Lecture notes Advanced Statistical Mechanics AP3021G

Jos Thijssen, Kavli Institute for Nanoscience Faculty of Applied Sciences Delft University of Technology

September 23, 2008



Delft University of Technology

Preface

This is a set of lecture notes which is intended as a support for students in my course 'advanced statistical mechanics'. This is a typical graduate course on the subject, including some non-equilibrium thermodynamics and statistical physics. The course has over the years been based on different books, but the informed reader will recognise the structure of the book by Pathria (*Statistical Mechanics*, 1992) in the first part (equilibrium phenomena) and from several chapters of the book by Bellac, Mortessange and Batrouni (*Equilibrium and non-equilibrium statistical thermodynamics*, 2004). Another important contribution is provided by the lecture notes by Hubert Knops for his statistical mechanics courses at Nijmegen. My lecture notes are therefore by no means original, but they intend to combine the parts of all the sources mentioned into a coherent and clear story.

However, this story does by no means qualify as a textbook, as it is too sketchy and superficial for that purpose. It is merely intended as a support for students following my lecture course. I hope it helps.

It should be noted that these notes do not fully cover the material of my course. I usually make a selection of about 80 % of the material in these notes, and fill the remaining time with additional topics, e.g. the exact solution of the Ising model in 2D or the epsilon-expansion. I intend to include these topics into the course, together with a discussion of polymers and membranes.

Contents

1	The	statistical basis of Thermodynamics			
	1.1	The macroscopic and the microscopic states			
	1.2	Contact between statistics and thermodynamics			
	1.3	Further contact between statistics and thermodynamics			
	1.4	The ideal gas			
	1.5	The entropy of mixing and the Gibbs paradox			
	1.6	The "correct" enumeration of the microstates			
2	Elements of ensemble theory				
	2.1	Phase space of a classical system			
	2.2	Liouville's theorem and its consequences			
	2.3	The microcanonical ensemble			
	2.4	Examples			
3	The	canonical ensemble 10			
	3.1	Equilibrium between a system and a heat reservoir			
	3.2	A system in the canonical ensemble			
	3.3	Physical significance of the various statistical quantities in the canonical ensemble 12			
	3.4	Alternative expressions for the partition function 14			
	3.5	Classical systems			
	3.6	Energy fluctuations in the canonical ensemble: correspondence with the micro-			
	27	canonical ensemble			
	3.1 2.0	Two theorems – the equipartition and the virtal			
	3.8	A system of classical narmonic oscillators			
	3.9				
	3.10	Thermodynamics of magnetic systems: negative temperature			
4	The	grand canonical ensemble 23			
	4.1	Equilibrium between a system and a particle-energy reservoir			
	4.2	Formal derivation of the grand canonical ensemble			
	4.3	Physical significance of the various statistical quantities			
	4.4	Examples			
5	Form	nulation of Quantum Statistics 28			
	5.1	Statistics of the various ensembles			
	5.2	Examples			
		5.2.1 Electron in a magnetic field 30			
		5.2.2 Free particle in a box			
	5.3	Systems composed of indistinguishable particles			
	5.4	The density matrix and the partition function of a system of free particles $\ldots \ldots 34$			

6	The theory of simple gases	37
	6.1 An ideal gas in other quantum-mechanical ensembles – occupation numbers	37
	6.2 Examples: gaseous systems composed of molecules with internal motion	39
-		12
7	Examples of quantum statistics	42
	7.1 Thermodynamics of free quantum gases	42
	7.2 Bose-Einstein systems	43
	7.2.1 Planck distribution	43
	7.2.2 Bose–Einstein condensation	44
	7.2.3 Phonons and the specific heat	45
	7.3 Fermions	46
	7.3.1 Degenerate Fermi gas	46
	7.3.2 Pauli paramagnetism	50
	7.3.3 Landau diamagnetism	51
8	Statistical mechanics of interacting systems: the method of cluster expansions	53
	8.1 Cluster expansion for a classical gas	53
	8.2 The virial expansion and the Van der Waals equation of state	59
9	The method of quantized fields	63
,	9.1 The superfluidity of helium	63
	9.2 The low-energy spectrum of helium	66
10	Introduction to phase transitions	68
	10.1 About phase transitions	68
	10.2 Methods for studying phase behaviour	
	10.3 Landau theory of phase transitions	75
	10.4 Landau Ginzburg theory and Ginzburg criterion	
	10.5 Exact solutions	
	10.6 Renormalisation theory	81
	10.7 Scaling relations	
	10.8 Universality	
	10.9 Examples of renormalisation transformations	90
	10.10Systems with continuous symmetries	
11	Irreversible processes: macroscopic theory	98
	11.1 Introduction	
	11.2 Local equation of state	
	11.3 Heat and particle diffusion	100
	11.4 General analysis of linear transport	102
	11.5 Coupling of different currents	105
	11.6 Derivation of hydrodynamic equations	106
12	Fluctuations and transport phenomena	100
14	12.1 Motion of particles	109
	12.1.1 Diffusion	110
	12.1.2. Thermal conductivity	112
	121.2 Viscosity	112
	12.1.5 (Beobly	•••••

iv

	12.2 The Boltzmann equation	113		
	12.3 Equilibrium – deviation from equilibrium	115		
	12.4 Derivation of the Navier–Stokes equations	117		
13	13 Nonequilibrium statistical mechanics			
	13.1 Langevin theory of Brownian motion	122		
	13.2 Fokker Planck equation and restoration of equilibrium	124		
	13.3 Fluctuations – the Wiener-Kintchine theorem	126		
	13.4 General analysis of linear transport	129		

1

The statistical basis of Thermodynamics

This chapter reviews material that you should have seen before in one way or another. Therefore it is kept very brief.

1.1 The macroscopic and the microscopic states

Notions of statistical mechanics:

- Extensive/intensive quantities: N, V are respectively the number of particles and the volume of the system. We let both quantities go to infinity, while keeping the ratio n = N/V constant. In that case, quantities which scale linearly with V (or N) are called *extensive*, while quantities which do not scale with V (or N) are called *intensive*. The density n = N/V is an example of an intensive quantity.
- A macrostate is defined by values of the macroscopic parameters which can be controlled. For a thermally and mechanically isolated system, these are *N*, *E* and *V*.
- A microstate is a particular state of a system which is consistent with the macrostate of that system. For an isolated classical system, a microstate is a set of positions and momenta which are consistent with the prescribed energy *E*, volume *V* and particle number *N*.
- The quantity $\Omega(N, V, T)$ is the number of microstates which are consistent with a particular macrostate. This number may not be countable, but we shall see that this problem is only relevant in the classical description – in a proper quantum formulation, the number of states within a fixed energy band is finite (for a finite volume).

1.2 Contact between statistics and thermodynamics

Two systems, 1 and 2 are in thermal contact. That is, their respective volumes and particle numbers are fixed, but they can exchange energy. The total energy is fixed, however, to an amount E_0 . In that case, the *total* system has a number of microstates which, for a particular partitioning of the total energy (E_1, E_2) , is given by

$$\Omega^{(0)}(N_1, V_1, E_1, N_2, V_2, E_2) = \Omega(N_1, V_1, E_1)\Omega(N_2, V_2, E_2),$$

with $E = E_1 + E_2$ constant. Because the particle numbers are very large, the quantity $\Omega^{(0)}$ is sharply peaked around its maximum *as a function of* E_1 . Therefore, the *most likely* value of E_1 is equal to *the average value* of E_1 . We find the most likely value by putting

$$\frac{\partial \ln \Omega^{(0)}(N_1,V_1,E_1,N_2,V_2,E_2)}{\partial E_1}$$

equal to 0. This leads to the condition for equilibrium:

$$\frac{\partial \ln \Omega(N_1, V_1, E_1)}{\partial E_1} = \frac{\partial \ln \Omega(N_1, V_1, E_2)}{\partial E_2}.$$

The partial derivative of $\ln \Omega$ with respect to energy is called β . We have

$$\beta = 1/(k_{\rm B}T)$$
 $S = k \ln \Omega(N, V, E).$

S is the *entropy* and *T* the *temperature*.

1.3 Further contact between statistics and thermodynamics

Similar to the foregoing analysis, we can study two systems which are not only in thermal equilibrium (i.e. which can exchange thermal energy) but also in mechanical equilibrium (i.e. which can change their volumes V_1 and V_2 while keeping the sum $V_1 + V_2 = V_0$ constant). We then find that, in addition to the temperature, the quantity

$$\eta = \frac{P}{k_{\rm B}T} = \frac{\partial \ln \Omega(N, V, E)}{\partial V}$$

is the same in both systems, i.e. pressure and temperature are the same in both.

If the systems can exchange particles (e.g. through a hole), then the quantity

$$\zeta = -\frac{\mu}{k_{\rm B}T} = \frac{\partial \ln \Omega(N, V, E)}{\partial N}$$

is the same in both. The quantity μ is known as the *chemical potential*.

In fact, *P* and μ are thermodynamic quantities. We have derived relations between these and the fundamental quantity $\Omega(N, V, E)$ which has a well-defined meaning in statistical physics (as do *N*, *V* and *E*) by using the relation

$$S = k_{\rm B} \ln \Omega$$

and the thermodynamic relation

$$dE = TdS - PdV + \mu dN$$

The following relations can be derived straightforwardly:

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

Here, $(\partial \dots / \partial \gamma)_{\alpha,\beta}$ denotes a partial derivative with respect to γ at constant α and β . Finally, you should know the remaining most important thermodynamic quantities:

• Helmholtz free energy

$$A = E - TS;$$

• Gibbs free energy

$$G = A + PV = E - TS + PV = \mu N;$$

• Enthalpy

$$H = E + PV = G + TS;$$

• Specific heat at constant volume

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_{N,V} = \left(\frac{\partial E}{\partial T}\right)_{N,V};$$

• Specific heat at constant pressure:

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_{N,P} = \left(\frac{\partial (E+PV)}{\partial T}\right)_{N,P} = \left(\frac{\partial H}{\partial T}\right)_{N,P}.$$

1.4 The ideal gas

If N particles in a volume V do not interact, the number of ways the particles can be distributed in that volume scales as V^N , i.e.

$$\Omega \propto V^N$$

Therefore

$$\frac{P}{T} = k_{\rm B} \left(\frac{\partial \ln \Omega(N, E, V)}{\partial V} \right)_{N, E} = k_{\rm B} \frac{N}{V}.$$

For a consistent derivation of the entropy, we consider a particular example: a quantum mechanical system consisting of particles within a cubic volume $V = L^3$ and with total energy E. The particles have wavefunctions

$$\Psi(x,y,z) = \left(\frac{2}{L}\right)^{3/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right).$$

with energy

$$E = \frac{\hbar^2}{2m} \frac{\pi^2}{L^2} \left(n_x^2 + n_y^2 + n_z^2 \right) = \frac{\hbar^2}{8mL^2} \left(n_x^2 + n_y^2 + n_z^2 \right).$$

For N particles, we have the relation

$$E = \frac{h^2}{8m} \sum_{j=1}^{N} \left(n_{j,x}^2 + n_{j,y}^2 + n_{j,z}^2 \right),$$

that is, the energy is the square of the distance of the appropriate point on the 3N dimensional grid. The number $\Omega(N, V, E)$ is the number of points on the surface of a sphere with radius $2mE/\hbar^2$ in a grid with unit grid constant in 3N dimensions. But it might occur that none of the grid points lies precisely on the sphere (in fact, that is rather likely)! In order to obtain sensible physics, we therefore consider the number of points in a spherical shell of radius $2mE/\hbar^2$ and thickness much smaller than the radius (but much larger than the grid constant). The number of points in such a grid is called Γ . The surface of a sphere of radius *r* in 3N dimensions is given by

$$\frac{2\pi^{3N/2}}{(3N/2-1)!}r^{3N-1}$$

Multiplying this by δr gives the volume of a spherical shell of thickness δr . We use the fact that each grid point occupies a unit volume to obtain the number of grid points within the shell. In order to

4

include only positive values for each of the $n_{j,\alpha}$, $\alpha = x, y, z$, we must multiply this volume by a factor 2^{-3N} . Using finally the fact that *N* is large, we arrive at the following expression for the entropy:

$$S(N,V,E) = Nk_{\rm B} \ln\left[\frac{V}{h^3} \left(\frac{4\pi mE}{3N}\right)^{3/2}\right] + \frac{3}{2}Nk_{\rm B}.$$

We have neglected additional terms containing the thickness of the shell – it can be shown that these are negligibly small in the thermodynamic limit. This expression can be inverted to yield the energy as a function of S, V and N:

$$E(S,V,N) = \frac{3h^2N}{4\pi mV^{2/3}} \exp\left(\frac{2S}{3Nk_{\rm B}} - 1\right).$$

This equation, together with $T^{-1} = (\partial S / \partial E)_{N,V}$, leads to the relations

$$E = \frac{3}{2}Nk_{\rm B}T, \quad C_V = \frac{3}{2}Nk_{\rm B}, \quad C_P = \frac{5}{2}Nk_{\rm B}.$$

From the last two relations, we find for the ratio of the two specific heats

$$\frac{C_P}{C_V} = \frac{5}{3}.$$

It can be verified that the change in entropy during an *isothermal* change of a gas (i.e. N and T constant) is

$$S_f - S_i = Nk_B \ln \left(V_f / V_i \right)$$

Furthermore, during an adiabatic change (i.e. N and S constant),

$$PV^{\gamma} = \text{const}; \quad TV^{\gamma-1} = \text{const}$$

with $\gamma = 5/3$. The work done by such an adiabatic process is given by

$$(dE)_{\text{adiab}} = -PdV = -\frac{2E}{3V}dV$$

These relations are specific examples of more general thermodynamic ones.

1.5 The entropy of mixing and the Gibbs paradox

If we mix two gases which, before mixing, were at the same pressure and temperature, then it turns out that after the mixing, the entropy has changed. This is to be expected because, when the two original gases consisted of different types of molecules, the entropy has increased tremendously by the fact that both species now have a much larger volume at their disposal. This difference is called the *mixing* entropy. A straightforward analysis, using the expression for the entropy derived in the previous section, leads to a mixing entropy ΔS :

$$\Delta S = k_{\rm B} \left[N_1 \ln \frac{V_1 + V_2}{V_1} + N_2 \ln \frac{V_1 + V_2}{V_2} \right].$$

Now consider the case where the two gases contain the same kind of molecules. According to quantum mechanics, two configurations obtained by interchanging the particles must be considered

as being identical. In that case, the mixing should not influence the entropy, so the above result for the mixing entropy cannot be correct. This paradox is known as the *Gibbs* paradox. It is a result of neglecting the indistinguishability. A more careful rederivation of the entropy, taking the indistinguishability of the particles into account, leads to the famous *Sackur-Tetrode formula*:

$$S(N,V,E) = Nk_{\rm B} \ln\left(\frac{V}{N}\right) + \frac{3}{2}Nk_{\rm B}\left\{\frac{5}{3} + \ln\left(\frac{2\pi mk_{\rm B}T}{h^2}\right)\right\}.$$

This formula is derived by multiplying Ω (the number of states) by 1/N! in order to account for the indistinguishability in case alle particles occupy different quantum states. This expression for the entropy leads to $\Delta S = 0$ for identical particles. The expression above for ΔS remains valid for non-identical particles.

Note that the process in which the wall is removed, changes the entropy, but does not correspond to any heat transfer, nor does it involve any work. The fact that the entropy changes without heat transfer is allowed, as the second law of thermodynamics states that $\Delta Q \leq T \Delta S$. The equals-sign only holds for reversible processes.

1.6 The "correct" enumeration of the microstates

This section argues how and why the indistinguishability of the particles should be included in the derivation of the entropy. For a system with n_1 particles in quantum state 1, n_2 particles in state 2 etcetera, it boils down to dividing the total number of states calculated for distinguishable particles, by

$$\frac{N!}{n_1!n_2!\dots}$$

In deriving the Sackur–Tetrode formula, we have taken the n_i to be either 0 or 1.

2

Elements of ensemble theory

2.1 Phase space of a classical system

The *phase space* is the space of possible values of the generalised coordinates and canonical momenta of the system. Remember the generalised coordinates can be any coordinates which parametrise the accessible coordinate space within perhaps some given constraints. In our case, we shall most often be dealing with a volume within which the particles must move, so the coordinates are simply the variables \mathbf{r}_i (*i* labels the particles) which are constrained to lie within *V*. The motion of the particles is determined by the Lagrangian, which is a function of the generalised coordinates q_j and their derivatives with respect to time \dot{q}_j :

$$L = L(q_j, \dot{q}_j, t).$$

The equations of motion are the Euler-Lagrange equations:

$$\frac{d}{dt}\frac{\partial L}{\partial \dot{q}_j} = \frac{\partial L}{\partial q_j}$$

The canonical momenta are defined as

$$p_j = -\frac{\partial L}{\partial \dot{q}_j}$$

and these can be used to construct the Hamiltonian:

$$H(p_j,q_j) = \sum_j p_j \dot{q}_j - L.$$

Note that *H* is a function of the p_j and q_j , but not of the \dot{q}_j , which nevertheless occur in the definition of *H*. In fact, the \dot{q}_j must be formulated in terms of q_j and p_j by inversion of the expression giving the p_j . For example, for a particle in 3D, we have

$$p_j = m \dot{q}_j,$$

for which \dot{q}_i can very easily be written in terms of the p_i .

The Euler-Lagrange equations of motion can now be formulated in terms of the Hamiltonian:

$$\dot{q}_j = rac{\partial H}{\partial p_j};$$

 $\dot{p}_j = -rac{\partial H}{\partial q_j}$

These equations are completely equivalent to the Euler-Lagrange equations. In fact, the latter are second order differential equations with respect to time, which are here reformulated as twice as many first-order differential equations. The Hamiltonian equations clearly give a recipe for constructing the time evolution in phase space given its original configuration. The latter is a point in phase space, from which a dynamical trajectory starts.

In statistical mechanics, we are interested in the probability to find a system in a particular point (q, p) ((q, p) is shorthand for all the coordinates). This probability is also called the *density func*tion $\rho(q, p; t)$. Any physical quantity is defined in terms of the dynamical variables p_j and q_j . The expectation value of such a quantity f can be written as

$$\langle f \rangle = \frac{\int f(q,p)\rho(q,p;t) \, d^{3N}p \, d^{3N}q}{\int \rho(q,p;t) \, d^{3N}p \, d^{3N}q},$$

where the denominator is necessary in the case where ρ is not normalised.

2.2 Liouville's theorem and its consequences

We are not interested in the individual dynamical trajectories of a system. Rather we want to know the probabilities to find our system in the points of phase space, i.e. the density function ρ , so that we can evaluate expectation values of physical quantities. Liouville's theorem is about the change in the course of time of the density function. Suppose we stay at some point (q, p) in phase space. At that time, the change of the density is

$$\frac{\partial \rho}{\partial t}$$

The density in some volume ω changes as

$$\int_{\omega} \frac{\partial \rho}{\partial t} \, d\omega$$

 $(d\omega \text{ is shorthand for } d^{3N}p d^{3N}q)$. This change can only be caused by trajectories starting within ω and moving out of it, or trajectories starting outside ω and moving in. The flux of phase space points is given by $\rho \mathbf{v}$, where \mathbf{v} is shorthand for the vector (\dot{p}, \dot{q}) : it is the velocity of the points in phase space.

The number of points leaving and entering the system per unit of time can be evaluated as

$$\int_{\sigma} \rho \mathbf{v} \cdot \hat{\mathbf{n}} \, d\sigma,$$

where σ is the boundary of ω . Using Gauss' theorem, this can be written as a volume integral:

$$\int_{\sigma} \operatorname{div}(\rho \mathbf{v}) \, d\omega$$

The flux of points across the boundary is the only cause of change in the density inside ω , as there are no 'sources' or 'sinks' (trajectories do not disappear or appear). From these considerations, and from the fact that the shape of ω can be arbitrary, we see that the following relation must hold:

$$\frac{\partial \rho}{\partial t} + \operatorname{div}(\rho \mathbf{v}) = 0$$

We now work out the second term:

$$\frac{\partial \rho}{\partial t} + \sum_{j} \left(\frac{\partial \rho}{\partial q_{j}} \dot{q}_{j} + \frac{\partial \rho}{\partial p_{j}} \dot{p}_{j} \right) + \rho \sum_{j} \left(\frac{\partial \dot{q}_{j}}{\partial q_{j}} + \frac{\partial \dot{p}_{j}}{\partial p_{j}} \right) = 0.$$

Using the equations of motion, the last group of terms is seen to vanish, and we are left with

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \sum_{j} \left(\frac{\partial\rho}{\partial q_{j}} \dot{q}_{j} + \frac{\partial\rho}{\partial p_{j}} \dot{p}_{j} \right) = \frac{\partial\rho}{\partial t} + \{\rho, H\} = 0,$$

where the expression on the left hand side can also be written as $d\rho(t)/dt$. It is useful to emphasise the difference between $\partial \rho/\partial t$ and $d\rho/dt$. The former is the change of the density function at a fixed point in phase space, whereas the latter is the change of the density function as seen by an observer moving along with the trajectory of the system. The last equation expresses the fact that such an observer does not see a change in the density. This now is Liouville's theorem.

The brackets $\{,\}$ are called the *Poisson brackets*. They are for classical mechanics what commutators are for quantum mechanics. In fact, the resulting equations for the classical density function and the quantum density operator in Heisenberg representation can be compared:

$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} + \{\rho, H\} \text{ (class.);}$$
$$\frac{d\rho}{dt} = \frac{\partial\rho}{\partial t} - \frac{i}{\hbar}[\rho, H] \text{ (quantum).}$$

The intimate relation between classical and quantum mechanics is helpful in formulating statistical mechanics.

We now define equilibrium as the condition that $\partial \rho / \partial t$ be equal to 0, so the question arises how this condition can be satisfied. One possibility is to have a density function which is constant in time and in phase space so that both $\partial \rho / \partial t$ and $[\rho, H]$ vanish. This is however not physically acceptable, as infinite momenta are allowed in that case. Another possibility is to have ρ not depending explicitly on time (this is mostly the case – it means that there is no external, time-dependent field) but being a function of H. This is usually assumed. It implies that for some particular value of H, every point in phase space compliant with that value, occurs equally likely. This is the famous *postulate of equal a priori probabilities*.¹

2.3 The microcanonical ensemble

Any particular choice for the density function is called an *ensemble*. This refers to the idea of having a large collection of independent systems, all having the same values for their controllable external parameters (energy, volume, particle number etcetera), but (in general) different microstates. The microstates all occur with a probability given by the density function – therefore, determining the average of a physical quantity over this ensemble of systems, corresponds to the expression given at the end of section 2.1.

For an isolated system, the energy is fixed, so we can write

$$\rho = \rho(H) = \delta[H(q, p) - E].$$

Obviously, there are some mathematical difficulties involved in using a delta-function - one may formulate this as a smooth function with a variable width which can be shrunk to zero.

The density function ρ gives us the probability that we find a system in a state (q, p), and we can use this in order to find the average $\langle f \rangle$ as described above. This average is called the *ensemble*

¹Parthia formulates this a bit differently on page 34, but I am not very happy with his description.

average. This is equal to the time average of the quantity f in the stationary limit. This result is called the *fundamental postulate of statistical mechanics*.

Obviously, the phase space volume accessible to the system is proportional to the number of microstates accessible to the system. If we consider phase space as continuous (as should be done in classical mechanics), however, that number is always infinite (irrespective of the number of particles). In quantum mechanics we do not have this problem, as the states are given as wavefunctions and not as points (q, p). The connection between the two can be made by considering wavepackets which are localised in both q-space and p-space. In view of the Heisenberg uncertainty relation, these packets occupy a volume $\sim h$ per dimension in phase space. Therefore, it appears that there is a fundamental volume h^{3N} which is occupied by quantum state of the system. Therefore, the relation between the number of states Γ and the occupied volume ω in phase space is given by

$$\Gamma = \omega/h^{3N}$$

For the microcanonical ensemble, Γ is the volume of a thin shell in phase space where the energy lies between $E - \Delta/2$ and $E + \Delta/2$. We call this shell $\Delta \omega$.

2.4 Examples

First we consider the case of N non-interacting point particles, that is an ideal classical gas. The number of states in the energy shell $\Delta \omega$ is given by:

$$\Delta\Gamma = \int_{\Delta\omega} d^{3N} p \, d^{3N} q.$$

As the potential vanishes, the integral over q yields V^N . The integral over the momenta can be evaluated using the results for an N-dimensional shell used in section 1.4, and we find for the number of states within the shell:

$$\Delta\Gamma = \frac{1}{(3N/2 - 1)!} \left[\frac{V}{h^3} (2\pi mE)^{3/2} \right]^N \frac{\Delta E}{E}.$$

In order to take the indistinguishability of the particles into account, we must divide this number by N!. The entropy can then be calculated as above, resulting in the Sackur–Tetrode formula.

Our general formalism also allows to evaluate the entropy of a single particle. As an example, we consider the harmonic oscillator:

$$H = \frac{p^2}{2m} + \frac{k}{2}q^2$$

From this equation, the points with constant energy are seen to lie on ellipses. In order to find the volume (in our 2D phase space this is a surface area), we can scale the coordinates in order to map the ellipse onto a circle:

$$q \to rac{q}{\sqrt{2E/m\omega}}, \quad p \to rac{p}{\sqrt{2mE}}$$

with, as usual, $\omega = \sqrt{k/m}$. Do not confuse this ω (angular frequency) with that representing the volume in phase space. Then the volume of the ellipse can be found to be

$$\Delta\Gamma = \frac{2\pi\Delta}{\omega}.$$

The canonical ensemble

3.1 Equilibrium between a system and a heat reservoir

Suppose we have a large, isolated system which we divide up into a very small one and the rest. The small subsystem can exchange energy with the rest of the system, but its volume and number of particles is constant. Consider a state *r* of the small subsystem with energy E_r . How likely is it to find the subsystem in this state? That depends on the number of states which are accessible to the rest of the system (this is called the *heat bath*), and this number is given as $\Omega(E - E_r)$, where *E* is the energy of the total system. Therefore, the multiplicity of the state with energy E_r is

$$P_r = \Omega(E - E_r).$$

We know that Ω of the heat bath is given as $\exp(S/k_{\rm B})$. We then have: use

$$P_r = \exp[S(E - E_r)/k_{\rm B}] = \exp\left\{\left[S(E) - \frac{\partial S(E)}{\partial E}E_r\right]/k_{\rm B}\right\} = \exp\left\{\left[S(E) - \frac{E_r}{T}\right]/k_{\rm B}\right\},$$

so that we obtain

$$P_r = P(E_r) \propto \exp(-E_r/k_{\rm B}T) = e^{-\beta E_r}$$

with $\beta = 1/k_{\rm B}T$. P_r is the Boltzmann distribution function.

As the subsystem is very small in comparison with the total system, its temperature will be determined by the latter. Therefore the temperature of the subsystem will be a control parameter, just as the number of particles N and its volume V. If we consider a set of systems which are all prepared with the same N, V and T, and with energies distributed according to the Boltzmann factor, we speak of a *canonical*, or (N, V, T) *ensemble*.

3.2 A system in the canonical ensemble

A more formal approach can be taken in the calculation of the canonical and other distributions that we shall meet hereafter, which is based on a very general definition of entropy. In a quantum mechanical formulation, this entropy is formulated terms of the quantum density operator as

$$S = -k_{\rm B} {\rm Tr} \, \rho \ln \rho$$

Writing

$$\rho = \sum_{r} |r\rangle P_r \langle r|$$

leads to the same expression as above

$$S = -k_{\rm B} \sum_r P_r \ln P_r.$$

The basic postulate now is that, given expectation values for external parameters, the density matrix will assume a form which maximises the entropy defined this way.

This expression for the entropy is often used in information theory. Furthermore, it turns out that expressions for the entropy that can be derived from more physical arguments are all compatible with this general expression.

Let us first note that the (NVE) ensemble is the most natural one to define in classical or quantum mechanics: the number of degrees of freedom is well-defined (via the particle number N) and the potential does not explicitly depend on time (the volume is fixed, i.e. the walls do not move). Then, the Hamiltonian is conserved and it can be identified with the energy. Now suppose that there is a number M of states with the prescribed energy. We must find the distribution P_r which makes S stationary under the constraint that P_r is normalised. This is done using a Lagrange multiplier λ . We define

$$F = S - \lambda \sum_{r=1}^{M} P_r$$

and now require F to be stationary:

$$\frac{\partial F}{\partial P_r} = -k_{\rm B}(1+\ln P_r) - \lambda$$

This leads to a family of solutions

$$P_r = \exp\left(-\frac{k_{\rm B}+\lambda}{k_{\rm B}}\right),\,$$

parametrised by λ . The P_r are thus all equal. We must now adjust λ such as to satisfy the constraint that P_r be normalised. This then leads to

$$P_r = \frac{1}{M}.$$

We see that for the microcanonical ensemble, the distribution which maximises the entropy is the one in which each state has the same probability of occurrence.

Instead of requiring that each of the parameters N, V or E be fixed, we may relax any of these conditions and require the *expectation value* to assume a certain value rather than the stronger condition that the parameter *may only assume* a certain value. We shall work this out for the energy. In the context of quantum mechanics, this is a bit tricky as we must calculate the variation of an operator. However, if we assume that the density operator can be written in the form

$$ho = \sum_{r} \ket{r} P_r \langle r
vert$$

with $|r\rangle$ being eigenstates of the Hamiltonian, the solution of the problem is similar to that of the classical case.

We now have an additional constraint, that is,

$$\langle E \rangle = \sum_{r} P_{r} E_{r}$$

is given. Here E_r is the energy of the state *r*. We now have *two* Lagrange multipliers, one for the energy (which we call $k_B\beta$) and one (again λ) for the normalisation:

$$F = S - \lambda \sum_{r} P_{r} - k_{\rm B} \beta \sum_{r} P_{r} E_{r}.$$

Following the same procedure as above, we find

$$P_r = \frac{1}{Q_\lambda} \exp(-\beta E_r).$$

Q – the partition function – is defined in terms of the multiplier λ – it serves merely to normalise the probability distribution.

The Lagrange parameter β which we can identify with $1/k_{\rm B}T$ serves as the parameter which can be tuned in order to adjust the expectation value of the energy to the required value. If we relax the particle number but fix its expectation value, we obtain

$$P_r = \frac{1}{Z_{\lambda}} \exp(-\beta E_r - \sigma N).$$

where σ can be identified with $-\beta\mu$, μ is the chemical potential.

Let us analyse the canonical partition function a bit further. The expectation value of the energy can be determined as

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Q$$

Using $P_r = \exp(-\beta E_r)/Q$, we can write the entropy as

$$S = -k_{\rm B}\sum_{r} P_r \ln P_r = -k_{\rm B}\sum_{r} P_r \left[-\ln Q - \beta E_r\right] = k_{\rm B} \ln Q - k_{\rm B} \beta \frac{\partial}{\partial \beta} \ln Q.$$

The transformation from S to $\ln Q$ which leads to this type of relation is known as the Legendere transformation.

Returning to the derivation of the canonical distribution function, we note that the function we have maximised can be written as

$$S - \lambda - T \langle E \rangle$$

where we have used $\sum P_r = 1$ and $\sum_r P_r E_r = \langle E \rangle$. Now we write this expression (disregarding the constant λ) as

$$-\frac{A}{T} = -\frac{E - TS}{T}.$$

The quantity A = E - TS is called the (Helmholtz) free energy. We see that this quantity was minimised as a function of P_r . We have:

The Boltzmann distribution is the distribution which minimises the Helmholtz free energy.

3.3 Physical significance of the various statistical quantities in the canonical ensemble

Let us first calculate the energy:

$$U = \langle E \rangle = rac{\sum_r E_r e^{-eta E_r}}{\sum_r e^{-eta E_r}}.$$

The denominator ensures proper normalisation, in particular it ensures that the average value of 1 is equal to 1.

Looking at the above equation, we see that we can write U as

$$U = \langle E \rangle = -\frac{\partial}{\partial \beta} \ln \sum_{r} e^{-\beta E_{r}}.$$

It is useful to define

$$Q_N = \sum_r e^{-\beta E_r};$$

Q is called the *partition function*. Let us relate the quantities we have seen so far to thermodynamics. For a system at constant *V*, *N* and *T*, we know for the Helmholtz free energy A = E - TS, that

$$dA = dU - TdS - SdT = -SdT - PdV + \mu dN.$$

From this, we have:

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}; \quad P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}; \quad \mu = \left(\frac{\partial A}{\partial N}\right)_{T,V}$$

From the first relation, we have:

$$U = A + TS = A - T\left(\frac{\partial A}{\partial T}\right)_{N,V} = -T^2 \left[\frac{\partial}{\partial T}\left(\frac{A}{T}\right)\right]_{N,V} = \left[\frac{\partial(A/T)}{\partial(1/T)}\right]_{N,V},$$

from which we can infer that

$$A = -k_{\rm B}T\ln Q_N.$$

By taking the temperature derivative of U we obtain the expression for the specific heat:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = -T^2 \left(\frac{\partial^2 A}{\partial T^2}\right)_{N,V}.$$

Moreover, from

$$dA = -SdT - PdV + \mu dN.$$

(see above), we see that if we keep the volume and the particle number constant, we have

$$dA = -PdV$$
,

that is, the change in free energy is completely determined by the work done by the system. The Hemholtz free energy represents the work which can be done by a closed, isothermal system.

We have seen that the probability P_r with which a configuration with energy E_r occurs, is given by the *Boltzmann factor*:

$$P_r = \frac{e^{-E_r/(k_{\rm B}T)}}{Q_N}.$$

The entropy can be calculated as

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = \frac{\partial (k_{\rm B}T\ln Q_N)}{\partial T} = k_{\rm B}\ln Q_N - \frac{U}{T}$$

We now replace U, which is the expectation value of E_r , by the expectation value of $-k_{\rm B}T \ln(Q_N P_r)$:

$$S = k_{\rm B} \ln Q_N - k_{\rm B} \left\langle \ln(Q_N P_r) \right\rangle = -k_{\rm B} \left\langle \ln P_r \right\rangle = -k_{\rm B} \sum_r P_r \ln P_r.$$

From this relation, it follows that the entropy vanishes at zero temperature ('third law of thermodynamics'). Furthermore, this relation has become the starting point for studying information theory, where entropy is a measure for the reliability of communication. This is obviously the same entropy as was introduced in the previous section.

3.4 Alternative expressions for the partition function

It is very important to realise that, when evaluating the sums over *states* r, we should not confuse those states with their energies. For a system with a strictly discrete spectrum, the energies E_i might occur with a multiplicity (degeneracy) g_i . In that case, when we evaluate the sum over some energy-dependent quantity, we have

$$\sum_r \to \sum_i g_i.$$

In fact, the probability of having an energy E_i is given by

$$P_i = \frac{g_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}}$$

In practice, the energy is usually continuous or almost continuous. In that case, g_i is replaced by the *density of states* g(E). This quantity is defined as follows:

Number of quantum states with energy between *E* and E + dE = g(E)dE.

In that case

$$P(E) = \frac{g(E)e^{-\beta E}}{\int_{-\infty}^{\infty} g(E)e^{-\beta E}dE}$$

3.5 Classical systems

We now show how to evaluate expectation values for a system consisting of interacting point particles. In the previous chapter it was argued that the sum over the available quantum states can be replaced by a sum over e volume ω in phase space, provided we divide by the 'unit phase space volume' h^{3N} and by N! in order to avoid over-counting of indistinguishable configurations obtained from each other by particle permutation. Therefore we have

$$Q_N = \frac{1}{h^{3N}N!} \int e^{-\beta H(q,p)} d^{3N} q d^{3N} p,$$

where

$$H(q,p) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V(q_1,\ldots,q_{3N}).$$

For the ideal gas, $V \equiv 0$. Note that the \mathbf{p}_i are vectors in 3D.

The expression for Q_N looks quite complicated, but the integral over the momenta can be evaluated analytically! The reason is that the exponential can be written as a product and the integral factorises into 3N Gaussian integrals:

$$\int e^{-\beta \sum_{i} p_{i}^{2}/(2m)} d^{3N} p = \int e^{-\beta p_{1}^{2}/(2m)} d^{3} p_{1} \int e^{-\beta p_{2}^{2}/(2m)} d^{3} p_{2} \dots \int e^{-\beta p_{N}^{2}/(2m)} d^{3} p_{N} \dots$$

The integral over one particle then factorises into one over p_x , one over p_y and one over p_z . Now we use the Gaussian integral result:

$$\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}},$$

in order to obtain:

$$Q_N = \frac{1}{N!} \left[\frac{(2\pi m k_{\rm B} T)^{(3/2)}}{h^3} \right]^N \int e^{-\beta V} d^{3N} q.$$

For an ideal gas, V = 0 and we can evaluate the remaining integral: it yields V^N (V is the volume of the system – do not confuse it with the potential!). Therefore, the partition function of the ideal gas is found as:

$$Q_N = \frac{1}{N!} \left[V \frac{(2\pi m k_{\rm B} T)^{(3/2)}}{h^3} \right]^T$$

3.6 Energy fluctuations in the canonical ensemble: correspondence with the micro-canonical ensemble

In the canonical ensemble, the energy can take on any possible value between the ground state and infinity. The actual probability with which a particular value of the energy occurs is proportional to

$$P(E) \propto g(E)e^{-E/kT}$$
.

The prefactor g(E) is the density of states – it is proportional to the $\Omega(E)$, i.e. the number of microstates at energy E. In general, we find that this quantity is a very strongly increasing function of the energy, whereas the Boltzmann function $\exp(-E/k_{\rm B}T)$ strongly *decreases* with energy. The result is that the probability distribution of the energy is very sharply peaked around its mean value $U = \langle E \rangle$. To show that the energy is indeed sharply peaked around U, we calculate the fluctuation. From statistics, we know that the width of the distribution is given by

$$(\Delta E)^2 = \langle E^2 \rangle - \langle E \rangle^2$$

From

$$U = \langle E \rangle = \frac{\sum_{r} E_{r} e^{-\beta E_{r}}}{\sum_{r} e^{-\beta E_{r}}}$$

where, as usual, $\beta = 1/k_{\rm B}T$, we see that

$$\frac{\partial U}{\partial \beta} = \left(\frac{\sum_{r} E_{r} e^{-\beta E_{r}}}{\sum_{r} e^{-\beta E_{r}}}\right)^{2} - \frac{\sum_{r} E_{r}^{2} e^{-\beta E_{r}}}{\sum_{r} e^{-\beta E_{r}}} = -(\Delta E)^{2}.$$

The quantity $\partial U/\partial \beta$ is equal to

$$\frac{\partial U}{\partial \beta} = k_{\rm B} T^2 \frac{\partial U}{\partial T} = k_{\rm B} T^2 C_V.$$

Realising that C_V is an extensive quantity, which scales linearly with N, we therefore have:

$$\frac{\Delta E}{U} = \frac{\sqrt{k_{\rm B}T^2C_V}}{U} \sim 1/\sqrt{N}.$$

In the thermodynamic limit $(N \to \infty)$, we see that the relative width becomes very small. Therefore, we see that the energy, which is allowed to vary at will, turns out to be almost constant. Therefore, we expect the physics of the system to be almost the same of that in the microcanonical ensemble (where the energy *is* actually constant).

This result is usually referred to as the 'equivalence of ensembles'.

3.7 Two theorems – the 'equipartition' and the 'virial'

The analysis of the classical gas in section 3.5 allows us to calculate the expectation value of the kinetic energy T. This is done as follows.

$$\langle T \rangle = \frac{\int \sum_{i} \frac{p_i^2}{2m} \exp\left[-\left(\sum_{i} \frac{p_i^2}{2m} + V(\mathbf{R})\right) / (k_{\rm B}T)\right] d^{3N} P d^{3N} R}{\int \exp\left[-\left(\sum_{i} \frac{p_i^2}{2m} + V(\mathbf{R})\right) / (k_{\rm B}T)\right] d^{3N} P d^{3N} R}.$$

All sums over *i* run from 1 to *N*; *R* and *P* represent all positions and momenta.

Obviously, the contributions to the result from each momentum coordinate of each individual particle are identical, and they can be evaluated using the same factorisation which led to the evaluation of the partition function of the ideal gas (the integrals over the coordinates R cancel). We obtain

$$\langle T \rangle = 3N \frac{\int \frac{p^2}{2m} \exp[-p^2/(2mk_{\rm B}T)]dp}{\int \exp[-p^2/(2mk_{\rm B}T)]dp} = \frac{3Nk_{\rm B}T}{2}.$$

This result is known as the *equipartition theorem*: it tells us that the kinetic energy for each degree of freedom is $k_BT/2$. In the book, this theorem is proven more generally.

The second theorem gives us an expression for the pressure P (the derivation given here is somewhat different from that of the book). We know that

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$$

(see above). Now we replace A by $-k_{\rm B}T \ln Q_N$:

$$P = k_{\rm B}T \frac{1}{Q_N} \frac{\partial Q_N}{\partial V}.$$

First we realise that the integral over the momenta is volume-independent – therefore only the part

$$\tilde{Q}_N = \int \exp[-U(\mathbf{r}_1,\ldots,\mathbf{r}_n)/(k_{\rm B}T)]d^3R$$

is to be considered (note that we call the potential function U – this is to avoid confusion with the volume V).

To evaluate the volume-dependence of this object, we write for the coordinates \mathbf{r}_i of the particles:

$$\mathbf{r}_{i} = V^{1/3} \mathbf{s}_{i};$$

that is, the coordinates \mathbf{s}_i are simply rescaled in such a way that they occupy a volume of the same shape as the \mathbf{r}_i , but everything is rescaled to a unit volume. Every configuration in a volume *V* has a one-to-one correspondence to a configuration of the \mathbf{s}_i . Therefore we can write:

$$\int \exp[-U(\mathbf{r}_1,\ldots,\mathbf{r}_n)/(k_{\rm B}T)]d^{3N}R = V^N \int \exp[-U(V^{1/3}\mathbf{s}_1,\ldots,V^{1/3}\mathbf{s}_N)/(k_{\rm B}T)]d^{3N}S$$

where the prefactor arises because of the change of integration variables.

Now, the derivative with respect to *V* can be evaluated:

$$\frac{\partial \tilde{Q}_N}{\partial V} = NV^{N-1}\tilde{Q}_N - \frac{V^{-2/3}}{3k_{\mathrm{B}}T} \int \sum_i \mathbf{s}_i \cdot \nabla_i U \exp\left[-U(V^{1/3}\mathbf{s}_1, \dots, V^{1/3}\mathbf{s}_N)/(k_{\mathrm{B}}T)\right] d^{3N}S.$$

Collecting all the terms we obtain

$$\frac{PV}{k_{\rm B}TN} = 1 - \frac{1}{3Nk_{\rm B}T} \left\langle \sum_{i=1}^{N} \mathbf{r}_i \cdot \frac{\partial U}{\partial \mathbf{r}_i} \right\rangle.$$

We see that for U = 0 we have $PV = Nk_BT$, which is well known for the ideal gas.

Very often interaction potentials are modelled as a sum over all particle pairs:

$$U(\mathbf{r}_1,\ldots,\mathbf{r}_N)=\sum_{i,j;j>i}^N u\left(\left|\mathbf{r}_i-\mathbf{r}_j\right|\right).$$

In that case, the rightmost term in the virial theorem can be rewritten as

$$\left\langle \sum_{i=1}^{N} \mathbf{r}_{i} \cdot \frac{\partial U}{\partial \mathbf{r}_{i}} \right\rangle = \frac{N(N-1)}{2} \left\langle r \frac{\partial u(r)}{\partial r} \right\rangle = \frac{N(N-1)}{2} \int_{0}^{\infty} r \frac{du}{dr} g(|\mathbf{r}_{1} - \mathbf{r}_{2}|) d^{3}r_{1} d^{3}r_{2},$$

where we have introduced the *pair correlation function*, g(r), which gives the probability of finding a particle pair at separation $r = |\mathbf{r}_2 - \mathbf{r}_1|$. The formal definition of g(r) is

$$g(r) = V^2 \frac{\int \exp\left[-\beta U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)\right] d^3 r_3 \dots d^3 r_N}{Q_N}$$

Because the particles are identical, we can take any pair instead of 1 and 2. For large separation r, g(r) tends to 1. The virial theorem can be reformulated in terms of the pair correlation function:

$$\frac{PV}{Nk_{\rm B}T} = 1 - \frac{2\pi N}{3Vk_{\rm B}T} \int_0^\infty g(r) \frac{\partial u(r)}{\partial r} r^3 dr.$$

3.8 A system of classical harmonic oscillators

Now we consider a classical system with an Hamiltonian given by

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \frac{m\omega^2}{2} q_i^2, N.$$

For this system, the partition function can be evaluated analytically as the Hamiltonian is a quadratic function of both the momenta and the coordinates. The calculation therefore proceeds analogous to that for the ideal gas where the Hamiltonian is a quadratic function of the momenta only. The result for oscillator system is:

$$Q_N = rac{1}{(eta \hbar \omega)^N},$$

where we have assumed that the oscillators are distinguishable. The free energy now follows as

$$A = -k_{\rm B}T\ln Q_N = Nk_{\rm B}T\ln\left(\frac{\hbar\omega}{k_{\rm B}T}\right).$$

From this we find

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T} = k_{\rm B}T \ln\left(\frac{\hbar\omega}{k_{\rm B}T}\right);$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T} = 0;$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = Nk_{\rm B}\left[\ln\left(\frac{k_{\rm B}T}{\hbar\omega}\right) + 1\right];$$

$$U = \left[\frac{\partial(A/T)}{\partial(1/T)}\right]_{N,V} = Nk_{\rm B}T.$$

From the last equation, we find

$$C_V = Nk_{\rm B} = C_P$$

The fact that $U = Nk_BT$ is in agreement with the equipartition theorem as the Hamiltonian has *two* independent quadratic terms (for *q* and *p*) instead of only one. It shows that for harmonic oscillators, the energy is equally divided over the potential and the kinetic energies.

Next we consider a collection of quantum harmonic oscillators in the canonical ensemble. This is simpler to evaluate than the classical case. The states for oscillator number i are labeled by n_i , hence

$$Q_N = \sum_{\{n_i\}} e^{-eta \hbar \omega \sum_i (n_i+1/2)},$$

where $\sum_{\{n_i\}}$ denotes a sum over all possible values of all numbers n_i . This partition function factorises in a way similar to the classical system, and we obtain:

$$Q_N = \left(\sum_n e^{-\beta\hbar\omega(n+1/2)}\right)^N = \left(\frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}\right)^N$$

From the partition function we obtain, similar to the classical case:

$$A = N \ln \left[\frac{\hbar \omega}{2} + k_{\rm B} T \ln \left(1 - e^{-\beta \hbar \omega} \right) \right].$$

And, from this,

$$\begin{split} & \mu = A/N; \\ & P = 0; \\ & S = Nk_{\rm B} \left[\frac{\beta \hbar \omega}{e^{-\beta \hbar \omega} - 1} - \ln \left(1 - e^{-\beta \hbar \omega} \right) \right]. \\ & U = N \left[\frac{\hbar \omega}{2} + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right]. \end{split}$$

And, finally

$$C_V = C_P = N k_{\rm B} (\beta \hbar \omega)^2 rac{e^{\beta \hbar \omega}}{\left(e^{\beta \hbar \omega} - 1
ight)^2}.$$

Interestingly, the quantum harmonic oscillator does not obey equipartition: we see that only the first term in the expression for the energy is in accordance with that theorem – the second term gives a positive deviation from the equipartition result.



Figure 3.1: The Langevin function. The dashed line is the graph of x/3.

3.9 The statistics of paramagnetism

Consider a system consisting of a set of magnetic moments. Each moment interacts with a magnetic field \mathbf{H} , but the interaction between the moments is neglected. In that case we can consider again a system of only one magnetic moment and construct the partition function for N moments by raising that for a single moment to the N-th power.

The interaction Hamiltonian is given by

$$H = -\boldsymbol{\mu} \cdot \mathbf{H}.$$

Note the difference between the Hamiltonian H and the field **H**. Without loss of generality we can take **H** along the *z*-direction so that

$$H = -\mu H \cos \vartheta$$
,

where ϑ is the angle between the moment and the *z*-axis.

The partition function can now be evaluated:

$$Q_1 = \int e^{\beta\mu H \cos\vartheta} \sin\vartheta d\vartheta d\varphi = 4\pi \frac{\sinh(\beta\mu H)}{\beta\mu H}.$$

We can also calculate the average value of the magnetic moment:

$$\overline{\mu}_{z} = \frac{\int_{0}^{2\pi} \int_{0}^{\pi} \mu e^{\beta \mu H \cos \vartheta} \cos \vartheta \sin \vartheta d\vartheta d\varphi}{\int_{0}^{2\pi} \int_{0}^{\pi} e^{\beta \mu H \cos \vartheta} \sin \vartheta d\vartheta d\varphi} = \mu \left[\coth(\beta \mu H) - \frac{1}{\beta \mu H} \right] = \mu L(\beta \mu H),$$

where L(x) is the Langevin function. It is shown in figure 3.1.

For high temperatures, that is, for small values of *x*, the Langevin function behaves as $L(x) \sim x/3$ (see figure 3.1), so we have

$$M = \frac{\mu^2}{3k_{\rm B}T}H.$$

The magnetic susceptibility is defined as

$$\chi = \frac{\partial M}{\partial H}$$

2.1.6

$$\chi = \frac{C}{T}$$

where C is the so-called *Curie constant*. This relation is known as the *Curie law* of paramagnetism. This law is found in nature for systems with high values of the angular momentum quantum number l, in which case the behaviour of the system approaches classical behaviour.

In the book, the situation of real quantum systems (with smaller values of l) is discussed further.

3.10 Thermodynamics of magnetic systems: negative temperature

The case of paramagnetic s = 1/2 spins is the easiest example of a quantum magnetic system. In that case, the spins assume values either $\hbar/2$ or $-\hbar/2$ when they are measured along an arbitrary axis. If we apply a magnetic field **H**, there are therefore two possible values of the energy for these two orientations – we call these energies ε and $-\varepsilon$. Therefore we immediately find that the partition sum is given as:

$$Q_N(oldsymbol{eta}) = \left(e^{-eta arepsilon} + e^{eta arepsilon}
ight)^N = \left[2\cosh(eta arepsilon)
ight]^N.$$

The fact that the term in brackets can simply be raised to the *N*-th power is a result of the fact that the spins do not interact mutually.

In the usual way we obtain the thermodynamic properties from the partition function:

$$A = -Nk_{\rm B}T\ln[2\cosh(\varepsilon/k_{\rm B}T)];$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{H} = Nk_{\rm B}\left\{\ln\left[2\cosh(\beta\varepsilon)\right] - \beta\varepsilon\tanh(\beta\varepsilon)\right\};$$

$$U = A + TS = -N\varepsilon\tanh(\beta\varepsilon)$$

$$M = -\left(\frac{\partial A}{\partial H}\right)_{T} = N\mu_{\rm B}\tanh(\beta\varepsilon),$$

where $\mu_{\rm B}$ is the Bohr magneton: the coupling constant between the spin and the external field, i.e.

$$\varepsilon = \mu_{\rm B} H$$
.

Finally we have

$$C_H = \left(\frac{\partial U}{\partial T}\right)_H = Nk_{\rm B}(\beta\varepsilon)^2/\cosh^2(\beta\varepsilon).$$

We see that U = -MH, as could be expected. In the next few figures we show the temperature dependence of *S*, *U*, *M* and *C*_{*H*}.

These graphs show several interesting features. The entropy vanishes for small temperature as it should; this shows that for low temperatures nearly all spins are in line with the field, so that the entropy is low. Also, the energy per spin is about $-\varepsilon$ which is in agreement with this picture.

When we increase the temperature, more and more spins flip over and the entropy and energy increase. There will be a particularly strong increase in the entropy near $k_{\rm B}T = \varepsilon$ as in that region the thermal energy is sufficiently strong for flipping the spins over. For high temperatures the spins assume more or less random orientations, and the entropy will approach a constant. The graph of the magnetisation is also easily explained now. The specific heat shows a maximum near $k_{\rm B}T = \varepsilon$ for the reason just explained.



Figure 3.2: Entropy versus temperature



Figure 3.3: Energy versus temperature

A striking feature of the energy graph is that it does not approach its maximum value, which is reached when all spins would be *antiparallel* to the field. In fact, when the energy is positive, the entropy will *decrease* with energy. This can be used in an experimental technique called *magnetic cooling*. In this technique, a strong magnetic field is suddenly reversed in order to bring the spins in a configuration where the majority is antiparallel to the field. In that case, the temperature is *negative*, as the entropy decreases with energy and $1/T = \partial S/\partial E$. This is not in contradiction with the laws of thermodynamics, as the system is far from equilibrium. In order to reach equilibrium, the temperature will return to positive values, and it therefore has to pass through absolute zero. The system is therefore extremely cold for some time.



Figure 3.4: Magnetisation versus temperature



Figure 3.5: Specific heat versus temperature

4

The grand canonical ensemble

4.1 Equilibrium between a system and a particle-energy reservoir

We derive the grand canonical distribution function (density function) in a way analogous to that of the canonical ensemble. We consider again a large, isolated system in which we define a subsystem, which can exchange not only energy, but also particles with the remainder of the large system (the remainder is again called a bath). Now we consider a state *s* of the subsystem consisting of N_r particles and an energy E_s . Just as in the derivation of the canonical ensemble, we note that the probability of occurrence of this state is proportional to the number of possible states of the bath:

$$P_{r,s} \propto \Omega(E - E_s, N - N_r).$$

Writing $\Omega = \exp(S/k_{\rm B})$ and realising that

$$\frac{\partial S}{\partial E} = \frac{1}{T}$$
$$\frac{\partial S}{\partial N} = -\frac{\mu}{T}$$

we obtain

$$P_{rs} \propto e^{S(E-E_s,N-N_r)/k_{\rm B}} \propto e^{-\beta E_s+\beta \mu N_r}$$



Figure 4.1: The grand canonical ensemble. The system under consideration (dashed square) can exchange energy and particles with its surroundings.

We see that the probability distribution is that of the canonical ensemble multiplied by an extra factor $\exp(\beta \mu N)$ and summed over *N*. The required normalisation factor is

$$\sum_{N=0}^{\infty} e^{\beta \mu N} \sum_{s} E_{s} e^{-\beta E_{s}} \equiv \mathscr{Z}.$$

The quantity \mathscr{Z} is called the grand canonical or grand partition function.

4.2 Formal derivation of the grand canonical ensemble

Using the principle of maximum entropy, we can again derive the probability for the grand canonical ensemble. We do this by requiring that the *expectation* values of E and N are given. Hence we must maximise the entropy

$$S = -k_{\rm B} \sum_{N} \sum_{r} p_r(N) \ln p_r(N)$$

under the condition that

$$\sum_{N}\sum_{r}p_{r}(N)E_{r}(N)=\langle E\rangle=U$$

is given and that

$$\sum_{N} N \sum_{r} p_{r}(N) = \langle N \rangle.$$

This then leads to a Lagrange function

$$F = S - \lambda \sum_{N} \sum_{r} p_{r}(N) - k_{\mathrm{B}} \beta \sum_{N} \sum_{r} p_{r}(N) E_{r}(N) - k_{\mathrm{B}} \beta \mu \sum_{N} N \sum_{r} p_{r}(N).$$

Taking the derivative with respect to $p_r(N)$ leads to

$$-k_{\rm B}\ln p_r(N) - k_{\rm B} - \lambda - k_{\rm B}\beta E_r(N) + k_{\rm B}\beta\mu N = 0,$$

leading to the distribution

$$p_r(N) = rac{e^{-eta E_r(N)+eta \mu N}}{\sum_N \sum_r e^{-eta E_r(N)+eta \mu N}},$$

as found in the previous section. The denominator in the last expression is called the *grand canonical partition function*

$$\mathscr{Z} = \sum_{N} \sum_{r} e^{-\beta E_r(N) + \beta \mu N}.$$

4.3 Physical significance of the various statistical quantities

We can relate the thermodynamic quantities using the grand canonical distribution function. First of all, we note that the grand partition function can be written as

$$\mathscr{Z} = \sum_{N=0}^{\infty} e^{\beta \mu N} Q_N(N,V,T)$$

where $Q_N(N,V,T)$ is the canonical partition function, which is related to the Helmholtz free energy *A* as

$$Q_N = e^{-A/k_{\rm B}T}.$$

The grand canoncial partition function can thus be written as

$$\mathscr{Z} = \sum_{N=0}^{\infty} e^{\beta(\mu N - A)}$$

Just as in the case of the energy in the canonical ensemble, the summand $e^{\beta(\mu N - A)}$ will be very sharply peaked near the equilibrium value \overline{N} of N, so that we may replace the sum by the summand at its peak value. In this way we find

$$k_{\rm B}T \ln \mathscr{Z} = \mu \overline{N} - A = \mu \overline{N} - U + TS.$$

Using the Euler relation from thermodynamics,

$$U = ST - PV + \mu N,$$

we find

$$k_{\rm B}T\ln \mathscr{Z} = PV \equiv k_{\rm B}Tq.$$

Note that we have been a bit sloppy in replacing the sum over *N* by its maximum value – we should have included a width here. However, this only leads to an additive constant in the relation between $\mu \overline{N} - A$ and $k_{\rm B}T \ln \mathscr{Z}$, which can be fixed by noting that for $\overline{N} = 0$, the right hand side should vanish, and the result obtained turns out to be correct.

Let us now calculate the average value of N using the density function:

$$\overline{N} = \frac{\sum_{N=0}^{\infty} N e^{\beta \mu N} e^{-A/k_{\rm B}T}}{\sum_{N=0}^{\infty} e^{\beta \mu N} e^{-A/k_{\rm B}T}} = k_{\rm B} T \left(\frac{\partial q(\mu, V, T)}{\partial \mu}\right)_{V, T}$$

Instead of the chemical potential μ , often the parameter $z = \exp(\beta\mu)$ is used. The parameter z is called the *fugacity*. The energy can be obtained as

$$\overline{U} = k_{\rm B} T^2 \left(\frac{\partial q(z, V, T)}{\partial T} \right)_{z, V}$$

Note that in the derivative with respect to *T*, the fugacity $z = \exp(\mu/k_B T)$ is kept constant (though it depends on *T*).

The relations with thermodynamic quantities can most easily be formulated as

$$N = \left(\frac{\partial k_{\rm B} T \ln \mathscr{Z}}{\partial \mu}\right)_{V,T}$$
$$P = \left(\frac{\partial k_{\rm B} T \ln \mathscr{Z}}{\partial V}\right)_{\mu,T}$$
$$S = \left(\frac{\partial k_{\rm B} T \ln \mathscr{Z}}{\partial T}\right)_{\mu,V}$$

4.4 Examples

We first calculate the grand canonical partition function of the ideal gas. We start from the canonical partition function, which has the form

$$Q_N(N,V,T) = \frac{V^N}{N!} \left(\frac{\sqrt{2\pi m k_{\rm B} T}}{h}\right)^{3N}.$$

Now

$$\mathscr{Z} = \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{V^N \left(2\pi m k_{\rm B} T\right)^{3N/2}}{h^{3N} N!} \sum_{N=0}^{\infty} \frac{\xi^N}{N!} = \exp(\xi)$$

with

$$\xi = V z \left(\frac{2\pi m k_{\rm B} T}{h^2}\right)^{3/2} \equiv V z \Lambda^{-3}.$$

The quantity $\Lambda = \sqrt{h^2/(2\pi m k_B T)}$ is called the *de Broglie wavelength* – it depends on *T* only. From this expression for the grand canonical partition function, the thermodynamic quantities can easily be evaluated using the relations given in the previous section.

$$P = \frac{zk_{\rm B}T}{\Lambda^3}$$

$$N = \frac{zV}{\Lambda^3}$$

$$U = zVk_{\rm B}T^2\frac{d\Lambda^{-3}}{dT}$$

$$S = -Nk_{\rm B}\ln z + zVk_{\rm B}\left[T\frac{d\Lambda^{-3}}{dT} + \Lambda^{-3}\right]$$

The first two of these relations can be combined into the well-known equation of state

$$PV = Nk_{\rm B}T.$$

Interestingly, this relation does not depend on Λ , so it holds for other, *uncoupled* systems too, such as a system consisting of indistinguishable harmonic oscillators.

In a solid, consisting of atoms vibrating around their eqilibrium position, the oscillators are *localised*. This has two important implications: first of all, they are distinguishable, and, secondly, the partition function of one such oscillator does not depend on the volume. This leads to the following form of the partition function:

$$Q_N(N,V,T) = (Q_1(T))^N$$

Writing

$$Q_1(T) \equiv \phi(T),$$

this leads straightfordly to

$$\mathscr{Z} = \sum_{N} z^{N} [\phi(T)]^{N} = \frac{1}{1 - z\phi(T)}.$$

We see that $z\phi(T)$ must be smaller than 1 in order for this sum to converge. From the partition sum the thermodynamic quantities can again be derived:

$$N = \frac{z\phi(T)}{1 - z\phi(T)};$$

$$U = \frac{zk_{\rm B}T^2\phi'(T)}{1 - z\phi(T)};$$

$$A = Nk_{\rm B}T\ln z + k_{\rm B}T\ln[1 - z\phi(T)];$$

$$S = -Nk_{\rm B}\ln z - k_{\rm B}\ln[1 - z\phi(T)] + \frac{zk_{\rm B}T\phi'(T)}{1 - z\phi(T)}.$$

Note that calculating the pressure for this system is nonsensical, as the grand partition function is independent of the volume (see Eq. (16) of Pathria, which you should forget as soon as possible). From the second of these equations, we see that

$$z\phi(T) = \frac{N}{1+N} \approx 1 - 1/N$$

for large N. This renders the other relations a bit simpler:

$$U/N = k_{\rm B}T^2\phi'(T)/\phi(T);$$

$$A/N = -k_{\rm B}T\ln\phi(T);$$

$$S/(Nk_{\rm B}) = \ln\phi(T) + T\phi'(T)/\phi(T)$$

For quantum harmonic oscillators, we have

$$\phi(T) = \sum_{n} e^{-\beta\hbar\omega(n+1/2)} = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} = \frac{1}{2\sinh(\beta\hbar\omega/2)}$$

For classical harmonic oscillators we have, on the other hand,

$$\phi = (\beta \hbar \omega)^{-1}$$

We now use these results in order to analyse the solid-vapour euqilibrium. Solid and vapour are in equilibrium when their chemical potentials are equal. For the gas, we have

$$z_g = \frac{N_g \Lambda^3}{V_g},$$

with Λ the de Broglie wavelength $h/\sqrt{2\pi m k_{\rm B}T}$.

For the solid, which we describe a system composed of many independent oscillators, we have

$$z_s = 1/\phi(T).$$

The equilibrium is achieved for a gas density

$$\frac{N_g}{V_g} = \frac{1}{\Lambda^3 \phi(T)}.$$

For low vapour density and high enough temperature, we therefore find

$$P = \frac{N_g}{V_g} k_{\rm B} T = \frac{1}{\Lambda^3 \phi(T)} k_{\rm B} T$$

which follows immediately from the ideal gas equation of state.

For 3D harmonic oscillators, we have

$$\phi(T) = [2\sinh(\hbar\omega/2k_{\rm B}T)]^{-3}$$

We have however not taken into account the fact that the energy at the equilibrium point of the harmonic oscillator describing an atom is *lower* than the energy of a gas atom: after all, the atom is bound to the solid, and we need a certain amount of energy to remove it from there and move it to the gas. As a result, we must include a factor $\exp(\beta\varepsilon)$ in the product $\phi(T)\Lambda^3$. We then arrive at an expression for the vapour pressure

$$P = k_{\rm B}T \left(\frac{2\pi m k_{\rm B}T}{h^2}\right)^{3/2} \left[2\sinh(\hbar\omega/2k_{\rm B}T)\right]^3 e^{-\beta\varepsilon}$$

We see that two parameters enter this equation: the energy difference ε and the frequency ω . These two parameters precisely determine shape and offset of the parabola's defining the energy felt by an atom in the solid.

Formulation of Quantum Statistics

Up to now, we have mainly considered classical statistical mechanics. Of course, sometimes we needed to take quantum mechanics into account in order to have well-behaved partition functions, where 'well-behaved' means in this context that entropy and (free) energies scale linearly with N, and also that integrals over phase space are dimensionless. Remember however that the density functions we have considered so far were essentially *classical*: we have derived Liouville's theorem from the classical (Hamilton) equations of motion, and inferred from that theorem that in equilibrium the density function depends on the Hamiltonian only: $\rho(q, p) = \rho[H(q, p)]$.

Now we shall consider statistical mechanics more strictly in the context of quantum mechanics. The analog of the density function now becomes the *density operator*. This operator can be useful when we do not know the actual state of the system, but only the set of possible states which the system can be in, together with the probability for the system to be in any of those states. The density operator is then

$$\hat{\boldsymbol{
ho}} = \sum_{i} p_i \ket{\psi_i} ra{\psi_i},$$

where p_i is the normalised probability for the system to be in state $|\psi_i\rangle$ ($\sum_i p_i \equiv 1$).

From the time-dependent Schrödinger equation

$$i\hbar \frac{\partial |\psi\rangle}{\partial t} = \hat{H} |\psi\rangle$$

and its Hermitian conjugate

$$-i\hbar\frac{\partial\left\langle |\psi|\right\rangle }{\partial t}=\langle\psi|\hat{H}$$

which hold for *any* state $|\psi\rangle$, we see that

$$i\hbar\frac{\partial\hat{\rho}}{\partial t} = i\hbar\sum_{i}p_{i}\left[\left(\frac{\partial}{\partial t}|\psi_{i}\rangle\right)\langle\psi_{i}| + |\psi_{i}\rangle\left(\frac{\partial}{\partial t}\langle\psi_{i}|\right)\right] = \sum_{i}p_{i}\left[\left(\hat{H}|\psi_{i}\rangle\right)\langle\psi_{i}| - |\psi_{i}\rangle\left(\langle\psi_{i}|\hat{H}\right)\right] = \hat{H}\hat{\rho} - \hat{\rho}\hat{H}.$$

From now on, we shall leave the hats from operators unless confusion may arise.

We see that we have an equation quite analogous to Liouville's theorem:

$$\dot{\rho} = \frac{\iota}{\hbar} [H, \rho].$$

This is called the *quantum Liouville theorem*. Just as in the classical case, we note that in equilibrium $\dot{\rho}$ must vanish. In case we have a stationary Hamiltonian (i.e. no explicit time dependence), we have $\rho = \rho(H)$.

We recall here that for any operator G, the expectation value is easily evaluated as

$$\langle G \rangle = \frac{\operatorname{Tr} \rho G}{\operatorname{Tr} \rho}.$$

Here, Tr is the *trace* operator. For any orthonormal basis $|\phi_n\rangle$, it is evaluated as

$$\operatorname{Tr} A = \sum_{n} \langle \phi_n | A | \phi_n \rangle.$$

In a finite-dimensional Hilbert space, the basis is finite, and the trace boils down to adding the diagonal elements of the matrix representation of the operator being traced.

Suppose we have an orthonormal basis set ϕ_n which forms a basis in our Hilbert space, Then we can express ρ with respect to this basis:

$$ho_{nm} = raket{\phi_n |
ho | \phi_m}$$
 .

This is the matrix representation. In a finite-dimensional Hilbert space, we therefore speak of the density *matrix* rather than an operator. In case we have a state $|\psi\rangle$ which can be expressed in this basis as

$$\left|\psi\right\rangle = \sum_{n} a_{n}(t) \left|\phi_{n}\right\rangle,$$

we have

The density matrix then reads

 $ho = \ket{\psi}ra{\psi}.$

$$\rho_{nm} = a_n(t)a_m^*(t).$$

In a many-particle system, the physical wavefunctions have coordinates $\mathbf{r}_1, \ldots, \mathbf{r}_N$. Also, spin degrees of freedom might be included. The wavefunction in general can therefore be written as $\psi(x_1, \ldots, x_N)$, where x_i is supposed to include all degrees of freedom of a single particle. Now suppose we have a complete set of basis states $\phi_n(x)$ (*n* might assume an infinite number of values, even continuum) for a single particle. Then a complete set of states for a system consisting of *N* particles is

$$\psi_{n_1,\ldots,n_N}(x_1,\ldots,x_N) = \phi_{n_1}(x_1)\phi_{n_2}(x_2)\ldots\phi_{n_N}(x_N).$$

A general state of the system is a linear combination of these basis states. In general, such a state is entangled.

5.1 Statistics of the various ensembles

Just as in the classical case, the density operator of a quantum system is given as

$$\rho = \delta [H - EI]$$

where *I* is the unit operator. In practice, we do not rigorously implement a delta-function, but instead, count the states in a narrow interval $(E, E + \Delta E)$. We can, instead of using the delta-function, also use the theta-function which is constant for all energies smaller than *E*, and zero for energies above *E*. As mentioned in the first chapter, it does not matter which representation we choose because, for large particle numbers, the dominant contributions to the entropy come from energies very close to *E* in the latter representation.

The entropy is given as

$$S = k_{\rm B} \ln \Gamma$$
,

where Γ is the number of states with energy in a narrow band $(E, E + \Delta E)$. In a basis of eigenstates of the Hamiltonian, the density matrix becomes diagonal:

$$\rho_{nn} = \begin{cases} 1/\Gamma & \text{ for } E_n < E; \\ 0 & \text{ for } E_n \ge E. \end{cases}$$

In the canonical ensemble, we have a density operator

$$\rho = Ce^{-\beta H}$$
.

If we express this operator with respect to an energy-basis, that is, an orthonormal basis of eigenfunctions of the Hamiltonian with eigenvalues E_n :

$$\rho_{mn} = C e^{-\beta E_n} \delta_{nm}$$

From this, the normalisation is easily found as

$$1/C = \operatorname{Tr} e^{-\beta \hat{H}} = \sum_{n} e^{-\beta E_n} = Q_N(T),$$

just as in the classical case.

The grand canonical ensemble is formulated using the *particle number operator* \hat{n} in addition to the Hamiltonian:

$$\rho = C e^{-\beta H + \beta \mu \hat{n}}$$

In most cases, the particle number operator commutes with the Hamiltonian. The grand canonical partition function is then found again as

$$1/C = \mathscr{Z}(\mu, V, T) = \sum_{N} e^{\beta \mu N} \sum_{s} e^{-\beta E_s} = \sum_{N} e^{\beta \mu N} Q_N(T).$$

5.2 Examples

5.2.1 Electron in a magnetic field

In order to practice the quantum formulation a bit, we calculate properties for some systems we have considered before in the classical context.

The first example is that of an electron in a magnetic field. We consider only the interaction of the magnetic moment with the magnetic field, and not the orbital degrees of freedom (i.e. the motion of the electron, perhaps in some potential). The calculation is most conveniently done in the canonical ensemble. Considering only a single spin, we have

$$H = -\mu_{\rm B}(\boldsymbol{\sigma} \cdot \mathbf{B}).$$

We work in the representation in which σ_z is diagonal. Then we can use the fact that the exponential of a diagonal operator is again a diagonal operator with the exponentials of its eigenvalues on the diagonal:

$$ho = rac{e^{-eta B \mu_{
m B} \sigma_z}}{{
m Tr}\,e^{-eta B \mu_{
m B} \sigma_z}} = rac{1}{e^{eta \mu_{
m B} B} + e^{-eta \mu_{
m B} B}} \left(egin{array}{c} e^{eta \mu_{
m B} B} & 0 \ 0 & e^{-eta \mu_{
m B} B} \end{array}
ight).$$

Then we obtain for the average expectation value of σ_z :

$$\langle \sigma_z \rangle = \operatorname{Tr} (\rho \sigma_z) = \frac{e^{\beta \mu_{\mathrm{B}} B} - e^{-\beta \mu_{\mathrm{B}} B}}{e^{\beta \mu_{\mathrm{B}} B} + e^{-\beta \mu_{\mathrm{B}} B}} = \tanh(\beta \mu_{\mathrm{B}} B).$$

A comparison with sections 3.9 and 3.10 shows that these results are correct.

5.2.2 Free particle in a box

We now consider a free particle in a box, governed by the Hamiltonian

$$H = \sum_{i} \frac{\mathbf{p}_i^2}{2m}.$$

Inside the cubic box of size L in which the particles move, the potential is zero; outside, we assume periodic boundary conditions. The eigenfunctions which are compliant with these boundary conditions are

$$\psi(\mathbf{r}) = \left(\frac{1}{L}\right)^{3/2} e^{i(k_x x + k_y y + k_z z)},$$

with $\mathbf{k} = 2\pi/L(n_x, n_y, n_z)$. The corresponding energies are

$$E(k) = \frac{\hbar k^2}{2m}.$$

We must choose a basis of the Hilbert space in order to evaluate the trace. First we choose as a basis the eigenfunctions which we denote as $|\mathbf{k}\rangle$:

$$\left\langle \mathbf{k} \left| e^{-\beta H} \right| \mathbf{k}' \right\rangle = e^{-\hbar^2 k^2 / (2mk_{\rm B}T)} \delta(\mathbf{k} - \mathbf{k}'),$$

so that the partition function becomes

$$Q_T = \operatorname{Tr} \left(e^{-\beta H} \right) = \sum_{\mathbf{k}} \left\langle \mathbf{k} \left| e^{-H/(k_{\mathrm{B}}T)} \right| \mathbf{k}' \right\rangle = \sum_{\mathbf{k}} e^{-\beta \hbar^2 k^2 / (2m)} \approx \frac{L^3}{(2\pi)^3} \int d^3 k \ e^{-\beta \hbar^2 k^2 / 2m} = V \left(\frac{m}{2\pi \beta \hbar^2} \right)^{3/2}.$$

That the transition from the sum to the integral requires an extra factor $L^3/(2\pi)^3$ can be seen as follows. On the grid of *k*-values, the volume occupied by a *k*-point is $(2\pi/L)^3$. The sum runs over the points in a certain volume. This is then equal to that volume (i.e. $\int d^3k$) divided by the volume per point.

It is instructive to derive the same partition function using the **r**-representation:

$$\begin{split} \left\langle \mathbf{r} \left| e^{-\beta H} \right| \mathbf{r}' \right\rangle &= \frac{1}{L^3} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot (\mathbf{r}' - \mathbf{r})} e^{-\hbar^2 k^2 / (2mk_{\rm B}T)} \\ &\approx \frac{1}{(2\pi)^3} \int d^3 k \; e^{i\mathbf{k} \cdot (\mathbf{r}' - \mathbf{r})} e^{-\hbar^2 k^2 / (2mk_{\rm B}T)} \\ &= \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2} \exp\left(-\frac{m}{2\beta\hbar^2} \left| \mathbf{r} - \mathbf{r}' \right|^2 \right). \end{split}$$
The Fourier integral will be discussed in the exercises. Using this, the partition function can be evaluated as $(1 + 1)^{3/2}$

$$Q_1(T) = \int \left\langle \mathbf{r} \left| e^{-\beta H} \right| \mathbf{r} \right\rangle d^3 r = V \left(\frac{m}{2\pi\beta\hbar^2} \right)^3$$

which is obviously the same as the one found above.

The quantity $\langle \mathbf{r} | \rho | \mathbf{r} \rangle$ which occurs in these expressions (remember $\rho = \exp(-\beta H)$) represents the probability density of finding the particle at position \mathbf{r} . Because we have periodic boundary conditions, this must not depend on \mathbf{r} , as we have found. On the other hand, the expression $\langle \mathbf{r} | \rho | \mathbf{r}' \rangle$ gives the probability that a particle suddenly moves from \mathbf{r} to \mathbf{r}' as a result of a thermal fluctuation.

Let us evaluate the expectation value of the energy. This is most easily evaluated in the \mathbf{k} -representation:

$$\langle H \rangle = \frac{\text{Tr} (He^{-\beta H})}{\text{Tr} (e^{-\beta H})} = \frac{1}{Q_1} \frac{V}{(2\pi)^3} \int \frac{\hbar^2 k^2}{2m} e^{-\hbar^2 k^2 / (2mk_{\rm B}T)} d^3 k = \frac{3}{2} k_{\rm B} T,$$

that is, equipartition is satisfied. We could also use

$$\langle H \rangle = -\frac{\partial \ln \operatorname{Tr} \left(e^{-\beta H} \right)}{\partial \beta}$$

which leads to the same result.

One might ask how general the equipartition theorem is. We have seen in the case of the quantum harmonic oscillator (see exercises and the next section) that the equipartition theorem does no longer hold for $k_{\rm B}T \stackrel{<}{\sim} \hbar \omega$. In order to check whether this theorem still holds for the kinetic energy only, we must evaluate

$$\langle T \rangle = \frac{\operatorname{Tr} \left[T e^{-\beta(T+V)} \right]}{\operatorname{Tr} \left[e^{-\beta(T+V)} \right]}.$$

The contributions from $\exp(-\beta V)$ in numerator and denominator do no longer cancel, as a result of the fact that *T* and *V* do not commute. Therefore, the equipartition theorem no longer holds in the quantum case.

5.3 Systems composed of indistinguishable particles

To fix the ideas, we start by considering the noninteracting case. Then, the Hamiltonian has the form

$$H = \sum_{n=1}^{N} H_n$$

where H_n only acts on the coordinates of particle *n*. The coordinates of the particles are denoted by

$$q=(q_1,q_2,\ldots,),$$

where q_n denotes the coordinate(s) of particle *n*. The eigenstates of the Hamiltonian then have the form

$$\psi_{\mathrm{E}}(q) = \prod_{n=1}^{N} u_n(q_n),$$

where

$$H_n u_n = \varepsilon_n u_n.$$

The total energy is given as

$$E=\sum_{n=1}^N \varepsilon_n.$$

Note that *n* denotes a particle, not a particular energy level. Now suppose that the particles are identical – in that case, the form of the Hamiltonians, and their spectra should be identical. Now suppose that we have *N* particles with energy *E*. As each of the particles occupues energies of the same spectrum, there might be more than one particle in the one state with energy ε_i . We must have:

$$N = \sum_{i} n_{i},$$
$$E = \sum_{i} \varepsilon_{i}.$$

The states can then be written as

$$\Psi_{\rm E}(q) = \prod_{m=1}^{n_1} u_1(q_m) \prod_{m=1}^{n_2} u_2(q_m) \dots$$

Now, if the particles are *identical*, we know that a permutation of them leaves the total Hamiltonian invariant. If this is the case, the Hamiltonian commutes with the permutation operator:

PH = HP.

If an operator commutes with the Hamiltonian, it must be possible to construct the eigenstates of the Hamiltonian in such a way, that they are simultaneously eigenstates of that operator. You might recall from your mathematics course that any permutation can be written as a product of particle exchanges (a particle exchange means that we exchange a particle pair, *i*, *j*, say). Let us call $P_{i,j}$ a particle exchange for the pair *i*, *j*. We obviously have $P_{i,j}^2 = 1$. Then also the eigenvalues λ of $P_{i,j}$ should satisfy $\lambda^2 = 1$. As we furthermore know that, since $P_{i,j}$ is Hermitian, λ is real, we must have $\lambda = \pm 1$. We see that the particle wavefunctions are either symmetric under particle exchange ($\lambda = 1$) of antisymmetric ($\lambda = -1$). It turns out that for a particular kind of particles, we have either one or the other possibility. Particles whose wavefunction is symmetric with respect to exchange, are called *bosons*; those which have antisymmetric wavefunctions are called *fermions*.

The fact that any permutation operator can be written as a product of exchanges, leads to the conclusion that always

$$P\psi_E = \pm \psi_E.$$

This notion directly leads to the conclusion that the microstates are invariant with respect to any permutation of the particles. Therefore, the numbers n_i , which tell us how many particles can be found in state *i*, define a microstate uniquely, and additional correction factors for proper counting should not be included in sums over the states.

Even if the particles interact, we can use the same representation (although the u_i are no longer eigenstates of single-particle Hamiltonians). The reason why interaction does not matter is that the products of single particle states form a basis of the Hilbert space for many particles, whether they interact or not.

Finally we note that, for fermions, we can construct wavefunctions constructed from singleparticle states u_i as follows:

$$\psi(q) = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_i(q_1) & u_i(q_2) & \dots & u_i(q_N) \\ u_j(q_1) & u_j(q_2) & \dots & u_j(q_N) \\ \vdots & \vdots & \ddots & \vdots \\ u_l(q_1) & u_l(q_2) & \dots & u_l(q_N) \end{vmatrix}$$

where the vertical bars |...| denote a determinant. This wavefunction is called a *Slater determinant*. The prefactor follows automatically from the normalisation condition (the u_i are considered to be normalised). In the case of Bosons, we have a similar expression, but the minus-signs in evaluating the determinant all turn into plus-signs.

Another way of writing the wavefunction is

$$\psi(q_1,\ldots,q_N)=\sum_P \delta^{[P]}Pu_i(q_1)u_j(q_2)\cdots u_l(q_N),$$

where \sum_{P} denotes a sum over *all possible* permutations, $\delta = 1$ for bosons and -1 for fermions and [P] is the sign of the permutation. The sign of the permutation is determined as the number of exchange operations it is composed of. Note that the permutation operator acts on the *arguments* q_n of the wavefunctions only, not on the labels i, j, \ldots Note that this state is not normalised in the case of bosons:

$$\langle \psi | \psi \rangle = n_1! n_2! \cdots$$

where n_1 etcetera are the occupation numbers of the different states. To see that this factor occurs indeed in the normalisation, look at a system consisting of two bosons, both in the same state u:

$$\psi = \frac{1}{\sqrt{N!}} [u(q_1)u(q_2) + u(q_2)u(q_1)] = \sqrt{2}u(q_1)u(q_2)$$

We see that the norm of this state is 2! = 2. For fermions we do not have this problem, as no two particles can be in the same state.

5.4 The density matrix and the partition function of a system of free particles

We know the wavefunctions already for a single particle (see section 5.3):

$$u_{\mathbf{k}}(q) = \frac{1}{L^{3/2}} e^{i\mathbf{k}\cdot\mathbf{r}}.$$

With the above definition of a many-particle basis function, we must therefore evaluate

$$\langle \mathbf{k}_1, \ldots, \mathbf{k}_N | \exp(-\beta H) | \mathbf{k}'_1, \ldots, \mathbf{k}'_N \rangle$$

where the states $|\mathbf{k}'_1, \dots \mathbf{k}'_N\rangle$ are (anti)symmetrised states.

In order to evaluate this equation we note the following:

- On the left hand side and on the right hand side, we have actually a sum over all permutations.
- For a particular permutation for *different* \mathbf{k}_i on the left hand side, the operator $\exp(-\beta H)$ in the middle forces the states on the right hand side to correspond in a one-to-one fashion to those on the left hand side.
- The normalising prefactors $1/\sqrt{N!}$ on the left and right hand side yield a factor 1/N!.

Combining all these considerations, we see that

$$\left\langle \mathbf{k}_{1},\ldots,\mathbf{k}_{N}\left|\exp(-\beta H)\right|\mathbf{k}_{1}^{\prime},\ldots,\mathbf{k}_{N}^{\prime}\right\rangle = e^{-\hbar^{2}(k_{1}^{2}+\cdots+k_{N}^{2})/(2mk_{\mathrm{B}}T)}\prod_{i=1}^{N}\delta(\mathbf{k}_{i}-\mathbf{k}_{i}^{\prime})$$

where the normalisation factor $n_1!n_2!...$ of the Slater determinant has already be divided out in order to work with normalised states. This factor amounts to 1 if all \mathbf{k}_i are different.

When taking the trace, we must sum over a state $\mathbf{k}_1, \ldots, \mathbf{k}_N$. Note that this sum must include a restriction such that for the set of permutations of the quantum numbers $\mathbf{k}_1, \ldots, \mathbf{k}_N$ only one member is chosen, otherwise we are overcounting. But we can relax any such restriction provided we divide by the number of possible permutations

$$\frac{N!}{n_1! \cdot n_2! \cdots}$$

Therefore we have as the final result

$$Q_N = \frac{1}{N!} \frac{L^{3N}}{(2\pi)^3} \left\{ \int \exp\left[-\hbar^2 k^2 / (2mk_{\rm B}T)\right] d^3k \right\}^N = \frac{1}{N!} \left(\frac{V}{\Lambda^3}\right)^N.$$

We see that we have obtained the correct expression of the partition function. Note that we have been sloppy in this calculation: if all **k** would be different, the result would be correct. But by integrating over all possile combinations $\mathbf{k}_1, \ldots, \mathbf{k}_N$, we have included the cases where two **k**'s are the same. If there is such overlap, the 3*N*-dimensional integral no longer factorises into *N* three-dimensional integrals. It turns out that the correction turns out to be very small when $V^{1/3} \gg \Lambda$: then for the vast majority of configurations, no two **k**'s overlap.

Obviously, we could have evaluated this partition function using the coordinate (\mathbf{r}) basis rather than the **k**-basis. The book uses this representation, but the calculation is more difficult. We shall work out here the example of a two-particle system. We first evaluate

$$\left\langle \mathbf{r}_{1},\mathbf{r}_{2}\left|e^{-\beta H}\right|\mathbf{r}_{1},\mathbf{r}_{2}\right\rangle = \frac{1}{2}\frac{L^{6}}{(2\pi)^{6}}\int\left\{1\pm\cos\left[\left(\mathbf{k}_{1}-\mathbf{k}_{2}\right)\cdot\left(\mathbf{r}_{1}-\mathbf{r}_{2}\right)\right]\right\}e^{-\beta\hbar^{2}\left(k_{1}^{2}+k_{2}^{2}\right)/(2m)}d^{3}k_{1}d^{3}k_{2}.$$

In this expression, the first term is the one where the particles are both on the left and right hand side of the matrix element in the same state (both either \mathbf{k}_1 or \mathbf{k}_2), and the second term corresponds to different states on the left and right hand side of the matrix element – the + sign is for bosons, the – for fermions. Evaluating the integrals we obtain

$$\left\langle \mathbf{r}_{1},\mathbf{r}_{2}\left|e^{-\beta H}\right|\mathbf{r}_{1},\mathbf{r}_{2}\right\rangle =\frac{1}{2\Lambda^{6}}\left[1\pm\exp(-2\pi(r_{12}/\Lambda)^{2})\right].$$

Taking the trace means that we must integrate over \mathbf{r}_1 and \mathbf{r}_2 :

$$Q_2 = \frac{1}{2\lambda^6} \int \left[1 + \exp(-2\pi (r_{12}/\Lambda)^2) \right] d^3 r_1 d^3 r_2 = \frac{1}{2} \left(\frac{V}{\Lambda^3} \right)^2 \left[1 \pm \frac{1}{2^{3/2}} \left(\frac{\Lambda^3}{V} \right) \right].$$

We see that the result reduces to the correct partition function for the case where $\Lambda \ll V^{1/3} = L$. The probability density for the particles to be at \mathbf{r}_1 and \mathbf{r}_2 can be considered for the boson- end fermi case. We define the *statistical potential* $v_s(r)$ as

$$e^{-\beta v_s(r_{12})} = \rho(\mathbf{r}_1, \mathbf{r}_2).$$

The statistical potential is shown in figure 5.1. We see that the potential has the correct behaviour in the sense that it prevents fermi particles to come close, and favours bose particles to come close.

It is instructive to repeat the calculation for the two-particle partition function in terms of the **k** basis. For bosons, we have a possible state for each combination $\mathbf{k}_1, \mathbf{k}_2$. In this case, for $\mathbf{k}_1 \neq \mathbf{k}_2$ the wavefunction is:

$$\psi = \frac{1}{\sqrt{2}} \left(\psi_{\mathbf{k}_1}(1) \psi_{\mathbf{k}_2}(2) + \psi_{\mathbf{k}_1}(2) \psi_{\mathbf{k}_2}(1) \right).$$



Figure 5.1: Statistical two-particle potential for bose (solid line) and fermi (dashed line) systems.

For $\mathbf{k}_1 = \mathbf{k}_2$, the wavefunction is:

$$\boldsymbol{\psi} = \boldsymbol{\psi}_{\mathbf{k}_1}(1)\boldsymbol{\psi}_{\mathbf{k}_1}(2).$$

Note that the two expressions differ by a factor $\sqrt{2}$.

For fermions, we have a possible state only when $\mathbf{k}_1 \neq \mathbf{k}_2$:

$$\psi = \frac{1}{\sqrt{2}} \left(\psi_{\mathbf{k}_1}(1) \psi_{\mathbf{k}_2}(2) - \psi_{\mathbf{k}_1}(2) \psi_{\mathbf{k}_2}(1) \right).$$

If we calculate the partition function, we must integrate over \mathbf{k}_1 and \mathbf{k}_2 , but we see that we must single out the contributions for $\mathbf{k}_1 = \mathbf{k}_2$. In general, for an operator *A* which is *diagonal* in phase space we have

$$\operatorname{Tr} A = \frac{1}{2} \left(\frac{V}{(2\pi)^3} \right)^2 \int A(\mathbf{k}_1, \mathbf{k}_2) d^3 k_1 d^3 k_2 \pm \frac{1}{2} \frac{V}{(2\pi)^3} \int A(\mathbf{k}, \mathbf{k}) d^3 k.$$

For the trace, this results in

$$\operatorname{Tr} e^{-\beta H} = \frac{1}{2} \left(\frac{V}{(2\pi)^3} \right)^2 \left(\frac{2\pi m k_{\mathrm{B}} T}{\hbar^2} \right)^3 \pm \frac{1}{2} \frac{V}{(2\pi)^3} \left(\frac{\pi m k_{\mathrm{B}} T}{\hbar^2} \right)^{3/2} = \frac{1}{2} \left(\frac{V}{(2\pi)^3} \right)^2 \left(\frac{2\pi m k_{\mathrm{B}} T}{\hbar^2} \right)^3 \left[1 \pm \frac{1}{2^{3/2}} \frac{\Lambda^3}{V} \right]$$

6

The theory of simple gases

In the last chapter we have laid the foundations for quantum statistical mechanics. Let us summarise the most important results here. A quantum state of a collection of identical particles is a fully antisymmetric (for fermions) or symmetric (bosons) many-particle state. Such a state can be constructed from single-particle states by a Slater determinant (in the case of fermions) or a symmetrised linear combination of products of single-particle states (bosons). In this chapter we shall work out further the case of non-interacting particles for which the partition functions usually factorise, thereby rendering a full analytic solution feasible.

6.1 An ideal gas in other quantum-mechanical ensembles – occupation numbers

Quantum states for ideal gases are *fully* characterised by specifying *how many particles there are in each available state*. From this it follows that, if we have a set of single-particle quantum states $|i\rangle$, the many-particle state is specified by the numbers n_i of particles in each such state. If we have N particles, we must have

$$\sum_{i} n_i = N.$$

If the single-particle states are eigenstates of the single particle Hamiltonian with energies ε_i , we can evaluate the energy of the system to be

$$E = \sum_{i} n_i \varepsilon_i.$$

The number of single-particle products in such a state is

$$\frac{N!}{n_1! \cdot n_2! \cdots}$$

In any sum over all the eigenstates, each set $(n_1, n_2, ...)$ should be counted *only once*.

In Maxwell-Boltzmann counting, we sum over all possible configurations for *distinguishable* particles and then divide by N! Therefore, the effective weight with which we take the configuration $(n_1, n_2, ...)$ into account is

$$g(n_1, n_2, \ldots) = \frac{1}{n_1! \cdot n_2! \cdots}$$

instead of the correct factor g = 1 which is taken into account in Bose-Einstein counting. The two are equivalent only if each state contains at most one particle, which occurs at high enough temperature and large enouh volume.

The canonical partition function can be evaluated as

$$Q(N,T) = \sum_{\{n_i\}}' g(n_1, n_2, \ldots) e^{-\beta \sum_i \varepsilon_i n_i}$$

where $\sum_{\{n_i\}}'$ denotes a sum over all configurations $(n_1, n_2, ...)$ with $\sum_i n_i = N$. Because of this last restriction, it is not easy to evaluate this partition function. Note that for Bose-Einstein (BE) and Fermi-Dirac (FD) statistics, the weight factor g = 1, and that for Maxwell-Boltzman statistics $g = 1/(n_1! \cdot n_2! \cdots)$.

In order to proceed, we look at the grand canonical partition function, where the restriction $\sum_i n_i = N$ does not come into play:

$$\mathscr{Z}(\mu,T) = \sum_{\{n_i\}} g(n_1,n_2,\ldots) e^{\beta \sum_i (\mu-\varepsilon_i)n_i}.$$

The nice property of this partition function is that it factorises into a product of sums over n_i . In the case of BE statistics:

$$\mathscr{Z}(\mu,T) = \sum_{n_1=0}^{\infty} e^{\beta(\mu-\varepsilon_1)n_1} \sum_{n_2=0}^{\infty} e^{\beta(\mu-\varepsilon_2)n_2} \cdots$$

Each of the factors is a geometric series which can be evaluated analytically:

$$\sum_{n=0}^{\infty} e^{\beta(\mu-\varepsilon)n} = \frac{1}{1-e^{\beta(\mu-\varepsilon)}}$$

Note, however, that in order for the grand canonical partition function to be well-defined, it is necessary that $\mu < \varepsilon_0$, where ε_0 is the ground state energy.

For FD statistics, the situation is even simpler: each of the n_i only assumes the values 0 or 1.

$$\sum_{n=0}^{1} e^{\beta(\mu-\varepsilon)n} = 1 + e^{\beta(\mu-\varepsilon)}$$

For Maxwell-Boltzmann counting, with $1/(n_1! \cdot n_2! \cdots)$, the factors are identified as the power series expansions of the exponential function:

$$\sum_{n=0}^{\infty} \frac{1}{n!} e^{\beta(\mu-\varepsilon)n} = \exp\left[e^{\beta(\mu-\varepsilon)}\right].$$

It is also possible to evaluate the average occupations of the levels. For Bose-Einstein statistics, we obtain:

$$\langle n_i \rangle = \frac{\sum_{n_1=0}^{\infty} e^{\beta(\mu-\varepsilon_1)n_1} \cdots \sum_{n_i=0}^{\infty} n_i e^{\beta(\mu-\varepsilon_i)n_i} \cdots}{\sum_{n_1=0}^{\infty} e^{\beta(\mu-\varepsilon_1)n_1} \cdots \sum_{n_i=0}^{\infty} e^{\beta(\mu-\varepsilon_i)n_i} \cdots}.$$

All factors in the numerator and the denominator are identical, except for the *i*-th factor, which yields:

$$\langle n_i \rangle = rac{\sum_{n_i=0}^{\infty} n_i e^{eta(\mu - \varepsilon_i)n_i}}{\sum_{n_i=0}^{\infty} e^{eta(\mu - \varepsilon_i)n_i}}$$

This can be evaluated as

$$\langle n_i \rangle = \frac{\partial}{\partial \beta(\mu - \varepsilon_i)} \ln \left[\frac{1}{1 - e^{\beta(\mu - \varepsilon_i)}} \right] = \frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1}.$$

This is the famous Bose-Einstein distribution function.

For Fermi-Dirac statistics, we obtain

$$\langle n_i
angle = rac{\partial}{\partial eta(\mu - arepsilon_i)} \ln \left[1 + e^{eta(\mu - arepsilon_i)}
ight] = rac{1}{e^{eta(arepsilon_i - \mu)} + 1}.$$



Figure 6.1: Bose-Einstein, Fermi-Dirac and Maxwell-Boltzmann distribution functions.

Finally, for Maxwell-Boltzmann counting, we have, not really surprisingly:

$$\langle n_i \rangle = \frac{\partial}{\partial \beta(\mu - \varepsilon_i)} \ln \left[\exp \left(e^{\beta(\mu - \varepsilon_i)} \right) \right] = e^{\beta(\mu - \varepsilon_i)}$$

In figure 6.1 we show the different distribution functions.

6.2 Examples: gaseous systems composed of molecules with internal motion

Consider a gas consisting of molecules with internal degrees of freedom. These can include electronic or nuclear spin, and vibrational or rotational motions of the nuclei. We neglect the interaction between different molecules, which is justified in the gas phase when their mutual separations are on average very large. We furthermore suppose that the thermal wavelength is much smaller than the system size, so that Boltzmann counting is justified.

In the usual way, we may factorise the partition function into partition functions of the individual molecules:

$$Q(N,T,V) = \frac{1}{N!} \left[Q(1,T,V) \right]^N$$

where the single-molecule partition function has the form:

$$Q(1,T,V) = V\left(\frac{2\pi mk_{\rm B}T}{h^2}\right)^{3/2} j(T)$$

To obtain this expression, it is necessary to split up the degrees of freedom: we consider the centre of mass coordinates separately from the internal degrees of freedom. The centre of mass coordinates of the molecules yield the free, ideal gas partition function, whereas the internal degrees of freedom generate the internal, molecular partition function j(T):

$$j(T) = \sum_{i} g_i e^{-\varepsilon_i/(k_{\rm B}T)}.$$

The factor g_i is the multiplicity (degeneracy) of the state *i*. We do not have to include the counting factor $1/n_1!$ since $n_1 \le 1$ in the regime considered.

For these systems,

$$P = -\frac{\partial A}{\partial V} = \frac{Nk_{\rm B}T}{V}.$$

Note that j(T) does not contribute to the pressure, as does not depend on the volume (which is natural, since j(T) includes only *internal* degrees of freedom). The energy can be evaluated as

$$E = \frac{3}{2}Nk_{\rm B}T + E_{\rm int},$$

where

$$E_{\rm int} = Nk_{\rm B}T^2 \frac{\partial}{\partial T} \ln j(T).$$

Also the specific heat at constant volume can be evaluated as

$$C_V = \frac{3}{2}Nk_{\rm B} + \frac{dE_{\rm int}}{dT}$$

Using $PV = Nk_{\rm B}T$, we obtain for the specific heat at constant pressure:

$$C_P = \left(\frac{\partial(E+PV)}{\partial T}\right)_{N,P} = \frac{5}{2}Nk_{\rm B} + \frac{dE_{\rm int}}{dT},$$

where we have again used the fact that the internal degrees of freedom do not depend on V.

Other quantities which can be evaluated are the chemical potential and the entropy:

$$S = S_{\text{ideal}} + Nk_{\text{B}} \left(\ln j + T \frac{\partial}{\partial T} \ln j \right);$$
$$\mu = \mu_{\text{ideal}} - k_{\text{B}} T \ln j.$$

We see that j always influences the values of these two quantities, whereas those of the energy and of the specific heat are determined only by the temperature-dependence of j.

Let us, as en example, consider a monatomic gas for which the electrons *or* the nuclei have spin *S*. We have

$$j = 2S + 1.$$

The spin does not influence the energy (if we neglect the (hyper)fine structure) and only the chemical potential and entropy are affected by the spin.

If on the other hand, the electron has orbital angular momentum in addition to its spin, then there is fine structure splitting. From quantum mechanics, we know that the fine structure energy correction is determined by the value of the quantum number J, which is the value of the total angular momentum. Calling the energy levels ε_J , we have

$$j = \sum_{J} (2J+1)e^{-\beta \varepsilon_J}$$

Diatomic molecules consist of two atoms. We then have additional degrees of freedom: two related to rotations and one to vibrations. We first consider the vibrations along the axis connecting the nuclei. As the atomic bonds are relatively stiff, the corresponding frequency is high: in fact the distance between the vibrational levels, $\hbar\omega$, is of the order of 10^3 K, which means that these vibrations can only be seen for temperatures of that order. We have already evaluated the partition function of the harmonic oscillator. It turned out that for $T \gg \hbar\omega$ the system satisfies equipartition, leading to

a constant specific heat, and that the specific heat for small temperatures decays to zero. The full behaviour is given by

$$C_V = Nk_{\rm B}(\beta\hbar\omega) \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

The temperature $\hbar \omega / k_{\rm B}$ is often denoted as $\theta_{\rm v}$: it is the temperature where the vibrations become noticeable in the specific heat.

A diatomic molecule can be considered as a 'rigid' rotator if we neglect the coupling between vibrations and rotations. The quantum mechanical energies for a rigid rotator are given as

$$E_l = \frac{\hbar^2 l(l+1)}{2I}$$

where I is the moment of inertia perpendicular to the molecular axis. Again we can define the temperature where rotations become important. This is

$$\theta_{\rm r} = \frac{\hbar^2}{2Ik_{\rm B}}.$$

This temperature is in general much lower than the vibrational temperature. The partition function for the rotations is

$$j_{\rm r} = \sum_{l=0}^{\infty} (2l+1) \exp\left[-\theta_{\rm r} l(l+1)/T\right].$$

For low temperatures, only the first few terms will contribute significantly to the partition function:

$$j_{\rm r}({\rm low} \ T) \approx 1 + 3e^{-2\theta_{\rm r}/T} + 5e^{-6\theta_{\rm r}/T} + \cdots$$

For high temperatures, the sum can be replaced by an integration:

$$j_{\rm r}({\rm high } T) \approx \int (2l+1) \exp\left[-\theta_{\rm r} l(l+1)/T\right] dl = \frac{T}{\theta_{\rm r}}$$

This results in a contribution $Nk_{\rm B}$ to the specific heat.

In summary we can say that

- At all temperatures, we see the effect of spin degeneracy in the entropy and the chemical potential.
- For low temperatures, fine structure effects may become noticeable in the specific heat.
- For high enough temperatures, first the rotational freedom will affect the specific heat.
- For even higher temperatures, the vibrational degrees of freedom will become noticeable.

If we disregard fine structure, we see that for $T < \theta_r, \theta_v$, we have

$$C_{V} = \frac{3}{2}Nk_{\rm B}, \text{ for } T \ll \theta_{\rm r}, \theta_{\rm v},$$

$$C_{V} = \frac{5}{2}Nk_{\rm B}, \text{ for } \theta_{\rm r} \ll k_{\rm B}T \ll \theta_{\rm v},$$

$$C_{V} = \frac{7}{2}Nk_{\rm B}, \text{ for } T \gg \theta_{\rm r}, \theta_{\rm v}.$$

7

Examples of quantum statistics

Quantum statistics involves either Bose–Einstein or Fermi–Dirac counting in the evaluation of physical quantities. Examples have been covered extensively in the statistical physics course of the third year (G. Bauer). Therefore, we restrict ourselves here to a brief review of the major applications.

7.1 Thermodynamics of free quantum gases

As we have seen in the exercises, we can write

$$\frac{N\lambda^3}{V} = \frac{1}{\pi^{3/2}} \int d^3x \, \frac{1}{e^{x^2 - \beta\mu} \pm 1},$$

where the + sign corresponds to Fermi, and the - sign to Bose statistics. Furthermore

$$\lambda = rac{h}{\sqrt{2\pi m k_{
m B}T}}.$$

In the classical limit for which μ is strongly negative, this leads to

$$n\lambda^3 = e^{\beta\mu} \mp \frac{1}{2^{3/2}} e^{2\beta\mu} + \cdots$$

This equation shows that when we keep the density fixed, strongly negative μ corresponds to high temperatures.

For the pressure, we have the expression

$$\frac{P}{k_{\rm B}T} = \frac{1}{V}\ln \mathscr{Z} = \pm \frac{1}{\lambda^3 \pi^{3/2}} \int d^3x \, \ln\left(1 \pm e^{-x^2 + \beta\mu}\right),$$

where the + sign is for fermions, and the - sign for bosons. In the classical limit, $e^{-x^2+\beta\mu} \ll 1$, this yields, after expanding to second order in $\exp(\beta\mu)$:

$$\frac{P}{k_{\rm B}T} = \frac{1}{\lambda^3 \pi^{3/2}} \left[\int d^3 x \, e^{-x^2} e^{\beta \mu} \mp e^{2\beta \mu} \int d^3 x \, e^{-2x^2} \right] = \frac{1}{\lambda^3} \left(e^{\beta \mu} \mp \frac{1}{2^{5/2}} e^{2\beta \mu} \right).$$

If we now substitute $e^{\beta\mu}$ by the expansion obtained above, we see that

$$P = nk_{\rm B}T\left(1\pm 2^{-5/2}n\lambda^3\right)$$

The first term is the classical results; the second term gives the quantum correction. For Fermions we have the plus-sign, which indicates that the particles seem to repel each other as a result of the Pauli principle. For Bosons (minus-sign) the pressure becomes smaller, indicating an effective attraction.

Finally we can derive the entropy:

$$S = -\left(\frac{\partial k_{\rm B}T\ln \mathscr{Z}}{\partial T}\right)_{\mu,V} = V\left(\frac{\partial P}{\partial T}\right)_{\mu,V}$$

Now we copy the lowest order term in the expansion found above for the pressure *P*:

$$S = V \frac{\partial}{\partial T} \left[(k_{\rm B}T)^{5/2} \left(\frac{m}{2\pi\hbar^2} \right)^{3/2} e^{\beta\mu} \right]$$
$$= \frac{V}{\lambda^3} e^{\beta\mu} \left[\frac{5}{2} k_{\rm B} - \frac{\mu}{T} \right].$$

Combining this with the classical relation $e^{\beta\mu} = n\lambda^3$ gives

$$S = Nk_{\rm B} \left[\frac{5}{2} + \ln(\lambda^3/n)\right],$$

which, for $\lambda = \sqrt{h^2/(2\pi m k_B T)}$ and $E/N = 3k_B T/2$ can be written in the form:

$$S = Nk_{\rm B} \left[\frac{3}{2} \ln \frac{E}{N} + \ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{4\pi m}{3h^2} \right) + 5/2 \right].$$

This is again the Sackur–Tetrode formula for the entropy of an ideal gas. The quantum corrections can be evaluated analogous to the case of the pressure. The result is

$$S = S_{\text{Class}} \pm \frac{1}{8\sqrt{2}} \lambda^3 N k_{\text{B}}.$$

7.2 Bose-Einstein systems

7.2.1 Planck distribution

Take an empty box in contact with a reservoir of temperature *T*. The reservoir can interact with the box by emitting electromagnetic (EM) field waves into it. In quantum language we say that photons can travel into the box. The photons carry energy $\hbar \omega$, with $\omega = c |\mathbf{k}|$. Which \mathbf{k} vectors are accessible is determined by the shape of the box. If we take a cube of size $L \times L \times L$, the \mathbf{k} vectors are $2\pi/L(n_x, n_y, n_z)$ with N_i integer. From the quantum theory of the elactromagnetic field, it follows that the photons are created and annihilated freely, so that there number cannot be controlled by a chemical potential. Creating a new photon in particular does not involve any cost except for its energy, so $\mu = 0$. Therefore, the number of modes available at frequency ω is given by

$$N(k)dk = 2 \cdot 4\pi k^2 dk L^3 / (2\pi)^3 = V \frac{\omega^2 d\omega}{c^3 \pi^2}.$$

In this expression, the factor of 2 arises from the fact that there are two transverse modes (only transverse modes are allowed by Maxwell's equations), and we have divided the volume of the spherical shell with thickness dk in **k**-space by the volume $(2\pi/L)^3$ of each **k**-point, and used $\omega = ck$. Now we use the fact that the photons are bosons (they are spin-1 particles) and we have for the energy radiated at frequencies between ω and $\omega + d\omega$:

$$u(\omega)d\omega = n(\omega)\hbar\omega d\omega = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3 d\omega}{e^{\hbar\omega/k_{\rm B}T} - 1}.$$

where the BE distribution is recognised, multiplied by the energy of the mode and the occupancy.



Figure 7.1: The Bose–Einstein function g.

7.2.2 Bose–Einstein condensation

The BE distribution is well defined only for values of μ below the ground state energy – otherwise, the occupancy becomes negative. Let us, for such an acceptable μ , evaluate the number of particles as a function of μ :

$$N = \sum_{\mathbf{k}} \frac{1}{e^{\beta(\hbar^2 k^2/(2m) - \mu)} - 1} \approx \frac{V}{(2\pi)^3} \int \frac{1}{e^{\beta(\hbar^2 k^2/(2m) - \mu)} - 1} 4\pi k^2 dk.$$

Reparametrising $\hbar^2 k^2/(2mk_BT)$, we obtain for the particle density

$$n\lambda^3 = \frac{4}{\sqrt{\pi}} \int_0^\infty \frac{x^2}{e^{x^2 - \beta\mu} - 1} dx \equiv g(\beta\mu)$$

Note that the integral depends on $\beta\mu$ only. In function 7.1, we plot the function $g(\beta\mu)$ as a function of $\beta\mu$. For $\beta\mu \to 0$ this function approaches the value 2.61.

This imposes a temperature-dependent *maximum* on the particle density – beyond this value, the analysis fails, and the only way out is by questioning the transition from the sum over **k** to an integral. In fact, this transition is not justified if $\varepsilon_0 - \mu$ really approaches the value 0, where ε_0 is the ground state energy (i.e. the energy corresponding to the longest wavelength). In that case we must split off the term corresponding to the ground state energy, which now is macroscopically occupied (that is, a finite fraction of the particles is in the ground state).

What happens is that the gas splits up into two parts. The normal part fills the energy levels according to the BE distribution in the usual way. This fraction corresponds to

$$n_{\rm normal}\lambda^3 = 2.61.$$

If the total particle density is greater than prescribed by this limit, the rest of the particles occupied the ground state. We therefore know that $n_G = n - n_{normal}$ particles *per unit volume* will be in the ground state. The occupation of the ground state is

$$Vn_{\rm G}=\frac{1}{e^{\beta(\varepsilon_{\rm G}-\mu)}-1}.$$



Figure 7.2: Pressure versus λ^3/n . The critical density corresponds to 1/2.61 on the horizontal axis.

We now can deduce that

$$\varepsilon_{\rm G} - \mu \approx 1/(\beta V n_{\rm G})$$

i.e., the larger the system, the closer the chemical potential will be to the ground state.

As we have seen in section 7.1, the pressure is given by

$$P = -\frac{k_{\rm B}T}{\lambda^3} \frac{4}{\sqrt{\pi}} \int dx \, x^2 \ln(1 - e^{-x^2 + \beta\mu}).$$

The x = 0 term no longer contributes, even when μ is close to ε , as the denominator in the formulae for the density is now replaced by the logarithm.

Now we keep the temperature constant, and let the density vary. For densities lower than the critical density, μ will vary and assume negative values. For densities higher than the critical value, $\mu = 0$ and the pressure remains constant. Figure 7.2 shows the pressure as a function of the inverse density.

7.2.3 Phonons and the specific heat

Phonons are lattice vibrations, and they can be understood by realising that the system of interacting atomic nuclei can be approximated by a *harmonic system*, i.e. a system of particles connected by harmonic springs. Close to the configuration of minimum potential energy, any system can be described in terms of harmonic interactions, and the excitations can be described in terms of a collection of *independent* harmonic oscillators (see the classical mechanics course). The energy for such a system can easily be found: we simply add up the expectation value of the energies of the oscillators at frequencies ω_i and at temperature T:

$$U(T) = \left[\Phi_0 + \sum_i \frac{\hbar \omega_i}{2} \right] + \sum_i \frac{\hbar \omega_i}{e^{\hbar \omega_i / (k_{\rm B}T)} - 1}.$$

The first term on the right hand side is the energy-offset, the second is the zero-point energy of the harmonic oscillator, and the rightmost term is the average energy due to the energy quanta $n\hbar\omega_i$.

We can evaluate the sums by transforming them into integrals, but Einstein avoided this in 1907 by requiring that there was approximately only one frequency, $\omega_{\rm E}$, at which the oscillators would vibrate. This leads directly to

$$C_V(T) = \frac{\partial U}{\partial T} = 3Nk_{\rm B}\frac{x^2e^x}{(e^x-1)^2},$$

where $x = \hbar \omega_{\rm E} / (k_{\rm B}T) = \theta_{\rm E} / (k_{\rm B}T)$. The parameter $\theta_{\rm E}$ is called the *Einstein temperature*.

For low temperatures, the Einstein result does not match the experimental results very well. At higher temperatures, however, it approaches the classical result $3Nk_{\rm B}$ (why?).

Peter Debye took the actual distribution of modes which we have already encountered above for the photons. This distribution is however cut off as there cannot be more modes than particles:

$$\int_0^{\omega_{\rm D}} V C \omega^2 d\omega = N.$$

The value of the proportionality constant depends on the sound speeds for transverse and longitudinal waves. Using the ω^2 distribution, The specific heat is found as

$$C_V(T) = 3Nk_{\rm B}D(x_0),$$

where $x_0 = \hbar \omega_D / (k_B T) = \theta_D / (k_B T)$. The parameter θ_D is called the *Debye temperature*. The Debye function D(x) is defined as

$$D(x_0) = \frac{3}{x_0^3} \int_0^{x_0} \frac{x^4 e^x}{(e^x - 1)^2} dx.$$

For low temperatures, the Debye result for the specific heat is

$$C_V(T) = C(T/\theta_{\rm D})^3.$$

For high temperatures, we can perform a Taylor expansion of the integrand in the expression for D which yields

$$D(x_0) \approx \frac{3}{x_0^3} \int_0^{x_0} x^2 dx = 1,$$

so that we find again

$$C_V \rightarrow 3Nk_B$$

as it should be for high temperature.

7.3 Fermions

7.3.1 Degenerate Fermi gas

The name 'degenerate Fermi gas' is used for a dense system consisting of noninteracting Fermions. Dense means that

$$n\lambda^3 = e^{\beta\mu}$$

is larger than 1. In that case, the chemical potential μ is positive. For T = 0, the distribution function has a square shape, and for small, but positive T, the square shape gets rounded of, as shown in figure 7.3. In the ground state, which is occupied for T = 0, all the one-particle levels are filled for energies smaller than μ . The chemical potential at T = 0 is called the *Fermi energy*, $\varepsilon_{\rm F}$. For particles



Figure 7.3: The Fermi distribution function for T = 0 and small, but positive T.

moving in a cubic box with side L, the particles fill up a sphere in k-space, since $E = \hbar^2 k^2 / (2m)$. The radius of this sphere is as usual related to the particle number:

$$N = 2 \frac{L^3}{(2\pi)^3} \frac{4\pi}{3} k_{\rm F}^3.$$

The factor 2 is for the particular case of electrons, and it takes care of the double spin-degeneracy. We conclude that

$$\varepsilon_{\rm F} = rac{\hbar^2 k_{
m F}^2}{2m} = rac{\hbar^2 (3n\pi^2)^{2/3}}{2m}.$$

From figure 7.3 it is clear that for positive *T*, the chemical potential will remain more or less constant. What happens is that some electrons with $\varepsilon < \varepsilon_F$ are excited to $\varepsilon > \varepsilon_F$. These excited electrons come from a band of width $\approx k_B T$ below the Fermi energy, and they occupy states in a band $k_B T$ above the Fermi energy. We speak of a degenerate Fermi gas when $k_B T \ll \varepsilon_F$. Degenerate Fermi gases are quite familiar: in a metal, the valence electrons have a fermi energy corresponding to about 50000 K, much larger than room temperature. In a particular kind of stars, the so-called 'white dwarfs', the electrons have a Fermi temperature of 10^7 K.

To show that the chemical potential for a degenerate electron gas deviates only to order $(k_B T/\epsilon_F)^2$ is not easy. We shall take this for granted here. If we do so, we can easily evaluate the specific heat of the degenerate electron gas. It is convenient to count the number of states at a specific energy – this is called the density of states. The number of **k**-points which lie in the range $k, k + \Delta k$ is given as

$$D(\varepsilon)\Delta\varepsilon = 2\frac{L^3}{(2\pi)^3}4\pi k^2\Delta k;$$

therefore

$$D(\varepsilon)\Delta\varepsilon = rac{V}{2\pi^2}\left(rac{2m}{\hbar^2}
ight)^{3/2}\sqrt{\varepsilon}\Delta\varepsilon,$$

which can also be written as

$$D(\varepsilon) = \frac{3}{2} N \varepsilon_{\rm F}^{-3/2} \sqrt{\varepsilon}$$

The total energy is now given by

$$\langle E \rangle = \int d\varepsilon D(\varepsilon) \varepsilon f(\varepsilon, T).$$

Using the fact that

$$N = \int d\varepsilon \, D(\varepsilon) f(\varepsilon, T),$$

we can write

$$\langle E \rangle = N \varepsilon_F + \int d\varepsilon D(\varepsilon) (\varepsilon - \varepsilon_F) f(\varepsilon, T).$$

If we take the derivative with respect to T and assume that μ is approximately temperature-independent (this is not quite correct, see below), we obtain:

$$C_{V} = \frac{\partial \langle E \rangle}{\partial T} = \frac{1}{k_{\rm B}T^2} \int_{0}^{\infty} d\varepsilon \, D(\varepsilon) \frac{\varepsilon - \varepsilon_{\rm F}}{\left(e^{(\varepsilon - \varepsilon_{\rm F})/(2k_{\rm B}T)} + e^{-(\varepsilon - \varepsilon_{\rm F})/(2k_{\rm B}T)}\right)^2}$$

Note that the integrand is small everywhere, except in a band $k_{\rm B}T$ around $\varepsilon_{\rm F}$. This allows us to take $D(\varepsilon_{\rm F})$ out of the integral. Changing to the integration variable $x = (\varepsilon - \varepsilon_{\rm F})/(k_{\rm B}T)$, we have

$$C_V = k_{\rm B}^2 T D(\varepsilon_{\rm F}) \int_{-\varepsilon_{\rm F}/(k_{\rm B}T)}^{\infty} \frac{x^2}{\left(e^{x/2} + e^{-x/2}\right)^2} dx$$

The lower boundary $\varepsilon_{\rm F}/(k_{\rm B}T)$ of the integral is large but negative – we replace it by $-\infty$. Using

$$\int_{\infty}^{\infty} \frac{x^2 \, dx}{(e^{x/2} + e^{-x/2})^2} = \frac{\pi^2}{3}$$

we have

$$C_V = \frac{\pi^2}{3} k_{\rm B}^2 T D(\varepsilon_{\rm F})$$

Substituting the value $D(\varepsilon_{\rm F}) = 3/2N/(k_{\rm B}T)$ we obtain:

$$C_V = \frac{\pi^2}{2} N k_{\rm B} \frac{T}{T_{\rm F}}$$

where the *Fermi temperature* T_F is defined by $\varepsilon_F = k_B T_F$. We see that the specific heats grows linearly with *T*. This growth stops only at the Fermi temperature, which, as we have seen, lies fairly high. For very high temperatures (higher than T_F), the specific heat saturates at $3Nk_B/2$. If we compare this with phonons, we see that for low temperature, where the specific heat due to the phonons, grows as T^3 , the electronic contribution dominates, whereas for temperatures well above the Debye, the phonon contribution saturates at $3Nk_B$, well above the maximum contribution of the electrons.

Although this calculation yields the correct result, a few things have been wiped under the carpet, in particular the fact that μ was replaced by $\varepsilon_{\rm F}$. We now present a correct calculation, which starts by expressing *N* as an integral over the function $\Delta(\varepsilon)$ which is an integral of the density of states over the energy:

$$\Delta(\varepsilon) = \int_0^\infty D(\varepsilon') d\varepsilon'.$$

Then we can write, using partial integration:

$$N = \int_0^\infty D(\varepsilon) f(\varepsilon, T) \, d\varepsilon = -\int_0^\infty \Delta(\varepsilon) \frac{f(\varepsilon, T)}{d\varepsilon} \, d\varepsilon.$$

The partial integration has the advantage that the energy derivative of f is nonzero only in a small interval around μ so that we can expand D around μ :

$$N = \int \left[\Delta(\mu) + (\varepsilon - \mu)D(\mu) + \frac{(\varepsilon - \mu)^2}{2}D'(\mu) \right] \frac{1}{k_{\rm B}T} \frac{1}{\left(e^{(\varepsilon - \mu)/(2k_{\rm B}T)} + e^{-(\varepsilon - \mu)/(2k_{\rm B}T)}\right)^2} d\varepsilon$$

We have used the prime ' to indicate a derivative with respect to T. Again selecting only the even integrands, we obtain two terms:

$$N = \Delta(\mu) + D'(\mu) \frac{\pi^2}{6} (k_{\rm B}T)^2,$$

where in the first term we could integrate directly as the integrand is proportional to the energyderivative of f, and in the second integral we have used the same result as was used in the simplified derivation.

The main observation now is to realize that, if we want to calculate the specific heat at constant density, the number of particles should be fixed. This implies that its derivative with respect to the temperature should vanish:

$$\frac{dN}{dT} = D(\mu)\mu' + D'(\mu)\frac{\pi^2}{3}k_{\rm B}^2T + D''(\mu)\mu'(k_{\rm B}T)^2\frac{\pi^2}{6}.$$

For low temperatures, the rightmost term is much smaller than the first two, so that we have

$$D(\mu)\mu' + D'(\mu)\frac{\pi^2}{3}k_{\rm B}^2T = 0.$$

We now perform a similar analysis for the specific heat, along the lines of our simple derivation above:

$$c_{V} = \int \varepsilon \frac{\partial f}{\partial T} d\varepsilon = \mu \int D(\varepsilon) \frac{\partial f}{\partial T} d\varepsilon + \int D(\varepsilon) (\varepsilon - \mu) \frac{\partial f}{\partial T} d\varepsilon$$

We have

$$rac{\partial f}{\partial arepsilon} = rac{1}{k_{\mathrm{B}}T^2} rac{arepsilon - \mu + T\mu'}{ig(e^{(arepsilon - \mu)/(2k_{\mathrm{B}}T)} + e^{-(arepsilon - \mu)/(2k_{\mathrm{B}}T)}ig)^2}.$$

Substituting this into the two integrals appearing in the expression for c_V , we obtain:

$$c_{V} = \mu \int \left[D(\mu) + (\varepsilon - \mu) D'(\mu) + \ldots \right] \frac{1}{k_{\mathrm{B}} T^{2}} \frac{\varepsilon - \mu + T\mu'}{\left(e^{(\varepsilon - \mu)/(2k_{\mathrm{B}}T)} + e^{-(\varepsilon - \mu)/(2k_{\mathrm{B}}T)} \right)^{2}} d\varepsilon + \int \left[D(\mu) + (\varepsilon - \mu) D'(\mu) + \ldots \right] (\varepsilon - \mu) \frac{1}{k_{\mathrm{B}} T^{2}} \frac{\varepsilon - \mu + T\mu'}{\left(e^{(\varepsilon - \mu)/(2k_{\mathrm{B}}T)} + e^{-(\varepsilon - \mu)/(2k_{\mathrm{B}}T)} \right)^{2}} d\varepsilon$$

Carefully analysing these integrals gives three dominant terms, where two arise from the first integral, and the third one from the second integral:

$$c_V = \mu \mu' D(\mu) + \mu D'(\mu) \frac{\pi^2}{3} k_{\rm B}^2 T + D(\mu) k_{\rm B}^2 T \frac{\pi^2}{3}$$

Using the relation obtained above from the vanishing temperature-derivative of the particle number *N* then yields:

$$c_V = D(\mu)k_{\rm B}^2 T \pi^2/3.$$

Substituting the explicit expression for the density of states yields the result obtained above.

Note that in this derivation, no reference to the explicit form of $D(\varepsilon)$ has been made.

In chapter 3 we have already considered paramagnetism (section 3.9 and 10). Here we shall consider the full quantum description for spin-1/2 fermions – you may think of electrons in a solid. Suppose we have no magnetic field. Then, all the properties of the electrons are determined by the density of states $D(\varepsilon)$ (see the previous section). Once we know this function, all relevant physical quantities can be determined. The important issue now is that this density of states does not depend on the spin degrees of freedom (this is a direct consequence of the fact that $\mathbf{B} = \mathbf{0}$). If the magnetic field is switched on, the only thing which changes is that the energies are shifted over $\pm \mu^* B$, where the sign depends on the spin. Note that μ^* is the magnetic moment – it should not be confused with chemical potential which is μ without the asterisk.

First we analyse how the chemical potential changes with the magnetic field. We do this by calculating the total number of particles and then require that this is constant:

$$N = N_+ + N_- = \sum_i \left[f_+(i) - f_-(i) \right]$$

where the sum is over the *orbital* states *i*; f_{\pm} are the Dirac functions for the appropriate spin state. A sum over the orbital states can however be replaced by an integral over the energy if we insert the density of states:

$$N = \frac{1}{2} \int d\varepsilon \, \left[D(\varepsilon) f(\varepsilon - \mu^* B) + D(\varepsilon) f(\varepsilon + \mu^* B) \right].$$

The integral is over the *orbital* energies, and the magnetic field only enters in the Fermi distribution functions. The factor 1/2 in front of the integral takes into account that $D(\varepsilon)$ includes up- and down spins. Now we assume that the field *B* is very small (i.e. μ^*B smaller than k_BT). Then we can expand the distribution functions about B = 0:

$$f(\boldsymbol{\varepsilon} \pm \boldsymbol{\mu}^* B) \approx f(\boldsymbol{\varepsilon}) \pm \boldsymbol{\mu}^* B f'(\boldsymbol{\varepsilon}) + \frac{(\boldsymbol{\mu}^* B)^2}{2} f''(\boldsymbol{\varepsilon}).$$

Substituting this back into the integral expression for N, we have

$$N = \int d\varepsilon \, D(\varepsilon) f(\varepsilon) + \mathcal{O}(B^2) + \dots$$

We see that to first order in *B* the density does not change if we keep the chemical potential constant; hence we conclude that μ varies with *B* only to second order.

We are interested in how the system reacts to an applied field, that is, we want to calculate the magnetisation as a function of the field strength B. The magnetisation is given as the difference between the number of spin-up and -down electrons:

$$M = \mu^* (N_+ - N_-) = \mu^* \sum_i [f_+(i) - f_-(i)]$$

where the sum is over the *orbital* states $i - f_{\pm}$ are the Dirac functions for the appropriate spin state. The sum over the orbital states can again be replaced by an integral over the energy:

$$M = \frac{\mu^*}{2} \int d\varepsilon \, \left[D(\varepsilon) f(\varepsilon_i - \mu^* B) - D(\varepsilon) f(\varepsilon_i + \mu^* B) \right].$$

Substituting the same Taylor expansion for the distribution functions as above, we obtain:

$$M = \mu^{*2} B \int_0^\infty d\varepsilon \, D(\varepsilon) f'(\varepsilon).$$

For small *T*, the Fermi function decays rapidly from 1 to 0 near the Fermi energy, hence $f'(\varepsilon) \approx -\delta(\varepsilon - \varepsilon_F)$. Using this, we obtain

$$M \approx \mu^{*2} BD(\varepsilon_{\rm F}).$$

The *magnetic susceptibility* χ tells us how the magnetisation varies with the field:

$$\chi = \frac{dM}{dB} = \mu^{*2} D(\varepsilon_{\rm F}).$$

We see that measuring the susceptibility at low temperatures tells us what the density of states near the Fermi level is.

For the free electron gas, the density of states was found in the previous section – we find for the susceptibility in this case

$$\chi = \frac{3}{2} \frac{\mu^{*2}}{\varepsilon_{\rm F}}.$$

For higher temperature, the susceptibility can be expanded in powers of $k_{\rm B}T$; the result is

$$\chi \approx \frac{3}{2} \frac{{\mu^*}^2}{\varepsilon_{\rm F}} \left[1 - \frac{\pi^2}{12} \frac{k_{\rm B}T}{\varepsilon_{\rm F}} + \cdots \right].$$

7.3.3 Landau diamagnetism

Electrons moving in a solid have a magnetic moment not only as a result of their spin, but also as a result of their orbit. This is called the *orbital magnetic moment*. If we apply a magnetic field in the *z*-direction, the particles will have quantized field levels associated with the *x*- and *y* degrees of freedom. In addition, they have an energy associated with their motion in the *z*-direction. The spectrum is given by

$$\varepsilon(j, p_z) = \frac{e\hbar B}{m}(j+1/2) + \frac{p_z^2}{2m}$$

This problem has been treated in the exercise class of your quantum course (believe it or not).

For evaluating particle numbers and magnetisations, we need to know the density of states, in other words the *multiplicity* of these levels. This holds in particular for the x and y degrees of freedom, as we can simply perform an integral over p_z when summing over all states. It can be argued that the multiplicity for the energy levels associated with the orbital motion in the xy plane is given by

$$D(j) = L_x L_y \frac{eB}{h}.$$

We can then evaluate the number of particles and the magnetic moment. This is most easily done by first evaluating the grand partition function:

$$\mathscr{Z} = \prod_{i} \left[1 + e^{\beta(\mu - \varepsilon_i)} \right].$$

We then have, with $z = \exp(\beta \mu)$:

$$\ln \mathscr{Z} = \sum_{i} \ln \left[1 + z e^{-\beta \varepsilon_i} \right]$$

The index *i* denotes the states, which for our particular problem are defined by p_z and *j*:

$$\ln \mathscr{Z} = \int \frac{L_z}{2\pi\hbar} dp_z \sum_{j=0}^{\infty} L_x L_z \frac{eB}{h} \ln \left[1 + z \exp\left\{ -\beta \left[\frac{e\hbar B}{m} (j+1/2) + \frac{p_z^2}{2m} \right] \right\} \right].$$

This partition function can be evaluated in the classical limit, where $z \ll 1$. Expanding the argument of the logarithm, we get

$$\ln \mathscr{Z} = \frac{zVeB}{h^2} \int e^{-\beta p_z^2/(2m)} dp_z \sum_{j=0}^{\infty} e^{-\beta e\hbar B(j+1/2)/m} = \frac{zVeB}{h^2} \left(2\pi m k_{\rm B}T\right)^{1/2} \frac{1}{2\sinh\left[e\hbar B/(2m k_{\rm B}T)\right]}.$$

Now the desired quantities can easily be evaluated. With $\lambda = h/(2\pi m k_{\rm B}T)$, $x = \beta Beh/(4\pi m)$ and $\mu_{\rm eff} = eh/(4\pi m)$, we have

$$N = z \frac{\partial \mathscr{Z}}{\partial z} = \frac{zV}{\lambda^3} \frac{x}{\sinh x}$$

and

$$M = \frac{1}{\beta} \frac{\partial}{\partial B} \ln \mathscr{Z} = \frac{zV}{\lambda^3} \mu_{\text{eff}} \left[\frac{1}{\sinh x} - \frac{x \cosh x}{\sinh^2 x} \right].$$

We can write

$$M = -N\mu_{\rm eff}L(x),$$

where L is the Langevin function

$$L(x) = \coth x - 1/x.$$

The result we have obtained is similar to that of 3.9, except for a *minus* sign. This means that the magnetisation is now opposite to the field – this effect is called *diamagnetism*.

8

Statistical mechanics of interacting systems: the method of cluster expansions

Up to this point we have considered ideal gases only. These were sometimes derived from interacting systems, such as systems with harmonic interactions (e.g. crystal lattices) which could be transformed to a system of independent oscillators.

In general, however, we cannot transform away the interaction like we have done in these harmonic systems. The interaction then plays a relevant role. In this chapter, we consider a method for evaluating the correct equation of state, which for a classical ideal gas reads:

$$PV = \alpha N k_{\rm B} T$$

with $\alpha = 3/2$ for a noninteracting system in 3 dimensions and $\alpha = 3$ for a system of uncoupled harmonic oscillators.

Relevant interactions are those which are described in terms of pair-interactions, i.e., which are written as

$$V(\mathbf{r}_1,\ldots,\mathbf{r}_N)=\sum_{i< j}u(|\mathbf{r}_i-\mathbf{r}_j|).$$

Important examples of pair interactions are the hard sphere interaction:

$$u(r) = \begin{cases} \infty & \text{ for } r < a; \\ 0 & \text{ for } r \ge a, \end{cases}$$

and the Lennard-Jones interaction

$$u_{\rm LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right].$$

This interaction is shown in figure 8.1.

8.1 Cluster expansion for a classical gas

In the analysis of the classical gas, we have seen that the partition function always factorises into an integral over the momenta, involving the kinetic energy, and an integral over the orbital coordinates:

$$Q_N(T) = \frac{1}{h^{3N}N!} \int \exp\left\{-\beta \left[\sum_{i=1}^N \frac{p_i^2}{2m} + V(q_1, \dots, q_N)\right]\right\} d^{3N}p d^{3N}q.$$



Figure 8.1: The Lennard-Jones potential.

The integral over the momenta can be performed analytically (it is a product of elementary Gaussian integrals):

$$Q_N(T) = \frac{1}{N!\lambda^{3N}} Z_N(T, V)$$

with

$$Z_N(T,V) = \int \exp\left[-\beta \sum_{i < j} u(r_{ij})\right] d^{3N}r$$

The *cluster expansion* is a way to systematically evaluate the so-called *configuration integral* Z_N .

So, how does it work? The idea behind the cluster expansion is to include first only the interactions between particle pairs, then between triplets, and larger and larger clusters. But if we want to neglect contributions beyond a certain cluster size, we must have some expressions which vanish rapidly beyond some interaction range. Clearly, the factors $\exp[-\beta u(r)]$ do not decay to zero – they will tend to 1 for large separation since the interaction then vanishes. Therefore we introduce the *Mayer functions f*, defined as

$$f(r) = \exp[-\beta u(r)] - 1,$$

which indeed decay to 0 for large r. Figure 8.2 shows the Mayer function for the Lennard-Jones potential.

Using the Mayer function, we immediately see that the configuration integral can be written as

$$Z(N,V,T) = \int d^{3N}r \ e^{-\beta \sum_{i < j} u(r_{ij})} = \int d^{3N}r \ \prod_{i < j} e^{-\beta u(r_{ij})} = \int d^{3N}r \ \prod_{i < j} [1 + f(r_{ij})].$$

We shall use the notation $f(r_{ij}) \equiv f_{ij}$ from now on.

If we write out the product occurring in the integral for Z, we obtain

$$\prod_{i < j} [1 + f_{ij}] = 1 + \sum_{i < j} f_{ij} + \sum_{i,j;k,l} f_{ij} f_{kl} + \sum_{i < j < k} f_{ij} f_{jk} f_{ki} + \cdots$$



Figure 8.2: The Lennard-Jones interaction potential and the Mayer function.



Figure 8.3: Some cluster configurations. The top left cluster corresponds to the lowest order term; the other two are the second order terms.

The sum with the prime \sum' is over all possible pairs *i*, *j* and *k*, *l* which are distinct. Note however that we still include configurations of the form *i*, *j*; *j*, *k*. In figure 8.3 we indicate the possibilities. Note that the actual expansion consists of a sum over *all possible* configurations. This means that we have a sum over *all distinct pairs* in the first order term, and a sum over all 'distinct pairs of distinct particle pairs', a sum over all possible triplets,

It is clear that the first order term contains N(N-1)/2 pairs. The second order term contains

N(N-1)(N-2)(N-3)/8 terms of the form corresponding to the upper right part of figure 8.3. This number is obtained as follows. For the first term we have N(N-1)/2 possibilities, and for each of these possibilities we have (N-2)(N-3)/2 for the second pair. In order to avoid double counting of these pairs (corresponding to interchanging pair 1 and pair 2) we must include one more factor 1/2, which leads to the required result. For the terms corresponding to the configuration in the lower left part of figure 8.3, we have N(N-1)(N-2)/2 possibilities, and for the lower right part we have N(N-1)(N-2)/6.

We work out the term

$$\int f(r_{12}) d^3r_1 d^3r_2 \dots d^3r_N.$$

Obviously, the integral over all coordinates except \mathbf{r}_1 and \mathbf{r}_2 can be performed directly, and we obtain

$$\int f(r_{12}) d^3r_1 d^3r_2 \dots d^3r_N = V^{N-2} \int f(r_{12}) d^3r_1 d^3r_2.$$

We rewrite the integral over \mathbf{r}_1 and \mathbf{r}_2 as one over \mathbf{r}_1 and $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$. The integral over \mathbf{r}_1 can be performed over \mathbf{r}_1 , which yields an additional factor V. As the interaction is short-ranged, and the volume is large, we do not have to impose additional conditions on the integration over \mathbf{r}_{12} , so we have

$$\int f(r_{12}) d^3r_1 d^3r_2 \dots d^3r_N = V^{N-1} \int f(r_{12}) d^3r_{12}.$$

Higher terms in the expansion are considered similarly.

Inserting the first two terms of the product expansion in the expression for the configuration integral and integrating over the coordinates, we obtain

$$Z = V^{N} + N(N-1)V^{N-1}\frac{1}{2!}\int d^{3}r f(r) + V^{N-2}\frac{N(N-1)(N-2)(N-3)}{8}\int d^{3}r_{1}d^{3}r_{2} f(r_{1})f(r_{2}) + V^{N-2}\frac{N(N-1)(N-2)}{2}\int d^{3}r_{1}d^{3}r_{2} f(r_{1})f(r_{2}) + V^{N-2}\frac{N(N-1)(N-2)}{6}\int d^{3}r_{1}d^{3}r_{2} f(r_{1})f(r_{2})f(r_{12}) + \cdots$$

The prefactors (the powers of V) arise from the integrations over the particles not present in the clusters and from the integration over one of the coordinates of each independent cluster itself.

Now we define

$$b_2 = \frac{1}{2} \int d^3 r f(r)$$

and

$$b_3 = 2b_2^2 + \frac{1}{3!} \int d^3r_1 d^3r_2 f(r_1)f(r_2)f(r_{12})$$

We then see, noting that

$$\int d^3r_1 d^3r_2 f(r_1) f(r_2) = 4b_2^2,$$

after some calculation that the expansion for the configuration integral can be written as

$$Z = V^{N} \left[1 + \frac{N(N-1)}{V} b_{2} + \frac{N(N-1)(N-2)(N-3)}{2V^{2}} b_{2}^{2} + \frac{N(N-1)(N-2)}{V^{2}} b_{3} + \dots \right]$$

Generally, the expansion is built up as follows. We label the different types of clusters by the index *j*. A single point (vertex) has label j = 1; two connected points have j = 2 etcetera. In table 8.1 we list the first five clusters. Obviously, b_3 defined above contains the contributions from diagrams 3a and 3b. We call n_j the number of vertices in a cluster of type *j*. The number of ways in which



Table 8.1: Different types of clusters, their labelling and the corresponding cluster integrals.

we can divide N particles into m_1 clusters of type 1, m_2 clusters of type 2, etcetera is given by the combinatorial factor

$$\frac{N!}{\prod_j m_j! (n_j!)^{m_j}}$$

Obviously, $N = \sum_{j} m_{j} n_{j}$. For each type of cluster, the *cluster integral* b_{j} is defined as

$$b_j(T) = \frac{1}{n_j! V} \sum_{\text{vertex permutations}} \int d^3 r_1 \cdots d^3 r_{n_j} \prod_{i,j} f_{ij}.$$

Now let's go back to the expansion containing only the terms to order V^{N-2} . If we calculate the free energy, we first have a contribution arising from the momenta, so that we have

$$A = -k_{\rm B}T \ln\left[\left(\frac{2\pi mk_{\rm B}T}{h^2}\right)^{3N/2}\frac{1}{N!}Z(N,V,T)\right].$$

Including the remaining terms, we obtain

$$A = -k_{\rm B}T \ln\left[\left(\frac{2\pi mk_{\rm B}T}{h^2}\right)^{3N/2} \frac{V^N}{N!}\right] - k_{\rm B}T \ln\left[1 + \frac{N(N-1)}{V}b_2 + \frac{N(N-1)(N-2)(N-3)}{2V^2}b_2^2 + \frac{N(N-1)(N-2)}{V^2}b_3\right].$$

Performing a Taylor expansion for the logarithm¹, we have

$$A = A_0 - k_{\rm B}T \left[\frac{N(N-1)}{V} b_2 + \frac{b_2^2}{V^2} \left(\frac{N(N-1)(N-2)(N-3)}{2} - \frac{N^2(N-1)^2}{2} \right) + \frac{N(N-1)(N-2)}{V^2} b_3 + \dots \right]$$

= $A_0 - k_{\rm B}T \left[\frac{N(N-1)}{V} b_2 - \frac{b_2^2}{V^2} (2N^3 - 5N^2 + 3N) + \frac{N(N-1)(N-2)}{V^2} b_3 + \dots \right].$

If we now use the fact that N - 1 etcetera can be replaced by N if N is large, we can write this expansion in terms of the density n = N/V:

$$A = A_0 - k_{\rm B} T N \left[n b_2 + n^2 (b_3 - 2b_2^2) + \dots \right].$$

Two important remarks are to be made at this stage:

- The coefficient of b_2^2 is proportional to N as a result of a cancellation of two terms proportional to N^2 . This cancellation must happen at all orders of the expansion in order to guarantee that the free energy scales linearly with N (it is an extensive variable).
- The second order term $b_3 2b_2^2$ corresponds to the triangle term

$$\frac{1}{3!}\int d^3r_1 d^3r_2 f(r_1)f(r_2)f(r_{12}).$$

This is a specific example of a feature which occurs at all levels: the diagrams remaining in the expansion do not contain any lines by which the diagram can be cut into two disjoint pieces. The remaing diagrams are called *star diagrams* or *irreducible* diagrams. For a general proof of this fact, you should consult the book of Mayer and Mayer.

Now that we have the partition function, the equation of state can be determined. Using

$$P = -\frac{\partial A}{\partial V}$$

we directly obtain

$$P = k_{\rm B} T n \left[1 - b_2 n - 2(b_3 - 2b_2^2)n^2 + \dots \right]$$

= $k_{\rm B} T n \left[1 + a_2 n + a_3 n^2 + \dots \right].$

¹This expansion should not be read as an expansion for small arguments, but as a formal expansion in terms which could perhaps be relatively large. The aim is merely to group terms with a particular power of n = N/V. A better way to perform the expansion is to move to the grand canonical ensemble, but we shall refrain from this step for simplicity.

The coefficients

$$a_{2} = -b_{2} = -\frac{1}{2} \int f(r) d^{3}r$$

$$a_{3} = -2b_{3} + 4b_{2}^{2} = -\frac{1}{3} \int f_{1}f_{2}f_{12}dr_{1}dr_{2}$$

etcetera, are called virial coefficients.

The virial coefficients contain information concerning the potential. In practice, an educated guess for the form of the potential is made, which contains several parameters. An example is the Lennard-Jones potential which contains two parameters: ε and σ . After measuring the pressure accurately as a function of the density, the parameters occurring in the potential can be fitted in order to match the virial coefficients for the model potential to the experimental results.

8.2 The virial expansion and the Van der Waals equation of state

In chapter 11 we shall concern ourselves with *phase transitions*. These are transitions which take place when the control parameters are changed and which cause the system to move from a phase with certain values for thermodynamic properties to a phase where these properties are significantly different. Common example of phase transitions are the liquid-gas transition and the solid-liquid transition. Also, in magnets phase transitions occur – there they are associated with a change in the magnetisation.

The first theory which explained the phenomenon of phase transitions was the Van der Waals theory from 1873. In fact, the Van der Waals theory is based on a particular equation of state, the form of which can heuristically be motivated as follows.

The ideal gas equation of state reads

$$PV = Nk_{\rm B}T.$$

Now the volume occurring in this equation is the total volume of the system. However, in practice, some fraction of this volume is excluded as the strong repulsive interaction for short particle separation prevents them from coming too close. This suggests that we replace the volume by V - Nb. It can be argued that $b \approx 4V_0$, where V_0 is the volume occupied by the 'hard core' of each particle. The fact that the particles have less space to move in, directly affects the entropic contribution to the free energy. In fact, the volume-dependent part of the entropic term for the ideal gas

$$S = k_{\rm B} N \ln V$$
,

is now replaced by

$$S = k_{\rm B} N \ln(V - Nb).$$

To guess the value of the parameter *b*, we note that for a spherical hard core of volume V_0 , the excluded volume is $8V_0$. Now let's put *N* particles in the volume *V*. The first particle does not experience the presence of other particles. The second particle however has only a volume $V - 8V_0$ at its disposal. For the third particle, only $V - 2 \cdot 8V_0$ is available etcetera. On average, the excluded volume is

$$\frac{1}{N} (0 + 8V_0 + 2 \cdot 8V_0 + \dots + (N-1) \cdot 8V_0) \approx 4NV_0$$

We see that $b \approx 4V_0$.

In addition to this effect, we note that the internal energy is reduced by the *attractive* part of the potential. This term will for each particle be proportional to the number of particles within the range of the potential. This number is in first approximation proportional to the density. For *all* particles we have

$$E = E_0 - N \frac{N}{V} a,$$

where E_0 is the internal energy of the ideal gas and *a* is determined by the details of the attractive potential. The value of the parameter *a* can be guessed as follows. Take a particular particle and calculate its interaction with the particles nearby. The result is

$$n\int u(r)d^3r.$$

So if we add up this contributions for all particles, and correcting for the double counting of pairs, we see that

$$a = -\frac{1}{2} \int u(r) d^3 r.$$

All in all, we find for the volume-dependent part of free energy

$$A = -\frac{aN^2}{V} - Nk_{\rm B}T\ln(V - Nb),$$

from which the equation of state follows as

$$P = -\frac{\partial A}{\partial V} = -a\left(\frac{N}{V}\right)^2 + Nk_{\rm B}T\frac{1}{V-Nb},$$
$$\left[P + a\left(\frac{N}{V}\right)^2\right](V-Nb) = Nk_{\rm B}T.$$

so

In figure 8.4, the pressure is shown as a function of the volume per particle for several tempera-
tures. We see that for large temperature, for a particular value for the pressure, only one temperature
can be found. For *T* below a treshold value
$$T_c$$
, *three* values for the density are possible. It turns out
that the middle value does not correspond to a thermodynamically stable phase, but the other two do.
Now suppose that we fix the temperature at some value below T_c and lower the pressure. When are
we at the leftmost branch of the curve, and when do we cross over to the right hand? The answer to
this question is given by a thermodynamical argument. Using

$$E = TS - PV + \mu N,$$

we have

$$\mu = \frac{E - TS + PV}{N}.$$

Using the thermodynamic relation

$$dE = TdS - PdV + \mu dN,$$

we obtain

$$d\mu = \frac{VdP - SdT}{N}.$$



Figure 8.4: Isotherms for the Van der Waals gas.

As we keep the temperature constant, we have

$$d\mu = \frac{1}{N} V dP.$$

If the phase on the left branch coexists with the phase on the right branch at a given pressure and temperature, the chemical potentials of these two phases should be equal. This means that we must have:

$$\int d\mu = \int V dP,$$

which means that the hatched area in figure 8.4 must be zero.

Now we compare the Van der Waals equation of state to the cluster expansion. Starting from

$$P = \frac{Nk_{\rm B}T}{V - Nb} - a\left(\frac{N}{V}\right)^2 = \frac{Nk_{\rm B}T}{V} \left[1 + \left(b - \frac{a}{k_{\rm B}T}\right)\left(\frac{N}{V}\right) + b^2\left(\frac{N}{V}\right)^2 + b^3\left(\frac{N}{V}\right)^3 + \dots\right].$$

Comparing this with the virial expansion for the pressure, we see that

$$a_2 = b - \frac{a}{k_{\rm B}T}$$
$$a_3 = b^2$$

etcetera.

Now let's work out the first virial coefficient a_2 for low temperatures:

$$a_2 = \frac{1}{2} \int (e^{-\beta u(r)} - 1) d^3 r \approx 4V_0 + \frac{1}{2k_{\rm B}T} \int u(r) d^3 r = b - \frac{a}{k_{\rm B}T}$$

We see that this matches precisely the expansion of the Van der Waals equation of state! This unfortunately does not hold for the higher orders. The Van der Waals expansion approximates the effect of the hard core by the series

$$1 + 4V_0n + 16V_0^2n^2 + 64V_0^3n^3 + \dots$$

whereas the correct series from the cluster expansion yields

$$1 + 4V_0n + 10V_0^2n^2 + 18.4V_0^3n^3 + \dots$$

The Van der Waals equation takes part of *all* higher virial coefficients into account. That is the reason why it can predict the phase transition behaviour rather well.

9

The method of quantized fields

9.1 The superfluidity of helium

If liquid helium is cooled down to a temperature of 2.17 K, it becomes a 'superfluid'. This means that helium which flows through a pipe, cannot lower its energy by interactions with the pipe, so that it moves without friction. This curious phenomenon can be understood using techniques of statistical quantum field theory.

Helium-4 consists of atoms, which normally have integer spin (spin=0). This means that these atoms could form a Bose-Einstein condensate at low temperatures. Strictly speaking however, the fact that helium forms a liquid at low temperatures, tells us that the interactions between the atoms become important, and so far, a Bose-Einstein (BE) condensate has been studied in the case of noninteracting particles. Nevertheless, a kind of BE condensation can also take place in the case of interacting systems, provided a description in terms of noninteracting particles is appropriate for the system at hand. You may compare this with the description of electrons as independent particles in the solid: we consider the particles moving in a potential which is represents the *average* interaction potential of each particle with its counterparts.

The phenomenon of superfluidity has been brought in connection with a BE condensate a long time ago. It is assumed that a finite fraction of particles occupies the same quantum state, and that this state does not experience any friction with walls. A way to see this is to consider a flow with speed v of helium thourgh a pipe of mass M. If we place ourselves in the rest frame of the liquid, we see the pipe moving with a speed v in the opposite direction. Now suppose that the liquid and the pipe exchange momentum \mathbf{p} . This implies that the momentum of the helium becomes \mathbf{p} (before the exchange, the helium was at rest) and that that of the pipe is decreased by an amount \mathbf{p} . The energy of the pipe with momentum \mathbf{P} is given as

$$E = \frac{P^2}{2M}$$

For the helium we assume a relation between energy and momentum given as $\Delta + \varepsilon(\mathbf{p})$, which can either be determined by experiment (scattering experiments) or theoretically.

We can now setup the energy balance between the helium and the pipe:

$$\varepsilon(\mathbf{p}) = \frac{\mathbf{P}^2}{2M} - \frac{(\mathbf{P} - \mathbf{p})^2}{2M}$$

From this we have, using $\mathbf{v} = \mathbf{P}/M$ and letting $M \to \infty$:

$$\boldsymbol{\varepsilon}(\mathbf{p}) = \mathbf{v} \cdot \mathbf{p} + \frac{\mathbf{p}^2}{2M} \approx \mathbf{v} \cdot \mathbf{p}.$$



Figure 9.1: Dispersion relation for helium.

It turns out that $\varepsilon(p)$ has a shape depicted in figure 9.1.

Now suppose that the pipe would cause excitations of the helium. Then, in order for the container to have available such an amount of energy, we should have

$$pv > \varepsilon(p)$$
.

It is seen from figure 9.1 that this is possible only in case the speed is large enough. The fastest speed at which no energy transfer is possible corresponds to the straight line in figure 9.1 which is tangent to the energy-momentum curve. For such low velocities, energy transfer is not possible which means that helium is superfluid.

If the energy-dispersion curve is measured, the critical velocity can be determined; it turns out to be 60 m/s, much higher than the critical velocity which was measured directly in experiments. The difference can be explained by considering rotational motion in the superfluid. It is in this context important to realise that if helium is superfluid as a result of BE condensation, only a finite fraction of the liquid is in the ground state, and the rest is in a normal state. We can express this by splitting the total density in a normal and a superfluid fraction:

$$ho=
ho_s+
ho_n$$

The superfluid fraction of the liquid consists of particles which are all in the same state $\Psi(\mathbf{r})$ which can be written in the form:

$$\Psi(\mathbf{r}) = a(\mathbf{r})e^{i\gamma(\mathbf{r})}.$$

The superfluid number density is given by

$$\rho_s(\mathbf{r}) = a^2$$

and the mass flow is given by the quantum mechanical expression of the flux:

$$\mathbf{j}(\mathbf{r}) = \frac{\hbar}{2im} \left[\Psi^*(\mathbf{r}) \nabla \Psi(\mathbf{r}) - \Psi(\mathbf{r}) \nabla \Psi^*(\mathbf{r}) \right] = \frac{\hbar}{m} a^2 \nabla \gamma(\mathbf{r}).$$

Given the fact that the flow is density \times velocity, we see that for the velocity we have

$$\mathbf{u}_s = \frac{\hbar}{m} \nabla \gamma(\mathbf{r}).$$

We see that the flow can be considered as a gradient of a function, just as the force is a gradient of a potential. The function $\gamma(\mathbf{r})$ plays the role of the potential. For such a flow we have

$$\nabla \times \mathbf{u}_s = 0$$

(In the analogue of classical mechanics this equation expresses the fact that the work done along a path only depends on the start and end point of that path). This last condition seems to prohibit circular flows. For example, in the case where the fluid would rotate in a cylinder, we should have at each point \mathbf{r} :

$$\mathbf{v} = \boldsymbol{\omega} \times \mathbf{r}; \quad \nabla \times \mathbf{v} = 2\boldsymbol{\omega},$$

where $\boldsymbol{\omega}$ is the angular velocity. We see that the second equation is certainly incompatible with a potential flow field (i.e. a flow derived from a potential as sketched above).

The expectation that superfluid helium cannot rotate was checked by putting helium inside a rotating cylinder ('rotating bucket experiment'). For a normal fluid, the meniscus assumes the shape

$$z(r) = \frac{\omega^2 r^2}{2g}$$

which can easily be checked by minimising the total energy of the fluid as a function of z(r). In experiments, although only the normal fraction was supposed to contribute to the rotation, causing the above relation to be modified to

$$z(r)=\frac{\rho_n}{\rho}\frac{\omega^2 r^2}{2g},$$

the experiment showed that also the superfluid fraction participated in the rotation.

The explanation for this fact comes from the notion that the function $\gamma(\mathbf{r})$ is not a usual potential: it is a *phase* and hence defined modulo 2π . Therefore, we may satisfy the condition

$$\nabla \times \mathbf{v} = 0$$

without the usual relation following from it:

$$\oint \mathbf{u}_s \cdot d\mathbf{l} \neq 0.$$

In order to prove the latter relation, we must assume that $\nabla \times \mathbf{v} = 0$ holds in a region of the plane without holes in it. We can circumvent this condition by assuming that the superfluid rotates around an axis, but that the 'core' of this 'vortex motion' is not superfluid.

When we follow a path surrounding the vortex core, we have

$$\oint \nabla \gamma \cdot d\mathbf{l} = 2\pi n, \quad n \text{ integer.}$$

Therefore we have

$$\oint \mathbf{u} \cdot d\mathbf{l} = \frac{nh}{m}.$$

From this, we read off two striking features: (i) the rotational velocity of a vortex is *quantized* and (ii) this velocity depends directly on Planck's constant.

9.2 The low-energy spectrum of helium

In this section we want to derive the low-energy spectrum of helium from the microscopic Hamiltonian:

$$\hat{H} = \sum_{\mathbf{k}} \frac{\hbar^2 k^2}{2m} b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + \frac{1}{2V} \sum_{\mathbf{k},\mathbf{k}',\mathbf{q}} v_{\mathbf{q}} b_{\mathbf{k}+\mathbf{q}}^{\dagger} b_{\mathbf{k}'-\mathbf{q}}^{\dagger} b_{\mathbf{k}'} b_{\mathbf{k}}.$$

In order to make the Hamiltonian tractable, we restrict ourselves to a delta-function potential, for which

 $v_{\mathbf{q}} = u_0$, for all \mathbf{q} .

Secondly, we analyze the system in the case where the part of the helium which is in the superfluid phase much larger than the part which is the normal phase. In fact, for N particles, we have N_0 in the superfluid phase, and we consider the case where

$$N - N_0 \ll N$$
.

In that case, an operator term containing $b_{\mathbf{k}+\mathbf{q}}^{\dagger}b_{\mathbf{k}'-\mathbf{q}}^{\dagger}b_{\mathbf{k}'}b_{\mathbf{k}}$ with $\mathbf{k}+\mathbf{q}$, $\mathbf{k}'-\mathbf{q}$, \mathbf{k} and \mathbf{k}' being nonzero, is negligible (it scales with $(N-N_0)^2$, in comparison to terms where two subscripts are zero, and which scales as $(N-N_0)$).

This means that we must single out all possibilities where at least two b's have subscript zero. This is possible in seven different ways:

- $\mathbf{q} = \mathbf{k} = \mathbf{k}' = 0;$
- q = -k, k' = 0;
- q = k', k = 0;
- $\mathbf{k} = \mathbf{k}' = 0; \mathbf{q} \neq 0;$
- $\mathbf{k} = \mathbf{q} = 0; \, \mathbf{k}' \neq 0;$
- $\mathbf{k}' = \mathbf{q} = 0, \, \mathbf{k} \neq 0;$
- $\mathbf{q} = \mathbf{k}' = -\mathbf{k} \neq 0.$

We then are left with $(\sum_{\mathbf{k}}' \text{ means that } \mathbf{k} = 0 \text{ is excluded})$:

$$\begin{split} \hat{H} &= \frac{u_0 N_0^2}{2V} + \sum_{\mathbf{k}}' \frac{\hbar^2 k^2}{2m} b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + \frac{u_0 N_0}{2V} \sum_{\mathbf{k}}' 4b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + b_{\mathbf{k}}^{\dagger} b_{-\mathbf{k}}^{\dagger} + b_{\mathbf{k}} b_{-\mathbf{k}} = \\ & \frac{u_0 [N_0^2 + 2N_0 (N - N_0)]}{2V} + \frac{u_0 N_0}{2V} \sum_{\mathbf{k}}' \frac{\hbar^2 k^2}{2m} b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + \sum_{\mathbf{k}}' 2b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + b_{\mathbf{k}}^{\dagger} b_{-\mathbf{k}}^{\dagger} + b_{\mathbf{k}} b_{-\mathbf{k}}. \end{split}$$

Using the fact that $N_0^2 + 2N_0(N - N_0)^2 \approx N^2$, we have

$$\hat{H} = \frac{u_0 N^2}{2V} + \sum_{\mathbf{k}}' \frac{\hbar^2 k^2}{2m} 2b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + \frac{u_0 N_0}{2V} \sum_{\mathbf{k}}' \left(2b_{\mathbf{k}}^{\dagger} b_{\mathbf{k}} + b_{\mathbf{k}}^{\dagger} b_{-\mathbf{k}}^{\dagger} + b_{\mathbf{k}} b_{-\mathbf{k}} \right).$$

For a fixed total number of particles, the first term is fixed and can be neglected. The fact that half of the term $4b_k b_k^{\dagger}$ in the potential energy has been split off and approximated, cannot be justified within the approach in which we analyse the low energy states. The correct treatment of the problem

should include the chemical potential, which precisely cancels this term. A correct treatment of this is presented in the book of Fetter and Walecka.

The question is now what the eigenvalues of this Hamiltonian are. To solve this problem, we note that the Hamiltonian is essentially a quadratic expression of the *b*-operators, and a quadratic form can be put in diagonal form by a linear transformation. In this case we must however take care that the linear transformations are chosen such that the operators still satisfy tractable commutation relations. The proper choice, first made by Bogoliubov, is:

$$b_{\mathbf{k}} = \eta_{\mathbf{k}} \cosh \theta_{\mathbf{k}} - \eta_{-\mathbf{k}}^{\dagger} \sinh \theta_{\mathbf{k}};$$

$$b_{-\mathbf{k}} = \eta_{-\mathbf{k}} \cosh \theta_{\mathbf{k}} - \eta_{\mathbf{k}}^{\dagger} \sinh \theta_{\mathbf{k}}.$$

It is straightforward to check that the η_k satisfy the proper boson commutation relations:

$$\left[\eta_{\mathbf{k}},\eta_{\mathbf{k}}^{\dagger}\right]=1.$$

If we substitute the new expression for the b_k in terms of the η_k into the Hamiltonian, we obtain an off-diagonal contribution:

$$\begin{split} H_{\text{o.d.}} &= -\sum_{\mathbf{k}}' \left[\frac{\hbar^2 k^2}{2m} + \frac{u_0 N_0}{V} \right] \cosh \theta_{\mathbf{k}} \sinh \theta_{\mathbf{k}} \left(\eta_{\mathbf{k}}^{\dagger} \eta_{-\mathbf{k}}^{\dagger} + \eta_{-\mathbf{k}} \eta_{\mathbf{k}} \right) + \\ & \frac{u_0 N_0}{V} \sum_{\mathbf{k}}' \left(\cosh^2 \theta_{\mathbf{k}} + \sinh^2 \theta_{\mathbf{k}} \right) \left(\eta_{\mathbf{k}}^{\dagger} \eta_{-\mathbf{k}}^{\dagger} + \eta_{-\mathbf{k}} \eta_{\mathbf{k}} \right). \end{split}$$

We see that these off-diagonal terms vanish when

$$\tanh 2\theta_{\mathbf{k}} = \frac{u_0 N_0/V}{\frac{\hbar^2 k^2}{2m} + u_0 N_0/V}.$$

Substituting this into the expression for the diagonal part, we are left with

$$H = \sum_{\mathbf{k}}' \sqrt{\left(\frac{\hbar^2 k^2}{2m}\right)^2 + 2\frac{u_0 N_0}{V} \frac{\hbar^2 k^2}{2m}} \eta_{\mathbf{k}} \eta_{\mathbf{k}}^{\dagger} + \sum_{\mathbf{k}}' \left[\sqrt{\left(\frac{\hbar^2 k^2}{2m}\right)^2 + \frac{2u_0 N_0}{V}} - \frac{\hbar^2 k^2}{2m} - \frac{u_0 N_0}{V} \right]$$

From this, we can immediately infer the energy eigenvalues with respect to the ground state:

$$E(\mathbf{k}) = \sqrt{\left(\frac{\hbar^2 k^2}{2m}\right)^2 + 2\frac{u_0 N_0}{V} \frac{\hbar^2 k^2}{2m}}$$

For small \mathbf{k} , we see that the second term in the square root dominates, and we see that the energy is linear in \mathbf{k} .

Note that the elementary excitations are linear combinations of the single-**k** modes which describe single-particle excitations: the elementary excitations describe excitation quanta, and are generally denoted as 'quasi-particles'. The simples example of a quasi-particle is the energy quantum of a harmonic oscillator. Here, a there is only a single vibrating particle. However, the theory does not see the difference between the energy quanta of this system and 'particles' of energy $\hbar\omega$ which can be created and destroyed by the ladder operators a_{\pm} .
10

Introduction to phase transitions

10.1 About phase transitions

The most common examples of phase transitions are the freezing and boiling of ordinary water. These transitions are associated with an abrupt change of the density in the case of boiling, and a sudden emergence of order in the case of freezing. These fascinating phenomena have for long time been poorly understood. It seems paradoxal that although we believe the world around us to be governed by smooth functions and differential equations leading to analytical solutions, we see such abrupt, non-analytic behaviour. In the first half of the twentieth century it has become clear that the reason for this nonanalytic behaviour lies in the fact that macroscopic objects (such as a glass of water) consist of large (almost infinite) numbers of molecules: a function depending on a paremeter, which is analytic for every finite value of that parameter, may become nonanalytic if the parameter becomes infinite.

A phase transition is always characterised by a sudden change in the degree or the type of order in the system. In order to analyse phase transitions, it is necessary to always identify a parameter which characterises the degree and/or type of order present in the system. This parameter is called the *order parameter*. In the case of the boiling of water, the density is the proper order parameter. In the case of freezing, it might be the structure factor.

The first theory of phase transitions which gave excellent results was the Van der Waals theory. We have discussed this at the end of chapter 8 of the notes and it is recommended that you go back and study this theory once again. There exist however other types of phase transitions than freezing and boiling, and an instructive system for studying phase transitions more generally is the system in which the degrees of freedom reside on lattice sites, and can assume only two different values, which we call + and -. The model describing such a system is the famous *Ising model*. In two dimensions, the system is formulated on a square lattice (in fact, different choices for the lattice can be made, but the square lattice is quite popular): on each lattic point, a spin-up or -down can be placed. For a $N \times N$ lattice, there are thus 2^{N^2} possible configurations. We may consider the spins as magnetic moments which obviously interact – usually, the interaction is limited to nearest neighbours. Furthermore, there may be an external magnetic field present which favours all spins to be either + or -. These considerations lead to the following Hamiltonian:

$$H = -K \sum_{\langle ij \rangle} s_i s_j - h \sum_i s_i.$$

What will be the behaviour of the model? To answer this questions, we start by examining the ground state, which will be the phase at absolute zero. The first interaction favours all spins to be equal: all spins + or all spins -. If the magnetic field *h* is zero, these two phases have the same energy and the system will choose either one or the other. For a positive field, the positive magnetisation will be favoured, whereas for negative field, the opposite sign is the stable phase. Now let us consider



Figure 10.1: The magnetisation of the Ising model as a function of temperature for zero field.

the h = 0 case at nonzero temperatures. This case is interesting because the Hamiltonian yields the same value for any particular configuration as for the one in which all spins are reversed. At very high temperatures, $\beta \rightarrow 0$, the interactions between the spins become irrelevant, and their values will be completely random. This means that the average *magnetisation*, defined as the average value of the spins, will be zero. One now might think that the magnetisation will decay with increasing temperature to reach zero at $T \rightarrow \infty$, but this turns out not to be the case. The magnetisation assumes a value zero above a *finite* temperature. The magnetisation is shown in figure 10.1.

The Ising transition occurs in two dimensions at $K/(k_BT) = 0.44...$ Suppose the system starts at high temperature and is then cooled down. When the system passes the transition temperature, the phase in which all spins have either the value +1 or -1 must be chosen. Which of the two will be the low-temperture phase is not known beforehand. Once the system chooses one of the two values, the symmetry between up- and down is broken. This phenomenon is called *symmetry breaking*, sometimes *spontaneous symmetry breaking*, as it is not imposed by changing the model itself – it is a well-known phenomenon which is relevant in many areas of physics and astronomy.

The behaviour close to the transition point is interesting. Physical quantities usually vary as broken algebraic power functions of the system parameters. As an example, consider the variation of the magnetisation when the transition temperature is approached from below. It turns that then in 2D and on a square lattice,

$$m \sim |T - T_c|^{1/8}$$
.

This behaviour is only one example of many similar ones. The parameter $\beta = 1/8$ (do not confuse this β with $1/(k_{\rm B}T)$!) is called *critical exponent*. There exist other critical exponents for other physical quantities and/or parameters:

$$\chi_m = \left(\frac{\partial m}{\partial h}\right)_T \propto |T - T_c|^{-\gamma};$$

$$c_h(T) \propto |T - T_c|^{-\alpha}$$

$$\xi(T) \propto |T - T_c|^{-\nu}$$

$$m(T) \propto (-T + T_c)^{\beta}; \quad T < T_c$$

and, moreover, we have an exponent for the behaviour of the magnetisation with varying small magnetic field at the transition temperature:

$$m(h, T_{\rm c}) = h^{1/\delta}.$$
 (10.1)

For the case of the two-dimensional Ising model on a square lattice, we know the values of the exponents from the exact solution:

$$\alpha = 0, \quad \beta = 1/8, \quad \gamma = 7/4, \\ \delta = 15, \quad v = 1.$$
 (10.2)

For nonzero magnetic field, the magnetisation will always be along the field, except for infinite temperature. The phase transition no longer occurs for nonzero field. If we consider however the magnetisation as a function of the external field for fixed temperature (which is taken below the phase transition temperature), then we see a sudden flip of the magnetisation which jumps from positive to negative or vice versa. This is also a phase transition, but of a different kind than the one described above, in which the magnetisation is a continuous function of the parameter which is changed (the temperature in that case). We shall from now on focus on the second kind of phase transition, which is called *critical, continuous* or *second order*, as opposed to transitions in which the order parameter jumps discontinuously, and which are called *first order* transitions. The order refers to the derivative of the (free) energy which jumps or is continuous.

10.2 Methods for studying phase behaviour

The results given in the previous section for the behaviour of the Ising model can be derived in various ways. First of all, the Ising model in two dimensions on a square lattice was solved for zero field analytically by Lars Onsager in 1944. This is one of the most important results obtained in theoretical physics of the 20th century. However, for nonzero field, no analytic solution is possible, although some progress has been made in recent years. Also for the Ising model on a triangular lattice, an analytic solution was obtained by Houtappel in 1950. For three dimensions, no such solutions exist, nor for Ising models including farther than nearest neighbour interactions.

Many results concerning spin models can be obtained using Monte Carlo techniques which are performed on a computer. In a nutshell, these methods boil down to the following: in a computer, a spin is chosen at random. Then the energy cost or gain associated with flipping that spin is calculated. Suppose this cost is ΔE . If $\Delta E < 0$, that is, if there is an energy *gain* by flipping the spin, the spin is actually flipped. If, on the other hand, there is an energy *cost* associated with the spin flip, then the spin is flipped with probability

$$P = \exp(-\beta \Delta E).$$

Performing a spin flip with this probability is done as follows. A random number between 0 and 1 is chosen. If this number is smaller than $\exp(-\beta\Delta E)$, the spin flip is carried out, the flip is performed, else the spin is not flipped. The Monte Carlo algorithm leads to configurations occuring with a probability proportional to $\exp(-\beta E)$ as required in the canonical ensemble. This can be seen as follows. Consider the probability $P_{\rho}(t)$ that at some instance of time *t*, the system is in some state ρ . The change in P_{ρ} is due to the combined effect of the system leaving the state ρ at the next step to enter a state σ , and entering the state ρ from any different state σ . The first type of event results in a decrease of P_{ρ} and the second one in a gain. All in all we have

$$P_{\rho}(t+1) - P_{\rho}(t) = \sum_{\sigma} \left[-T(\rho \to \sigma) P_{\rho} + T(\sigma \to \rho) P_{\sigma} \right]$$

where $T(\rho \to \sigma)$ is the probability to go to state σ provided the system was in a state ρ . If the probability distribution P_{ρ} becomes stationary, we have

$$\frac{T(\rho \to \sigma)}{T(\sigma \to \rho)} = \frac{P_{\sigma}}{P_{\rho}}$$

For the Boltzmann distribution, we have

$$\frac{P_{\sigma}}{P_{\rho}} = \exp\left[-\beta(E_{\sigma} - E_{\rho})\right] = \exp\left(-\beta\Delta E\right).$$

The Monte Carlo method is flexible in the sense that in principle any dimension and many types of interaction can be treated in this way, but in practice, the results are subject to statistical errors and will be not infinitely accurate. It is however important that apart from the finite size of the system, no systematic approximation is introduced.

A method for obtaining analytic results is the *mean field approximation*. This approximation occurs in many different forms, but always boils down to replacing the interactions between a particular particle and its neighbours by the average value of the interactions between that particle and all its neighbours. We shall now sketch the mean field approximation for the Ising model. On the Ising lattice, each site has a number of neighbours, which we call q, the *coordination number*. For the (hyper)cubic lattice in D dimensions, the coordination number is 2^D which gives indeed 2 neighbours in 1 dimension, 4 neighbours in 2D and 8 in 3D. We can rewrite the Hamiltonian in the form:

$$\begin{split} H &= K \sum_{\langle i,j \rangle} (s_i - m + m)(s_j - m + m) - h \sum_i s_i = \\ &- \frac{K}{2} q N m^2 - (h + K q m) \sum_i s_i - K \sum_{\langle i,j \rangle} (s_i - m)(s_j - m) \approx -\frac{K}{2} q N m^2 - (h + K q m) \sum_i s_i. \end{split}$$

(the number *N* represents the number of lattice sites). In the last expression, we have neglected the quadratic contribution of fluctuations of the magnetisation around its equilibrium value. We want to find the average magnetisation $m = \langle s_i \rangle$, where s_i is the average value of the spin, which does not depend on *i* for a homogeneous Hamiltonian (we assume the Hamiltonian satisfies periodic boundary conditions so that a site on the edge of the lattice couples to the corresponding site on the opposite edge, see figure 10.2). This can easily be done as the partition function has been reduced to that of uncoupled spins, interacting with a 'field' which incorporates the contribution from the average magnetisation. Now we can evaluate the free energy by factorising the partition function:

$$F = -k_{\rm B}\ln Z = -k_{\rm B}T\ln\left\{e^{-\beta KqNm^2/2}\prod_{i}\sum_{s_i}\left[e^{\beta(qmK+h)s_i}\right]\right\}.$$

This expression can be evaluated as

$$F = \frac{K}{2}qNm^2 - k_{\rm B}TN\ln\left\{2\cosh\left[(Kqm + h)/k_{\rm B}T\right]\right\}$$

Note that this expression for the free energy still contains the unknown average magnetisation *m*. We can evaluate this from our mean-field Hamiltonian:

$$m = \langle s_i \rangle = \frac{e^{\beta(qmK+h)} - e^{-\beta(qmK+h)}}{e^{\beta(qmK+h)} + e^{-\beta(qmK+h)}} = \tanh\beta(qmK+h).$$



Figure 10.2: Periodic Boundary conditions in the Ising model.



Figure 10.3: The self-consistency relation for the Ising model for different values of the parameter $qJ = \beta qK$.

We see that this is a self-consistency relation for m: on the right hand side, m is the average magnetisation which we imposed before evaluating the very same quantity, which we have evaluated as the result on the left hand side. Obviously, the two should be the same. In figure 10.3, we show the leftand right hand side as a function of m for h = 0 and for different values of the parameter $\beta qK \equiv qJ$. The self-consistent values for the magnetisation correspond to acceptable values. We see that the number of such points depends on the value of qJ. For qJ < 1, there is only one intersection point, at m = 0. For qJ > 1, there are three such points, two of which have opposite nonzero values of m, and still the point at m = 0. Which of these three points will the system choose. Considering the free energy, it turns out that the m = 0 corresponds to a higher value of the free energy than the nonzero values, which give an equal value of the free energy. Therefore, the system will choose one of these two. The phase diagram is therefore the same as the one described in the previous section, except for the location of the critical point, which now lies at $\beta K = 1/q$, which is 0.25 in two dimensions. We can now calculate the critical exponents for the Ising model. First we analyse the magnetisation as a function of temperature. We can expand the tanh function on the right hand side:

$$m = qJm - \frac{1}{3}(qJ)^3m^3 + \dots$$

from which we obtain, writing $qJ = T_c/T$:

$$m = \pm \sqrt{3} \sqrt{1 - \left(\frac{T}{T_c}\right)}.$$

Thus we see that the exponent β is found to be 1/2, quite different from the exact result $\beta = 1/8$ for 2D (see above). It seems that the mean field approximation can cause large errors in the exponents. For 3D, the exponent β is 0.324, which is already quite a bit closer to the mean field value. It turns out that for dimensions greater than four, ordinary critical points have indeed $\beta = 1/2$. In general, the mean field approximation becomes better with increasing dimension. The reason behind this is that in the mean field approximation, we neglect *correlations*. This means that the values of the neighbours of a + spin differs from those of the neighbours of a - spin. Above, we have however replaced these values by *m*, irrespective of the value of s_i . In higher dimensions (or when a spin has very many neighbours) these correlations become less important and the mean field result becomes more and more reliable. Mean field theory is very successful in systems with long range interactions.

Now let us calculate the other critical exponents. Now we study how *m* varies with *h* at the critical point. This means that we must set qJ = 1 and then include the magnetic field into the expression for *m* and see how the latter varies with *h*. The procedure is similar to that followed in calculating β : we simply must replace qJm by $m + h/k_{\rm B}T$

$$m = (m + \frac{h}{k_{\rm B}T}) - \frac{1}{3}(m + \frac{h}{k_{\rm B}T})^3,$$

from which it follows that

$$m = \left(\frac{3h}{k_{\rm B}T}\right)^{1/3},$$

giving $\delta = 3$, to be compared with $\delta = 15$ for the 2D Ising model on a square lattice.

The magnetic susceptibility is defined as

$$\chi = \left(\frac{\partial m}{\partial h}\right)_T.$$

Differentiating the self-consistency relation at arbitrary *T* with respect to *h* and then putting $h \rightarrow 0$ yields

$$\chi = \left(\frac{T_c}{T}\chi + \frac{1}{T}\right)\left(1 - m^2\right),\,$$

from which we have

$$\chi = \frac{1 - m^2}{k_{\rm B} \left[T - T_c (1 - m^2) \right]}.$$

For $T > T_c$, m = 0 and we see that $\chi \sim |T - T_c|$, hence $\gamma = 1$, to be compared with $\gamma = 7/4$ for the 2D Ising model on a square lattice.

For $T < T_c$, the calculation of the exponent proceeds a bit differently. We have $m \approx \sqrt{3/T_c}(T_c - T)^{1/2}$; putting this into the above equation leads to

$$\chi = \frac{1}{k_{\rm B}(T_c - T)}$$

which again leads to $\gamma = 1$.

Finally, we consider the exponent of the specific heat. First we note that the energy for h = 0 is given by

$$E = \frac{\partial \beta F}{\partial \beta} = -\frac{1}{2} K q N m^2$$

where we have used the self-consistency relation to replace the tanh occurring in the second term by m. The specific heat is calculated as

$$C_h = \left(\frac{\partial E}{\partial T}\right)_h = 0 \text{ for } T > T_c,$$

where we have used the fact that m = 0 for $T > T_c$. For $T < T_c$, we have

$$C_h = \frac{3}{2} \frac{KqN}{T_c} = \frac{3}{2} k_{\rm B} N.$$

This tells us that the critical exponent $\alpha = 0$, which is the same as in the 2D Ising model on the square lattice.

The behaviour of correlations is generally seen from the *correlation function* This function is defined as

$$g(|\mathbf{r}_i - \mathbf{r}_j|) = \langle s_i s_j \rangle = \frac{1}{Z} \sum_{\{i\}} s_i s_j \exp(-\beta H).$$

Note that now, *i* and *j* are not necessarily neighbours. For short distances, using the absolute value on the left hand side is not justified as the expression on the right hand side is anisotropic. For longer distances however, the correlation function becomes more or less isotropic, and the absolute values are justified. The shape of the correlation function is nearly always exponential, with a typical length scale, which is called the *correlation length*, ξ :

$$g(r) \sim \exp(-r/\xi) - m^2.$$

The term m^2 is the value which we expect for long distances: the average values of the spins s_i and s_j are not correlated and equal to the single-site average m. The distance ξ over which the correlations decay increases when the critical point is increased. In fact, we have seen above that the correlation length diverges near the transition point according to a scaling law with the critical exponent v = 1. At the critical point, the correlation function changes from exponential to algebraic:

$$g(r) \sim \frac{1}{r^x},$$

where *x* is another example of a critical exponent.

If the correlation function decays with a given exponent ξ , a rescaling of the physical space will change the correlation length accordingly. If however, we have an algebraic decay of the correlation function, it does not change its shape under a recaling $r \rightarrow br$:

$$g(br) \sim \frac{1}{b^x} \frac{1}{r^x} \sim \frac{1}{r^x}.$$

This behaviour is a manifestation of the fact that the system is *scale invariant*. If we would look at an Ising model from a distance from nearby, and we would not notice the anisotropy of the lattice at short scales, the picture looks the same. *Fractals* are examples of scale-invariant objects. An Ising model at the critical point is an example of a fractal structure.

10.3 Landau theory of phase transitions

Suppose we fix the magnetisation of our Ising model to the value *m*. When we evaluate the partition function, we can no longer sum over all possible configurations with $s_i = \pm$, but we must restrict ourselves to those configurations for which the total magnetisation sums up to *Nm*. If we do so, the free energy as calculated from this partition function is the free energy evaluated for the particular value of the magnetisation we started with. Note the difference with the mean field approximation: there we started with calling *m* the average magnetisation which was to be calculated; here we fix a priori the magnetisation to its predefined value. From the expression for the free energy:

$$F = -k_{\rm B}T \ln Z, \text{ with}$$
$$Z = \sum_{\{s_i\}}' \exp\left[J \sum_{\langle i,j \rangle} s_i s_j + bm\right],$$

where $b = \beta h$ and the primed sum denotes the restricted sum over the configurations with magnetisation *m*, we see that

$$F = -hm - k_{\rm B}T \ln \sum_{\{s_i\}}' \exp \left[J \sum_{\langle i,j \rangle} s_i s_j\right].$$

Note that the second term should be even in m as it does not have any preference for up- or down directions. Close to the critical point, the magnetisation is small, and we may expand the free energy in m;

$$F = -hm + q + rm^2 + sm^4 + \dots$$

The Taylor coefficients q, r, s, ... depend on temperature. In fact, instead of temperature, we prefer using the *reduced temperature t* as a parameter:

$$t = \frac{T - T_c}{T_c}.$$

Close to the critical point *t* is small.

A system at fixed temperature will occupy, at its equilibrium, states which correspond to a minimum of the free energy. Therefore, if we now relax the value m, we know that the minima of F as a function of m correspond to equilibrium. Cutting off the expansion beyond the fourth order term, in order for the free energy to be acceptable, we should have s > 0, otherwise the free energy would be lowest at large m which is clearly invalid close to the critical point. The parameter q furthermore can be set to zero by a suitable redefinition of the zero of energy, which as usual does not affect the physics of the problem. We furthermore study first the case where h = 0. We then have

$$F = rm^2 + sm^4,$$

with s > 0. Note that r and s are functions of the temperature t. In figure 10.4 we show F(m) for several values of q. We see that for r > 0 there is only one minimum of the free energy at m = 0. This



Figure 10.4: The free energy in the Landau expansion for various r.

minimum turns into a maximum for r < 0 and is accompanied by two minima at $\pm m_s$, where m_s is the value of the spontaneous magnetisation.

From the Landau theory, we can again derive the critical exponents. For example, the exponent β is found by analysing how *m* goes to zero when *t* approaches 0. The assumption is that the Taylor coefficients are regular functions of *t*. We know that criticality corresponds to t = 0 and r(t) = 0. Around t = 0, *r* and *s* behave as

$$r(t) = r_1 t, \quad s = s_0 + s_1 t,$$

where r_1 , s_0 and s_1 are some constants which do not depend on t. We assume that r_1 is nonzero. The minimum of the Landau expansion for the free energy is found at $m = \pm \sqrt{\frac{-r}{2s}}$. Substituting the expansions for r and s we obtain, for small t:

$$m \propto t^{1/2}$$
, hence $\beta = 1/2$

the same as in the mean field approximation.

Another exponent that we can find is δ . This exponent tells us how the magnetisation varies with h at the critical point for small magnetic field. Usually, we would expect this magnetisation to vary linearly with h, but here we find a different behaviour, just as in the mean field theory. At the critical point, r = 0, so F varies with m as

$$F = -hm + sm^4$$

We see that

$$m \propto h^{1/3}$$
,

so that $\delta = 3$, as in the mean field approach. Also for the other critical exponents, the mean field values are found.

We see that the critical exponents from the Landau theory and for the mean field approach are the same. This is not surprising, as it can be shown that the mean field free energy can be expanded in a series which is equal to the Landau expansion. Taking the expression found above:

$$F = \frac{K}{2}qNm^2 - k_{\rm B}TN\ln\left\{2\cosh\left[(Kqm + h)/k_{\rm B}T\right]\right\}.$$

and expanding this in terms of *m*, we find:

$$F = q + rm^2 + sm^4 + \dots$$

with $q = -k_{\rm B} \ln 2$, $r = Kq(1 - Kq/k_{\rm B}T)$, $u = Kq/3(Kq/k_{\rm B}T)^3$.

In the Landau theory it is assumed that the free energy is determined by the average value of the magnetisation. In reality, the fluctuations of the magnetisation must be considered as well. The fact that these fluctuations were neglected is an approximation similar to the mean field approximation. This explains why the mean field exponents were recovered in the Landau theory.

10.4 Landau Ginzburg theory and Ginzburg criterion

In order to obtain more insight into the approximations made in formulating the Landau theory, we now formulate a *mesoscopic* form of this theory. The idea behind this formulation is as follows. We divide the volume of the system up into cells which are very small in comparison to the system volume, but still large enough to contain many spins (in the case of a gas/liquid, these subvolume must contain many particles). Then the average spin in such a cell is a continuous variable which we shall call $m(\mathbf{r})$: \mathbf{r} is the location of the cell, and *m* assumes values between -1 and +1. As we are interested in phenomena close to the critical point, we are dealing with small values of $m(\mathbf{r})$, and within each cell, the energy (Hamiltonian) may be described by a Landau expansion as in the previous section. However, writing up such a Hamiltonian for each *isolated* cell, means that we neglect the couplings between neighbouring cells. This coupling will depend on the difference between the magnetisation in these cells; moreover, it will not depend on the sign of that difference, even in the presence of an external field. Therefore, this contribution can be cast in the form

$$\alpha \left[m(\mathbf{r}') - m(\mathbf{r}) \right]^2 + \beta \left[m(\mathbf{r}') - m(\mathbf{r}) \right]^4 + \dots$$

where \mathbf{r} and \mathbf{r}' are the coordinates of neighbouring cells. Keeping only the lowest order term in this expansion, we have, after replacing the difference by a gradient and integrating over the volume:

$$H = \int \left\{ k \left[\nabla m(\mathbf{r}) \right]^2 + h(\mathbf{r})m(\mathbf{r}) + rm^2(\mathbf{r}) + sm^4(\mathbf{r}) \right\} d^3r.$$

This form of the Hamiltonian reproduces the results of the previous section is $m(\mathbf{r})$ does not vary with \mathbf{r} . Note that the magnetic field *h* varies with position. The possibility to vary *h* and *m* with position enables us to evaluate the correlation function, defined as

$$g(\mathbf{r}) = \langle m(\mathbf{r}_0)m(\mathbf{r}_0+\mathbf{r})\rangle - \langle m(\mathbf{r}_0)\rangle^2$$
.

For a homogeneous system, the term on the right hand side does not depend on \mathbf{r}_0 .

A full calculation of the free energy starting from this Hamiltonian is difficult because of the presence of the m^4 term – the way to proceed is by a diagramatic expansion as done in Wilson's renormalisation theory, which is beyond the scope of this course. However, we can assume the critical behaviour found in the previous section to be valid and use our new Hamiltonian only to evaluate the correlation function. This is important because the integral over the correlation function is precisely the term which was neglected in the mean field theory. We therefore obtain a consistency criterion fo this theory.

The correlation function with the Landau-Ginzburg Hamiltonian is found as follows. We take a magnetic field which only couples to the spin located at $\mathbf{r} = 0$. This means that we have a term

 $hm(\mathbf{r} = 0)$ in the Hamiltonian. Now we evaluate the magnetisation at some point \mathbf{r} (not necessarily at the origin):

$$m(\mathbf{r}) = \frac{\int \prod_{\mathbf{r}} dm(\mathbf{r}') \exp\left\{-\beta \left[\int H\left(\{m(\mathbf{r}')\}\right) d^3r + hm(0)\right\}\right] m(\mathbf{r})}{\int \prod_{\mathbf{r}} dm(\mathbf{r}') \exp\left\{-\beta \left[\int H\left(\{m(\mathbf{r}')\}\right) d^3r + hm(0)\right]\right\}}.$$

The correlation function is then given by

$$\beta g(\mathbf{r}) = \frac{dm(\mathbf{r})}{dh} = \beta \left[\langle m(\mathbf{r})m(0) \rangle - \langle m(\mathbf{r}) \rangle \langle m(0) \rangle \right]$$

- / >

so if we find $m(\mathbf{r})$ as a function of h, we only have to evaluate its derivative in order to find the correlation function.

We find $\langle m(\mathbf{r}) \rangle$ by requiring that only the contribution which maximises the Boltzmann should be counted in evaluating the equilibrium value. This is the solution $m(\mathbf{r})$ which minimises

$$\int H(\{m(\mathbf{r})\}) d^3r + hm(0).$$

Varying $m(\mathbf{r})$ by $\delta m(\mathbf{r})$ we have

$$\int \left\{ 2rm(\mathbf{r})\delta m(\mathbf{r}) + 4sm^3\delta m(r) + 2k\nabla m(\mathbf{r})\nabla \left[\delta m(\mathbf{r})\right] + h\delta m(\mathbf{r})\delta(\mathbf{r}) \right\} d^3r = 0.$$

We apply Green's theorem to the term with the gradients, and require that $\delta m(\mathbf{r})$ vanishes at the boundary of the system in order to find the equation

$$-k\nabla^2 m(\mathbf{r}) + rm(\mathbf{r}) + 2sm^3(\mathbf{r}) + \frac{h}{2}\delta(\mathbf{r}) = 0.$$

Remember r is a parameter of the Hamiltonian – it does not denote $|\mathbf{r}|$. For h = 0 we recover the Landau result

$$m(\mathbf{r}) = m_0 = 0$$
 for $T > T_c(r > 0)$ and
 $m(\mathbf{r}) = m_0 = \sqrt{\frac{-r}{2s}}$ for $T < T_c(r < 0)$.

For small *h*, we can write

 $m(\mathbf{r}) = m_0 + h\boldsymbol{\varphi}(\mathbf{r}),$

and because $g(\mathbf{r}) = dm/dh$, we may identify $\varphi(\mathbf{r})$ with $g(\mathbf{r})$.

Substituting this in our differential equation we obtain

$$abla^2 g(\mathbf{r}) - rac{r}{k} g(\mathbf{r}) = rac{1}{2k} \delta(\mathbf{r}) ext{ for } T > T_c ext{ and }
abla^2 g(\mathbf{r}) + 2rac{r}{k} g(\mathbf{r}) = rac{1}{2k} \delta(\mathbf{r}) ext{ for } T < T_c.$$

The solution for these equations is

$$g(\mathbf{r})=\frac{1}{8k\pi r}e^{-r/\xi},$$

where

$$\xi = \begin{cases} \sqrt{\frac{k}{r}} & \text{for } T > T_c \text{ and} \\ \sqrt{\frac{-k}{2r}} & \text{for } T < T_c. \end{cases}$$

Since *r* is proportional to $T - T_c$ (see previous section), we see that the critical exponent v = 1/2.

At the critical point, we must use r = 0 in the differential equations for g:

$$\nabla^2 g(\mathbf{r}) = \frac{h}{k} \delta(\mathbf{r})$$

which is recognised as the electrostatic problem of finding the potential of a point charge. The solution is well known:

$$g(\mathbf{r}) \sim \frac{1}{|\mathbf{r}|},$$

which gives an exponent $\eta = 0$.

For dimension other than 3, the above result can be generalised to

$$g(\mathbf{r}) \sim \frac{1}{r^{d-2+\eta}},$$

still yielding $\eta = 0$.

The required result enables us now to estimate the term which was neglected in Landau (or mean field) approximation: the spatial fluctuation of the magnetisation. The relative importance of this fluctuation can be estimated as follows:

$$\frac{\int_{a}^{\xi} g(\mathbf{r}) d^{d} r}{\int_{a}^{\xi} m_{0}^{2} d^{d} r} \sim \frac{\int_{a}^{\xi} \frac{1}{|\mathbf{r}|^{d-2}} d^{d} r}{\xi^{d} m_{0}^{2}} \sim \frac{\xi^{2-d}}{m_{0}^{2}}.$$

For *T* approaching T_c from below, we have $m_0 = \sqrt{-r/s}$, which leads to

$$rac{\xi^{2-d}}{m_0^2} \sim rac{r^{-(2-d)/2}}{r} = r^{(d-4)/2}.$$

We see that the fluctuations can safely be neglected for d > 4. For smaller dimensions, we can expect corrections to the classical exponents.

10.5 Exact solutions

Another way for studying phase transitions is by exact solutions. Quite a few spin models on regular lattices have been solved exactly. Exact solutions are generally quite difficult to obtain, and we shall refrain from treating them in detail here, but sketch the ideas and apply them to the simple case of the one-dimensional Ising model. The partition function of this model can be written as

$$Z = \sum_{\{s_i=\pm 1\}} \exp\left(J\sum_{i=1}^N s_i s_{i+1} + B\sum_{i=1}^N s_i\right) = \sum_{\{s_i=\pm 1\}} \prod_{i=1}^N \exp\left(Js_i s_{i+1} + Bs_i\right).$$

We use periodic boundary conditions, so that $s_{N+1} \equiv s_1$. Now we define the **transfer matrix** as follows

$$T_{s_{i},s_{i+1}} = \exp\left[Js_{i}s_{i+1} + \frac{B}{2}(s_{i}+s_{i+1})\right] = \langle s_{i}|T|s_{i+1}\rangle$$

where we have used Dirac notation in the last expression. We can now rephrase the partition function as follows

$$Z = \sum_{\{s_i=\pm 1\}} \langle s_1 | T | s_2 \rangle \langle s_2 | T | s_3 \rangle \langle s_3 | \dots | s_{N-1} \rangle \langle s_{N-1} | T | s_N \rangle \langle s_N | T | s_1 \rangle$$

which, using the fact that $\sum_{s} |s\rangle \langle s|$ is the unit operator, can immediately be written in the form

$$Z = \operatorname{Tr} T^N$$
.

It is easy to see that T is a real, symmetric matrix. Therefore its eigenvalues are real. The largest (in absolute value) eigenvalue is called λ_1 , and the second largest is λ_2 etcetera. Then

$$Z = \sum_{i=1}^N \lambda_i^N.$$

For large N, the contribution from the largest eigenvalue will dominate the sum, and therefore we have

$$Z \approx \lambda_1^N$$
.

We now can calculate the average value of some spin s_i somewhere in the Ising chain. It is easy to see that this is given by

$$\langle s_i \rangle = \sum_{\{s_i = \pm 1\}} \langle s_1 | T | s_2 \rangle \langle s_2 | T | s_3 \rangle \langle s_3 | \dots | s_i \rangle s_i \langle s_i | T \dots | s_{N-1} \rangle \langle s_{N-1} | T | s_N \rangle \langle s_N | T | s_1 \rangle$$

Using again the fact that an expression like this is dominated by the eigenvector with the largest eigenvalue of T, we obtain

$$\langle s_i \rangle = \frac{\langle \phi_1 | s_i | \phi_1 \rangle}{\langle \phi_1 | \phi_1 \rangle}.$$

where ϕ_1 is the – normalised – eigenvector corresponding to the largest eigenvalue λ_1 of T.

Slightly more difficult is the evaluation of the correlation function

$$g_{ij} = \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle.$$

We assume j > i and $j - i \ll N$. Then

$$g_{ij} = \frac{\left\langle s_1 | T^{i-1} | s_i \right\rangle s_i \left\langle s_i | T^{j-i} | s_j \right\rangle s_j \left\langle s_j | T^{N-j+1} | s_1 \right\rangle}{\lambda_1^N} - \left(\frac{\left\langle \phi_1 | s | \phi_1 \right\rangle}{\left\langle \phi_1 | \phi_1 \right\rangle} \right)^2.$$

If we follow the same argument as we used in the calculation of the partition function, we would replace the transfermatrix by its largest eigenvalue. However, in that case, the second term cancels against the first and the result is zero. The main contribution to the transfer matrix comes from the second largest term in of the first part. This the term in which we replace the part between *i* and *j* (the term T^{j-i}) by the second largest eigenvalue of *T*. This eigenvalue is λ_2 . Therefore, we are left with

$$g_{ij} = \left(\frac{\lambda_2}{\lambda_1}\right)^{j-i} \left[|\langle \phi_1 | s | \phi_2 \rangle|^2 - (\langle \phi_1 | s | \phi_1 \rangle)^2 \right].$$

We see that *g* decays exponentially with correlation length

$$\xi = \ln \frac{\lambda_1}{\lambda_2}.$$

This correlation length becomes infinite when $\lambda_1 = \lambda_2$, i.e. when the largest eigenvalue becomes *degenerate*. Above we have indicated that the critical point is characterised by a divergence of the correlation length, so we identify the critical point with the point where the eigenvalues of *T* become



Figure 10.5: Kadanoff's droplet picture for the Ising model.

degenerate. Important in this respect is the *Frobenius theorem*. This theorem tells us that the largest eigenvalue of a symmetric matrix with all positive elements is nondegenerate. Therefore, the one-dimensional Ising model does not have a critical phase transition. In general, a model which has only a finite number of degrees of freedom in the direction perpendicular to the transfer-matrix direction, never exhibits critical behaviour.

The situation is different in the two-dimensional Ising model, if this becomes infinitely large. Then the transfer matrix becomes infinite, and Frobenius theorem no longer applies. The two dimensional Ising model can be solved exactly using the transfer matrix method (Onsager 1944, Schulz, Mattis and Lieb, 1964). Baxter (1982) has written a book about exactly solved models in statistical mechanics.

Working out the transfer matrix for the 1D model and its eigenvalues is left as an exercise.

10.6 Renormalisation theory

Close to a critical phase transition, the correlation length diverges. This does not mean that there is no structure characterised by length scales smaller than the correlation length. Kadanoff has characterised the critical phase by a **droplet model**. For the Ising model above the critical temperature, this droplet picture incorporates large regions (droplets) of one spin direction, which contain smaller droplets of the opposite spin, and these droplets contain in turn smaller droplets with the first spin direction etcetera. Thus we have droplets, within droplets, within droplets, ..., as shown in figure 10.5. The largest droplets are of a size of the order of the correlation length. For $T < T_c$ the picture is similar, but there we see droplets with spin opposite to the direction of the overall magnetisation, the largest of which are of a size comparable to the correlation length.

The foregoing description suggests that a critical model is *scale invariant*, as argued above in section 11.2 in connection with the divergence of the correlation length and the shape of the correlation function (power law). The scale invariance of a model at its critical point is the notion which lies at the basis of the renormalisation theory which is described in this section. We shall discuss the general ideas behind this theory by considering an Ising model with nearest neighbour coupling J and next



Figure 10.6: Example of a coarsening procedure as is performed in a renormalisation transformation

nearest neighbour coupling K (including a factor $1/(k_BT)$):

$$H = -k_{\rm B}T \left(J \sum_{\langle i,j \rangle} s_i s_j + K \sum_{\langle \langle i,j \rangle \rangle} s_i s_j\right)$$

where $\langle i, j \rangle$ denotes nearest neighbour pairs, whereas $\langle \langle i, j \rangle \rangle$ are the next-nearest neighbour pairs. We study the model in the *J*, *K* space.

In a renormalisation transformation we try to formulate the model on a coarser scale. Specifically, we want to formulate the partition function in terms of new spins which are defined on a lattice with a larger length scale, as in figure 10.6. The coarse spins are denoted as *t* instead of *s*. The *t*-spins are located at the centers of a subset of the plaquettes of the lattice. The spins *t* can assume the values ± 1 , just as in the ordinary Ising model. These values are determined by the values of the spins at the corners of the plaquette according to the following rules:

- If $s_1 + s_2 + s_3 + s_4 > 0$ then t = 1;
- If $s_1 + s_2 + s_3 + s_4 < 0$ then t = -1;
- If $s_1 + s_2 + s_3 + s_4 = 0$ then t = -1 or 1, the actual value is chosen at random with probabilities 1/2 for both values.

Now suppose we fix the values of t on each plaquette. Then we can assign an energy to this configuration using the following rule:

$$\exp(-\beta H'\{t_k\}) = \sum_{\{s_i\}} e^{-\beta H(\{s_i\})} W(t_k, s_1^{(k)}, s_2^{(k)}, s_3^{(k)}, s_4^{(k)})$$

where $\{t_k\}$ is a configuration of plaquette-spins t_k , k denotes the plaquettes, $s_i^{(k)}$ denotes the spins surrounding plaquette k, and W are the probabilities to have a spin t given the values of the four corner spins – these probabilities follow directly from the rules given above:

• $W(t = 1, s_1, s_2, s_3, s_4) = 1$ if $s_1 + s_2 + s_3 + s_4 > 0$;

- $W(t = -1, s_1, s_2, s_3, s_4) = 1$ if $s_1 + s_2 + s_3 + s_4 < 0$;
- $W(t, s_1, s_2, s_3, s_4) = 1/2$ for $t = \pm 1$ if $s_1 + s_2 + s_3 + s_4 = 0$.

For all other configurations, the weight factors W are zero.

We have now merely defined a new interaction for the t_k . Now we show what we can do with this new interaction. We calculate the partition function for the t_k :

$$\sum_{\{t_k\}} e^{-\beta H'(\{t_k\})} = \sum_{\{t_k\}} \sum_{\{s_i\}} e^{-\beta H(\{s_i\})} W(t_k, s_1^{(k)}, s_2^{(k)}, s_3^{(k)}, s_4^{(k)})$$

We can now move the sum over the configurations $\{t_k\}$ to the right as the term $e^{-\beta H(\{s_i\})}$ does not depend on the t_i :

$$\sum_{\{t_k\}} e^{-\beta H'(\{t_k\})} = \sum_{\{s_i\}} e^{-\beta H(\{s_i\})} \sum_{\{t_k\}} W(t_k, s_1^{(k)}, s_2^{(k)}, s_3^{(k)}, s_4^{(k)}).$$

Now we note that the sum over $\{t_k\}$ of the weights W for any *fixed* configuration of the four spins $s_1^{(k)}, s_2^{(k)}, s_3^{(k)}, s_4^{(k)}$ equals 1 (the W have been designed this way). Thus,

$$\sum_{\{t_k\}} e^{-\beta H'(\{t_k\})} = \sum_{\{s_i\}} e^{-\beta H(\{s_i\})} = Z.$$

We see that the new spins t_k form a model with a partition function which is *exactly* the same as the original one which was defined in terms of the s_i . A problem is that the form of H' might differ from H. Let us however assume that we can approximate H' – up to an additive constant – reasonably well by a form similar to H, but with different values of the interaction constants. We shall come back to this point later. This means that in going from the s_i to the t_k , the coupling constants J and K are mapped onto new ones, J' and K'. Then we repeat this procedure over and over.

It is important to realise that what we have done is a clever *scale transformation*, as the distance between two neighbouring *t*-spins is twice that between two s_i spins. We say that we have integrated out all degrees of freedom at length scale of the lattice constant *a* and are left with a new Hamiltonian of the same form as the original one, but with a lattice constant 2a, and new values of the coupling constants. This transformation is the **renormalisation transformation**.

Now let us consider the renormalisation transformation in the J, K plane. Under a renormalisation transformation, a point J, K is mapped onto a new point J', K'. How will these points transform? We consider a few special cases.

• Consider a point where J and K are large (low-temperature case). Then only few spins s_i might deviate from the majority value, which we take +1 to be specific. If we calculate the t_k , even when an isolated spin $s_i = -1$ is found at the corner of the plaquette, the plaquette spins will be +1. Therefore, the t_k are *more* likely to assume the majority value than the s_i , hence the new coupling constants J' and K' describing the *t*-spins will be *larger* than J and K respectively. In other words, in the low temperature, the renormalisation transformation causes the temperature to go down.

Another way to understand this is to imagine that we color the + spins red and the - spins blue. In the low temperature phase, most of the lattice is single-colored (either red or blue), with small spots of minority color. If we look at the lattice from a distance so that we no longer distinguish the fine detail, the lattice looks either red or blue, and the small deviating color spots have dissapeared. Therefore it looks like a system at T = 0.



Figure 10.7: Renormalisation flow.

At high temperatures, the effective couplings J and K are weak. The average spin value is 0 – there is no net magnetisation. The system will consist of patches of a single color – these patches have a size larger than the lattice constant a because the spins still feel the ferromagnetic interaction. If we coarsen however, near the edges of such a patch, the new spins t on the coarser lattice will assume random values as on the edge there are about as many spins + as there are −. This means that the edge becomes fuzzier. After a few renormalisation steps, the edges have become broader and broader and finally these regions where the t spins are randomly +1 or −1 cover the whole lattice. We see that the t seem to live in a system at higher temperature than the system of the s spins, in other words, the small couplings J and K transform into even smaller values J' and K'.

Again, when we look from a distance at a lattice at the lattice consisting of red and blue patches, we see in the end a mixture of red and blue, or, in other words, the rescaling has made the patches smaller, and in the end they have the same size as the (new) lattice constant, so we have a system at infinite temperature.

Now we can imagine what the flow diagram generated by the renormalisation transformation in the J, K plane looks like: there is a flow towards the origin J = K = 0 and there is a flow towards infinity $J = K = \infty$. We therefore have opposite flows towards two *fixed points*. Both fixed points have an *attraction basin* which is the region of points which flow eventually towards the fixed points. Obviously, the two attraction basins must be separated by a line, called *separatrix*. Points on that line must flow along that line. By extending the arguments above for describing the flow in the J, K plane, we can see that for J = 0, K > 0, a positive coupling J will be generated in the renormalisation transformation, and the reverse is also true: from the point J > 0, K = 0 we move to a point where both are positive. Collecting all this information we have the picture shown in figure 10.7. We see that there are three fixed points. Two of these (at zero and infinity) are so-called *trivial* fixed points where the physics of the model is easy to understand and relatively trivial. Then there is a third fixed point on the separatrix. The entire separatrix is interpreted as a line consisting of critical points, because it separates the low- from the high temperature phase.

So far, we have only discussed the mechanics of the renormalisation transformation but have not derived any useful result from it. To proceed, we consider the partition function in more detail. The free energy is related to the partition function by

$$F = -k_{\rm B}T\ln Z.$$

Therefore, the free energy per spin f = F/N (for N spins) satisfies:

$$e^{-\beta N f(J,K)} = Z(J,K).$$

Now we can write Z as the partition function of the Ising model either in terms of the 'original' spins s_i , or in terms of the coarsened spins t_k , as shown above:

$$e^{-\beta N f(J,K)} = \sum_{\{t_k\}} e^{-H'(J',K')-C} = e^{-\beta N' f(J',K')-C}.$$

The constant *C* is the difference between the original and the renormalised Hamiltonian. This constant also depends on *J* and *K*. There is a clear relation between *N* and N':

$$N' = N/2^{d}$$

as can be seen directly from the renormalisation procedure. To keep the discussion general, we relax the rescaling constant 2 to assume any value larger than 1, and call it *l*. The result we can infer for the free energy per spin is:

$$f(J,K) = l^{-d} f(J',K') + c$$

where $c = k_{\rm B}TC/N$.

We can analyse the transformation of the correlation in a similar fashion. The renormalisation transformation leaves the physics at length scales beyond the scales over which we have integrated out the degrees of freedom, essentially invariant, so the correlation length does not change under the renormalisation transformation. However, if we measure the correlation length in units of the grid constant, we must realise that the latter scales with l, so

$$\xi(K',J') = \xi(K,J)/l.$$

Now let us analyse the behaviour of the transformation close to the (nontrivial) fixed point. Points on the separatrix flow to that point under the renormalisation transformation, whereas points in a direction perpendicular to that line flow away from the fixed point. To describe the behaviour near the fixed point, we linearise the renormalisation transformation. If we call the coordinates of the fixed point J^*, K^* , we have

$$(J^* + \Delta J, K^* + \Delta K) \xrightarrow{\operatorname{RT}} (J^* + \Delta J', K^* + \Delta K').$$

To first order in ΔJ and ΔK , $\Delta J'$ and $\Delta K'$ can be written as

$$\left(\begin{array}{c} \Delta J'\\ \Delta K'\end{array}\right) = A \left(\begin{array}{c} \Delta J\\ \Delta K\end{array}\right),$$

where A is a 2×2 matrix whose elements do not depend on ΔJ and ΔK . If we diagonalise the matrix A, we find two real eigenvalues, λ and μ . One of these, say λ , corresponds to the points on the separatrix and will be smaller than 1. This means that the corresponding eigenvector lies along the

sepatrix at the fixed point. The other, μ , will be larger than 1 and the corresponding eigenvector lies in the outflowing direction.

Now there exists an important theorem by Wegner which says that the eigenvalues λ and μ must have the following dependence on *l*:

$$\lambda = l^{y};$$
$$\mu = l^{z}.$$

The corresponding eigenvectors are called *Wegner scaling fields*. We call these scaling fields *s* (corresponding to λ) and *t* (corresponding to μ). Repeated application of the transformation leads to the rule:

$$s^{(n)} = l^{ny}s;$$

$$t^{(n)} = l^{nz}t.$$

Since $\lambda < 1$ and $\mu > 1$, we must have y < 0 and z > 0. The indices y and z are called *scaling indices*.

Note that close to the critical point, J and K can be reparametrised in terms of s and t. For the correlation length we therefore have:

$$\xi(s,t) = l^n \xi(l^{ny}s, l^{nz}t).$$

Choosing now *n* such that $l^{nz}t = 1$, we have

$$\xi(s,t) = t^{-1/z} \xi(t^{-y/z}s,1).$$

For $t \rightarrow 0$, and using the fact that y/z < 0 (see above), we have

$$\xi(s,t) = t^{-1/z}\xi(0,1) \equiv \frac{A}{t^{1/z}}.$$

From the renormalisation flow plot, we can infer thet *t* must be related to the temperature, as varying the temperature corresponds to moving on a straight line through the origin. We therefore can identify

$$t=\frac{T-T_c}{T_c},$$

and we see that the critical exponent v is given by 1/z.

We have seen that near a fixed point, there is an outward flow, corresponding to a positive scaling index (eigenvalue > 1) and a negative scaling index (eigenvalue < 1). Scaling fields with positive indices are called *relevant*, those with negative indeces are *irrelevant*, and those with index 0 are called *marginal*. Note that any point on the separatrix moves under the renormalisation transformation eventually to the fixed point. Therefore, the behaviour at long length scales of these points is dominated by the properties of this fixed point.

Other critical exponents follow from a similar analysis of the free energy. To analyse these exponents, it is useful to expand the parameter space to include the magnetic field *B* (including the factor $1/k_{\rm B}T$):

$$f = f(J, K, B).$$

Therefore, we have three scaling fields, which we denote as s, t and h. Note that the corresponding scaling field must be relevant, as the magnetic field breaks the symmetry and destroys the critical

87

behaviour. If it were irrelevant, there would be points corresponding to nonzero field which would flow to the fixed point, and therefore these points would be critical, which, as we know, is not the case. We call v the scaling index, associated with h. The direction corresponding to h is perpendicular to the plane of the renormalisation flow plot in figure 10.7.

We call the scaling fields *s*, *t* and *h*. The interpretation of these fields is as follows:

- *t* corresponds to the temperature,
- *h* corresponds to the magnetic field,
- *s* corresponds to a particular combination (e.g. the ratio) of *J* and *K*.

If we are at a critical point and change either the temperature or the field, we destroy the criticality. However, a judicious change of both J and K keeps the system at the critical point.

We have seen before that the free energy per spin transforms as

$$f(s,t,h) = l^{-d} f(s',t',h') + c(s,t,h).$$

We now neglect c(s,t,h) as this is a regular function, and we are interested in the part of the free energy which contains singularities, as these determine the critical properties. After *n* renormalisation transformations, we have

$$f_{\rm sing}(s,t,h) = l^{-nd} f_{\rm sing}(l^{ny}s, l^{nz}t, l^{nv}h).$$

Again we take $l^{nz}t = 1$. Therefore we have

$$f_{\text{sing}}(s,t,h) = t^{d/z} f(st^{-y/z},\pm 1,ht^{-v/z}).$$

From this expression we can derive the critical exponents in terms of the scaling indices. We may first note that again $st^{-y/z}$ will approach 0 (see the discussion concerning the correlation length).

First, we calculate the exponent α for the specific heat per particle. This is found from the free energy per particle as

$$C_h = \left(\frac{\partial^2 f}{\partial t^2}\right)_{h=0}$$

Restricting attention to the singular part of f, we see that

$$C_h \propto t^{d/z-2}$$

so that

$$\alpha = 2 - d/z$$

The exponent β describes the behaviour of the magnetisation when the critical temperature is approached from below. Recall that the magnetisation is given by

$$m = \left(\frac{\partial f}{\partial h}\right)_{h=0}$$

The contribution to the magnetisation arising from the singular part of the free energy is therefore

$$m \propto t^{d/z} t^{-\nu/z}$$
.

so the exponent β is found as

$$\boldsymbol{\beta} = (d - v)/z.$$

For the susceptibility exponent γ , we find

$$\chi = \frac{dm}{dh} = \frac{\partial^2 f}{\partial h^2} \propto t^{d/z} t^{-2\nu/z},$$

and we have

$$\gamma = -(d-2v)/z.$$

Finally, the exponent δ describes how the magnetisation varies with the applied magnetic field. In order to find this exponent, we choose *n* such that $l^{nv}h = \pm 1$. Then,

$$f_{\rm sing}(s,t,h) = |h|^{d/\nu} f(s|h|^{-y/\nu},t|h|^{-z/\nu},\pm 1),$$

so that

$$m=|h|^{d/\nu-1},$$

yielding

$$\delta = \frac{v}{d-v}.$$

A different kind of analysis enables us to find the critical exponent associated with the correlation function, which, as we anticipated above, decays algebraically with distance *at the critical point*. The decay is defined in terms of a critical exponent η :

$$g(r) \sim rac{1}{r^{d-2+\eta}}$$

Now we note that the susceptibility χ is related to the correlation function by the relation

$$\chi = \int g(r) d^d r.$$

This relation is derived as follows.

$$\int g(r)d^d r \approx \sum_{\mathbf{r}} \langle s(0)s(\mathbf{r}) \rangle - N \langle s(0) \rangle^2,$$

where use has been made of the translation invariance of the system. Given the fact that the magnetisation is given as

$$m = \frac{\sum_{\mathbf{r}} s(\mathbf{r} = 0) \exp\left[H_0\left(\{s(\mathbf{r})\}\right) + h\sum_{\mathbf{r}} s(\mathbf{r})\right]}{\sum_{\mathbf{r}} \exp\left[H_0\left(\{s(\mathbf{r})\}\right) + h\sum_{\mathbf{r}} s(\mathbf{r})\right]}$$

and using $\chi = dm/dh$, we see that

$$\chi = \frac{\sum_{\mathbf{r}} s(\mathbf{r}=0) \sum_{\mathbf{r}} s(\mathbf{r}) \exp\left[H_0\left(\{s(\mathbf{r})\}\right) + h \sum_{\mathbf{r}} s(\mathbf{r})\right]}{\sum_{\mathbf{r}} \exp\left[H_0\left(\{s(\mathbf{r})\}\right) + h \sum_{\mathbf{r}} s(\mathbf{r})\right]} - N\left[\frac{\sum_{\mathbf{r}} s(\mathbf{r}=0) \exp\left[H_0\left(\{s(\mathbf{r})\}\right) + h \sum_{\mathbf{r}} s(\mathbf{r})\right]}{\sum_{\mathbf{r}} \exp\left[H_0\left(\{s(\mathbf{r})\}\right) + h \sum_{\mathbf{r}} s(\mathbf{r})\right]}\right]^2,$$

where the first term derives from the numerator, and the second from the denominator in the expression for *m*. We recognise the right hand side of this equation as $\int g(r) d^d r$.

Now the exponent η can be derived by evaluating the contribution from the algebraic component of g(r) in the integral. In order to do this properly, we must realise that the algebraic decay sets in beyond a distance of the order of the lattice constant a, and that, close to the critical point, where the correlation length ξ is large but finite, this decay persists up to the distance ξ , but vanishes beyond. Therefore we have

$$\chi \propto t^{(d-2\nu)/z} = \int_a^{\xi(t)} \frac{1}{r^{d-2+\eta}} r^{d-1} dr,$$

where the angular degrees of freedom have been separated out from the integral, as the integrand depends only on r. From this, and from

$$\xi \propto t^{-\nu} = t^{-1/z},$$
$$t^{(d-2\nu)/z} \propto \xi^{2-\eta} \propto t^{(\eta-2)/z},$$

we see that

. .

so that

$\eta = d + 2 - 2v.$

10.7 Scaling relations

In the previous section, we have seen that the critical behaviour is governed by the positive scaling indices z and v, i.e. the indices corresponding to the relevant scaling fields. There are only two such fields, but there are six critical exponents. Therefore, the exponents must be related among each other. Inspecting the expressions for these exponents, we have

•
$$v = 1/z; \ \alpha = 2 - d/z, \text{ so}$$

• $\alpha = 2 - d/z; \ \beta = (d - v)/z; \ \gamma = -(d - 2v)/z, \text{ so}$
 $\alpha + 2\beta + \gamma = 2.$
• $\beta = (d - v)/z; \ \gamma = -(d - 2v)/z; \ \delta = v/(d - v) \text{ so}$
 $\beta(\delta - 1) = \gamma.$
• $\gamma = -(d - 2v)/z; \ v = 1/z; \ \eta = d + 2 - 2v, \text{ so}$
 $\gamma = (2 - \eta)v.$

It is clear that the critical exponents of the Ising model ($\alpha = 0$, $\beta = 1/8$, $\delta = 15$, $\nu = 1$, $\eta = 1/4$, $\gamma = 7/4$ satisfy these scaling relations for d = 2 whereas the mean-field or Landau exponents ($\alpha = 0$, $\beta = 1/2$, $\delta = 3$, $\nu = 1/2$, $\eta = 0$) satisfy these relations for d = 4.

10.8 Universality

Suppose that we add new interactions or fields to the Hamiltonian. 'New' here means that they cannot be expressed in terms of the interactions and fields already present in the Hamiltonian. These new terms then have their own parameters, so the total parameter space of the model acquires extra dimensions. Obviously the effect of the new terms strongly depends on whether they are relevant, irrelevant or marginal. If the new fields are relevant, then their presence will move the system away from the critical point under the renormalisation transformation. If the terms are irrelevant they have *absolutely no effect* on the critical exponents. If they are marginal, this means that the fixed point lies on a line of critical points, and on this line, the critical exponents may vary. The important notion here is that adding irrelevant fields leaves the critical exponents unchanged. All the models which differ from the original one by irrelevant terms, have the same critical behaviour. The class of models which is governed by one and the same fixed point is called the *universility class* of the system.



Figure 10.8: The renormalisation transformation for the triangular lattice in 2 dimensions.

10.9 Examples of renormalisation transformations

As an example of a renormalisation transformation, we consider the Ising model in two dimensions on a triangular lattice. The reason we choose this lattice is that the transformation is simpler than for the square lattice. The transformation is shown in figure 10.8. We take for the interaction only nearest neighbour couplings into account, and take the magnetic field equal to zero. Two neighbouring coarse plaquettes are arranged as shown on the right hand side of figure 10.8. The plaquette spins are chosen according to the majority rule: the plaquette spin is the same as the majority of spin values at the three corners of the plaquette. If both plaquette spins are positive, then the sum of the Boltzmann weights corresponding to all possible configurations, given that the two + values of the plaquette spins is

$$e^{-H(+,+)} = e^{8J} + 3e^{4J} + 2e^{2J} + 3 + 6e^{-2J} + e^{-4J}.$$

H includes the factor $1/k_{\rm B}T = \beta$. The total number of weights on the right hand side adds up to 16, since both plaquettes have four possible configurations given their majority spin. For opposite spins we have

$$e^{-\beta H(+,-)} = 2e^{4J} + 2e^{2J} + 4 + 6e^{-2J} + 2e^{-4J}.$$

Therefore, calling the plaquette spins t_i we have a Hamiltonian of the form

$$H_{\text{renormalised}}(\{t_i\}) = \sum_{\langle i,j \rangle} J' t_i t_j,$$

where J' obviously includes the factor $-\beta$ and where the renormalised coupling constant J' is given by the requirement

$$e^{2J'} = rac{e^{-H(+,+)}}{e^{-H(+,-)}},$$

which leads to the following explicit form of J'(J).

$$J' = \frac{1}{2} \ln \left[\frac{e^{8J} + 3e^{4J} + 2e^{2J} + 3 + 6e^{-2J} + e^{-4J}}{2e^{4J} + 2e^{2J} + 4 + 6e^{-2J} + 2e^{-4J}} \right].$$



Figure 10.9: Renormalised coupling constant J' as a function of the original coupling constant J of the Ising model.

In figure 10.9, the renormalised coupling constant is plotted as a function of J. There is a fixed point at the value $J \approx 0.365$. The exact solution for the Ising model on a triangular lattice gives a value 0.274.

The slope of the plot of the function J'(J) turns out to be 1.544 – this is the value of the eigenvalue λ . It then follows directly that the scaling index z = 0.79, to be compared with the exact value of 1.0. It is straightforward to include the magnetic field into this renormalisation procedure. This leads to a scaling index for the magnetisation of 2.02 (exact value 1.8750). All in all these values are encouraging. Moreover, this procedure can be extended straightforwardly to encompass larger and larger clusters (Niemeyer and Van Leeuwen) and the values obtained in this way are within less then a percent of the exact ones.

10.10 Systems with continuous symmetries

Another example of a system for which a renormalisation transformation can be carried out is the *XY* model. This model has physical realisations in superfluid helium films and arrays of superconducting islands separated by Josephson junctions. Moreover, the model can be mapped onto a roughening model, which describes the roughening of a crystal surface with increasing temperature.

The model is formulated on a 2D lattice; the degrees of freedom have a 2π periodicity: they can be viewed as the angles of unit vectors which in turn can be considered as 'planar spins' (see figure 10.10). The Hamiltonian of the model is given by

$$H = -K \sum_{\langle i,j \rangle} \cos(\theta_i - \theta_j).$$

This Hamiltonian favours the spins to be aligned ($\theta_i = \theta_j$).

The behaviour at low temperatures of this models is dominated by two types of excitations. The first type of excitations are *spin waves*. These are excitations of the form

$$\theta(\mathbf{r}) = A \exp(i\mathbf{k} \cdot \mathbf{r})$$



Figure 10.10: The XY model with planar spins on a square lattice.

with wavelengths $2\pi/|\mathbf{k}|$ much larger than the lattice spacing *a*. In that case we can approximate the cosine occurring in the Hamiltonian by a quadratic expression:

$$H \approx -K \sum_{\langle i,j \rangle} \left[1 - \frac{1}{2} (\theta_i - \theta_j)^2 \right].$$

The first terms in the square brackets add up to a constant which does not influence the model. Keeping the second term leads to the so-called *Gaussian model*, as the Boltzmann factor has a Gaussian form.

The Gaussian model can be solved exactly by Fourier transforming the variables θ_i . We set

$$\tilde{\theta}(\mathbf{k}) = \frac{1}{L} \sum_{i} \theta(\mathbf{r}_{i}) e^{i\mathbf{k}\cdot\mathbf{r}_{i}}$$

where we assume that we are dealing with an $L \times L$ square lattice. Then,

$$heta(\mathbf{r}_i) = \sum_{\mathbf{k}} ilde{ heta}(\mathbf{k}) e^{-i\mathbf{k}\cdot\mathbf{r}_i}$$

Therefore, we obtain

$$\sum_{i} \left[\theta(\mathbf{r}_{i}) - \theta(\mathbf{r}_{i} + a\hat{\mathbf{x}})\right]^{2} = \sum_{i} \left[\sum_{\mathbf{k}} \tilde{\theta}(\mathbf{k}) \left(e^{-i\mathbf{k}\cdot\mathbf{r}_{i}} - e^{-i\mathbf{k}\cdot(\mathbf{r}_{i} + a\hat{\mathbf{x}})}\right)\right]^{2}$$

Using the fact that, since **k** assumes the values $\mathbf{k} = \frac{2\pi}{aL}(n_x, n_y)$, we have

$$\sum_{i} e^{i\mathbf{k}\cdot\mathbf{r}_{i}} = N\delta_{\mathbf{k},\mathbf{0}},$$

we obtain

$$\sum_{i} \left[\theta(\mathbf{r}_{i}) - \theta(\mathbf{r}_{i} + a\hat{\mathbf{x}})\right]^{2} = \sum_{\mathbf{k}} \left[2 - 2\cos(ak_{x})\right]\tilde{\theta}(\mathbf{k})\tilde{\theta}(-\mathbf{k})$$

Including the terms which are neighbours along the y direction, and taking $|\mathbf{k}|$ small, we have

$$H = -\frac{K}{2} \sum_{\mathbf{k}} k^2 \tilde{\theta}(\mathbf{k}) \tilde{\theta}(-\mathbf{k}).$$

Defining $J = \beta K$, the partition function can be written as

$$Z = \int_{-\infty}^{\infty} \prod_{\mathbf{k}} \tilde{\theta}_k \exp\left[\frac{J}{2}k^2 \tilde{\theta}(\mathbf{k}) \tilde{\theta}(-\mathbf{k})\right].$$

This is a product of Gaussian integrals which can be evaluated analytically to yield

$$Z = \prod_{\mathbf{k}} \frac{\pi}{Jk^2}.$$

For the free energy we then find

$$F = -k_{\rm B}T\ln Z = -k_{\rm B}T\int\ln\frac{2\pi}{Jk^2}\,d^3k.$$

The integral has a lower bound corresponding to $2\pi/(La)$ and an upper bound of $2\pi/a$. We refrain from working it out but emphasise that this free energy is an analytical function of temperature (which is hidden in the parameter *J*) so there is no phase transition.

Surprisingly, the model is critical for all temperatures! This can be seen by working out the correlation function

$$\langle \cos[\theta(\mathbf{r}) - \theta(0)] \rangle = \left\langle e^{i[\theta(\mathbf{r}) - \theta(0)]} \right\rangle$$

(the sin term disappears as a result of antisymmetry). As the action (Hamiltonian) is quadratic in θ_k , we can evaluate this expectation value.

$$\left\langle e^{i(\theta_{\mathbf{r}}-\theta_{0})}\right\rangle = \left\langle e^{\frac{i}{N}\sum_{\mathbf{k}}\left(e^{i\mathbf{k}\cdot\mathbf{r}}-1\right)\theta_{\mathbf{k}}}\right\rangle = \frac{\int\prod_{\mathbf{k}}d\theta_{\mathbf{k}}e^{i\mu_{\mathbf{k}}\theta_{\mathbf{k}}}e^{-\frac{J}{2}\sum_{\mathbf{k}}k^{2}|\theta_{\mathbf{k}}|^{2}}}{\int\prod_{\mathbf{k}}d\theta_{\mathbf{k}}e^{-\frac{J}{2}\sum_{\mathbf{k}}k^{2}|\theta_{\mathbf{k}}|^{2}}}$$

with $\mu_{\mathbf{k}} = e^{i\mathbf{k}\cdot\mathbf{r}} - 1$.

We see that the expressions in the numerator and denominator factorize. For the numerator we can work out a factor. We write $\theta_{\mathbf{k}} = X + iY$ and $\mu_{\mathbf{k}} = \mu_1 + i\mu_2$. Furthermore, we realise that $\theta(-\mathbf{k}) = \theta^*(\mathbf{k})$ and similar for $\mu_{\mathbf{k}}$. Finally, we combine the integrals over \mathbf{k} and $-\mathbf{k}$ into a single integral over \mathbf{k} , which now runs over half the reciprocal space only, to obtain

$$\int e^{i(\mu_{\mathbf{k}}\theta_{k}+\mu_{-\mathbf{k}}\theta_{-\mathbf{k}}} e^{-Jk^{2}\theta_{\mathbf{k}}\theta_{-\mathbf{k}}} d\theta_{\mathbf{k}} = \int e^{2i(\mu_{1}X-\mu_{2}Y)} e^{-Jk^{2}(X^{2}+Y^{2})} dX dY.$$

We see that the two integrals factorise. For the integral over *X* we have

$$\int e^{2i\mu_1 X} e^{-Jk^2 X^2} dX = \int \exp\left[-Jk^2 \left(X - i\frac{\mu_1}{Jk^2}\right)^2\right] \exp\left(-\frac{\mu_1^2}{Jk^2}\right).$$

The Gaussian integral gives precisely the same result as the corresponding Gaussian integral occurring in the denominator, so after dividing this factor out, the result is

$$\exp\left(-\frac{\mu_1^2}{Jk^2}\right).$$

For the integral over *Y*, we obtain

$$\exp\left[-\frac{\mu_2^2}{Jk^2}\right].$$

multiplying both terms gives

$$\exp\left[-\frac{|\mu_{\mathbf{k}}|^2}{Jk^2}\right].$$

Carrying out the product over \mathbf{k} over the *entire* reciprocal space, and realising that the product of exponentials can be written as the exponential of the sum, we obtain

$$g(\mathbf{r}) = \exp\left[-\frac{1}{2J}\sum_{\mathbf{k}}\frac{|\boldsymbol{\mu}_{\mathbf{k}}|^2}{k^2}\right] = \exp\left[-\frac{1}{2J}\sum_{\mathbf{k}}\frac{2-2\cos(\mathbf{k}\cdot\mathbf{r})}{k^2}\right].$$

Let us call the result of the sum $f(\mathbf{r})$:

$$f(\mathbf{r}) = \sum_{\mathbf{k}} \frac{2 - 2\cos(\mathbf{k} \cdot \mathbf{r})}{k^2}$$

Then, in the continuum limit:

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) f(\mathbf{r}) = \sum_{\mathbf{k}} 2\cos(\mathbf{k} \cdot \mathbf{r}) = 2N\delta_{\mathbf{r},\mathbf{0}}.$$

This is recognised as the Poisson equation for a line charge (or a point charge in two dimensions). The solution of this equation is

$$f(\mathbf{r}) = \frac{1}{\pi} \ln r,$$

so that we find for the correlation function

$$g(\mathbf{r}) = g(r) \propto e^{-\ln(r)/(2\pi J)} = \frac{1}{r^{1/(2\pi J)}}$$

We see that this correlation is critical (power law).

In fact, the Hamiltonian favours spins to be aligned. However, the spin waves can be formed at such low energy cost that they will destroy any attempt to build up a real 'long range order', in which the expectation value for spins very far apart approaches a constant. This is an example of the Mermin-Wagner theorem (1966) which states that systems with continuous symmetry cannot exhibit long range order.

In addition to spin-waves, the XY model can exhibit excitation of a vortex character. First we study a single vortex as in figure 10.11. The energy of such a vortex can be calculated as follows. Consider a circle of radius *a* around the center of the vortex. The number of spins on that ring will be of order $2\pi r/a$ where *r* is the lattice constant. The difference between neighbouring spin angles will therefore be $2\pi/(2\pi r/a) = a/r$. The energy stored in the spins around the circle is therefore

$$E(r) \approx 2\pi \frac{r}{a} \frac{K}{2} \left(\frac{a}{r}\right)^2 \approx \frac{K\pi a}{r}.$$

For the total energy, we must integrate this for radii up to the order of the system size R, and we obtain

$$E_{\text{total}} \sim \pi K \ln(R/a).$$



Figure 10.11: An isolated vortex in the XY model.

The entropy associated with a single vortex is proportional to the logarithm of the number of ways we can place the vortex on the lattice:

$$S \sim k_{\rm B} \ln(R/a)^2$$
.

The free energy of a single vortex can therefore be estimated to be

$$F = E - TS = (\pi K - 2k_{\rm B}T)\ln(R/a).$$

We see that for low temperatures, it *costs* free energy to build up an isolated vortex, whereas for high temperatures, free energy is *gained* when a vortex is formed. We therefore expect a sudden, spontaneous proliferation of vortices when the temperature exceeds a particular value, which we associate with a phase transition.

To see what the situation is like in the two-vortex case, we first note that a vortex centered at \mathbf{r}_0 is described by a solution of the equation:

$$abla imes
abla [m{ heta}(\mathbf{r})] = \pm 2\pi \delta(\mathbf{r} - \mathbf{r}_0).$$

It can be rigourously shown that the vortex system behaves as a system of charges in two dimensions. The vortices have two possible winding directions, corresponding to positive and negative charges. A vortex pair of opposite sign has a total energy of

$$E_{\text{pair}} = -\pi J e_i e_j \ln \left| \mathbf{r}_i - \mathbf{r}_j \right|$$

where $e_i, e_j = \pm 1$. Therefore, two vortices have a *finite* energy (as opposed to a single vortex) and the entropy helps these pairs to proliferate at low temperatures.

The vortex system can be described by a so-called *Coulomb gas* in two dimensions: this is a gas consisting of charges which float on the lattice. The picture we have developed so far of the behaviour of this model is that at low temperatures, the system will for charge dipoles and therefore be an insulator. Beyond a transition temperature of the order of $T_c = \pi K/(2k_B)$, the dipoles will 'melt' and free charges will occur: the insulator becomes a conductor.



Figure 10.12: Renormalisation flow for the Coulomb gas. The transision point lies at $J = 2/\pi$.

Kosterlitz and Thouless have performed a renormalisation procedure to analyse the Coulomb gas model. The Hamiltonian is

$$-\pi J \sum_{i,j} e_i e_j V(|\mathbf{r}_i - \mathbf{r}_j|) + \mu \sum_i e_i^2$$

The second term is added to have the freedom of changing the chemical potential of the charges. The renormalisation transformation can also be obtained using a self-consistency requirement for the linearly screened, or effective potential. This potential is defined as the free energy associated with two infinitesimal charges placed at **0** and **r**. If the system is an insulator ($T < T_c$), the potential with still be logarithmic, but with a prefactor given by the dielectric constant. For high temperatures, when free charges can exist, the system becomes a conductor and the potential acquires an exponential form.

Defining $z = \exp(\mu)$, the renormalisation equations have the form

$$\frac{dJ}{dl} = -4\pi^2 J^2 z^2;$$
$$\frac{dz}{dl} = (2 - \pi J)z.$$

The flow diagram is shown schematically in figure 10.12. Suppose we start at some values for J and z. In the low-temperature phase, the renormalisation trajectory brings us to a point with equivalent critical behaviour. We see that we end up at z = 0, i.e. a phase with very low vortex density and a *renormalised coupling constant* \tilde{J} . In this phase, the correlation function is simply

$$g(r) = \exp(-\pi \tilde{J} \ln r) = r^{-\pi J}.$$

This is therefore a critical phase. Beyond the critical temperature, the behaviour of the system corresponds to that of a system with an infinite concentration of vortices and high temperature. This is a disordered phase. The transition temperature lies at $\tilde{J} = 2/\pi$, as anticipated above on the basis of a simple energy-entropy balance argument.

What consequences does this have for physics? We shall describe the vortex physics of superfluid helium films. These films are essentially two-dimensional, and they carry a particular density of (quasi)-particles which are all in the same quantum state, which is characterised as

$$\psi(\mathbf{r}) = a(\mathbf{r})e^{i\gamma(\mathbf{r})}$$

As we have seen in chapter 10, we can have vortices associated with a rotation of the phase around a centre where the superfluid density $\rho(\mathbf{r}) = a^2(\mathbf{r})$ vanishes. On page 63, we have found for the superfluid velocity:

$$\mathbf{u}_s = \frac{\hbar}{m} \nabla \gamma(\mathbf{r}).$$

Outside the vortex centres, the superfluid density is roughly constant, so we can evaluate the kinetic energy for the superfluid fraction as

$$H = \frac{m\rho}{2} \int u_s^2(\mathbf{r}) d^2 r = \frac{\hbar^2}{2m} \rho \int \left[\nabla \gamma(\mathbf{r})\right]^2 d^2 r.$$

The phases $\gamma(\mathbf{r})$ have the same property as the degrees of freedom in the *XY* model, in the sense that they are periodic with period 2π . This means that the phase can exhibit vortices. The coupling constant is

$$J = \frac{\hbar^2}{m} \frac{\rho}{k_{\rm B}T}.$$

What is measured in experiment is the renormalised coupling constant which, as we infer from the last equation, is in fact the superfluid density. At the phase transition, \tilde{J} jumps from the value $2/\pi$ to zero. This implies that the measured superfluid density jumps from

$$\rho_{\rm crit} = \frac{2k_{\rm B}Tm}{\pi\hbar^2}$$

to zero. This has been confirmed experimentally by Bishop and Reppy in 1978.

Similar phenomena have been observed for coupled arrays of Josephson junctions (Herre van der Zant) and for surface roughening transitions.

Irreversible processes: macroscopic theory

11.1 Introduction

Up to this point, we have been exclusively concerned with equilibrium statistical mechanics. If we consider a system in equilibrium, and identify a subvolume within this system of size (much) larger than the correlation length, we find that the thermodynamic properties within this system are equivalent to that of the entire system. However, if we are not yet in equilibrium, this may no longer hold, and neighbouring subsystems will have different thermodynamic properties. The systems will however tend to equalise these properties, by exchange of energy, momentum, or other quantities. This exchange can be formulated in terms of *fluxes* of the quantity under consideration.

Now consider such subcells inside some larger system. We focus on a particular quantity A_i within subcell a. Note that a necessary condition for defining A_i is that the subcell must be much larger than the microscopic length scale (atomic correlation length) and much smaller than the distance over which thermodynamic quantities vary – we then are in the *hydrodynamic limit*. If A_i is a conserved quantity (for example particle number, energy) then a change of $A_i(a)$ may take place through two mechanisms: (i) a loss or increase due to A_i flowing to or from neighbouring cells b; (ii) a loss or increase due to some source or sink for the quantity A_i inside the cell. For example, particles may move from one cell to another [process (i)] or the cell may be connected to a source or drain of particles [process (ii)].

The conservation law for quantity A_i can be formulated as

$$\frac{dA_i(t)}{dt} = -\sum_{b \neq a} \Phi_i(a \to b) + \Phi_i(\text{sources} \to a).$$

The quantities Φ_i represent *fluxes*: their dimension is the dimension of A_i per unit of time.

Now suppose that A_i can be defined in terms of a *density* ρ_i :

$$A_i(a,t) = \int_{V(a)} \rho_i(t) \, d^3r$$
(11.1)

for any cell *a* much larger than the correlation length. Then we may also define a local flux j_i and source term σ such that the conservation law above may be formulated, using the divergence theorem, in terms of ρ_i , j_i and σ_i :

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \mathbf{j}_i = \boldsymbol{\sigma}_i.$$

11.2 Local equation of state

When we want to consider the flow of a quantity A_i in the sense of the previous section, we must take this A_i to be extensive, as can be seen by expression (11.1). We have seen in the beginning of

this course, that with each extensive variable, there is a conjugate, intensive variable. As an example we may consider the energy, which is the quantity which flows from one cell to the other, and its conjugate variable temperature, which will change in the two cells as a result of energy transport, but which is not subject to a conservation law as in the previous section.

As the distinction between extensive quantities and their intensive, conjugate partners is quite explicit in the study of nonequilibrium and transport, it is convenient to take the entropy as the statistical potential: this potential is defined in terms of *extensive* quantities and the corresponding intensive quantities can be determined as derivatives of the entropy:

$$\frac{\partial S}{\partial E} = \frac{1}{T}; \quad \frac{\partial S}{\partial N} = -\frac{\mu}{T}; \quad \frac{\partial S}{\partial V} = \frac{P}{T}.$$

The last relation is irrelevant for our purposes as we do not consider the volume as a flowing quantity. What may flow, however, is the momentum of the particles in our subvolume, so we must consider the entropy for fixed volume, particle number, energy *and* total momentum **p**. Note that **p** is an extensive quantity. It can be shown that the entropy does not change when we impart an equal velocity to all particles in our system. The energy measured with respect to the system box, will however change by an amount $p^2/2m$. Therefore we have:

$$S(E,\mathbf{p}) = S(E-p^2/(2m),\mathbf{0}).$$

We find the derivative with respect to the momentum component p_i as follows:

$$\frac{\partial S(E,\mathbf{p})}{\partial p_i} = -\frac{\partial S(E,\mathbf{0})}{\partial E}\frac{p_i}{m} = -\frac{u_i}{T},$$

where u_i is the mean velocity.

In more general terms, we call the conjugate variable of an extensive variable A_i , γ_i :

$$\gamma_i = \frac{\partial S}{\partial A_i}.$$

As S is extensive, as are the extensive quantities A_i , we have

$$S(\lambda A_i) = \lambda S(A_i).$$

Taking the derivative with respect to λ and then setting $\lambda \equiv 1$, we have

$$S = \sum_{i} A_i \frac{\partial S}{\partial A_i} = \sum_{i} \gamma_i A_i.$$

For the local quantities, this is

$$\sum_{i} \int_{V} \rho_{i}(\mathbf{r},t) \gamma_{i}(\mathbf{r},t) d^{3}r = S.$$

From this, we see that

$$\gamma_i(\mathbf{r},t) = \frac{\delta S}{\delta \rho_i(\mathbf{r},t)}.$$

Summarizing, we see that there exist pairs of conjugate variables, one of which is intensive, and the other extensive. Intensive partners of extensive variables are found by taking the derivative of the entropy S with respect to the extensive variable. The variation of the intensive variable drives the transport of the extensive variable. An obvious example is temperature difference which drives the transport of energy.

We are usually interested in small deviations from equilibrium, and in that case we may postulate a linear relation between the driving force, or *affinity*, which is the difference of the intensive variable in neighbouring cells and the current $\Phi_i(a \rightarrow b)$:

$$\Phi_i(a \to b) = \sum_j L_{ij} [\gamma_j(b) - \gamma_j(a)].$$

This can be cast into a local form by taking the volumes *a* and *b* very small and dividing by the volume: then the current $j_{\alpha}^{i}(\mathbf{r},t)$ can be related to the gradient of the affinity γ_{i} along the cartesian direction α :

$$j^{i}_{\alpha}(\mathbf{r},t) - j^{i,\mathrm{eq}}_{\alpha}(\mathbf{r},t) = \sum_{j,\beta} L^{\alpha\beta}_{ij}(a,b) \partial_{\beta} \gamma_{j}(\mathbf{r},t).$$

In this chapter, we shall always use α, β for cartesion directions.

11.3 Heat and particle diffusion

We can apply the general analysis of the previous sections to the particular examples of particle and heat diffusion. As already mentioned, the heat diffusion is driven by the gradient of the temperature. We assume that energy is the only flowing quantity – this type of transport is called thermal conduction. Note that we do not include particle transport. The heat current can be directly derived using the results of the last section:

$$j_{\alpha,E}(\mathbf{r},t) = \sum_{\alpha\beta} L_{EE}^{\alpha\beta} \partial_{\beta} \left(\frac{1}{T}\right).$$

In an isotropic medium the relation between temperature and heat current is given by the familiar relation

$$\mathbf{j}_E(\mathbf{r},t) = -\kappa \nabla(T),$$

where κ is the *thermal conductivity*. We see that in this case the tensor $L_{EE}^{\alpha\beta}$ is diagonal:

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

The conservation law leads to an interesting result. The energy density is called ε , and together with the expression for the current just derived, it enters in the conservation equation to give

$$\frac{\partial \varepsilon}{\partial t} + \kappa T^2 \nabla \cdot \nabla \left(\frac{1}{T}\right) = 0.$$

We need a so-called constitutive equation to relate ε to the temperature. This is

$$\varepsilon = cT$$
,

where c is the specific heat (per unit volume), which we assume to be independent of temperature. We then obtain

$$c\frac{\partial T(\mathbf{r},t)}{\partial t} - \kappa \nabla^2 \left[T(\mathbf{r},t)\right] = 0$$

This is the famous *heat*, or *diffusion equation*. The solution with initial condition $T(\mathbf{r}, t = 0) = \delta^3(\mathbf{r})$ is given as

$$T(\mathbf{r},t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left[-r^2/(4Dt)\right],$$

with $D = \kappa/c$. This solution shows that sharp features (delta functions) decay to smooth shapes in the course of time.

For particle diffusion in a system with uniform temperature (i.e. no energy transport), we can focus on the particle transport. This is driven by μ/T according to the previous section. The current is related to the gradient of this driving force by the linear response relation:

$$j_{\alpha,N}(\mathbf{r},t) = -\sum_{\beta} L_{NN}^{\alpha\beta} \partial_{\beta} \left(\frac{\mu(\mathbf{r},t)}{T} \right).$$

Just as in the previous section, we may compare this with the familiar expression

$$\mathbf{j}_N(\mathbf{r},t) = -D\nabla n,$$

known as *Fick's law*. This comparison necessitates an additional step, which involves another relation between μ and n. This relation is

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

where κ_T is the isothermal compressibility. In fact, this compressibility indicates how difficult it is to compress a material, and its definition is

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right).$$

From the Gibbs-Duhem relation

$$Nd\mu + SdT - VdP = 0,$$

it is seen that

$$\left(\frac{\partial P}{\partial \mu}\right)_T = n,$$

so that we obtain

$$\frac{1}{\kappa_T} = -\frac{V}{N} \left(\frac{\partial P}{\partial (V/N)} \right)_T = n \left(\frac{\partial P}{\partial n} \right)_T = n \left(\frac{\partial P}{\partial \mu} \right)_T \left(\frac{\partial \mu}{\partial n} \right)_T = n^2 \left(\frac{\partial \mu}{\partial n} \right)_T,$$

which proves the relation used above.

All in all, we obtain for the current

$$\mathbf{j}_N(\mathbf{r},t) = -\frac{L_{NN}}{T} \frac{1}{\kappa_T n^2} \nabla n(\mathbf{r},t).$$

Hence we find

$$D = \frac{\partial \mu}{\partial n L_{NN}} = \frac{L_{NN}}{n^2 \kappa_T T}.$$

The particle conservation equation then leads to a diffusion equation similar to that for the heat transport obtained above.

11.4 General analysis of linear transport

Suppose we have a homogeneous, isotropic fluid at rest and in equilibrium. Obviously, the enetropy is maximal, as we are in equilibrium. Now we imagine a box that we move at uniform velocity along the fluid. Obviously, our imaginary box does not change the physics of the problem, and within the box the fluid is still in equilibrium. However, the fluid now moves, hence energy and momentum are transported through the walls of our imaginary box. Also, entropy will move in- and outside. We know however that the net flux, which gives us the change of energy, momentum, entropy and so on, vanishes. All these currents are therefore reversible, non-dissipative currents.

Now imagine another process in which we place many particles at the centre of a box. The particles will diffuse from the centre to fill the box homogeneously (if we are in the gas phase). If we now imagine again a box in the system, for example a box surrounding the centre, we have again currents of energy, momentum, entropy, etcetera, but these currents will no longer be reversible. In particular, we know that the entropy is not conserved, and that it will increase in the entire box. Therefore, if we divide the system in two parts, there will be an *exchange* of entropy, but as an exchange does not change the total entropy, in addition in each box there will be an increase or decrease which is not cancelled by an opposite change in the other box. We have distinguished reversible and non-reversible currents. The latter are associated with an increase of entropy, and therefore with heat generation. The problem of non-reversible, or dissipative, currents is of particular interest from now on.

We shall now analyse the transport problem in a general way. Fluctuations of a system from the equilibrium state can be related to the transport properties of that system. The analysis proceeds as follows. Suppose we have an isolated system, which tends to maximise its entropy. The entropy depends on extensive quantities A_i . We call \tilde{A}_i the values for which the entropy assumes its maximum.

Fluctuations correspond to deviations of the A_i from their equilibrium values. The corresponding variation in the entropy can be expanded in a Taylor series:

$$S(A_1,\ldots,A_N) = S(\tilde{A}_1,\tilde{A}_2,\ldots,\tilde{A}_N) + \frac{1}{2}\sum_{i,j}\frac{\partial^2 S(\tilde{A}_1,\tilde{A}_2,\ldots,\tilde{A}_N)}{\partial A_i\partial A_j}(A_i-\tilde{A}_i)(A_j-\tilde{A}_j) + \ldots$$

From now on, we shall confine ourselves to the case where the system is close enough to equilibrium to justify dropping the higher order terms in the expansion. The fact that the first-order term is not included is due to the fact that S was expanded around its *maximum* – hence, the first derivatives are all zero. The fact that the entropy strives to its maximum is the driving force which causes fluctuations to dampen out.

Recalling that

$$S = k_{\rm B} \ln \Omega$$

where Ω is the number of states accessible to the system, and combining this with the fundamental postulate if statistical mechanics, which says that each of these states is equally probable, we have for the probability of having a state where the quantities $a_i = A_i - \tilde{A}_i$ are nonzero, the following expression:

$$P(a_1,\ldots,a_N) = \frac{\exp\left(-\sum_{ij}\frac{\pi_i}{2}a_ia_j\right)}{\int_{-\infty}^{\infty}da_1\cdots da_N\exp\left(-\sum_{ij}\frac{\pi_i}{2}a_ia_j\right)},$$

where

$$\gamma_{ij} = -\frac{1}{k_{\rm B}} \sum_{i,j} \frac{\partial^2 S(\tilde{A}_1, \tilde{A}_2, \dots, \tilde{A}_N)}{\partial A_i \partial A_j}$$

Note that the fact that S has a maximum implies that the matrix γ_{ij} has positive eigenvalues.

From this we can derive a simple expression for correlation functions of the a_i . Note that

$$\frac{1}{P}\frac{\partial P}{\partial a_i} = \frac{1}{k_{\rm B}}\frac{\partial S}{\partial a_i}.$$

Taking the average on the left and right hand side with respect to the distribution P we obtain

$$\left\langle a_i \frac{\partial S}{\partial a_i} \right\rangle = \int da_1 \cdots da_N a_i \frac{\partial S}{\partial a_i} P = k_{\rm B} \int da_1 \cdots da_N a_i \frac{\partial P}{\partial a_i}$$

Integrating by parts the integral on the right hand side leads to

$$\left\langle a_i \frac{\partial S}{\partial a_i} \right\rangle = -k_{\rm B}$$

Moreover, for $i \neq j$ we find along the same lines:

$$\left\langle a_i \frac{\partial S}{\partial a_j} \right\rangle = 0.$$

You may object that the first derivative of S with respect to the a_i is zero. This is true at the maximum, but near that maximum, we find

$$\frac{\partial S}{\partial a_i} = \sum_j \gamma_{ij} a_j$$

Using this we rewrite the result above as

$$\sum_{k}\gamma_{ik}\left\langle a_{k}a_{j}\right\rangle =k_{\mathrm{B}}\delta_{ij}.$$

The entropy changes in the course of time as

$$\frac{dS}{dt} = \sum_{i} \dot{a}_{i} \frac{\partial S}{\partial a_{i}} = \sum_{i} \dot{a}_{i} \gamma_{i},$$

where we have used the definition of the affinity γ_i (see above). We know that the entropy strives towards becoming maximal, and the way to reach this maximum is by changing the values of the a_i . This change only stops when $\partial S/\partial a_i = \gamma_i$ is zero. In a linear response Ansatz, we have the following relation between the γ_i and the time-derivative of a_i :

$$\dot{a}_i = \sum_j L_{ij} \gamma_j.$$

This equation relates the rate of change of a_i to the affinities γ_j . The rate of change of a_i is often called a *current*, and the affinities are called *generalised forces*. Now it is however time to object: above, we used a different picture, in which a current was really associated with the *flow* of a quantity, and hence had a direction, and this flow was related to the *spatial variation* of the affinity [in electrical terms: with the *electric field* = spatial variation of the potential (=affinity)]. How can we translate the above analysis to the problem of currents?
The key is to not consider the flowing quantities A_i themselves as variables, but their first *moments*:

$$\mathbf{m}_i = \int_V \boldsymbol{\rho}_i(\mathbf{r},t) \mathbf{r} \, d^3 r.$$

Now suppose that this moment changes in time. If its α component increases, the slope of *A* in the increasing direction r_{α} , increases. This can only happen when there is a net current. Hence we see that $\mathbf{j}_i \propto \dot{\mathbf{m}}_i$. Therefore, the present analysis directly carries over to currents and their driving forces.

Now we consider the expectation value

$$\begin{split} \left\langle a_i(t+\tau)a_j(t) \right\rangle &= \left\langle a_i(t)a_j(t) \right\rangle + \tau \left\langle \dot{a}_i(t)a_j(t) \right\rangle \\ &= \left\langle a_i(t)a_j(t) \right\rangle + \tau \sum_m L_{im} \left\langle \frac{\partial S}{\partial a_m} a_j(t) \right\rangle \\ &= \left\langle a_i(t)a_j(t) \right\rangle - \tau L_{ij}k_{\rm B}. \end{split}$$

We see that the linear transport coefficients L_{ij} are found as the time correlation functions of the fluctuations:

$$L_{ij} = \frac{-1}{k_{\rm B}\tau} \left[\left\langle a_i(t+\tau)a_j(t) \right\rangle - \left\langle a_i(t)a_j(t) \right\rangle \right].$$

From this, using time-reversibility of the correlation function,

$$\langle a_i(t+\tau)a_j(t)\rangle = \langle a_i(t-\tau)a_j(t)\rangle$$

we see that the transport coefficients must be symmetric:

$$L_{ii} = L_{ii}$$

This nontrivial property follows from what is called *microscopic reversibility* as it reflects symmetry properties of microscopic correlation functions which follow from the underlying time reversal symmetry of the microscopic dynamics. This relation is used a lot by chemists to construct phenomenological systems of equations which describe exchange of thermal energy, particle species, momentum etcetera. Onsager received the Nobel prize for this formulation of non-equilibrium transport.

We can analyse further the relation between L_{ij} and the correlator. Suppose we had in the above derivation not multiplied $a_i(t + \tau)$ with $a_j(t)$ but with $a_j(0)$. In that case, we arrive at the result:

$$L_{ij} = \frac{-1}{k_{\rm B}\tau} \left[\left\langle a_i(t+\tau)a_j(0) \right\rangle - \left\langle a_i(t)a_j(0) \right\rangle \right] = \frac{-1}{k_{\rm B}\tau} \left[\left\langle a_i(t)a_j(-\tau) \right\rangle - \left\langle a_i(t)a_j(0) \right\rangle \right]$$

where we have used time translation symmetry.

Now we approximate finite differences by time derivatives:

$$L_{ij} \approx \frac{1}{k_{\rm B}} \left\langle a_i(t) \dot{a}_j(0) \right\rangle = \frac{1}{k_{\rm B}} \int_0^t \left\langle \dot{a}_i(t') \dot{a}_j(0) \right\rangle dt'.$$

If we take t much larger than the correlation time, we see that

$$L_{ij} \approx \frac{1}{k_{\rm B}} \int_0^\infty \left\langle \dot{a}_i(t') \dot{a}_j(0) \right\rangle dt'.$$

104

11.5 Coupling of different currents

In section 11.3, we have studied linear transport of a single quantity: either the energy or the particle density. In this section we study the simultaneous occurence of such currents, which according to the general theory may be coupled, under the restriction that the coupling constants are symmetric according to microscopic reversibility. Then we analyse the relation between drift and diffusion within the context of the general formulation.

As a first example, we consider flow of energy and current at the same time. Suppose we have a system consisting of *fixed* scattering centres, and light particles scattering off these centres. The scattering is considered to be elastic, so the energy of the light particles does not change. However, the total momentum of the light particles changes at the collisions and is absorbed by the scatterers, which are not included in the currents under study. Examples of such systems are the scattering of electrons off impurities in a solid, or of neutrons off heavy atoms.

The formalism enables us to directly formulate the currents using the transport coefficients:

$$\mathbf{j}_{E} = L_{EE} \nabla \left(\frac{1}{T}\right) + L_{EN} \nabla \left(\frac{-\mu}{T}\right);$$
$$\mathbf{j}_{N} = L_{NN} \nabla \left(\frac{-\mu}{T}\right) + L_{NE} \nabla \left(\frac{1}{T}\right).$$

Microscopic reversibility (the 'Onsager relation') tells us that $L_{NE} = L_{EN}$. Thermal conductivity is the process which takes place when there is no particle current. This implies that

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

Substituting this into the equation for the energy current, we obtain

$$\mathbf{j}_{E}(\mathbf{r},t) = \frac{-1}{T^{2}L_{NN}} \left(L_{EE}L_{NN} - L_{NE}^{2} \right) \nabla T$$

We see that, even when there is no net flow of particles, the fact they are allowed to move alters the thermal conductivity

$$\kappa_T = \frac{1}{T^2 L_{NN}} \left(L_{EE} L_{NN} - L_{NE}^2 \right)$$

with respect to that found in section 11.3.

We now turn to a problem in which there is only a single current, which now is driven by the chemical potential and by en electric field. The flowing quantity is the charge, and the current is the familiar electric current. If an electric potential can be considered to be more or less constant over the subvolume, the energy levels will be shifted by that potential. For the particles, this effect is indistinguishable from an shift of the chemical potential which in the grand canonical ensemble is a kind of 'zero point' energy which is assigned to every particle. From this we infer that

$$\mu = -T\frac{\partial s}{\partial n} = \mu_0 + e\Phi,$$

where e is the charge of the particles, n is the number density N/V and s is the entropy density S/V.

The current which we calculated in section 11.3 can directly seen to be modified:

$$\mathbf{j}_{\rm el}(\mathbf{r},t) = -\frac{e}{T}L_{NN}\nabla\mu_0(\mathbf{r},t) - \frac{e^2L_{NN}}{T}\nabla\Phi(\mathbf{r},t) = -e\frac{L_{NN}}{T}\frac{\partial\mu_0(\mathbf{r},t)}{\partial n}\nabla n(\mathbf{r},t) + \frac{e^2L_{NN}}{T}\mathbf{E}$$

where \mathbf{E} is the electric field. We see that the current is composed of a diffusive part, equal to that found in section 11.3, and a *drift* part which is caused by the electric field.

In a stationary system, the density will be uniform, and the first term vanishes. This then leads to Ohm's law:

$$\mathbf{j}_{\rm el}(\mathbf{r},t) = \frac{e^2 L_{NN}}{T} \mathbf{E} = \sigma_{\rm el} \mathbf{E}.$$

We see that conductivity $\sigma_{\rm el} = e^2 L_{NN}/T$. In section 11.3, we have seen that

$$D=\frac{\partial\mu}{\partial n}L_{NN},$$

so that we have

$$D = \frac{\partial \mu}{\partial n} T \sigma_{\rm el} / e^2.$$

For an ideal gas, we have

$$\frac{\partial \mu}{\partial n} = \frac{k_{\rm B}T}{n},$$

which leads to

$$D = k_{\rm B} T \sigma_{\rm el} \frac{1}{ne^2}.$$

This is an example of an *Einstein relation* which between the diffusion constant *D* and a transport coefficient σ . Note that this is a striking result: the way in which particles can diffuse through a medium determines their behaviour under a driving force completely. This can even be put on a more general level: the transport coefficient is related to dissipation (the current generates heat through the resistivity of the material), whereas the diffusion tells us how much the particle positions fluctuate in equilibrium. There exists theorems which establish general relations between equilibrium fluctuations on one hand, and transport phenomena on the other – they go under the name of *fluctuation dissipation theorems*.

11.6 Derivation of hydrodynamic equations

In this section, we derive hydrodynamic equations. These equations describe the flow of a fluid. We confine ourselves to the simplest case of isotropic fluids, consisting of structureless particles (i.e. no electric or magnetic dipoles or charges). The archetypical material is liquid argon. During the flow, the particles will collide and exchange energy and momentum. We have, however, at these collisions, conservation of momentum and energy (in addition to the trivial particle conservation: the particles do not undergo chemical reactions).

Mass conservation is expressed by the relation

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r},t) = 0.$$

where ρ is the mass density. The current represents the average motion of the particles. We call the average velocity in a small subvolume **u**, which is an intrinsic quantity. In terms of **u**, the mass flow is $\mathbf{j} = \rho \mathbf{u}$, so we have

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} + \nabla [\rho(\mathbf{r},t)\mathbf{u}(\mathbf{r},t)] = 0.$$

106

Working out the gradient, we see that

$$\frac{\partial \rho}{\partial t} + \rho \nabla \cdot \mathbf{u} + (\mathbf{u} \cdot \nabla)\rho = 0.$$

Now we consider the momentum flow. The momentum density is $\rho \mathbf{u}$. The conservation of the α -component of the momentum is expressed by

$$\frac{\partial \rho u_{\alpha}}{\partial t} + \sum_{\beta} \partial_{\beta} \mathscr{P}_{\alpha\beta} = 0.$$

Here, \mathscr{P} is a tensor containing the viscous forces which change the momentum.

Writing out the first term and using the mass conservation law, we obtain

$$\rho \frac{\partial u_{\alpha}}{\partial t} - u_{\alpha} \left[\rho \nabla \cdot \mathbf{u} + (\mathbf{u} \cdot \nabla) \rho \right] + \sum_{\beta} \partial_{\beta} \mathscr{P}_{\alpha\beta} = 0.$$

After some manipulation, the second and third term of this equation can be rewritten to arrive at

$$\rho \frac{\partial u_{\alpha}}{\partial t} + \rho \sum_{\beta} (u_{\beta} \partial_{\beta}) u_{\alpha} - \sum_{\beta} \partial_{\beta} (\rho u_{\alpha} u_{\beta}) + \sum_{\beta} \partial_{\beta} \mathscr{P}_{\alpha\beta} = 0.$$

The quantity $\rho u_{\alpha}u_{\beta}$ is the flow along the Cartesian direction β of the α -component of the momentum.

Now consider a small volume V within the fluid. The flow of momentum across the boundaries of this small volume determines the rate of change of the momentum inside this volume. But the rate of change of the total momentum is the net force acting on the volume. Therefore we have

$$\int_{S} \rho u_{\alpha} \sum_{\beta} u_{\beta} da_{\beta} = \int_{V} \partial_{\beta} \left(\rho u_{\alpha} u_{\beta} \right) d^{3} r = \mathbf{F},$$

where S is the surface bounding V; $d\mathbf{a}$ is a outward normal vector to the surface and we have used the divergence theorem to get the second experession. We see that the term occurring in our momentum conservation equation is simply the force. The effect of momentum flow across the boundary is called the *pressure*. Therefore, $\rho u_{\alpha} u_{\beta}$ is called the pressure tensor, which, in equilibrium, has the form

$$\rho u_{\alpha} u_{\beta} = P \delta_{\alpha\beta}$$

where P is the scalar pressure for the isotropic fluid.

Now we are left with the viscous tensor $\mathscr{P}_{\alpha\beta}$. Based on the general theory, this must be driven by the affinity of the particle number, momentum and energy, that is, by μ , T and u_{α} . We first make the assumption that our fluid is *isothermal*, i.e. the temperature does not vary in space. Furthermore we assume that the main contribution to the momentum is due to its own affinity, that is, to u_{α} . Finally, we should construct $\mathscr{P}_{\alpha\beta}$ such that it be isotropic and symmetric in α and β . This leads to the two possibilities

$$\delta_{\alpha\beta}(\nabla \cdot \mathbf{u})$$
 and $\partial_{\alpha}u_{\beta} + \partial_{\beta}u_{\alpha}$.

Both have their own transport coefficient, which are called viscosities.

Usually, the first of these is replaced by the linear combination

$$\frac{1}{2}\left(\partial_{\alpha}u_{\beta}+\partial_{\beta}u_{\alpha}\right)-\frac{1}{3}\delta_{\alpha\beta}(\nabla\cdot\mathbf{u}).$$

Now we can write down the conservation equations for the momentum:

$$\frac{\partial \mathbf{u}}{\partial t} + (\mathbf{u} \cdot \nabla)\mathbf{u} + \frac{1}{\rho}\nabla P = \frac{\eta}{\rho}\nabla^2 \mathbf{u} + \frac{1}{\rho}\left(\frac{\eta}{3} + \zeta\right)\nabla\left(\nabla \cdot \mathbf{u}\right).$$

This is the Navier-Stokes equation for the momentum flow. In good approximation, we can put *P* equal to $\rho k_{\rm B}T$ so that this turns into a closed equation.

The flow of entropy and energy can be expressed in a separate equation, using a similar analysis.

108

12

Fluctuations and transport phenomena

Up to this moment, we have restricted ourselves to equilibrium phenomena. In this chapter we shall concentrate on fluctuations from the equilibrium phase and on transport phenomena. The latter are intrinsically outside of the domain of equilibrium phenomena: transport does – on average – not occur in equilibrium.

12.1 Motion of particles

Particles move under the influence of their counterparts. The motion of a particle can be split into three contributions:

- A motion caused by an external force acting on the particles. This is called the *drift*.
- A motion on top of the drift, and which is the result of thermal fluctuations. This motion occurs also in equilibrium.
- A drag induced by the interaction of a particular particle with the other particles.

The main message of this chapter is that these three types of motion are strongly related. Therefore, from studying the fluctuations in an equilibrium system, we can deduce the transport properties, which are clearly the non-equilibrium properties of the system.

If a system is moved out of equilibrium, it will take some time before equilibrium is restored. Initially, a *local equilibrium* will be realised. This means for example that if we stir a liquid, in a small subvolume of the liquid, the particles will be distributed according to the distribution:

$$P(\mathbf{v}) = \exp\left[-m(\mathbf{v} - \mathbf{u})^2/(2k_{\rm B}T)\right]$$

where \mathbf{u} is the average velocity (also called the *wind velocity*) of the subvolume. Two neighbouring subvolumes will have different average velocities, but if we wait long enough, these velocities become equal.

We now focus on dilute systems, i.e. systems in which the particles move freely most of the time and experience collisions with their counterparts every now and then. In this context it is useful to speak of the *mean free path*, *l*, and of the *free flight time*, τ , which are related according to

$$l = \langle |v| \rangle \tau$$
,

where $\langle |v| \rangle$ is the average absolute velocity. The meaning of these quantities is related to what happens between two collision events: the average time between two collisions is the free flight time, and the average distance a particle travels during that time is the mean free path.



Figure 12.1: The volume a particle 'sees' when travelling through the system.

The free flight time can be calculated if we know the scattering cross section of the particles in the system, their density, and their average velocity.

A particle 'sees' other particles within a tube of cross section equal to the scattering cross section σ_{scat} and of length $\langle |v| \rangle t$. The average number of encounters is then given by the volume of this tube times the particle density – see figure 12.1. From this we infer directly that

$$\tau = \frac{t}{N} = \frac{t}{\langle |v_{\rm rel}| \rangle t \sigma_{\rm scat} n} = \frac{1}{\langle |v_{\rm rel}| \rangle \sigma_{\rm scat} n}$$

In this formula, $\langle |v_{rel}| \rangle$ is not the average velocity, but the average *relative* velocity between the particles, and we should correct for this. If we carry out the average for relative velocities, based on a Maxwell velocity distribution, we find

$$\langle |v_{\rm rel}| \rangle = \sqrt{2} \langle |v| \rangle$$

and we have

$$\tau = \frac{1}{\sqrt{2} \langle |v| \rangle \, \sigma_{\text{scat}} n}$$

12.1.1 Diffusion

In agreement with what has been said in the previous section, we can distinguish two mechnisms for transport of particles through a gas or liquid: diffusion, which is caused by thermal fluctuations kicking the particles in arbitrary directions, and *drift* caused by an external force. First we focus on diffusion.

We shall derive the diffusion equation for one dimension. A particle is placed on the *x*-axis and performs a step in some random direction at regular time intervals. We want to evaluate the probability $\rho(x,t)dx$ of finding the particle at time *t* in the interval dx located at *x*. To that end, we set up a Master equation similar to that introduced in connection with the Monte Carlo method. We take the step size equal to *a* and the time step equal to *h*. The probability that at each time step a jump to the left or right is made, is called α , and the particle will remain at its position with probability $1 - 2\alpha$. The probability density satisfies the following equation:

$$\rho(x,t+h) - \rho(x,t) = \alpha \left[\rho(x+a,t) + \rho(x-a,t) - 2\rho(x,t) \right] \approx \alpha a^2 \frac{\partial^2 \rho(x,t)}{\partial x^2},$$

where we have taken the small-a limit in the last expression. Taking also h small, we may approximate the left hand side by the time derivative in order to obtain:

$$\frac{\partial \rho(x,t)}{\partial t} = D \frac{\partial^2 \rho(x,t)}{\partial x^2}$$

where D is the diffusion constant, which can be seen to take on the value

$$D = \alpha \frac{a^2}{h}.$$

By interpreting *a* as the mean free path and *h* as the free flight time, and taking $\alpha = 1$, which seems to be the natural choice for this case, we have

$$D=\frac{l^2}{\tau}.$$

We can also calculate the *flux*, which is the net number of particles moving from one position to its neighbouring position. The flow to the right is given by

$$\alpha a \rho(x,t)$$

and that to the left by

$$\alpha a \rho (x+a,t)$$

The factors *a* in front of the ρ 's in these equation come from the fact that ρ is in fact defined as the number of particles *per unit length*. Keeping the same convention in the derivation of the diffusion equation does not alter the result, as an extra factor *a* would have to be included in both the left- and right hand side.

Therefore, we find for the flux:

$$J = \alpha a \frac{\rho(x,t) - \rho(x+a,t)}{h} \approx -\alpha \frac{a^2}{h} \frac{\partial \rho}{\partial x} = -D \frac{\partial \rho}{\partial x},$$

which can be generalised in 3D to

$$\mathbf{J} = -D\nabla \rho(\mathbf{r}, t).$$

This relation is known as *Fick's law of diffusion*. If the diffusion constant depends on position, the diffusion equation reads

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} + \nabla \left(D(\mathbf{r}) \nabla \right) \rho(\mathbf{r},t) = 0.$$

The solution to the diffusion equation with initial condition that there *is* a particle at the origin at t = 0, is

$$\rho(x,t) = \frac{1}{\sqrt{4\pi Dt}} e^{-x^2/(4Dt)}$$

The shape of this distribution is Gaussian at all times, with a width which grows proportional to \sqrt{t} . For t = 0 this reduces to a delta-function. It is obvious that the width should increase in time as the position of the particle should become more and more uncertain in the course of time. In 3D, we have

$$\rho(\mathbf{r},t) = \frac{1}{(4\pi Dt)^{3/2}} e^{-r^2/(4Dt)}$$

We can calculate the average square displacement of a particle in one dimension (the average displacement is obviously zero because of symmetry):

$$\left\langle \left(\Delta x\right)^2 \right\rangle = 2Dt,$$

in 3D this becomes 6Dt.

12.1.2 Thermal conductivity

In order to study the transport of thermal energy, we consider a system like in the previous subsection, but with a temperature gradient in the *z*-axis, which is realised by putting the system in between two planes perpendicular to the *z*-axis, which are kept at different temperatures, T_1 and T_2 .

Now let us consider a plane at height z. Particles will cross this plane, coming either from above or from below the plane. The average height at which these particles last collided was

$$h = \ell \frac{v_z}{v},$$

After this last collision, the particles have an energy which is the average energy for the height $z - \ell v_z/v$. The flux of energy through the plane at height z is therefore given by

$$j_E = \int n(v) v_z \varepsilon \left(z - \ell \frac{v_z}{v} \right) d^3 v.$$

where $\varepsilon(z)$ is the average energy of a particle at height z. Performing a Taylor expansion for ε around z gives

$$j_E = \int n(v) v_z \left[\varepsilon(z) - \ell \frac{v_z}{v} \frac{d\varepsilon(z)}{dz} \right] d^3 v.$$

Now we may substitute the Maxwell distribution for n(v) to obtain, after some manipulation:

$$j_E = -\frac{1}{3}n\left\langle v \right\rangle \ell \frac{d\varepsilon(z)}{dz}$$

Now we write $\varepsilon = cT$ where c is the specific heat per molecule. Then we find for the energy flux

$$j_E = -\frac{1}{3}n\left\langle v \right\rangle \ell c \frac{dT(z)}{dz}$$

and therefore, the thermal conductivity is given by

$$\kappa_T = \frac{ncl \langle v \rangle}{3}.$$

12.1.3 Viscosity

Now we consider the transport of momentum tangential to a plane across that plane. To fix the ideas, imagine a constant *z* plane. We want to study the transport of momentum p_x across that plane. This is given by

$$P_{xz} = \int p_x v_z n(v) d^3 v$$

Similar to the previous section, we note that the average momentum of the particles moving across, is

$$p_x = mu_x \left(z - \ell \frac{v_z}{v} \right).$$

Inserting this into the above expression for P_{xz} , we obtain

$$P_{xz} = \int m\left(u_x(z) - \frac{v_z}{v}\frac{du_x(z)}{dz}\right)n(v)v_zd^3v,$$

which directly leads to

$$P_{xz} = -\frac{1}{3}nm \langle v \rangle \,\ell \frac{du_x(z)}{dz}.$$

Therefore, we find for the viscosity

$$\eta = \frac{1}{3} nm \langle v \rangle \ell$$

12.2 The Boltzmann equation

We now turn to a central topic in nonequilibrium statistical mechanics: the *Boltzmann equation*. This is a more formal and consistent formulation of the ideas treated in the previous section. The Boltzmann equation describes the motion of a collection of particles in a hydrodynamic cell: that is, a cell which contains many molecules but which is much smaller than the scale over which hydrodynamic quantities vary appreciably. The central quantity is the number of particles in such a cell of size d^3r and velocity within the volume d^3v in velocity-space. This quantity is called the *distribution function* $f(\mathbf{r}, \mathbf{v}, t)$:

$$f(\mathbf{r}, \mathbf{v}, t)d^3r d^3v =$$
 number of particles within d^3r and velocity within d^3v .

If we consider the dilute limit as in the previous section, we consider the particles as moving freely for some average time τ and then colliding with each other. First we consider the question how f changes with time if we disregard the collisions.

There are two issues which we have to consider: first the particles move in space due to the fact that they have a velocity and they change their velocity as a result of some (external) force which acts on them. Do not confuse this force with the interactions between the particles: we save those for the collisions which are not taken into account til further notice. The change of position and speed has a direct effect on f. However, the volume elements d^3r and d^3v may also change in time. However, as the particles move independently of each other, each particle is subject to a Hamiltonian evolution which, by Liouville's theorem, keeps the volume element $d^3r d^3v$ constant.

Therefore we have

$$f(\mathbf{r}(t+\Delta t),\mathbf{v}(t+\Delta t),t+\Delta t) = f(\mathbf{r}+\mathbf{v}\Delta t,\mathbf{v}(t)+\frac{\mathbf{F}}{m}\Delta t,t+\Delta t) = f(\mathbf{r},\mathbf{v},t)+\mathbf{v}\cdot\nabla_{\mathbf{r}}f(\mathbf{r},\mathbf{v},t)+\frac{\mathbf{F}}{m}\cdot\nabla_{\mathbf{v}}f(\mathbf{r},\mathbf{v},t)+\frac{\partial}{\partial t}f(\mathbf{r},\mathbf{v},t).$$

If we are in equilibrium, f only depends on \mathbf{r} and \mathbf{v} , and not explicitly on time. In that case we have

$$\mathbf{v} \cdot \nabla_{\mathbf{r}} f(\mathbf{r}, \mathbf{v}, t) + \frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{v}} f(\mathbf{r}, \mathbf{v}, t) = 0,$$

which, using $\mathbf{F} = \nabla_{\mathbf{r}} V(\mathbf{r})$ allows for a solution

$$f(\mathbf{r}, \mathbf{v}) = \exp\left\{-\beta\left[\frac{mv^2}{2} + V(\mathbf{r})\right]\right\},\$$

which does not look too unfamiliar.

The interactions between the particles must also be taken into account. This is done in the dilute limit, in which the particles collide every now and then. The collisions will result in a loss and an increase of the distribution function $f(\mathbf{r}, \mathbf{v}, t)$: a collision at \mathbf{r} may have a particle with velocity \mathbf{v} as an end product, or a collision may change the velocity \mathbf{v} to some other velocity.

For the frequency of occurrence of a collision we have derived

$$\tau = \frac{1}{n|\mathbf{v}|\boldsymbol{\sigma}},$$

where σ is the total collision cross section. Now we need a more refined expression, which includes the in- and outgoing velocity. This means that we must replace the total collision section by the differential one, which depends on the difference between the in- and outgoing angle. More specifically, if we travel along with one of the incoming particles, this particles is a target at rest and we see the other particle hitting it. $\Omega = (\vartheta, \varphi)$ are the polar angles of the difference between in- and outgoing velocity of the incoming particle.

More generally, we introduce a transition amplitude

$$P(\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}'_1, \mathbf{v}'_2)$$

which gives us the probability density that *given* two particles which collide with incoming velocities \mathbf{v}_1 and \mathbf{v}_2 , the result is outgoing particles with velocities \mathbf{v}'_1 and \mathbf{v}'_2 . This probability density must satisfy several requirements:

• Time reversal symmetry:

$$P(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}_1', \mathbf{v}_2') = P(-\mathbf{v}_1', -\mathbf{v}_2', -\mathbf{v}_1, -\mathbf{v}_2).$$

As the probability distribution is in general symmetric under reversal of all velocities (space inversion symmetry), we also may write

$$P(\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}'_1, \mathbf{v}'_2) = P(\mathbf{v}'_1, \mathbf{v}'_2, \mathbf{v}_1, \mathbf{v}_2).$$

• *P* should respect the general conservation laws for momentum and energy. Hence, if the particles all have the same mass *m*:

$$\mathbf{v}_1 + \mathbf{v}_2 = \mathbf{v}_1' + \mathbf{v}_2';$$

and

 $v_1^2 + v_2^2 = {v'}_1^2 + {v'}_2^2.$

Using

$$2(v_1^2 + v_2^2) = (\mathbf{v}_1 + \mathbf{v}_2)^2 + (\mathbf{v}_1 - \mathbf{v}_2)^2,$$

which also holds for \mathbf{v}'_1 and \mathbf{v}'_2 , and using momentum conservation, we may reformulate energy conservation as

$$|\mathbf{v}_1 - \mathbf{v}_2| = |\mathbf{v}_1' - \mathbf{v}_2'|.$$

Therefore the transition probability density $P(\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}'_1, \mathbf{v}'_2)$ vanishes unless the velocities satisfy momentum and energy conservation.

We first analyse the loss of the distribution $f(\mathbf{r}, \mathbf{v}, t)$ due to collisions occurring in a small time interval Δt . This loss is caused by collisions with particles with a velocity \mathbf{v}_2 at \mathbf{r} . The probability that two such particles meet in this time interval is given by

$$f(\mathbf{r},\mathbf{v},t)f(\mathbf{r},\mathbf{v}_2,t)|\mathbf{v}-\mathbf{v}_2|\Delta t.$$

Therefore, the loss term due to the collisions can be written as

$$I_{-}(\mathbf{v}) = \Delta t f(\mathbf{r}, \mathbf{v}, t) \int f(\mathbf{r}, \mathbf{v}_{2}, t) |\mathbf{v} - \mathbf{v}_{2}| P(\mathbf{v}, \mathbf{v}_{2}; \mathbf{v}_{1}', \mathbf{v}_{2}') d^{3} v_{2} d^{3} v_{1}' d^{3} v_{2}'.$$

The gain term to $f\mathbf{r}, \mathbf{v}, t$ due to the collisions results from collisions of particles with any velocities \mathbf{v}_1 and \mathbf{v}_2 which results in one of the outgoing particles having end velocity \mathbf{v} . A similar analysis as for the loss term results in a gain term

$$I_{+} = \Delta t \int f(\mathbf{r}, \mathbf{v}_{1}, t) f(\mathbf{r}, \mathbf{v}_{2}, t) |\mathbf{v}_{1} - \mathbf{v}_{2}| P(\mathbf{v}_{1}, \mathbf{v}_{2}; \mathbf{v}, \mathbf{v}_{2}') d^{3}v_{1} d^{3}v_{2} d^{3}v_{2}'.$$

To be able to combine this expression conveniently with I_{-} we use time reversal symmetry to swap the arguments of the collision distribution P and rename the integration variables to obtain

$$I_{+} = \Delta t \int f(\mathbf{r}, \mathbf{v}_{1}', t) f(\mathbf{r}, \mathbf{v}_{2}', t) |\mathbf{v} - \mathbf{v}_{2}| P(\mathbf{v}, \mathbf{v}_{2}; \mathbf{v}_{1}', \mathbf{v}_{2}') d^{3}v_{1}' d^{3}v_{2}' d^{3}v_{2}.$$

Combining the loss and gain term, we arrive at the final form of the Boltzmann equation, including collisions:

$$\frac{\partial}{\partial t}f + \mathbf{v} \cdot \nabla_{\mathbf{r}} f = I_{\text{coll}}(f),$$

with

$$I_{\text{coll}} = \int |\mathbf{v} - \mathbf{v}_2| P(\mathbf{v}, \mathbf{v}_2; \mathbf{v}_1', \mathbf{v}_2') \left[f(\mathbf{r}, \mathbf{v}_1', t) f(\mathbf{r}, \mathbf{v}_2', t) - f(\mathbf{r}, \mathbf{v}, t) f(\mathbf{r}, \mathbf{v}_2, t) \right] d^3 v_2 \, d^3 v_1' \, d^3 v_2'.$$

It is important to realise that in this derivation, we have assumed that the probability for two particles with velocity \mathbf{v}_1 and \mathbf{v}_2 , is given by the product of the single particle distribution functions:

$$\operatorname{Prob}(\mathbf{r},\mathbf{v}_1,\mathbf{v}_2,t) = f(\mathbf{r},\mathbf{v}_1,t)f(\mathbf{r},\mathbf{v}_2,t).$$

This implies a neglect of velocity correlations: a probability depending on \mathbf{v}_1 and \mathbf{v}_2 which cannot be written as the above product is excluded. This implicit assumption goes by the name *molecular chaos*.

Note furthermore that the collision term does not affect the number density – it only influences the velocity distribution.

We end this section by writing up the Boltzmann transport equation, which includes the collision term derived above:

$$\frac{\partial}{\partial t}f(\mathbf{r},\mathbf{v},t) + \mathbf{v} \cdot \frac{\partial}{\partial \mathbf{r}}f(\mathbf{r},\mathbf{v},t) + \frac{\mathbf{F}}{m} \cdot \frac{\partial}{\partial \mathbf{v}}f(\mathbf{r},\mathbf{v},t) = \int |\mathbf{v}-\mathbf{v}_2| P(\mathbf{v},\mathbf{v}_2;\mathbf{v}_1',\mathbf{v}_2') \left[f(\mathbf{r},\mathbf{v}_1',t)f(\mathbf{r},\mathbf{v}_2',t) - f(\mathbf{r},\mathbf{v},t)f(\mathbf{r},\mathbf{v}_2,t)\right] d^3$$

12.3 Equilibrium – deviation from equilibrium

For equilibrium we now that, in the absence of the collision term, the local distribution function is the Boltzmann distribution. If we add the collision term, it should not affect the equilibrium distribution. That this is indeed the case follows from the fact that

$$f(\mathbf{r}, \mathbf{v}_{1}', t)f(\mathbf{r}, \mathbf{v}_{2}', t) - f(\mathbf{r}, \mathbf{v}, t)f(\mathbf{r}, \mathbf{v}_{2}, t) = n^{2}(\mathbf{r}) \left\{ \exp\left[-m\left(\mathbf{v}_{1}'^{2} + \mathbf{v}_{2}'^{2}\right)/(2k_{\mathrm{B}}T)\right] - \exp\left[-m\left(\mathbf{v}^{2} + \mathbf{v}_{2}^{2}\right)/(2k_{\mathrm{B}}T)\right] \right\} = 0,$$

where the last equality follows from energy conservation at the collision.

If we deviate from equilibrium, the collisions should drive us back to equilibrium. This process is expressed in terms of a new quantity H, which is commonly refered to as the Boltzmann function.¹

The Boltzmann function is defined as

$$H(t) = \int f(\mathbf{r}, \mathbf{v}, t) \ln f(\mathbf{r}, \mathbf{v}, t) d^3 r d^3 v$$

It is clear that this quantity is related to the entropy by

$$H = -k_{\rm B}S.$$

¹Usually people view *H* as a character of the latin alfabet. Boltzmann however used the Greek capital form of eta (η).

The quantity H is a function of time only, so we may calculate dH/dt. We can now evaluate

$$\frac{dH}{dt} = \int \frac{\partial f}{\partial t} \left(1 + \ln f\right) d^3 r \, d^3 v$$

From now on we shall use the obvious abbreviations:

$$f(\mathbf{r}, \mathbf{v}_1, t) \equiv f_1; \quad f(\mathbf{r}, \mathbf{v}'_1, t) \equiv f_{1'}$$

and so on. Furthermore

$$|\mathbf{v}_1 - \mathbf{v}_2| P(\mathbf{v}_1, \mathbf{v}_2 \to \mathbf{v}_1', \mathbf{v}_2') \equiv \tilde{P}(1, 2 \to 1', 2').$$

We then have, after substituting Boltzmann's equation in the equation for dH/dt:

$$\frac{dH}{dt} = -\int \dot{\mathbf{r}} \cdot \nabla_{\mathbf{r}} f_1 \left[1 + \ln f_1\right] d^3 r \, d^3 p_1 + \int \tilde{P}(1, 2 \to 1', 2') \left(f_{1'} f_{2'} - f_1 f_2\right) \left(1 + \ln f_1\right) d^3 r D v;$$

where Dv stands for $d^3v_1 d^3v_2 d^3v'_1 d^3v'_2$.

Integrating the first term and assuming that f vanishes if we are far away (outside the volume), we keep only the second integral. By using symmetry under exchanging coordinates 1 and 2, we obtain

$$\frac{dH}{dt} = \int \tilde{P}(1,2,\to 1',2') \left(f_{1'}f_{2'} - f_1f_2\right) \left(1 + \ln f_2\right) d^3r \, Dv.$$

We can add the two last expressions for the time derivative to obtain

$$\frac{dH}{dt} = \int \tilde{P}(1,2,\to 1',2') \left(f_{1'}f_{2'} - f_1f_2\right) \left(1 + \frac{1}{2}\ln f_1f_2\right) d^3r \, Dv.$$

As a final step, we use the time reversal symmetry property according to which the swap $1, 2 \leftrightarrow 1', 2'$ should not change the integral. This leads to another expression for the time derivative of the Boltzmann function:

$$\frac{dH}{dt} = \int \tilde{P}(1,2,\to 1',2') \left(f_1 f_2 - f_{1'} f_{2'}\right) \left(1 + \frac{1}{2} \ln f_{1'} f_{2'}\right) d^3 r \, Dv.$$

Adding this new form to the old one leads to

$$\frac{dH}{dt} = \int \tilde{P}(1,2,\to 1',2') \left(f_{1'}f_{2'} - f_1f_2\right) \frac{1}{4} \ln \frac{f_1f_2}{f_{1'}f_{2'}} d^3r \, Dv \le 0$$

The inequality on the right hand side follows from the fact that $(y - x)\ln(x/y)$ is always less than or equal to zero.

We see that H monotonically decreases. Furthermore, H is a positive number. Therefore, H will decrease in time until it has reached its minimum value. This value corresponds to the equilibrium state. So what does this state look like? It is reached when

$$f_1 f_2 = f_{1'} f_{2'},$$

or,

$$\ln f_1 + \ln f_2 = \ln f_{1'} + \ln f_{2'}.$$

In a homogeneous system, the equilibrium distribution does not depend on \mathbf{r} , and the last condition for equilibrium must be satisfied for the *f*'s being functions of the momentum coordinate. As we know that momentum and energy are conserved during collisions, this requirement can be satisfied for any function *f* of the form

$$\ln f(\mathbf{p}) = A + \mathbf{b} \cdot \mathbf{p} + C \frac{p^2}{2m},$$

in other words

$$f(\mathbf{p}) = \exp\left(A + \mathbf{b} \cdot \mathbf{p} + C\frac{p^2}{2m}\right)$$

This is the general form of the Maxwell distribution of a gas with a nonzero total momentum.

12.4 Derivation of the Navier–Stokes equations

In this section we present a derivation of the Navier–Stokes equations from an approximate Boltzmann equation through a Chapman–Enskog procedure.

If the particles would simply flow according to their initial velocity, without interaction, equilibrium would never be reached: the role of the collisions is to establish *local equilibrium*, that is, a distribution which is in equilibrium in a small cell with fixed volume, constant temperature, density and average velocity \mathbf{u} . We know this equilibrium distribution; it was derived in the previous section:

$$f^{\text{eq}}(\mathbf{r}, \mathbf{v}) = f(\mathbf{r}) \exp\left[-m(\mathbf{v} - \mathbf{u})^2 / (2k_{\text{B}}T)\right], \qquad (12.1)$$

which holds for cells small enough to justify a constant potential. We have neglected external forces which would change the velocities for simplicity – they can be included straightforwardly. Once the liquid is in (local) equilibrium, the collisions will not push it away from equilibrium. It can be shown that the collisions have the effect of increasing the entropy – hence they generate heat.

Before we continue, we note that the mass must *always* be conserved, whether there are collisions or not. The mass density is found as

$$\rho(\mathbf{r},t) = \int mf(\mathbf{r},\mathbf{v},t) \, d^3v. \tag{12.2}$$

Its evolution can be calculated by integrating the Boltzmann equation, multiplied by the single particle mass *m*, over the velocity:

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} + \int m \mathbf{v} \cdot \nabla_{\mathbf{r}} f(\mathbf{r},\mathbf{v},t) \, d^3 v = \int \left(m \frac{df}{dt}\right)_{\text{collisions}} d^3 v.$$
(12.3)

The second term of this equation can be written as $\nabla \cdot \mathbf{j}(\mathbf{r},t)$ where \mathbf{j} denotes the mass flux, or momentum density, of the fluid:

$$\mathbf{j}(\mathbf{r},t) = \int \mathbf{v}mf(\mathbf{r},\mathbf{v},t)d^3v = \rho \mathbf{u},$$
(12.4)

where **u** is the average local velocity. The collisions change the velocity distribution, but not the mass density of the particles – hence the right hand side of (12.3) vanishes and we obtain the familiar continuity equation:

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r},t) = 0.$$
(12.5)

Another interesting equation describes the conservation of momentum. We would like to know how $\mathbf{j}(\mathbf{r},t)$ changes with time. This is again evaluated straightforwardly by multiplying the Boltzmann

equation by **v** and integrate over the velocity. Using the indices α and β for the Cartesian coordinates, we obtain

$$\frac{\partial j_{\alpha}}{\partial t} + \int m v_{\alpha} \sum_{\beta} v_{\beta} \partial_{\beta} f(\mathbf{r}, \mathbf{v}, t) d^{3} v = \int m v_{\alpha} \left(\frac{df}{dt}\right)_{\text{collisions}} d^{3} v, \qquad (12.6)$$

where ∂_{β} denotes a derivative with respect to the coordinate r_{β} . For the right hand side, a similar statement can be made as for the equivalent term in the mass equation: although individual particles involved in a collision change their momenta, the *total* momentum is conserved at the collisions. After thus putting the right hand side to zero, we write (12.6) in short hand notation as

$$\frac{\partial j_{\alpha}}{\partial t} + \partial_{\beta} \mathscr{P}_{\alpha\beta} = 0, \qquad (12.7)$$

where we have introduced the momentum flow tensor

$$\mathscr{P}_{\alpha\beta} = \int m v_{\alpha} v_{\beta} f(\mathbf{r}, \mathbf{v}, t) d^{3} v, \qquad (12.8)$$

and where we have used the Einstein summation convention in which repeated indices (in this case β) are summed over. The derivative with respect to r_{β} is in our notation denoted by ∂_{β} .

Assuming that we are in equilibrium, we can evaluate the momentum tensor by substituting for $f(\mathbf{r}, \mathbf{v}, t)$ the form (12.1):

$$\mathscr{P}_{\alpha\beta}^{\mathrm{eq}} = \int m v_{\alpha} v_{\beta} n(\mathbf{r}) \exp\left[-m(\mathbf{v}-\mathbf{u})^{2}/(2k_{\mathrm{B}}T)\right] d^{3}v = \rho(\mathbf{r}) \left(k_{\mathrm{B}}T \delta_{\alpha\beta} + u_{\alpha}u_{\beta}\right).$$
(12.9)

This result can be derived by separately considering $\alpha = \beta$ and $\alpha \neq \beta$, and working out the appropriate Gaussian integrals. Noting that $\rho k_B T$ equals the pressure *P*,¹ we arrive at the following two equations:

$$\frac{\partial \rho(\mathbf{r},t)}{\partial t} + \nabla \cdot \mathbf{j}(\mathbf{r},t) = 0 \text{ (mass conservation);}$$
(12.10a)

$$\frac{\partial(\rho \mathbf{u})}{\partial t} + \nabla_{\mathbf{r}} \cdot (P\mathbf{I} + \rho \mathbf{u}\mathbf{u}) = 0 \text{ (momentum conservation).}$$
(12.10b)

Using the first equation, we can rewrite the second as

$$\frac{\partial \mathbf{u}(\mathbf{r},t)}{\partial t} + [\mathbf{u}(\mathbf{r},t) \cdot \nabla_{\mathbf{r}}] \mathbf{u}(\mathbf{r},t) = -\frac{1}{\rho(\mathbf{r},t)} \nabla_{\mathbf{r}} P(\mathbf{r},t).$$
(12.11)

The equations (12.10a) and (12.10b) or (12.11) are the *Euler equations* for a fluid in equilibrium.

When the fluid is not everywhere in local equilibrium, the collisions will drive the system towards equilibrium – hence their effect can no longer be neglected. As mentioned above, the additional currents which arise on top of the equilibrium ones increase the entropy and are therefore called *dissipative*. Hence these terms describe the viscous effects in the fluid.

We now split the distribution function into an equilibrium and a nonequilibrium part:

$$f(\mathbf{r}, \mathbf{v}, t) = f^{\text{eq}}(\mathbf{r}, \mathbf{v}) + f^{\text{noneq}}(\mathbf{r}, \mathbf{v}, t).$$
(12.12)

The equilibrium term satisfies (12.1).

¹Here, we consider the fluid as an ideal gas; a realistic equation of state may be used instead.

How can we represent the effect of the collision term? There is an approach due to Maxwell, which is based on the assumption that *all relaxation processes have the same, or are dominated by a single, relaxation time* τ . In that case:

$$\left(\frac{df(\mathbf{r},\mathbf{v},t)}{dt}\right)_{\text{collisions}} = -\frac{f(\mathbf{r},\mathbf{v},t) - f^{\text{eq}}(\mathbf{r},\mathbf{v})}{\tau} = -\frac{f^{\text{noneq}}}{\tau}.$$
 (12.13)

As mentioned above, the collisions do not change the mass conservation equation, which should always be valid. The equation for the flux will however acquire a contribution from the nonequilibrium part of the distribution function, as we shall see. The mass flux can still be written as $\rho \mathbf{u}$. Moreover, the collisions leave the total momentum unchanged.

The flux **j** occurring in the mass conservation equation also occurs in the momentum conservation equation. In this second equation, the momentum flux $\mathscr{P}_{\alpha\beta}$ occurs, which we have calculated above *assuming equilibrium*. If we consider the evolution of this flux using the Boltzmann equation, we see that the collision effects enter explicitly in this momentum flux.

To find the lowest-order contribution to a systematic expansion of the density, we replace n on the left hand side of the Boltzmann equation by its equilibrium version:

$$\frac{\partial f^{\text{eq}}(\mathbf{r}, \mathbf{v})}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} f^{\text{eq}} = -\frac{f^{\text{noneq}}(\mathbf{r}, \mathbf{v}, t)}{\tau}.$$
(12.14)

This is an *explicit* equation for the nonequilibrium term. It can be shown that this is an expansion in the parameter ℓ/L , where ℓ is the mean free path, and *L* is the typical length scale over which the hydrodynamic quantities vary. Note that if we integrate this equation over the velocity, the right hand side vanishes as the collisions do not affect the mass density.

The momentum flux is defined in (12.8). This is calculated from the density $f(\mathbf{r}, \mathbf{v}, t)$ and it can therefore be split into an equilibrium and nonequilibrium part. The equilibrium part was calculated in Eq. (12.9), and the nonequilibrium part will now be calculated using (12.14):

$$\mathscr{P}_{\alpha\beta}^{\text{noneq}} = \int m v_{\alpha} v_{\beta} n^{\text{noneq}} d^3 v = -\tau \left[\int m v_{\alpha} v_{\beta} \frac{\partial f^{\text{eq}}}{\partial t} d^3 v + \int m v_{\alpha} v_{\beta} \mathbf{v} \cdot \nabla_{\mathbf{r}} f^{\text{eq}} d^3 v \right], \qquad (12.15)$$

where we have again used the notation ∂_{α} for a derivative with respect to the α -component of **r**. Before we proceed to work out (12.15) further, we note that the tensor $\mathscr{P}_{\alpha\beta}^{\text{noneq}}$ has an important property: its trace vanishes. This can be seen by writing out this trace:

$$\sum_{\alpha} \mathscr{P}_{\alpha\alpha}^{\text{noneq}} = \int v^2 f^{\text{noneq}}(\mathbf{r}, \mathbf{v}, t) d^3 v.$$
(12.16)

Realizing that this expression represents the change in the average kinetic energy due to the collisions, we immediately see that it vanishes as the (instantaneous) collisions leave the total energy invariant:

$$\mathrm{Tr}\mathscr{P}^{\mathrm{noneq}} = 0. \tag{12.17}$$

For the calculation of the nonequilibrium stress tensor, Eq. (12.15), we use the following equations, which can easily be seen to hold for the equilibrium distribution:

$$\int m f^{\rm eq}(\mathbf{r}, \mathbf{v}) d^3 v = \rho(\mathbf{r}); \qquad (12.18a)$$

$$\int m(v_{\alpha} - u_{\alpha})(v_{\beta} - u_{\beta})f^{\text{eq}}(\mathbf{r}, \mathbf{v})d^{3}v = \rho \frac{k_{\text{B}}T}{m}\delta_{\alpha\beta} = P\delta_{\alpha\beta}; \qquad (12.18b)$$

$$\dot{u}_{\alpha} = -\sum_{\beta} u_{\beta} \partial_{\beta} u_{\alpha} - \frac{1}{\rho} (\partial_{\alpha} P); \qquad (12.18c)$$

where in the last equation it is understood that the velocities are those evaluated for the equilibrium distribution: this equation is the Euler equation, (12.11) which can also be written as $\partial_t \mathscr{P}^{eq}_{\alpha\beta}$ (we use ∂_t to denote a partial derivative with respect to time).

We first work out the first term in the square brackets on the right hand side in (12.15). After some manipulation, using Eqs. (12.9), (12.10a) and (12.10b), this can be written as

$$\partial_{t}\mathscr{P}_{\alpha\beta}^{eq} = \partial_{t} \left(P \delta_{\alpha\beta} + \rho u_{\alpha} u_{\beta} \right) = \dot{P} \delta_{\alpha\beta} - \sum_{\gamma} \left[\partial_{\gamma} (\rho u_{\gamma}) u_{\alpha} u_{\beta} + \rho u_{\alpha} u_{\gamma} (\partial_{\gamma} u_{\beta}) + \rho u_{\beta} u_{\gamma} (\partial_{\gamma} u_{\alpha}) \right] - u_{\beta} \partial_{\alpha} P - u_{\alpha} \partial_{\beta} P. \quad (12.19)$$

The second term in the square brackets of (12.15) can be written, using the quantity $w_{\alpha} = v_{\alpha} - u_{\alpha}$, in the form [see also (12.9) and (12.18b)]:

$$\int (u_{\alpha} + w_{\alpha})(u_{\beta} + w_{\beta})(u_{\gamma} + w_{\gamma})\partial_{\gamma}n^{\text{eq}}(\mathbf{r}, \mathbf{v}) d^{3}v = \partial_{\gamma} \left(u_{\alpha}u_{\beta}u_{\gamma} + u_{\alpha}P\delta_{\beta\gamma} + u_{\beta}P\delta_{\beta\gamma} + u_{\gamma}P\delta_{\alpha\beta} \right). \quad (12.20)$$

The second term can now be worked out and yields

$$\sum_{\gamma} \left[u_{\alpha} u_{\beta} u_{\gamma} \partial_{\gamma} \rho + \rho u_{\beta} u_{\gamma} (\partial_{\gamma} u_{\alpha}) + \rho u_{\alpha} u_{\gamma} (\partial_{\gamma} u_{\beta}) + \rho u_{\alpha} u_{\beta} (\partial_{\gamma} u_{\gamma}) + \partial_{\gamma} (P u_{\gamma}) \delta_{\alpha\beta} + \partial_{\gamma} (P u_{\alpha}) \delta_{\beta\gamma} + \partial_{\gamma} (P u_{\beta}) \delta_{\alpha\gamma} \right]$$
(12.21)

Adding the two terms of Eq. (12.15), many terms occuring in the last equations cancel – the ones that remain are [(12.19) and (12.21)]:

$$P(\partial_{\beta}u_{\alpha} + \partial_{\alpha}u_{\beta}) + \delta_{\alpha\beta} \left\{ \dot{P} + \sum_{\gamma} \left[u_{\gamma}(\partial_{\gamma}P) + P\partial_{\gamma}u_{\gamma} \right] \right\}.$$
 (12.22)

The terms

$$\dot{P} + \sum_{\gamma} u_{\gamma}(\partial_{\gamma}P) \tag{12.23}$$

can be calculated using (12.18b) and the equilibrium distribution. When we write this term out, we obtain, again with $w_{\alpha} = v_{\alpha} - u_{\alpha}$:

$$\frac{\partial}{\partial t} \int mw^2 f \, d^3 v + \sum_{\gamma} u_{\gamma} \partial_{\gamma} \int mw^2 f \, d^3 v = \int mw^2 \left(\frac{\partial f}{\partial t} + \sum_{\gamma} u_{\gamma} \partial_{\gamma} n\right) \, d^3 v = \frac{1}{\tau} \int mw^2 f^{\text{noneq}} \, d^3 v. \quad (12.24)$$

This is the trace of the tensor

$$\frac{1}{\tau} \int m w_{\alpha} w_{\beta} f^{\text{noneq}} d^3 v.$$
(12.25)

Now we use the fact that $Tr \mathscr{P}^{noneq}$ vanishes. This can only happen when the trace occurring in the last equation cancels the trace of the remaining terms in the expression for \mathscr{P}^{noneq} . This tensor must therefore be

$$\mathscr{P}^{\text{noneq}} = -P\tau \left(\partial_{\alpha} u_{\beta} + \partial_{\beta} u_{\alpha} - \frac{2}{3} \delta_{\alpha\beta} \partial_{\gamma} u_{\gamma} \right).$$
(12.26)

Using this, we can formulate the momentum conservation equation, with $v = \tau k_{\rm B} T/m$, as

$$\frac{\partial u}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} = \frac{1}{\rho} \nabla P + v \nabla^2 \mathbf{u} + \frac{1}{3} v \nabla (\nabla \cdot \mathbf{u}).$$
(12.27)

The mass conservation equation and the momentum conservation equation together are insufficient to give us the four unknown field: ρ , **u** and *P*. We need therefore an additional equation, which may be $\rho = \text{constant}$ for an incompressible fluid, or $P \propto \rho$ for the isothermal case. Note that the case where $\rho = \text{const}$ also implies $\nabla \cdot \mathbf{u} = 0$ from the continuity equation, which in turn causes the last term in the last equation to become negligible.

Nonequilibrium statistical mechanics

13.1 Langevin theory of Brownian motion

In this section we consider the Langevin equation, which describes Brownina motion on a microscopic level. Consider a solution containing polymers or ions which are much heavier than the solvent molecules. As the kinetic energy is on average divided equally over the degrees of freedom, the ions or polymers will move much more slowly than the solvent molecules. Moreover, because of their large mass, they will change their momenta only after many collisions with the solvent molecules and the picture which emerges is that of the heavy particles forming a system with a much longer time scale than the solvent molecules. This difference in time scale can be employed to eliminate the details of the degrees of freedom of the solvent particles and represent their effect by forces that can be treated in a simple way. This process can be carried out analytically through a projection procedure but here we shall sketch the method in a heuristic way.

How can we model the effect of the solvent particles without taking into account their degrees of freedom explicitly? When a heavy particle is moving through the solvent, it will encounter more solvent particles in the front than in the back. Therefore, the collisions with the solvent particles will *on average* have the effect of a friction force proportional and opposite to the velocity of the heavy particle. This suggests the following equation of motion for the heavy particle:

$$m\frac{d\mathbf{v}}{dt}(t) = -\gamma \mathbf{v}(t) + \mathbf{F}(t)$$
(13.1)

where γ is the friction coefficient and **F** the external or systematic force, due to the other heavy particles, walls, gravitation, etc. The motion of fluid particles exhibits strong time correlations and therefore the effects of their collisions should show time correlation effects. Time correlations affect the form of the friction term which, in Eq. (13.1), has been taken dependent on the *instantaneous* velocity but which in a more careful treatment should include contributions from the velocity at previous times through a memory kernel:

$$m\frac{d\mathbf{v}}{dt}(t) = -\int_{-\infty}^{t} dt' \ \gamma(t-t')\mathbf{v}(t') + \mathbf{F}(t).$$
(13.2)

This form of the equation must also hold for lighter particles. In order to avoid complications we shall proceed with the simpler form (13.1). In the following we shall restrict ourselves to a particle in one dimension; the analysis for more particles in two or three dimensions is similar.

Equation (13.1) has the unrealistic effect that if the external forces are absent the heavy particle comes to rest, whereas in reality it executes a Brownian motion. To make the model more realistic we must include the rapid variations in the force due to the frequent collisions with solvent particles on top of the coarse-grained friction force. We then arrive at the following equation:

$$m\frac{dv}{dt}(t) = -\gamma v(t) + F(t) + R(t)$$
(13.3)

where R(t) is a 'random force'. Again, the time correlations present in the fluid should show up in this force, but they are neglected once more and the force is subject to the following conditions.

• As the average effect of the collisions is already absorbed in the friction, the expectation value of the random force should vanish:

$$\langle R(t) \rangle = 0. \tag{13.4}$$

• The values of *R* are taken to be uncorrelated:

$$\langle R(t)R(t+\tau)\rangle = 0 \quad \text{for } \tau > 0. \tag{13.5}$$

• The values of *R* are distributed according to a Gaussian:

$$P[R(t)] = (2\mathscr{P}\langle R^2 \rangle)^{-1/2} \exp(-R^2/2\langle R^2 \rangle).$$
(13.6)

Now let us discretise time. All these above assumptions can then be summarised in the following prescription for the probability for a set of random forces to occur between t_0 and t_1 :

$$P[R_i(t)]_{t_0 < t < t_1} \sim \exp\left(-\frac{1}{2q} \int_{t_0}^{t_1} dt \ R_i^2(t)\right)$$
(13.7)

with q a constant to be determined.

In the discretised time case, we may assume that the random force is constant over each time step: at step n, the value of the random force is R_n . For this case, the correlation function for the R_n reads

$$\langle R_n R_m \rangle = \frac{\int dR_n dR_{n+1} \dots dR_m \exp\left(-\frac{1}{2q} \sum_{l=n}^m R_l^2 \Delta t\right) R_n R_m}{\int dR_n dR_{n+1} \dots dR_m \exp\left(-\frac{1}{2q} \sum_{l=n}^m R_l^2 \Delta t\right)}$$
(13.8)

which yields the value 0 for $n \neq m$, in accordance with the previous assumptions. For n = m we find the value $q/\Delta t$, so we arrive at

$$\langle R_n R_m \rangle = \frac{q}{\Delta t} \delta_{nm}.$$
 (13.9)

For the continuum case $\Delta t \rightarrow 0$ (13.9) converges to the δ -distribution function

$$\langle R(t)R(t+\tau)\rangle = q\delta(\tau).$$
 (13.10)

We now return to the continuum form of the Langevin equation (13.3) with $F(t) \equiv 0$. This can be solved analytically and the result is

$$v(t) = v(0) \exp(-\gamma t/m) + \frac{1}{m} \int_0^t \exp\left[-(t-\tau)\gamma/m\right] R(\tau) d\tau.$$
 (13.11)

Because the expectation value of R vanishes we obtain

$$\langle v(t) \rangle = v(0) \exp(-\gamma t/m)$$
 (13.12)

which is to be expected for a particle subject to a friction force proportional and opposite to the velocity.

The expectation value of v^2 is determined in a similar way. Using (13.10) and (13.3) we find

$$\left< [v(t)]^2 \right> = v_0^2 \exp(-2\gamma t/m) + \frac{q}{2\gamma m} (1 - e^{-2\gamma t}/m),$$
 (13.13)

which for large t reduces to

$$\left< \left[\nu(\infty) \right]^2 \right> = \frac{q}{2\gamma m}.$$
 (13.14)

According to (13.11), v depends linearly on the random forces R(t) and as the latter are distributed according to a Gaussian, the same will hold for the velocity – the width is given by (13.14), so we have

$$P[v(t)] = \left(\frac{\gamma m}{\mathscr{P}q}\right)^{1/2} \exp[-mv(t)^2 \gamma/q]$$
(13.15)

for large t. This is precisely the Maxwell distribution if we write

$$q = 2k_{\rm B}T\gamma,\tag{13.16}$$

so this equation defines the value of q necessary to obtain a system with temperature T. In section 12.4 we shall discuss Langevin types of equations in a more formal way, using the Fokker-Planck equation.

The velocity autocorrelation function can also be obtained from (13.11):

$$\langle v(0)v(t)\rangle = \langle v(0)^2 \rangle e^{-\gamma t/m}.$$
(13.17)

The absence of a long time tail in this correlation function reflects the oversimplifications in the construction of the Langevin equation, in particular the absence of correlations in the random force and the fact that the frictional force does not depend on the 'history' of the system.

The results presented here are easily generalised to more than one dimension. However, including a force acting between the heavy particles causes problems if this force exhibits correlations with the random force, and Eq. (13.16) is no longer valid in that case. Such correlation effects are often neglected and the systematic force is simply added to the friction and the Langevin term.

A further refinement is the inclusion of memory kernels in the forces, similar to the approach in Eq. (13.2). In that case, the random force is no longer uncorrelated – it is constructed with correlations in accordance with the fluctuation-dissipation theorem:

$$\langle R(0)R(t)\rangle = \langle v^2 \rangle \gamma(t).$$
 (13.18)

However, this equation is again no longer valid if external forces are included.

13.2 Fokker Planck equation and restoration of equilibrium

In the previous section we have formulated an equation for a single particle which diffuses and which feels a force \mathbf{F} which tries to establish some distribution which differs from the homogeneous one. This force may be derived from a stationary potential. The stationary solution for the velocity equation, in which the random force is neglected, is

$$\mathbf{v} = -\frac{\mathbf{F}}{\gamma},$$

that is, the force tries to increase the velocity along the force direction, and the friction counteracts this and in the end there is a balance between that friction and the force. We now establish an equivalent of the diffusion equation which includes the effect of a driving force. The flux due to diffusion is

$$\mathbf{j}_{\text{diff}} = -D\nabla \boldsymbol{\rho}(\mathbf{r}, t),$$

124

and the flux due to the driving force, or *drift flux* is given by

$$\mathbf{j}_{\text{drift}} = \boldsymbol{
ho}(\mathbf{r},t) \frac{\mathbf{F}(\mathbf{r},t)}{\gamma}.$$

A well-known example of the last relation is *Ohm's law*, where the flux (current) is linearly related to the force (which is proportional to the applied electric field).

The diffusion equation can be derived from the requirement that the flux through the surface A of a volume V equals the change in density inside that volume:

$$\frac{d}{dt}\int_{V}\rho(\mathbf{r},t)d^{3}r = -\int_{A}\mathbf{j}_{\text{total}}\cdot d\mathbf{A}$$

where \mathbf{A} is a unit vector perpendicular to a surface element dA. Using Gauss', or divergence theorem, we can rewrite the right hand side as a volume integral:

$$\int_{V} \frac{\partial}{\partial t} \rho(\mathbf{r}, t) d^{3}r = -\int_{V} \nabla \cdot \mathbf{j}_{\text{total}} d^{3}r.$$

As this must hold for *any* volume within the system, we obtain the *continuity equation*:

$$\frac{\partial}{\partial t}\boldsymbol{\rho}(\mathbf{r},t) + \nabla \cdot \mathbf{j}_{\text{total}}(\mathbf{r},t) = 0.$$

Now we can substitute the expressions above for the diffusive and the drift flux:

$$\frac{\partial}{\partial t}\boldsymbol{\rho}(\mathbf{r},t) = \nabla \cdot \left[D\nabla - \frac{\mathbf{F}}{\gamma} \right] \boldsymbol{\rho}(\mathbf{r},t).$$

Recalling the relation

$$\gamma = \frac{k_{\rm B}T}{D}$$

from the previous section, we have

$$\frac{\partial}{\partial t}\boldsymbol{\rho}(\mathbf{r},t) = \nabla \cdot \boldsymbol{D} \left[\nabla - k_{\rm B} T \mathbf{F} \right] \boldsymbol{\rho}(\mathbf{r},t).$$

This equation is called the *Fokker–Planck* equation. We can check whether this equation makes sense by investigating whether, in a closed system with some external potential, the density will be distributed according to the Boltzmann distribution. This turns out to be the case, as is clear from the fact that for

$$\mathbf{F} = \frac{\nabla \rho_0(\mathbf{r})}{k_{\rm B} T \rho_0(\mathbf{r})}$$

the Fokker–Planck distribution will yield a stationary distribution $\rho_0(\mathbf{r})$ which is realised for long times. This can be checked by putting the left hand side of the Fokker–Planck equation to zero, and checking that the right hand side vanishes for

$$\rho(\mathbf{r},t) = \rho_0(\mathbf{r}).$$

If we now substitute for $\rho_0(\mathbf{r})$ the Boltzmann factor:

$$\rho_0(\mathbf{r}) = \exp\left[-V(\mathbf{r})/(k_{\rm B}T)\right]$$

and realise that for

$$\mathbf{F}(\mathbf{r}) = -\nabla V(\mathbf{r}).$$

we see that indeed the Boltzmann distribution is the correct stationary distribution. In fact, this result tells us again that the relation $\gamma = k_{\rm B}T/D$ must be valid: if the proportionality factor would be different, the Boltzmann distribution would not be found as the stationary distribution. This relation is known as the *Einstein relation*.

Using the expression for the drift current, we can calculate transport coefficients. First we analyse electric transport which is due to the acceleration of charges by an electric field. There is a stationary situation when the diffusion current cancels the drift current. For an electric field along the *x*-direction:

$$J_{\rm drift} = eD \frac{d\rho(\mathbf{r})}{dx},$$

The electric field is minus the gradient of the potential $V(\mathbf{r})$, which determines the charge density $\rho(\mathbf{r})$:

$$\boldsymbol{\rho}(\mathbf{r}) = \rho_0 e^{-eV(\mathbf{r})/(k_{\rm B}T)},$$

hence

$$\frac{d\rho(\mathbf{r})}{dx} = \frac{eE_x}{k_{\rm B}T}\rho(\mathbf{r})$$

from which we find for the conductivity

$$\sigma = \frac{e^2 D \rho(\mathbf{r})}{k_{\rm B} T}.$$

This is essentially the famous Drude formula. The expression for the electric drift current:

$$J_{\rm el} = \frac{e^2 E_x \rho(\mathbf{r})}{\gamma}$$

gives the same result provided that

$$\frac{D}{k_{\rm B}T} = \frac{1}{\gamma},$$

in accordance with what was found above. It should be noted that the above derivation is performed in the context of a stationary equilibrium state, where the net current should be zero indeed. If the boundary conditions are such that there is a source and drain (the contacts), then a net current survives.

13.3 Fluctuations – the Wiener-Kintchine theorem

In our discussion of the Langevin equation, we have encountered a fluctuating quantity: the random force. There we have assumed that this random force had no time correlation. In this section we shall study fluctuating quantities which are correlated in time. Consider a quantity A (you may think of a more realistic random force in the Langevin equation) which has an average value of 0 but which fluctuates in time. The autocorrelation function is defined as

$$K(s) = \langle A(t)A(t+s) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T A(t)A(t+s)dt.$$

This is a time averaged quantity. The quantity K(s) satisfies the property

$$K(s) = K(-s),$$

as can readily be checked by inspecting its definition.

We expect furthermore that, since $\langle A(t) \rangle = 0$, the autocorrelation correlation function vanishes for large values of *s*, and that it will attain its maximum for s = 0 (then the integrand in the average is always positive). It turns out that the autocorrelation function is intimately related to the so-called *spectral density*, defined in terms of the Fourier transform of *A* in the time domain. The latter is defined as

$$\tilde{A}(\omega) = \frac{1}{\sqrt{T}} \int_0^T A(t) e^{i\omega t} dt.$$

where the limit $T \to \infty$ is implicitly assumed – a convention we shall adhere to from now on. Usually, A is such that A^2 is related to some energy. For example, in the case where A is a component of an electric field, A^2 is the contribution of that component to the energy stored in the oscillating field.

The spectral density of the variable A is defined as

$$S(\boldsymbol{\omega}) = \langle \tilde{A}(\boldsymbol{\omega})\tilde{A}^*(\boldsymbol{\omega}) \rangle.$$

We can evaluate the right hand side as follows:

$$S(\omega) = \frac{1}{T} \left\langle \int_0^T \int_0^T A(t) e^{i\omega t} A(t') e^{-i\omega t'} dt dt' \right\rangle = \frac{1}{T} \int \int \left\langle A(t) A(t+s) \right\rangle e^{i\omega t} e^{-i\omega(t+s)} dt ds$$

where the shift of the integration variable was made possible because the quantity in brackets is known to be K(s), which has a finite width. If we take the limit for $T \to \infty$, we find

$$S(\boldsymbol{\omega}) = \int_{-T/2}^{T/2} K(s) e^{-i\omega s} ds \equiv K(\boldsymbol{\omega}).$$

This relation is known as the *Wiener-Kintchine theorem*. Note the absence of the factor 1/T in front of the Fourier transform of *K*. If the width of K(s) is called τ , then the width of $K(\omega)$ will be $1/\tau$ (reminiscent of the Heisenberg uncertainty relation in quantum mechanics).

Let us now come back to the Langevin equation, but refrain from imposing a non-coherence for the random force. The equation of motion

$$m\dot{v} = -\gamma v + R(t)$$

with R the random force still holds. As we have seen, the solution of this equation can be written as

$$mv(t) = e^{-\gamma t/m} \int_0^t e^{\gamma t'/m} R(t') dt'$$

where we have assumed that the initial velocity was zero. We now evaluate the average kinetic energy:

$$\frac{m}{2}\left\langle v^{2}(t)\right\rangle = \left\langle \frac{1}{2m}e^{-2\gamma t/m}\int_{0}^{t}e^{\gamma t_{1}/m}R(t_{1})dt_{1}\int_{0}^{t}e^{\gamma t_{2}/m}R(t_{2})dt_{2}\right\rangle$$

where the expectation value is over the different possible realisations of the random force.

Using the fact that

$$\langle R(t_1)R(t_2)\rangle = K_F(t_2-t_1),$$

is short-ranged so that $t_1 \approx t_2$ and taking the limit of large t, we obtain, using the variables

$$T = \frac{t_1 + t_2}{2}$$
 and $\tau = t_2 - t_1$,

$$\langle E_{\rm kin} \rangle = \frac{e^{-2\gamma t/m}}{2m} \int_0^t e^{2\gamma t} \int_0^t e^{2\gamma T/m} dT \int K(\tau) d\tau = \frac{\mathscr{P}}{2\gamma} \tilde{K}_F(0) \left(1 - e^{-2\gamma t/m}\right)$$

which, for $t \rightarrow \infty$ reduces to

$$\langle E_{\rm kin} \rangle = \frac{1}{2\gamma} \tilde{K}(0).$$

As before, we may put the kinetic energy equal to $k_{\rm B}T/2$ to obtain

$$\gamma = \frac{1}{k_{\rm B}T} \tilde{K}_F(0).$$

As mentioned before, this friction exponent directly determines the value of the transport coefficients, such as the electric conductivity.

Now we shall focus on this last example, and instead of the $\omega = 0$ case, analyse the frequency dependence. To this end, we replace the expectation value of $v^2(t)$ on which the above derivation was based, by the autocorrelation function. We have evaluated this function in section 12.3; the result obtained there was

$$\langle v(0)v(t)\rangle = \frac{k_{\rm B}T}{2m}e^{-\gamma|t|/m},$$

where the equipartition theorem has been used to rewrite $\langle v^2(0) \rangle$ in terms of $k_B T$. The Fourier transform of this gives us

$$K_{\nu}(\omega) = \frac{k_{\rm B}T}{\gamma} \frac{1}{1 + (\omega m/\gamma)^2}$$

According to the Wiener-Kintchine theorem, this is related to the power spectrum:

$$\left< |\nu(\omega)|^2 \right> = \frac{k_{\rm B}T}{\gamma} \frac{1}{1 + (\omega m/\gamma)^2}$$

This formula implies that the spectrum of the current power, induced by the fluctuations, is flat, i.e. it does not depend on ω for frequencies (much) smaller than m/γ , which is the inverse relaxation time of the electrons. This means that we have white noise up to this limit.

In the previous section, we have derived the result

$$\gamma = \frac{1}{k_{\rm B}T} \tilde{K}_{\nu}(0).$$

The parameter γ determines the transport properties, such as the conductance. In particular, we have

$$j = nev = ne^2 \frac{E}{\gamma}$$

where E is a component of the electric field. Therefore, the conductance is found as

$$\sigma = rac{ne^2}{\gamma} = rac{ne^2k_{
m B}T}{ ilde{K}_{
m v}(0)}.$$

This means that we can evaluate the transport coefficient σ from the autocorrelation function for the velocities. This is a striking result: the autocorrelation function is a property of the *equilibrium* system – from this, we can evaluate the transport coefficient, which is a *non-equilibrium* property.

128

The Wiener Kintchine theorem has an important application in electric circuits. Consider for example an inductance in some electric circuit. The electric energy stored in the inductance is given by the expression

$$E_{\rm el}=\frac{L}{2}I^2.$$

It is generally assumed that the *total* energy of the circuit can be written as

$$E_{\text{total}} = E_{\text{el}}(I) + \text{ other terms}$$

where the 'other terms' do not depend on *I*. This means that *I* acts as a generalised coordinate of the Hamiltonian, and it should therefore satisfy the equipartition theorem

$$\frac{LI^2}{2} = \frac{k_{\rm B}T}{2}.$$

The power stored in a mode with frequency ω is

$$\frac{L}{2}\langle I^2(\boldsymbol{\omega})\rangle = J(\boldsymbol{\omega}).$$

In equilibrium, the total power should yield

$$\int \frac{L}{2} \left\langle I^2(\omega) \right\rangle d\omega = \frac{k_{\rm B}T}{2},$$

therefore, for frequencies (much) smaller than those corresponding to the relaxation time of the circuit, we must have white noise analogously to the case discussed above, and the power containes within a frequency window $d\omega$ should be

$$\int \frac{L}{2} \left\langle I^2(\omega) \right\rangle d\omega = \frac{k_{\rm B}T}{2} d\omega$$

This result is known as *Nyquist's theorem*.

13.4 General analysis of linear transport

Quite generally, fluctuations of a system from the equilibrium state can be related to the transport properties of that system. The analysis proceeds as follows. Suppose we have an isoalted system, which tends to maximise its entropy. The entropy depends on how the energy and the particle density, and perhaps some other quantities, are distributed in space. We can store the information concerning these distributions in a set of numbers – you may think of the Fourier coefficients of the energy and/or denisty distribution. We call these numbers x_i and we call \tilde{x}_i the values for which the entropy assumes its maximum.

Fluctuations correspond to deviations of the x_i from their equilibrium values. The corresponding variation in the entropy can be expanded in a Taylor series:

$$S(x_1,\ldots,x_N) = S(\tilde{x}_1,\tilde{x}_2,\ldots,\tilde{x}_N) + \frac{1}{2}\sum_{i,j}\frac{\partial^2 S(\tilde{x}_1,\tilde{x}_2,\ldots,\tilde{x}_N)}{\partial x_i \partial x_j}(x_i - \tilde{x}_i)(x_j - \tilde{x}_j) + \dots$$

The fact that the first-order term is not included is due to the fact that S was expanded around its maximum – hence, the first derivatives are all zero. The fact that the entropy strives to its maximum is the driving force which causes fluctuations to dampen out.

Recalling that

$$S = k_{\rm B} \ln \Omega$$
,

where Ω is the number of states accessible to the system, and combining this with the fundamental postulate if statistical mechanics, which says that each of these states is equally probable, we have for the probability of having a state where the quantities $a_i = x_i - \tilde{x}_i$ the following expression:

$$P(a_1,\ldots,a_N) = \frac{\exp\left(-\sum_{ij}\frac{\eta_j}{2}a_ia_j\right)}{\int_{-\infty}^{\infty} da_1\cdots da_N \exp\left(-\sum_{ij}\frac{\eta_j}{2}a_ia_j\right)},$$

where

$$\gamma_{ij} = \frac{1}{k_{\rm B}} \sum_{i,j} \frac{\partial^2 S(\tilde{x}_1, \tilde{x}_2, \dots, \tilde{x}_N)}{\partial x_i \partial x_j}$$

Note that the fact that S has a maximum implies that the matrix γ_{ij} has positive eigenvalues.

From this we can derive a simple expression for correlation functions of the a_i . Note that

$$\frac{1}{P}\frac{\partial P}{\partial a_i} = \frac{1}{k_{\rm B}}\frac{\partial S}{\partial a_i}.$$

Taking the average on the left and right hand side with respect to the distribution P we obtain

$$\left\langle a_i \frac{\partial S}{\partial a_i} \right\rangle == \int da_1 \cdots da_N a_i \frac{\partial S}{\partial a_i} P = k_{\rm B} \int da_1 \cdots da_N a_i \frac{\partial P}{\partial a_i}$$

Integrating by parts the integral on the right hand side leads to

$$\left\langle a_i \frac{\partial S}{\partial a_i} \right\rangle = -k_{\rm B}$$

Moreover, for $i \neq j$ we find along the same lines:

$$\left\langle a_i \frac{\partial S}{\partial a_j} \right\rangle = 0.$$

You may object that the first derivative of S with respect to the a_i is zero. This is true at the maximum, but near that maximum, we find

$$\frac{\partial S}{\partial a_i} = \sum_j \gamma_{ij} a_j.$$

Using this we rewrite the result above as

$$\sum_{ij}\gamma_{ik}\left\langle a_{k}a_{j}\right\rangle =k_{\mathrm{B}}\delta_{ij}.$$

As a_i represents a fluctuation in some quantity, we can identify $\delta \dot{x}_i$ as some kind of *current* (below we shall consider an example). The entropy changes in the course of time as

$$\frac{dS}{dt} = \sum_{i} \delta \dot{a}_i \frac{\partial S}{\partial a_i},$$

which suggests that we can interpret $\partial S/\partial a_i = X_i$ as the *driving force* corresponding to that current. Now we assume a linear relationship between the forces X_i and their resulting deviations a_i :

$$J_i = \dot{a}_i = \sum_j L_{ij} \frac{\partial S}{\partial a_j} = \sum_j L_{ij} X_j.$$

Now we consider the expectation value

$$\begin{split} \left\langle a_i(t+\tau)a_j(t) \right\rangle &= \left\langle a_i(t)a_j(t) \right\rangle + \tau \left\langle \delta \dot{a}_i(t)\delta x_j(t) \right\rangle \\ &= \left\langle a_i(t)a_j(t) \right\rangle + \tau \sum_m L_{im} \left\langle \frac{\partial S}{\partial a_m} a_j(t) \right\rangle \\ &= \left\langle a_i(t)a_j(t) \right\rangle + \tau L_{ij}k_{\rm B}. \end{split}$$

We see that the linear transport coefficients L_{ij} are found as the correlation functions of the fluctuations:

$$L_{ij} = \frac{1}{k_{\rm B}\tau} \left[\left\langle a_i(t+\tau)a_j(t) \right\rangle - \left\langle a_i(t)a_j(t) \right\rangle \right].$$

From this, we see that the transport coefficients must be symmetric:

$$L_{ij} = L_{ji}$$
.

This nontrivial property follows from what is called *microscopic reversibility* as it reflects symmetry properties of microscopic correlation functions which follow from the undrlying time reversal symmetry of the microscopic dynamics.

We can analyse further the relation between L_{ij} and the correlator. Suppose we had in the above derivation not multiplied $a_i(t + \tau)$ with $a_i(t)$ but with $a_i(0)$. In that case, we arrive at the result:

$$L_{ij} = \frac{1}{k_{\rm B}\tau} \left[\left\langle a_i(t+\tau)a_j(0) \right\rangle - \left\langle a_i(t)a_j(0) \right\rangle \right] = \frac{1}{k_{\rm B}\tau} \left[\left\langle a_i(t)a_j(-\tau) \right\rangle - \left\langle a_i(t)a_j(0) \right\rangle \right]$$

where we have used time translation symmetry.

Now we approximate finite differences by time derivatives:

$$L_{ij} \approx -\frac{1}{k_{\rm B}} \left\langle a_i(t) \dot{a}_j(0) \right\rangle = -\frac{1}{k_{\rm B}} \int_0^t \left\langle \dot{a}_i(t') \dot{a}_j(0) \right\rangle dt'.$$

If we take t much larger than the correlation time, we see that

$$L_{ij} \approx -\frac{1}{k_{\rm B}} \int_0^\infty \left\langle \dot{a}_i(t') \dot{a}_j(0) \right\rangle dt'.$$

Recall that \dot{a}_i is the current j_i , and we see that we have found an expression for the linear transport coefficient L_{ij} in terms of a time correlation function of the currents:

$$L_{ij} \approx -\frac{1}{k_{\rm B}} \int_0^\infty \left\langle J_i(t') J_j(0) \right\rangle dt'.$$

How does this relate to a specific process, such as diffusion? First we must identify the dependence of the entropy on the density. The parameters a_i are here the coordinates of the particles in the system. We use the thermodynamic relation

$$TdS = -\mu dN + dE - \frac{1}{T}\sum_{i} X_{i}a_{i}.$$

In this expression, the first two terms are always present, and the last term is used to store additional contributions resulting from external forces. The resulting fluxes are not necessarily the fluxes which are of interest to us. In particular, they are not spatial fluxes, but simply time derivatives. However, we can derive relations for spatial fluxes through some trick as we shall now show. It is clear that for the entropy density *s* we have

$$\frac{ds}{dt} = \frac{\partial s}{\partial t} + \nabla \cdot \mathbf{j}_s,$$

where \mathbf{j}_s is the *entropy flux*, which tells us how much entropy flows through a wall per unit area. For the particle density we have a similar formula, which, together with the conservation of particle density gives

$$\frac{\partial \boldsymbol{\rho}}{\partial t} + \nabla \cdot \mathbf{j} = 0.$$

We assume that similar conservation laws hold for the other quantities occuring in the problem.

From the thermodynamic relation above, we have

$$\frac{\partial s}{\partial t} = -\frac{\mu}{T}\frac{\partial \rho}{\partial t} + \frac{1}{T}\frac{\partial E}{\partial t} - \sum_{i}\frac{X_{i}}{T}\frac{\partial a_{i}}{\partial t}.$$

Then we see, after replacing all time derivatives by the appropriate fluxes, using the conservation laws that

$$\frac{ds}{dt} = -\nabla\left(\frac{\mu}{T}\right)\mathbf{j} + \nabla\left(\frac{1}{T}\right)\mathbf{j}_E - \sum_i \left(\frac{X_i}{T}\right)\mathbf{J}_i.$$

This is of the same form as found above provided that we interpret the quantities

$$-\nabla\left(\frac{\mu}{T}\right), \quad \nabla\left(\frac{1}{T}\right), \quad \nabla-\left(\frac{X_i}{T}\right)$$

as forces for the appropriate fluxes. We immediately see that the driving force for heat transport is the gradient of 1/T, and that of particle transport is the gradient of $-\mu/T$. Provided we do not apply a temperature gradient to the system, we have for the driving force for the particle flux:

$$-\frac{1}{T}\nabla\mu.$$

The linear relationship between the current and this force can be cast in the form

$$J_i = -\frac{1}{T} \sum_j \tilde{L}_{ij} \frac{\partial \mu}{\partial x_j},$$

where *i* and *j* assume the values 1,2 and 3. With the tilde \sim we have indicated that the transport coefficient may deviate from the coefficient of the Onsager relation, because the current is not a time derivative. We use

$$J_i(\mathbf{r},t) = \rho(\mathbf{r},t)v_i(\mathbf{r},t)$$

and the fact that any time correlation function of the currents is dominated by the velocity time correlation function. The latter is given as

$$\langle v_i(t)v_j(0)\rangle = \langle v^2(0)\rangle e^{-t/\tau}\delta_{ij}$$

where $\tau = D$, the diffusion coefficient. Integrating this over time gives

$$\tilde{L}_{ij} = \frac{1}{k_{\rm B}} \int_0^\infty \left\langle v_i(t) v_j(0) \right\rangle dt = \frac{1}{k_{\rm B}} \tau \delta_{ij} = \frac{D}{k_{\rm B}} \delta_{ij}.$$

So we see that

$$v_i = -\frac{1}{\rho} \frac{D}{k_{\rm B}T} \frac{\partial \mu}{\partial x_i},$$

so that

$$J_i = -\frac{D}{k_{\rm B}T}\frac{\partial\mu}{\partial x_i}.$$

In order to arrive at the diffusion equation, we must realize that, for low densities,

$$\mu(\rho) = \mu(\rho_0) + k_{\rm B}T \ln\left[\frac{\rho}{\rho_0}\right],\,$$

so that we obtain

$$J_i = D \frac{\partial \rho}{\partial x_i},$$

 $\mathbf{J} = D\nabla \rho$.

hence

Adding an electric term

$$-\frac{1}{T}V(x)qd\rho(x)$$

to the expression for the entropy, gives us the force on particles with charge q in a potential:

$$\mathbf{J} = \frac{D}{k_{\rm B}} \left[\frac{\partial \mu}{\partial x_i} + \frac{q}{T} E \right]$$

nicely in line with our previous results.

The Onsager formulation provides an abstract framework from which the various forces and currents can quickly be derived.