

Equilibrium Versus Nonequilibrium

What do we mean by the terms equilibrium, far from equilibrium, local equilibrium, etc.? It is first important to point out that we mean more by “equilibrium” than just “steady state”. We will be studying many phenomena that are time independent (perhaps after a transient dynamic period) and so may be called steady state. But these phenomena are also sensibly characterized as “far from equilibrium”. More precise terms would be “thermodynamic equilibrium” and “far from thermodynamic equilibrium”, etc. Thus, this book is concerned with the phenomenon of “pattern formation far from thermodynamic equilibrium”. To proceed we need to understand these terms in more detail.

In this chapter we discuss the basic ideas of equilibrium versus nonequilibrium. It is informative to do this through a review of the fundamental formulation of the thermodynamics of macroscopic systems. This is not intended to be an exhaustive introduction to thermodynamics, and the reader is referred to standard Thermodynamics textbooks for a more complete treatment.

Much of the remainder of this book is concerned with understanding the properties of physical systems described by macroscopic dynamical equations of motion that are nonlinear partial differential equations, such as the equations of fluid flow, or heat and concentration diffusion. Since these equations are quite familiar and may be motivated phenomenologically, they provide a completely adequate starting point for most of the discussion. However in this chapter we will delve deeper and discuss the connection of these macroscopic dynamical descriptions to the more fundamental issues of equilibrium and nonequilibrium thermodynamics.

We will discuss the issues of equilibrium versus nonequilibrium in the context of macroscopic systems, i.e. systems where the size and the scale of the phenomena of interest are much bigger than the molecular scale, so that an enormous number of particles are involved. Such systems form the main focus of this book. For these systems the discussion may be given within the framework of thermodynamics, because although globally they are *far* from equilibrium, they are locally, i.e. over small but still macroscopic regions, *near* thermodynamic equilibrium. This allows us to write down a description of the dynamics in terms of macroscopic equations of motion that are partial differential equations for the spatial and temporal variation of usual thermodynamic quantities such as density and temperature. The macroscopic descriptions of diverse systems, from physics to chemistry, have much in common, and this gives a certain unity to our discussion. For microscopic systems on the other hand, on the scale of the basic molecular constituents, a much more difficult statistical mechanics treatment would be needed. This treatment is likely to be quite specific to each system. The study of microscopic systems far from equilibrium is much less well advanced.

At the end of the chapter we review some ideas from thermodynamics and statistical physics that will be useful in later chapters. We briefly discuss the residual effects of the molecular nature of matter that lead to small stochastic or noise terms in the macroscopic equations: usually the size of the noise terms is tiny, and they do not play an important role in macroscopic pattern formation, but there are a few examples where this is not the case. Next we touch on the topic of phase transitions in equilibrium systems, partly for completeness

in understanding what variables are needed to completely define the thermodynamic state of an equilibrium system, and partly because the study of pattern formation benefits from ideas and questions first thought about in this context. Finally we compare and contrast the ideas of bifurcations and phase transitions, and remark that pattern forming systems show elements from both types of theories.

2.1 Equilibrium

2.1.1 A recipe for equilibrium

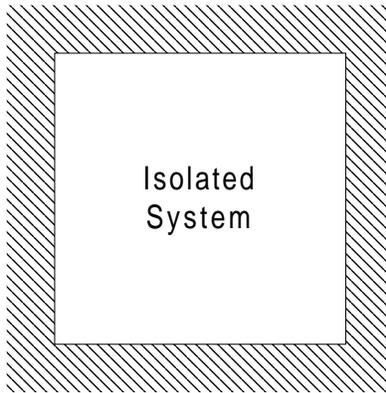


Fig. 2.1. System isolated from rest of universe.

We first need to define what we mean by an equilibrium system (i.e. a system in thermodynamic equilibrium). We can create a system that illustrates the definition in the following way. Take a system of interest, and isolate it from all contact with the remainder of the universe. There seems no problem in principle with doing this. Certainly we could imagine improving the isolation (thicker walls etc.) until further improvement has a negligible effect on the system. We would test this by making observations on the system, delicate enough not to themselves significantly perturb the system, to measure the state of the system. Now wait. Wait long enough that again there is negligible effect on the observed quantities of waiting longer. (Some quantities that we might measure might fluctuate in time: then we would demand that their statistical properties no longer change as we wait longer.) Eventually the system reaches what we will call thermodynamic equilibrium. How long do we have to wait? Typically we might expect transient effects to die out quite rapidly. For example a prepared non-Maxwellian distribution of velocities in a gas may return close to the equilibrium Maxwellian distribution in a time comparable to the collision time between molecules—a very short time typically 10^{-9} seconds at room temperature and pressure. On the other hand we might encounter much longer relaxation times. For example if we take a large box of gas but now prepare it in a state where one half of the box is at higher density than the other half, there will be an oscillatory motion of the gas that we call sound, that decays on much longer time scales, perhaps seconds or longer. Usually we will not have any doubt when we have waited long enough, although there are some counter examples to this, where the characterization as equilibrium or nonequilibrium may not be clear. An example is familiar window glass, and other similar very slowly relaxing systems that are now called “glassy”.

2.1.2 Role of Conserved Quantities

How can we prepare two similar systems in the identical equilibrium state? On what properties of the system does the equilibrium state depend? Clearly these properties must be ones that do not change even in the very long waiting time. We can immediately make a list of such quantities: these are the ones that are conserved by the dynamics of the isolated system, namely the ones satisfying the familiar conservation laws. Examples are the total number of particles, or the total energy. In some situations other quantities may be conserved: for example, depending on the geometry of the system, the momentum or angular momentum may be conserved. In addition there may be dependence on the volume of the system.

As an example consider a box containing a gas or liquid. Then it is a familiar result that specifying the amount of a one component gas or liquid (i.e. the number of molecules) N , the volume V , and the energy E , is sufficient to completely determine the equilibrium state. This means that if these quantities are the same for two similar systems, then all other macroscopic or statistically averaged quantities will also be the same. More generally, the thermodynamic properties of an isolated system are completely determined by the volume and the values of the conserved quantities of the system. These are therefore known as thermodynamic variables. (Below we will see that in ordered states at temperatures below certain phase transitions it is appropriate to introduce additional thermodynamic variables known as order parameters.)

2.1.3 Entropy and the condition for equilibrium

The second law of thermodynamics introduces a new thermodynamic variable called the entropy S that is a unique function of the thermodynamic state and is useful in characterizing the equilibrium state and the approach to equilibrium. (The entropy is also useful in understanding the partition of energy into work and heat.) For the one-component gas or liquid the entropy is a unique function of the energy, volume and number of molecules:

$$S = S(E, V, N). \quad (2.1)$$

The entropy of a system is extensive—it increases proportionately as like pieces are added to the system—and is additive between systems, so that the entropy of two uncoupled or weakly coupled systems is the sum of the individual entropies. Increasing entropy is intuitively associated with increasing disorder. Statistical mechanics gives the microscopic significance as the logarithm of the number of microscopic configurations consistent with the macroscopic thermodynamic state, e.g. defined by E, V, N , with a proportionality constant that is the Boltzmann constant k_B .

A simple example will show how the entropy is related to the condition for equilibrium. Consider an isolated system divided into two weakly coupled halves. Initially the system is in thermodynamic equilibrium, but we now take the system away from equilibrium by transferring an energy ΔE from one half to the other. If the two halves were isolated from one another, as well as from the rest of the universe, the energy of each subsystem would be conserved, and the perturbation would not relax. For weak coupling the time scale for the relaxation will be correspondingly long. In fact for macroscopic systems, the weak coupling automatically arises as a surface to volume ratio—the coupling of the subsystems is only over the area of contact, whereas the energy ΔE is distributed over the volume of the subsystem.

Since the relaxation between the systems is slow, we can suppose that at any time during the relaxation, the state of each subsystem is closely approximated by the state it would be in if it were isolated with energy content equal to the instantaneous value of the (relaxing) energy, i.e. E_1 for the first subsystem and E_2 for the second subsystem, with a fixed total energy E

$$E_1 + E_2 = E. \quad (2.2)$$

There is then some particular partition of the total energy E_1^{eq}, E_2^{eq} that corresponds to the thermodynamic

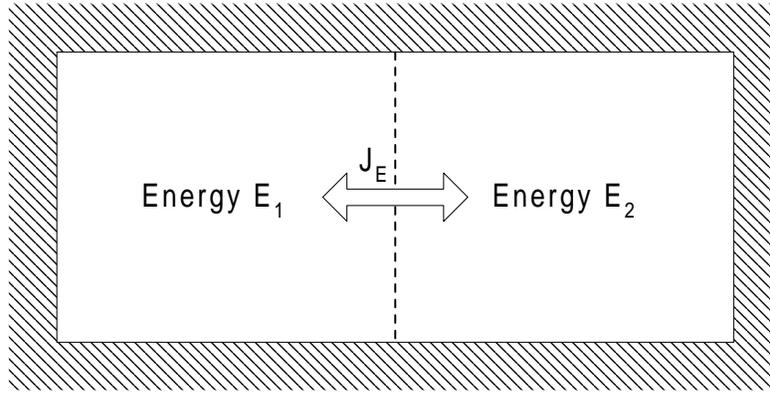


Fig. 2.2. Two subsystems of an isolated system in contact by energy exchange.

equilibrium state of the whole system. (The true equilibrium state of the combined system would also involve fluctuations of the energy partition about these values. However, for macroscopic systems the fluctuations are small—proportional to $1/N^{1/2}$ with N the number of particles in the system—and so this difference may be neglected.)

The second law of thermodynamics (justified by statistical mechanics) tells us that the entropy S increases in the approach to equilibrium and is maximized in the equilibrium state. The total entropy of the system is to a very good approximation the sum of the component entropies

$$S = S_1(E_1) + S_2(E_2) = S_1(E_1) + S_2(E - E_1) \quad (2.3)$$

where $S_1(E_1)$, the entropy of subsystem 1, can again be evaluated as if system 1 were completely isolated with energy content E_1 , etc. The equilibrium state is given by maximizing S with respect to E_1 with the constraint of fixed total energy E , Eq.(2.2). In greater generality the entropy is a function of all the conserved variables of the isolated system. The equilibrium condition for two weakly coupled macroscopic subsystems is then the maximization of the entropy with respect to the partition of each conserved variable that can flow between the subsystems.

2.1.4 Conjugate thermodynamic variables

The maximization of the entropy with respect to the energy partition is simply given by differentiating Eq.(2.3) with respect to E_1 , i.e. the equilibrium condition is

$$T_1 = T_2, \quad (2.4)$$

where a new variable we call the temperature T is defined by

$$\frac{1}{T} = \frac{dS}{dE}. \quad (2.5)$$

where implicitly we are holding all other variables such as the volume of the system constant. (To derive this expression we use the final form of the equality in Eq.2.3) and note that $\partial S_2(E - E_1)/\partial E_1$ is $-\partial S_2(E)/\partial E|_{E=E-E_1}$.) Note that since S and E are functions of the thermodynamic state, so too is T : the temperature is another thermodynamic variable. Through this idea of the equilibrium of subsystems

under the exchange of quantities of the conserved variables we are thus led to the introduction of conjugate thermodynamic variables, in this case the temperature T conjugate to the energy E .

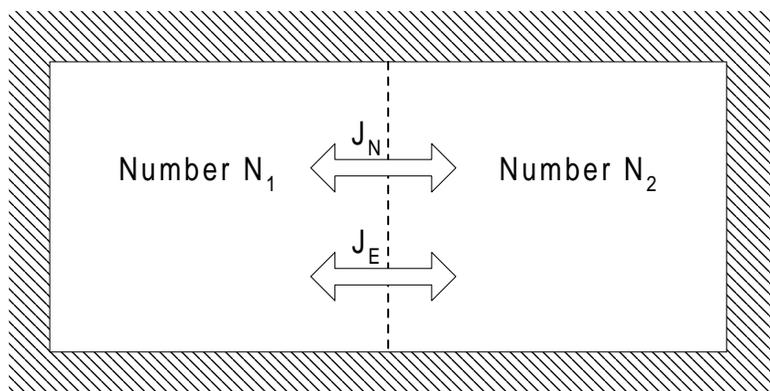


Fig. 2.3. Two subsystems of an isolated system that can exchange both particles and energy.

Generalizing this idea to subsystems that can exchange particles as well as energy introduces the chemical potential μ conjugate to the number of particles N (actually by convention $-\mu/T$) so that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V}, \quad \frac{\mu}{T} = - \left(\frac{\partial S}{\partial N} \right)_{E,V}. \quad (2.6)$$

Systems that can exchange particles as well as energy are in equilibrium when both the temperatures and chemical potentials are equal. Depending on the physical system there might be other conserved quantities and corresponding conjugate fields that are equal in equilibrium, for example a velocity \vec{V} conjugate to the momentum \vec{P} (a fluid will come into equilibrium with containing walls when the velocities are equal), a magnetic field \vec{H} conjugate to a conserved magnetization \vec{M} , etc.

Expressing the differential of the entropy in terms of its partials we can write an equation that is known as the thermodynamic identity

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN + \dots \quad (2.7)$$

or in its more conventional form

$$dE = TdS - PdV + \mu dN + \dots \quad (2.8)$$

We have included the “ PV ” work done for a change of volume, and the \dots allows for other conserved quantities which may be present depending on the system. It is convenient to write the thermodynamic identity in the general form

$$dS = - \sum_i X_i dY_i \quad (2.9)$$

with Y_i the conserved variables (taking a small liberty and including the volume in the list of conserved variables) and X_i the conjugate fields.

Note that the conserved quantities are extensive variables, whereas the conjugate fields are intensive variables.

2.1.5 Equilibrium in contact with “baths”

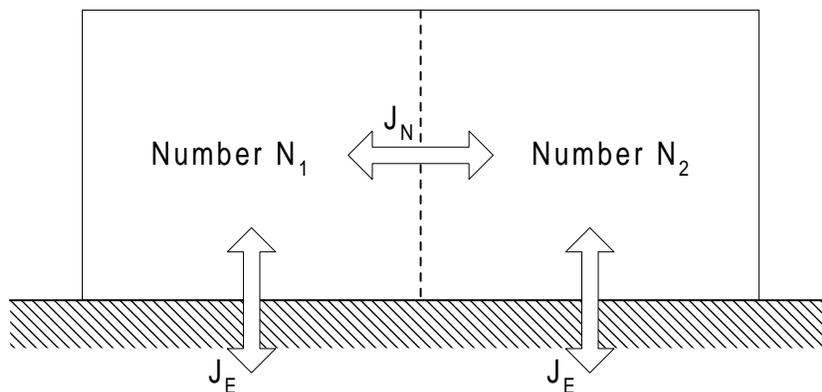


Fig. 2.4. Equilibrium in contact with a heat bath (i.e. at fixed temperature).

The equilibrium of two subsystems occurs at equal temperature, chemical potential, etc. If we now consider just one of the subsystems as the system of interest, we arrive at a second construction scheme for equilibrium: a system in contact with a source of energy at temperature T , a source of particles at chemical potential μ etc., will come to an equilibrium state at long times. Since we do not want the energy and particles absorbed by the system to affect the parameters T and μ we will require that the sources be arbitrarily large, and call them “baths”. If the system itself is large enough, the equilibrium defined in this way is essentially the same as the equilibrium of the isolated system. There are some differences—obviously the energy of the system can fluctuate if it is in contact with an energy bath at some temperature, but not if it is isolated—but these fluctuations are tiny for macroscopic systems.

2.1.6 Thermodynamic Potentials

There are certain advantages in formulating calculations at fixed temperature, for example, rather than fixed energy. As is shown in any standard thermodynamic text, a useful procedure is to introduce a new thermodynamic potential called the free energy F related to the energy by what is known as a Legendre transformation

$$F(T, N, V) = E - TS. \quad (2.10)$$

By straightforward differentiation and using the thermodynamic identity Eq.(2.8) this leads to the differential form

$$dF = -SdT - PdV + \mu dN + \dots. \quad (2.11)$$

Now we can ask about the equilibration of two subsystems that are both in contact with an energy reservoir at temperature T . For example we can ask for the equilibrium configuration of the partition of the total number of particles N between the two subsystems. The equilibrium condition is then to minimize the total free energy $F = F_1(N_1) + F_2(N - N_1)$ with respect to N_1 , holding the temperature T and the volume V fixed—it is easy to see from Eq.(2.11) that this reproduces the result of equal chemical potentials. (The fact that the free energy is *minimized* at fixed T whereas the entropy is *maximized* is simply a result of the choice of the sign convention used in defining F .)

Various other thermodynamics potentials can be introduced by appropriate Legendre transforms depending on the choice of independent variables. We do not need to go into the full details here. The main point to make is that the equilibrium of an isolated system, or of a system in contact with appropriate baths to fix temperature etc., is given by finding the stationary point of an appropriate thermodynamic potential which is a function of the thermodynamic variables and is additive between macroscopic subsystems. These minimization or maximization principles provide powerful tools for determining the properties of equilibrium systems. At a macroscopic level they provide a global description of the whole system. At a microscopic level expressions for the thermodynamic potentials can be written down directly in terms of the energy expression for the individual particles: evaluating the rich consequences of these expressions is the domain of statistical physics. A major difficulty of the study of systems far from equilibrium is that simple minimization principles do not seem to exist.

2.2 Nonequilibrium

Having defined a system in (thermodynamic) equilibrium, a nonequilibrium system is anything else! Thus a system that is neither simply isolated from the rest of the universe, nor in contact with a constant temperature, and/or chemical potential bath, will be nonequilibrium. A system that is in the transient before reaching equilibrium is also nonequilibrium, for example a plasma with a non-Maxwellian velocity distribution. An interesting nonequilibrium situation that will arise in later examples is a system in contact with *two* constant temperature baths that are at *different* temperatures. The nonequilibrium state may also be maintained by external fields, such as the electric field driving an electric current around a conducting loop.

Features that may be associated with nonequilibrium are dynamics (for example the transient relaxation towards equilibrium), and currents of the conserved quantities from one part of the system to another. Indeed we have seen that the lifetime of the nonequilibrium state is likely to be very short unless there are macroscopic disturbances in the conserved quantities away from the equilibrium distribution. Accompanying these disturbances will be macroscopic currents of the conserved quantities.

A particularly interesting nonequilibrium situation is one in which there is no time dependence (i.e. a steady state situation), but one in which currents of the conserved variables are flowing, driven by injection at one boundary and subtraction at another. Since the dynamics of the system are dissipative, there will usually be an injection of energy, energy currents within the system, sometimes a transformation between different forms of energy (e.g. mechanical or chemical to heat), and then the subtraction of energy to maintain the steady state. For example the system in contact with two heat baths at different, but constant, temperatures, will exhibit energy currents transporting heat between the two baths. Such sustained non-equilibrium states provide the opportunity of accurate experimental and theoretical investigation, and are the main focus of this book.

2.3 Near equilibrium

There are many powerful ideas and tools for studying equilibrium systems. This is the subject of many textbooks on thermodynamics and statistical mechanics. It might be expected that nonequilibrium systems that are *near* equilibrium, i.e. generated by small perturbations from equilibrium ones, are also amenable to treatment, and this is indeed the case. We have seen that there may be very different time scales associated with the relaxation towards equilibrium. We will try to understand the slow relaxation processes occurring on time scales much longer than typical microscopic time scales. This idea goes under the general label of the Onsager approach. The slowly relaxing degrees of freedom are the ones corresponding to the quantities of macroscopic subsystems that are the conserved variables of the isolated system.

Let us first return to our simple example of a system divided into two subsystems by a partition that allows

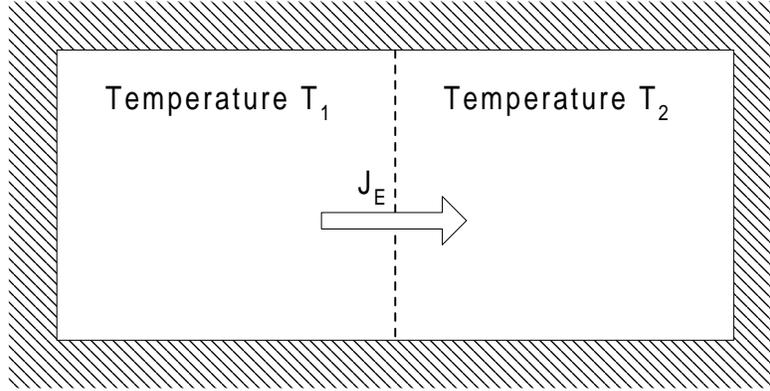


Fig. 2.5. Relaxation of a temperature difference.

energy to flow weakly between the two subsystems, but no flow of the other conserved quantities. The equilibrium of the two subsystems is then given by the equality of the temperatures $T_1 = T_2$. Clearly, if we prepare the system with the two subsystems at different temperatures, this is a nonequilibrium state, and we expect an energy current to flow between the subsystems moving the system towards equilibrium. The situation is particularly simple for small temperature differences $\delta T = T_2 - T_1$ about a mean temperature $T_1 \simeq T_2 \simeq T$, because then the energy current J_E between the subsystems should be proportional to the small temperature difference by simple Taylor expansion (it is zero for no temperature difference)

$$J_E = -K \delta T. \quad (2.12)$$

(Let us define J_E as positive if it is *from* subsystem 1 *to* subsystem 2.) Here K is a “kinetic coefficient” that depends on the strength of the coupling of the two subsystems.

Equation (2.12) can then be used to describe the relaxation process. The energy current gives us the rate of increase of energy on one side, and the rate of decrease on the other side. Since other conserved densities are fixed, the temperatures of the subsystems will change at a rate proportional to the rate of change of energy

$$\dot{T}_1 = \dot{E}_1/C_1 = -J_E/C_1 \quad (2.13a)$$

$$\dot{T}_2 = \dot{E}_2/C_2 = J_E/C_2 \quad (2.13b)$$

where C_1 is the thermal capacity of subsystem 1, the proportionality constant relating small changes of temperature to small changes of energy content. A key point is that since the relaxation *between* the systems is slow, each system may be taken as internally in equilibrium, so that the proportionality constant between changes of energy and temperature is the *equilibrium* value of the specific heat. Thus we find

$$\delta \dot{T} = -(K/C) \delta T \quad (2.14)$$

with $C^{-1} = C_1^{-1} + C_2^{-1}$ giving an effective combined thermal capacity. This equation yields *exponential* relaxation with a time constant

$$\tau = C/K \quad (2.15)$$

given by macroscopic quantities—we use the knowledge that δT is small to recognize that we may take C and K to be constants, equal to their values at the mean temperature T .

Since the energy current is the process of the approach to equilibrium, the entropy must increase in this relaxation. Using the thermodynamic identity we have

$$\dot{S} = \dot{S}_1(E_1) + \dot{S}_2(E_2) \quad (2.16)$$

$$= \frac{1}{T_1} \dot{E}_1 + \frac{1}{T_2} \dot{E}_2 \quad (2.17)$$

$$\simeq -J_E \delta T / T^2 \quad (2.18)$$

$$= K (\delta T / T)^2 \quad (2.19)$$

where in the third step we have kept terms up to first order in δT . Thus the second law of thermodynamics, that the entropy increases as an isolated system returns to equilibrium, tells us that the kinetic coefficient K must be positive.

The results are readily generalized to study continuum dynamics. Considering only the temperature and energy variables, a macroscopic system is in equilibrium when the temperature is uniform in space. Correspondingly, a spatially varying temperature will lead to an energy flow, and for small, slowly varying, perturbations the energy current will be proportional to the gradients of the temperature. It is useful to introduce the energy density (energy per unit volume) e , and the energy current density \mathbf{j}_E (so that the energy flow across a surface S is $\int_S \mathbf{j}_E \cdot d\mathbf{S}$). The conservation of energy now takes the form

$$\partial_t e = -\nabla \cdot \mathbf{j}_E. \quad (2.20)$$

(using the notation ∂_t for the partial derivative $\partial/\partial t$) where the energy current is proportional to the spatial gradient of the temperature

$$\mathbf{j}_E = -K \nabla T \quad (2.21)$$

with K the familiar thermal conductivity (not the same constant as in Eq.(2.12)). Again the law of increase of entropy places constraints on the coefficient, namely that K must be positive. The equations of motion Eqs.(2.20,2.21) are closed if we know how the energy density depends on the temperature. This relationship is again taken to be the same one as in equilibrium, i.e. by the appropriate specific heat, since the dynamical equations already represent the leading order expansion in the deviation from equilibrium. The dynamical equations are linear, and for a given finite physical system the evolution will be the sum of exponentially decaying modes of the system. (An infinite system has an infinite number of modes, and the relaxation may then be nonexponential.)

Equation (2.21) is the familiar equation for the conduction of heat, and could easily be written down from phenomenological considerations. This allows us to make the obvious but important point that the familiar macroscopic equations of continuum mechanics, heat and particle diffusion etc., that we will later use, are fully consistent with the general principles of thermodynamics. In particular, in *any* solution to the macroscopic dynamical equations, a positive rate of entropy production is guaranteed by the formalism.

If we assume that the thermal conductivity K is independent of temperature over the range encountered in an experiment, and also relate changes in the energy density e to changes in temperature through the specific heat per unit volume C that may also be considered temperature independent, the two equations (2.20) and (2.21) can be combined into the single equation

$$\partial_t T = \kappa \nabla^2 T \quad (2.22)$$

with $\kappa = K/C$. This equation takes the form of a time dependent *diffusion equation* for the temperature, and the energy density e satisfies an identical equation. The coefficient κ , with the dimensions of a diffusion constant, is known as the thermal diffusivity. Since equations like (2.20) and (2.21) are a direct consequence of a conservation law and a flux proportional to gradients, we will see diffusion equations, or diffusion terms

supplemented by additional terms describing other physical phenomena, commonly appear as equations for pattern forming systems.

To summarize, we have learned from a simple example the following results:

- A state near equilibrium decays exponentially towards equilibrium.
- The dynamics is given by equations of motion that are on the one hand the usual phenomenological equations (in our simple example the heat current proportional to temperature difference) and on the other hand derivable from the fundamental laws of thermodynamics. Necessarily the equations of motion are consistent with the laws of thermodynamics.
- The law of the increase of entropy places constraints on the *coefficients of the dynamical equations*, not on the solutions to the equations. Any solution to the dynamical equations necessarily is consistent with the law of the increase in entropy, and we do not gain *additional* constraints on the solutions by applying this law.

These results may be extended to the general case of coupled equations for more than one conserved quantity. For example in a fluid we need to consider the thermodynamic consequences of the conservation of mass and momentum as well, leading to the familiar equations of fluid dynamics (including viscous dissipation etc.). The general approach is the subject of the following étude.

Étude: Approach to equilibrium for the multivariable case. Suppose there are M conserved quantities Y_i . The equilibrium state for two discrete subsystems is given by equality of the M conjugate fields X_i

$$X_{i1} = X_{i2} \quad (2.23)$$

and for small deviations from equilibrium, $\delta X_i = X_{i2} - X_{i1}$ small, we expect currents $J_{Y_i} = \dot{Y}_{i2} = -\dot{Y}_{i1}$ of the Y_i proportional to these differences

$$J_{Y_i} = - \sum_j \gamma_{ij} \delta X_j. \quad (2.24)$$

The requirement of positive entropy production leads to constraints on the coefficients γ_{ij} . In addition, through the profound idea of relating the decay of prepared initial states to the dynamics of internal fluctuations Onsager showed that there are relationships between the off diagonal coefficients. These relationships depend on the time reversibility of the microscopic dynamics, and the form of the relationship depends on the signature of the variable Y_i under time reversal (a density is invariant, a velocity changes sign etc.). If Y_i and Y_j have the same signature under time reversal, then the γ matrix elements are symmetric

$$\gamma_{ij} = \gamma_{ji} \quad (\text{same time reversal signature}) \quad (2.25)$$

otherwise they are antisymmetric

$$\gamma_{ij} = -\gamma_{ji} \quad (\text{opposite time reversal signature}). \quad (2.26)$$

As in the simple case of thermal relaxation we can follow the dynamics approaching equilibrium. The changes of the variables X_{i1} will be proportional to the changes of the amounts of the conserved quantities Y_{j1}

$$\delta X_{i1} = \sum_j \beta_{ij1} \delta Y_{j1}, \quad (2.27)$$

with β an inverse susceptibility matrix, a generalization of the inverse thermal capacity.

The the dynamics is now given by

$$\delta \dot{X}_i = \dot{X}_{i2} - \dot{X}_{i1} \quad (2.28)$$

$$= \sum_j (\beta_{ij2} \dot{Y}_{j2} - \beta_{ij1} \dot{Y}_{j1}). \quad (2.29)$$

If we write

$$\beta = \beta_1 + \beta_2 \quad (2.30)$$

as the combined inverse susceptibility matrix, we finally find

$$\delta \dot{X}_i = - \sum_j (\beta\gamma)_{ij} \delta X_j. \quad (2.31)$$

The solution to this set of linear ordinary differential equations with constant coefficients is the sum of exponentially decaying solutions, with the decay rates given by the eigenvalues of the $\beta\gamma$ matrix—again we have *exponential* decay towards equilibrium. Complex eigenvalues correspond to decaying oscillations.

We can now look at the rate of entropy production in the dynamics:

$$\dot{S} = - \sum_i X_{i1} \dot{Y}_{i1} - \sum_i X_{i2} \dot{Y}_{i2} \quad (2.32)$$

$$= - \sum_i (X_{i2} - X_{i1}) J_{Y_i} \quad (2.33)$$

$$= \sum_{ij} \gamma_{ij} \delta X_i \delta X_j. \quad (2.34)$$

The ij and ji terms corresponding to variables of different time signature cancel in this sum. The remaining sum must be positive definite, and this provides the constraints on the values of the dissipative kinetic coefficients γ_{ij} . With these constraints on the *coefficients* satisfied, any solution of the dynamical equations Eq.(2.31) necessarily corresponds to a positive entropy production.

The generalization to the continuum limit proceeds as before. In the continuum limit the macroscopic system is in equilibrium when all the conjugate fields X_i are uniform in space. Correspondingly, spatially varying values of these fields will lead to currents of the conserved quantities. We introduce the density of the conserved quantities y_i (the quantity of Y_i per unit volume), and the corresponding current \mathbf{j}_{Y_i} such that the conservation law is

$$\partial_t y_i = -\nabla \cdot \mathbf{j}_{Y_i}. \quad (2.35)$$

For small, slowly varying perturbations the currents are proportional to the spatial gradients of the conjugate fields

$$\mathbf{j}_{Y_i} = - \sum_j \gamma_{ij} \nabla X_j \quad (2.36)$$

with γ a matrix of transport coefficients. The off-diagonal matrix elements are less familiar, and are analogous to thermoelectric coefficients. One example that is encountered in the study of convection in fluids that are mixtures of two components, such as water and alcohol, is that a gradient of *temperature* may drive a current in the *impurity concentration*. There are constraints on the γ_{ij} from the requirement of positive entropy production, and Onsager symmetry relationships depending on the time reversal characteristics of the variables y_i .

2.4 Far from equilibrium

The Onsager theory of near equilibrium leads to perturbations that decay exponentially towards equilibrium. This results derives simply from the assumption of small perturbations, so that only terms linear in the deviation from equilibrium are retained. We may characterize a system as far from equilibrium when the linearization is no longer valid and deviations from the linearization lead to qualitatively new effects. A key feature of these systems is that the equations of motion will be nonlinear, since the linear expansion must necessarily break down. Thus we no longer have the useful tools of global thermodynamics and linearization, and the study of these systems correspondingly becomes much harder.

We will concentrate almost entirely on systems that although far from equilibrium *globally*, are near equilibrium *locally*. This allows us to treat the systems using the equations derived from the Onsager approach to nonequilibrium thermodynamics, or equivalently the standard equations of fluid dynamics, chemical reaction and diffusion, etc. The appropriate systems are macroscopic ones in which for example the temperature deviations across the system are “large”, but the spatial gradients of the temperature are “small”. Temperature differences on a characteristic microscopic scale (e.g. the mean free path for collisions

in a gas) will be small. We may then take pieces of the system that are small enough that the linearization procedure above is sufficiently accurate, but large enough that a macroscopic description is also sufficiently accurate. Thus locally the currents of the conserved quantities are proportional to the gradients of the conjugate fields, with the same coefficients as introduced above (maybe depending on the local values of the temperature etc.). Furthermore the conjugate variables vary only slightly across these subsystems, so that the relationship between changes in the conserved densities and the conjugate variables, such as the specific heat relating energy and temperature changes, may again be taken to be the equilibrium equation of state. Thus the equations of motion will again be given by Eq.(2.20) and Eq.(2.21) (or more generally by Eq.(2.35) and (2.36)), but with coefficients C and K (or γ and β) that in general are functions of the local conjugate variables (the temperature T or more generally the X_i). Again these dynamical equations and the Onsager constraints on the kinetic coefficients guarantee positive entropy production in *any* solution of the dynamical equations.

In practice, rather than pursuing the formal Onsager approach, the equations of motion are often written down from phenomenological considerations. In some cases, motivated by the aim of simple tractable equations that perhaps capture specific aspects of a problem, grossly simplified “model” equations may be used, for which there is no direct connection to an underlying thermodynamic system. It is therefore useful to consider issues such as equilibrium versus nonequilibrium directly from the form of the dynamical equations. Here the important issue is whether the equations are dissipative or conservative. Dissipative macroscopic systems we associate with a relaxation towards a single state or a reduced set of states from a broad range of initial conditions. In the language of dynamical systems we expect phase space volumes to contract in time. These equations must display a sense of time, and so are not invariant under time reversal. Conservative macroscopic systems are invariant under time reversal, and so do not show a systematic trend towards a subset of states as time advances. Phase space volumes are preserved by the dynamics. Pattern formation is the spontaneous development of spatial structures from a wide range of initial conditions. We would expect this tendency to be stronger in dissipative systems.

2.5 Thermal fluctuations

The familiar macroscopic equations of fluid dynamics, thermal and particle diffusion etc. can be thought of as averages over the underlying microscopic molecular dynamics. At macroscopic length scales the root mean square fluctuations about the mean values are much smaller than the mean values by factors of order $N^{-1/2}$ where N is the number of molecular degrees of freedom in the averaging volume. This is because the fluctuations tend to cancel in the summation to form the macroscopic variable. For the length scales of order mm, cm, or larger of most pattern forming systems the size of the fluctuating corrections to the macroscopic deterministic equations are very small indeed.

There are some situations however where the residual fluctuations are important. One example is in answering how the growing perturbation about an unstable solution is initiated—in principle even an unstable solution may persist indefinitely if there is nothing to give an initial small kick away to establish a perturbation that then continues to grow. In almost all cases the small kick is supplied by experimental imperfections such as slight deviations of the geometry from the ideal, or an imperfectly controlled environment or initial condition—or from another point of view the idea that a precise solution exists but is unstable is a theoretical oversimplification, so that there is no issue of where an initial kick might come from. In some systems however very careful experiments can be done to eliminate these “external” sources driving the unstable mode, and uncover the intrinsic driving due to thermal fluctuations even on the mm length scale. In addition, for phenomena at smaller length scales, the residual effects of molecular fluctuations may be more apparent. One example is the formation of side branches in the dendritic growth of crystals apparent in the pictures of

snowflakes in Chapter 1: as we will explain further in Chapter 12 there is good evidence that side branches develop through the selective amplification of thermal noise at the tip of the dendrite.

Fortunately we do not have to revert to molecular theory to include these small fluctuation effects. The constraint that the fluctuating forces must yield a distribution of the thermodynamics variables given by the Boltzmann factor (i.e. probability proportional to $\exp(-\beta E)$ with $\beta = 1/k_B T$ with k_B the Boltzmann constant and E the energy, or more precisely the free energy, of the fluctuation), and the observation that the stochastic effects due to individual molecular collisions act on time scales very short compared to the macroscopic phenomenon of interest, are sufficient to pin down the strength and character of the fluctuating forces. A profound result of statistical mechanics known as the fluctuation-dissipation theorem in fact directly relates the strength of the fluctuating forces to the dissipative kinetic coefficients in the macroscopic equations, and to the temperature. Examples the reader may be familiar with are the expression for the voltage noise source associated with any electrical resistance known as Johnson noise, and the random forces on a particle immersed in a fluid that lead to Brownian motion. The precise expression for the fluctuation corrections to the equations of fluid dynamics and heat flow can be found in Vol. 6 of the Landau and Lifshitz series on Theoretical Physics. We emphasize again though, that it is only in very careful experiments designed specifically to seek out the phenomenon, or in a very small number of examples of patterns in nature that are at micron length scales, that these fluctuating forces arising from the tiny residual effects of molecular fluctuations not quite cancelling in averages over macroscopic regions become evident.

2.6 Phase transitions and broken symmetries

The idea of phase transitions is important in equilibrium physics, and analogous phenomena play an equally important role in the formation of structures in nonequilibrium systems. Phase transitions are also important to our discussion because they lead to states that require additional thermodynamic variables for a complete characterization, requiring us to expand our list of thermodynamic variables introduced above, through the idea of broken symmetries. Again an analogous idea is key in the study of pattern formation far from equilibrium.

We first review ideas about phase transitions with broken symmetries in a rather artificial but very simple model. This type of model was actually important in the development of the understanding of phase transitions, and captures many of the important aspects of the physics.

Consider a simple thermodynamic system made up of a large number N of spins s_i (which we can just think of just as arrows) that are arranged on a simple lattice (e.g. a cubic lattice in 3 dimensional space). Suppose that each spin s_i can only point in two directions, “up” $s_i = +1$ or “down” $s_i = -1$. (This would be the case for spin $\frac{1}{2}$ quantum spins where the up-down direction is an arbitrary choice of the quantization directions, or for other spins in a system with anisotropy energies such as crystal field energies that favor two degenerate opposite orientations with respect to others.) Now suppose that there is an energy of interaction between nearest neighbor spins that is lower if the spins are parallel. This means the total energy can be written

$$E = -J \sum_{\substack{i,j \\ n.n.}} s_i s_j \quad (2.37)$$

with J the strength of the interaction and the sum running over all nearest neighbor pairs. This gives us a simple model of a ferromagnet, known as the Ising model.

At high temperatures $k_B T \gg J$ where thermal fluctuations $k_B T$ are much larger than this interaction energy, the interaction will be unimportant, and the individual spins will fluctuate randomly up or down. The total macroscopic spin, $S = \langle \sum_i s_i \rangle$ summed over all lattice sites and averaged over thermal fluctuations, will be zero.

On the other hand at low temperatures the interaction favors parallel alignment of spins. At low enough temperatures the interaction will dominate, and the system will tend to its ground state. However we see that there are two possible degenerate ground states in which all the spins are parallel: all spins up or all spins down. The total spin S is either N or $-N$. In principle, since the two configurations are degenerate, we might imagine the physical state to be one with equal probability of residing in the two possibilities. However because of the macroscopic difference between the two configurations, if we prepare the system in one state (say $S = +N$) there would be essentially zero chance of the system fluctuating to the degenerate configuration $S = -N$. This is true at any temperature for which S is $O(N)$ and N is macroscopic (e.g. 10^{23} for a system size of order cm), since the energy barrier E_b between the two states will also be a macroscopic quantity, and the probability of fluctuations between the configurations, proportional to the Boltzmann factor $e^{-E_b/k_B T}$ will be horrendously small.

A unique characterization of the thermodynamic state of the spin system at low temperatures therefore requires the usual conserved variables, and in addition an “order parameter” that takes the value “up” or “down” and tells us which of the two macroscopically different configurations the system is in. (It is conventional to include the strength of the ordering in the definition of the order parameter: thus we could use the mean spin S , where the sign tells us the direction of the ordering, and the magnitude tells us the strength of the ordering.)

To summarize, the interacting spin system undergoes a phase transition as the temperature is lowered through some transition temperature T_c . Above this temperature the system is “disordered” and the order parameter (the macroscopic spin or “magnetization”) $S = 0$. Below this temperature the system becomes “ordered” with $|S|$ taking on a value that is macroscopic (extensive). The two possible signs of S give degenerate, equivalent states, and either one may be “chosen” by the system. This is an example of a “broken symmetry” since the ordered state (S either up or down) does not have the full symmetry of the interactions (which are invariant under changing the sign of all the spins) and of the high temperature phase. The value of the transition temperature T_c is set by the strength of the interaction. For example for our spins on a cubic lattice the transition temperature is $T_c \simeq 3.4J$.

A generalization of this example is where the spins are arrows that can point in any direction, and the interaction between neighboring spins (now vectors of some fixed magnitude) \vec{s}_i and \vec{s}_j depends only on the relative orientation $\vec{s}_i \cdot \vec{s}_j$. Again at high temperatures the system will be disordered, with $\vec{S} = \langle \sum_i \vec{s}_i \rangle = 0$. Below some transition temperature we might find an ordered state with $|\vec{S}| = O(N)$. Now the average spin may point in any direction and we need to define an order parameter that specifies this direction (\vec{S} is a suitable order parameter). The different directions are macroscopically different, but equivalent*. We call this an example of a broken *continuous* symmetry (here the symmetry of rotations).

The formation of crystals is another example of a broken continuous symmetry. In this case the symmetry of continuous translations is broken: it is useful to think of the atoms in the crystal as having a definite mean position (together with small thermal fluctuations about these fixed positions), even though the underlying interactions are invariant under all translations. This example will have direct analogies in pattern formation in systems far from equilibrium. The familiar rigidity of a solid against shear is directly related to the broken symmetry. Once we have specified the position of one lattice site, there is a preferred (lowest energy or free energy) position of all other lattice sites, and a motion away from the preferred position, for example due to a shear of the solid, costs energy—the solid has elasticity. To incorporate this energy into the thermodynamic description we would need to expand the list of variables Y_i in the thermodynamic identity Eq.(2.9) to include the components of the shear strain, and the corresponding new conjugate variables X_i would be the components of the shear stress.

* There are subtleties in terms of thermal fluctuations between nearby states known as spin waves that make this transition less robust than in the discrete spin case. As a consequence the ordered state does not occur at finite temperature for one or two dimensional arrays of spins, but does occur at finite temperature for three dimensional lattices.

2.7 Bifurcations and phase transitions

In the theory of nonlinear dynamical systems the notion of bifurcations is introduced. A bifurcation is a qualitative change in the character of solutions that occurs at particular parameter value. The study of bifurcations in the equations describing systems far from equilibrium will be a prominent feature of the following chapters. On the other hand a phase transition is the qualitative change in behavior of a *thermodynamic* system at a particular parameter value (e.g. temperature). What is the relationship between bifurcations and phase transitions?

First let us stress the formal differences. Mathematical bifurcation theory is derived for finite dimensional phase spaces (i.e. a finite number of ordinary differential equations describing the time evolution of the finite number of dynamical degrees of freedom of the system). On the other hand phase transitions strictly occur only in the thermodynamic limit of an infinite size system with an infinite number of dynamical degrees of freedom. This is because phase transitions occur in the presence of thermal fluctuations, and only in the infinite system limit can there be sharp, qualitative changes of behavior in the face of such noise. Since bifurcation theory usually treats macroscopic degrees of freedom, the influence of noise is not usually considered: typically noise which appears additively in the dynamical equations would eliminate the bifurcation, and the behavior would be smooth on varying parameters with no sudden qualitative change of behavior.

There is however some overlap between the two phenomena. For example the “mean field theory” of a phase transition, where the thermal fluctuations are neglected, yields a description of the phase transition that can be considered a bifurcation. (The description is in terms of equations for a single variable, the order parameter introduced above.) Since mean field theory is sufficient to give us much of our intuition about phase transitions, this means that there are many concepts that carry over between the description of phase transitions and bifurcations.

The study of pattern formation uses aspects of both the theory of phase transitions and bifurcation theory. In as much as macroscopic equations of motion are used and thermal fluctuations are ignored, bifurcation theory is an important tool. On the other hand, if we consider the ideal limit of an infinite system (so that the complications of boundary effects can be neglected) and allow for the presence of thermal fluctuations or other noise such as deterministic chaos, we would expect to recover many of the phenomena of phase transitions, such as diverging fluctuations and perhaps non-rational power law dependences on parameters near the transition point.

Exercises

- 2.1 Discuss whether the following are examples of equilibrium or nonequilibrium systems and give arguments to justify your conclusions:
 - (a) A metallic rod under tension;
 - (b) A wood table with rich grain texture;
 - (c) A beaker of water rotating on a turntable;
 - (d) Water between two concentric cylinders, with the inner one rotating and the outer one fixed;
 - (e) A superconducting magnet with a persistent current;
 - (f) An electromagnet attached to a battery;
 - (g) A lake with a frozen surface.
- 2.2 Consider two cubic meter volumes of air in glass containers with walls 1mm thick. One contains air at 100°C and the other contains air at 0°C. If the two cubes are placed into contact what is the time scale for the temperatures to equilibrate. Is it reasonable to assume that the gas within one container is internally close to equilibrium during this dynamic process?

- 2.3 Carefully derive the equality of chemical potentials as the additional equilibrium condition (as well as the equality of temperatures) for two macroscopic systems that can exchange particles and energy.
- 2.4 In metals the electrons fill energy states up to a maximum energy known as the Fermi energy, which is then equal to the chemical potential of the electron in the metal. The work function tells us the cost to remove an electron at the Fermi energy and take it out of the metal. If I allow two metals with work functions 4eV and 5eV to come into equilibrium what is the electrostatic potential difference that is set up between the metals. Can I connect wires to each metal making an electrical circuit and use the potential difference as a battery?
- 2.5 Present arguments for how “slow” the spatial variation of the temperature in a gas at room temperature and atmospheric pressure should be for the expression $\mathbf{j}_E = -K\nabla T$ to be a good approximation.
- 2.6 **Thermoelectric effects:** The charge transferred between two electrical conductors and the voltage between them are a conserved quantity and the conjugate thermodynamic variable. Thermoelectric coefficients quantify the interplay between temperature differences and charge flow (electrical currents) and voltage differences and energy flow (heat currents). Find out about the various thermoelectric effects—the Seebeck, Peltier and Thomson effects—and show how to understand them within the formulation introduced in the étude in section 2.3. Find values of the thermoelectric coefficients between a pair of metals, and verify the constraints established by the Onsager relationships.
- 2.7 Give a formal derivation of the diffusion equation for the concentration c of an impurity dissolved in a liquid

$$\partial_t c = D\nabla^2 c \quad (\text{E2.1})$$

starting from the basic laws of thermodynamics along the lines of the derivation leading to Eq.(2.22), carefully explaining any approximations made.

- 2.8 A solution to the diffusion equation in the previous exercise is

$$c = \frac{N}{8(\pi Dt)^{3/2}} \exp\left(\frac{-r^2}{4Dt}\right) \quad (\text{E2.2})$$

giving the solution for the spreading of N impurity molecules concentrated at the origin at time zero. Consider the thought experiment of opening a bottle of perfume in one corner of a room with no air currents and asking when someone in the opposite corner would first smell the perfume? The mathematics says that someone should smell the perfume instantly since the solution immediately develops a tail out to infinity, but this can't possibly be the case physically because of finite propagation speeds. What goes wrong with the mathematical description, and what is a physically sensible estimate for when a sensitive nose would first smell the perfume?

- 2.9 A simple model for some chemical and biological systems that might yield patterns is described by a set of reaction-diffusion equations for some fields (concentrations etc.) of the form

$$\partial_t u_i = \sum_j a_{ij} u_j + D_i \nabla^2 u_i + \dots \quad (\text{E2.3})$$

where the a_{ij} are rate constants and the D_i are diffusion constants. Estimate by *dimensionless analysis* the length scale on which a stationary pattern might form and the velocity at which a wave pattern might propagate for the following systems:

- The “Belousov-Zhabotinski” reaction for which $a \sim 0.2\text{s}^{-1}$, $D \sim 2 \times 10^5 \text{cm}^2\text{s}^{-1}$;
- The axon of the giant squid for which $a \sim 3 \times 10^3 \text{s}^{-1}$, $D \sim 3.4 \times 10^2 \text{cm}^2\text{s}^{-1}$;
- Cardiac action potentials for which $a \sim 3 \times 10^2 \text{s}^{-1}$, $D \sim 0.6 \text{cm}^2\text{s}^{-1}$;
- Cyclic AMP waves in slime mold for which $a \sim 10^{-2} \text{s}^{-1}$, $D \sim 4 \times 10^{-6} \text{cm}^2\text{s}^{-1}$;
- The spread of a rabies epidemic by foxes for which $a \sim 160 \text{year}^{-1}$, $D \sim 200 \text{km}^2 \text{year}^{-1}$;

(Here a and D denote typical entries in the a_{ij} and D_i matrices.)

In examples (iii)(b) and (iii)(c) the “diffusion constant” D is actually given by $(CR)^{-1}$ where C is the capacitance per unit length and R is the resistance per unit length of nerve or muscle fibre. Show that this combination does indeed have the dimensions of a diffusion constant.

2.10 Write down the general equations for the energy and impurity currents in a system with small temperature and chemical potential gradients.

2.11 Suppose in the Ising spin model discussed in this chapter the anisotropy energy favoring the “up” and “down” orientations rather than a “sideways” orientation is of the form

$$E_A = J_A(1 - \cos^2 \theta) \quad (\text{E2.4})$$

with θ the angle of the fixed length spin from the vertical. Then $\theta = 0$ corresponds to spin up, and $\theta = \pi$ to spin down, and these states have equal anisotropy energy $E_A = 0$. On the other hand an orientation of $\theta = \pi/2$ has the positive energy E_A . For simplicity we suppose $J_A = J$.

Estimate the probability for all the spins in a 1cm^3 sample to rotate together from the nearly-all-aligned-up state to the degenerate nearly-all-aligned-down state at a temperature $T = 0.1\text{J}/k_B$. How small would you have to make the sample for the Boltzmann probability factor to be (a) 10^{-12} and (b) 10^{-6} .

Can you think of any lower energy pathways connecting the two states?

2.12 One way to derive the Onsager relationships between the transport coefficients γ_{ij} for the continuum description Eq.(2.36) is to consider the amplitudes $X_j^{(q)}$ and $y_j^{(q)}$ of a long wave length sinusoidal variation of the conserved densities and the conjugate variables as thermodynamic variables, i.e.

$$X_j = X_j^{(q)} \cos qx \quad (\text{E2.5})$$

$$y_j = y_j^{(q)} \cos qx. \quad (\text{E2.6})$$

With these definitions:

- Write down the thermodynamic identity including the variables $X_j^{(q)}$ and $y_j^{(q)}$ for a system of volume V . (Assume q is small so that the wavelength is macroscopic, but that q^{-1} is small compared to the system size.)
- Write down the time dependence of the $y_j^{(q)}$ in terms of the $X_j^{(q)}$ and the transport coefficients γ_{ij} using the continuum equations Eq.(2.35), (2.36).
- Using these two parts, and the discussion of the Onsager relationships for discrete variables, you should now be able to derive the Onsager relationships for γ_{ij} .
- Derive the constraints on the γ_{ij} from requiring the positivity of the entropy production.