}

$$\underline{Q} = S (\mathbf{nn} - \frac{1}{3}\delta) . \quad (4.2)$$

Below the nematic-isotropic transition temperature degree of uniaxial ordering is regarded as having a fixed value as it is a fast variable and quickly returns to its minimum free energy value. The direction of the ordering \mathbf{n} has a very slow relaxation time for long wavelength perturbations so is treated in hydrodynamic formulations.

The homogeneous part of the free energy can be written down on phenomenological grounds by ensuring that the symmetries of the order parameter are respected. The result is

$$f_L = \frac{1}{2}a(T - T^*)Q_{ij}Q_{ij} + \frac{1}{3}bQ_{ij}Q_{jk}Q_{ki} + \frac{1}{4}C(Q_{ij}Q_{ji})^2 + \dots \quad (4.3)$$

Spatial distortions of the director field have an associated energetic cost calculated in the continuum theory from the Frank elastic energy [8]

$$2W_d = K_1(\nabla \cdot \mathbf{n})^2 + K_2(\mathbf{n} \cdot \nabla \times \mathbf{n})^2 + K_3(\mathbf{n} \times \nabla \times \mathbf{n})^2 = K\nabla \mathbf{n} : (\nabla \mathbf{n})^T. \quad (4.4)$$

These elastic terms known as splay, twist and bend respectively and they are responsible for local torques on the director due to spatial gradients in the director field. A simplifying approximation often made is known as the one constant approximation where it is assumed that $K_1 = K_2 = K_3 = K$, resulting in the final equality above. The elastic free energy can also be written in terms of \underline{Q}

$$f_F = L_1Q_{ij,k}Q_{ij,k} + L_2Q_{ij,j}Q_{ik,k}. \quad (4.5)$$

4.2 Equations of Motion

There are several different formulations of the equations of motion for liquid crystals. Leslie-Ericksen theory for example describes the hydrodynamics of uniaxial nematics by considering the orientation of the nematogens only [9–11]. However, the equations of motion can be framed more generally in terms of the order parameter \underline{Q} . The effect of shear flow on the phase transition from isotropic to nematic phase can then be investigated. We follow the approach of Olmsted here in discussing the equations of motion of the order parameter [12].

In equilibrium thermodynamics the thermodynamic potentials can be used to specify the state of the system when we know intensive variables e.g. when it is in contact with an external heat reservoir. The principle of maximum entropy can be converted to one of minimum free energy in this case. Similarly in the non-equilibrium case we can relate the entropy production to the free energy production.

$$dS_T = d[S_s + S_r] = dS_s + \frac{1}{T_r}dU_r \quad (4.6)$$

$$= -\frac{1}{T_r}[dU_s - T_r dS_s] = -\frac{1}{T_r}dF \quad (4.7)$$

where we have made use of the fact that the system is closed, so $dU_s = -dU_r$. The free energy production will have parts from both the energy and entropy flux, and the entropy production

$$\dot{F} = \dot{E} - T\dot{S} = - \int \mathbf{J}_E \cdot d\mathbf{S} + T \int \mathbf{J}_S \cdot d\mathbf{S} - T \int \sigma_s dV \quad (4.8)$$

The free energy can also be written in terms of the Landau and Frank contributions that were discussed above

$$F = \int_{\Omega} \left(\frac{1}{2} \rho v^2 + f_L(\underline{Q}) + f_F(\nabla \underline{Q}) \right) dV. \quad (4.9)$$

Typically when we look at the phenomenological free energy like this we minimise it with respect to the order parameter \underline{Q} (with constraints such as \underline{Q} remain traceless, and symmetric). This can be done using the functional derivative:

$$\underline{H} = - \frac{\delta F}{\delta \underline{Q}} = - \frac{\partial f_L}{\partial \underline{Q}} + \nabla \cdot \frac{\partial f_F}{\partial \nabla \underline{Q}}, \quad (4.10)$$

where \underline{H} is the molecular field and describes the change in the free energy for small deviations in the order parameter. In equilibrium we have $\underline{H} = 0$.

In the non-equilibrium case we imagine deforming the system $\mathbf{r} \rightarrow \mathbf{r}' = \mathbf{r} + \mathbf{u}$. The relation between the two coordinate systems is then given by

$$\nabla' = \frac{\partial \mathbf{r}}{\partial \mathbf{r}'} \cdot \nabla = (\underline{\delta} + \nabla \mathbf{u})^{-1} \cdot \nabla \approx (\underline{\delta} - \nabla \mathbf{u}) \cdot \nabla. \quad (4.11)$$

When we distort the system the points \mathbf{r} and \mathbf{r}' are identified so they must have the same order parameter $\underline{Q}(\mathbf{r}) = \underline{Q}'(\mathbf{r}')$ (see figure 4.2). The free energy of the deformed system is then given by

$$F' = \int_{\Omega} \left(f_L(\underline{Q}'(\mathbf{r}')) + f_F(\nabla' \underline{Q}'(\mathbf{r}')) \right) dV' \quad (4.12)$$

$$= \int_{\Omega} \left(f_L(\underline{Q}(\mathbf{r})) + f_F((\underline{\delta} - \nabla \mathbf{u}) \cdot \nabla \underline{Q}(\mathbf{r})) \right) \det(\underline{\delta} + \nabla \mathbf{u}) dV \quad (4.13)$$

Now if we vary \underline{Q} to minimise the free energy then the following results

$$\delta F = \int dV \left[\frac{\partial f_L}{\partial \underline{Q}} : \delta \underline{Q} + \frac{\partial f_F}{\partial \nabla \underline{Q}} : \left(\nabla \delta \underline{Q} - \nabla \mathbf{u} \cdot \nabla \underline{Q} \right) \right] \quad (4.14)$$

$$= \int dV \left[\left(\frac{\partial f_L}{\partial \underline{Q}} - \nabla \cdot \frac{\partial f_F}{\partial \nabla \underline{Q}} \right) : \delta \underline{Q} - \frac{\partial f_F}{\partial \nabla \underline{Q}} : (\nabla \mathbf{u} \cdot \nabla \underline{Q}) \right] \quad (4.15)$$

$$= \int dV \left(-\underline{H} : \delta \underline{Q} + (\underline{\sigma}^d - P\underline{\delta}) : \nabla \mathbf{u} \right). \quad (4.16)$$

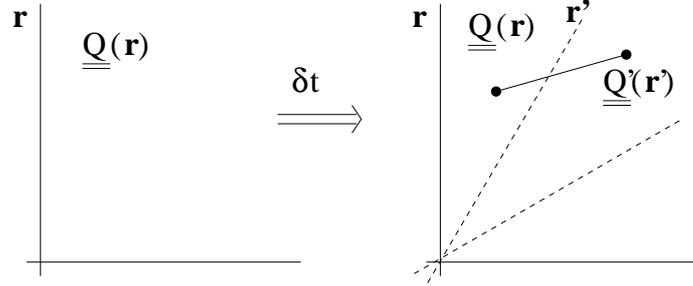


Figure 4.1: The distortion of the liquid crystal order parameter after deforming the space by $\mathbf{r} \rightarrow \mathbf{r}' = \mathbf{r} + \mathbf{u}(\mathbf{r})$.

The distortion stress and the pressure described above are both reversible stresses: $\underline{\underline{\sigma}}^r = \underline{\underline{\sigma}}^d - P\underline{\underline{\delta}}$. The irreversible stresses arising from dissipative effects also contribute to the total stress: $\underline{\underline{\sigma}} = \underline{\underline{\sigma}}^r + \underline{\underline{\sigma}}^i$. We can use the total stress to substitute into the free energy for the reversible stress. If we then take a total time derivative, then the following equation is produced:

$$\frac{dF}{dt} = \int dV \left(-\underline{\underline{H}} : \underline{\underline{\dot{Q}}} + (\underline{\underline{\sigma}} - \underline{\underline{\sigma}}^i) : \nabla \mathbf{v} \right). \quad (4.17)$$

If we integrate the term $\underline{\underline{\sigma}} : \nabla \mathbf{v}$ by parts then we obtain $-\nabla \cdot \underline{\underline{\sigma}} \cdot \mathbf{v} = -\rho \frac{d\mathbf{v}}{dt} \cdot \mathbf{v}$, where use has been made of the equation of motion $\rho D_t \mathbf{v} = \nabla \cdot \underline{\underline{\sigma}}$. This term cancels out with the kinetic energy term in the free energy, so does not need to be considered. Consequently the entropy production term can be written as follows:

$$T\sigma_s = \underline{\underline{\sigma}}^i : \nabla \mathbf{v} + \underline{\underline{H}} : \underline{\underline{\dot{Q}}}. \quad (4.18)$$

In this expression it is helpful to split up the stress into symmetric and anti-symmetric parts: $\underline{\underline{\sigma}}^i = \underline{\underline{\sigma}}^{i(a)} + \underline{\underline{\sigma}}^{i(s)}$. The antisymmetric part can be expressed in terms of an axial vector $\sigma_{\alpha\beta}^{(a)} = \frac{1}{2}\epsilon_{\alpha\beta\gamma}I_\gamma$. Now the bulk viscous torque is not caused by elastic terms, but due to force balance they must be equal to the elastic terms, just as $kx = \eta\dot{x}$ for an overdamped spring. Consequently we substitute for the viscous terms using the elastic terms:

$$I_\lambda = H_{\alpha\beta}(\epsilon_{\lambda\alpha\mu}Q_{\mu\beta} + \epsilon_{\lambda\beta\mu}Q_{\alpha\mu}) \quad (4.19)$$

Using this substitution we obtain the following expression for the entropy production

$$T\sigma_s = \underline{\underline{\sigma}}^{i(s)} : \nabla \mathbf{v} + \underline{\underline{H}} : \underline{\underline{K}} \quad (4.20)$$

where $\underline{\underline{K}} = \underline{\underline{\dot{Q}}} - ((\nabla \mathbf{v})^{(a)} \cdot \underline{\underline{Q}} - \underline{\underline{Q}} \cdot (\nabla \mathbf{v})^{(a)})$. We are now in a position to construct the linear constitutive equations, and apply the Onsager equations.

Here the fluxes are $\underline{\sigma}^i$ and \underline{K} . The forces are the molecular field \underline{H} and the velocity gradient $\nabla \mathbf{v}$. The linear relation between the fields can be expressed as follows:

$$\sigma_{\alpha\beta}^{i(s)} = \Gamma_{\alpha\beta\lambda\rho}^1 (\nabla \mathbf{v})_{\lambda\rho}^{(s)} + M_{\alpha\beta\lambda\rho}^1 H_{\lambda\rho}^{(s)} \quad (4.21)$$

$$K_{\alpha\beta} = \Gamma_{\alpha\beta\lambda\rho}^2 (\nabla \mathbf{v})_{\lambda\rho}^{(s)} + M_{\alpha\beta\lambda\rho}^2 H_{\lambda\rho}^{(s)}. \quad (4.22)$$

As we have seen in the previous section the Onsager relations arising from time reversal properties demand that $M_{\alpha\beta\lambda\rho}^1 = -M_{\lambda\rho\alpha\beta}^2$ and $\Gamma_{\alpha\beta\lambda\rho}^i = \Gamma_{\lambda\rho\alpha\beta}^i$. The symmetry and tracelessness of the forces and fluxes also demand various properties of these coupling matrices: $M_{\alpha\alpha\lambda\rho}^i = \Gamma_{\alpha\alpha\lambda\rho}^i = 0$, $M_{\alpha\beta\lambda\rho}^i = M_{\beta\alpha\lambda\rho}^i = M_{\alpha\beta\rho\lambda}^i$ and $\Gamma_{\alpha\beta\gamma\rho}^i = \Gamma_{\beta\alpha\gamma\rho}^i = \Gamma_{\alpha\beta\rho\gamma}^i$. These symmetry relations vastly reduce the number of phenomenological parameters necessary to describe the system. Only 3 viscosity coefficients are required.

4.3 Shear flow and phase transitions

The system of equations described in the previous section can be solved numerically [12]. For low shear rates the phase transition remains discontinuous, but as we increase the shear rate above a critical value the phase transition becomes continuous.

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