Theory Option

Statistical Mechanics

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Books: (i) *Statistical Physics Part I*, L.D. Landau & E.M. Lifschitz (Butterworth-Heinemann £32.99); (ii) *Statistical Physics*, F., Mandle (Wiley £24.95) (iii) *Statistical Mechanics of Phase Transitions*, J., Yeomans, (Oxford £24.95)

1 What's it all about?

A beaker full of water, a diamond, a wire, or a litre of helium are all complex dynamical systems with well defined bulk properties such as volume V, pressure P, temperature T, thermal conductivity κ, electrical conductivity σ, etc. We know experimentally that these properties are connected to one another by relations – for example an equation of state that links V, P and T – and we would like to connect these with our understanding of the dynamics of the systems. That is, we wish to start from the concept that a diamond is composed of carbon atoms arranged in a tretragonal lattice and derive expressions for a diamond's coefficient of thermal expansion, and its compressibility, thermal conductivity etc, in terms of say its temperature and pressure. Statistical mechanics is the branch of knowledge that enables us to achieve this goal. We shall restrict our attention to the sub-branch of equilibrium statistical mechanics, in which we assume that the system under study is in 'thermal equilibrium'. In practice this means that we are excluding problems in which different parts of the system are at different temperatures or pressures, or, worse still, cannot be characterized by a temperature at all. The restriction to thermal equilibrium is not a very severe one from the point of view of terrestrial experiments, but it is very limiting in astrophysics because significant departures from thermal equilibrium are common in the Universe at large.

The system under study is described mathematically by specifying its Hamiltonian H. This is the usual quantum operator associated with energy. What will be unfamiliar about H is its complexity: it typically describes a system that has $\sim 10^{24}$ dynamical variables. For example, the simplest non-trivial model of a diamond would involve the positions $\mathbf{q}_i$ and momenta $\mathbf{p}_i$ of $N \sim 10^{24}$ carbon atoms, each of which is connected by springs to its four nearest neighbours. Hence the Hamiltonian would be of the form

$$H = \sum_{i=1}^{N} \left(\frac{\mathbf{p}_i^2}{2m} + \tfrac{1}{4} \sum_{j=1}^{4} k[|\mathbf{x}_i - \mathbf{x}_{n_i(j)}| - a]^2 \right). \tag{1.1}$$

Here a is the natural length of each CC bond, $n_i(j)$ is a function that returns the index of the jth neighbour of atom i and the factor $1/4$ compensates for the fact that each spring is included twice in the sums over atoms. This vast Hamiltonian operates on wavefunctions that may be taken to depend on the N vector variables $\mathbf{x}_i$: $\psi(\mathbf{x}_1, \dots, \mathbf{x}_N)$. The eigenstates $|\alpha\rangle$ of this vast operator are the states in which the crystal as a whole has well defined energy. We are unlikely to have explicit expressions for the wavefunctions of these stationary states, but we shall pretend that we do.

The thermodynamic properties of the system turn out to depend strongly on the distribution over energy of the stationary states $|\alpha\rangle$. The energy levels of a finite system such as a crystal will be discrete, but the spacing between adjacent energy levels becomes smaller and smaller as we consider larger and larger crystals, and in the **thermodynamic limit** of crystals that are arbitrarily large, the energy levels form a continuum. In this limit the system's thermodynamics depends on the **density of states** $g(E)$, which is such that the number of quantum states with energies in the range $(E, E + \mathrm{d}E)$ is

$$\mathrm{d}N = g(E)\,\mathrm{d}E. \tag{1.2}$$

Which quantum state is our system in? We do not know, and we are not likely to find out, because exquisite accuracy in the measurement of the energy would be required to pick one state from the continuum of possible ones. By the uncertainty principle, a measurement of E to sufficient accuracy would require an indefinite period of time, and is entirely impracticable. Moreover, it is likely that many energy levels are highly degenerate, so measurement of the energy would have to be followed by further measurements of other observables before we could determine $|\alpha\rangle$ unambiguously. So we accept that we do not know which state the system is in and settle for the probability p_α that if we *were* to make the necessary measurements, the system *would* be found in the state $|\alpha\rangle$.

We identify the internal energy U of thermodynamics with the expectation value of the energy that is associated with the probability distribution $\{p_\alpha\}$:[1]

$$U = \sum_\alpha p_\alpha E_\alpha. \tag{1.3}$$

The energy eigenvalues E_α will depend on thermodynamic variables such as the volume: if we compress a beaker of water, we increase each E_α by some amount $(\partial E_\alpha/\partial V)\mathrm{d}V$ that we could in principle determine from quantum mechanics. Similarly, the energy levels of a wire depend on the wire's length l. If the compression or stretching is slow, we know from quantum mechanics that the system will remain in the αth eigenstate of $H(t)$ as the system is deformed. Consequently, the probabilities p_α do not change during a slow, or 'adiabatic' deformation. By equating the change in the beaker's energy to the work $-P\mathrm{d}V$ that we do during the compression, we find that the pressure is given by

$$P = -\sum_\alpha p_\alpha \frac{\partial E_\alpha}{\partial V}. \tag{1.4}$$

Similarly, the tension in a wire is given by

$$\tau = \sum_\alpha p_\alpha \frac{\partial E_\alpha}{\partial l}. \tag{1.5}$$

We'll want to apply our results to magnetic systems. The energy levels E_α of a magnetic system depend on the magnetic field $\mathbf{B}$, so $\mathbf{B}$ plays a role analogous to that of the volume V of a fluid. The magnetization $\mathbf{M}$ plays a role analogous to P in that it represents the response of the system to an imposed field $\mathbf{B}$ at a given temperature. If we increase the field by $\mathrm{d}\mathbf{B}$, the system's energy changes by

$$\mathrm{d}U = -\mathbf{M}\cdot\mathrm{d}\mathbf{B}, \tag{1.6}$$

where the minus sign arises because the energy is lowest when $\mathbf{M}$ is parallel to $\mathbf{B}$ (magnets align with the imposed field). Comparing this last expression for $\mathrm{d}U$ with the derivative of (1.3) for an adiabatic change, we find that

$$\mathbf{M} = -\sum_\alpha p_\alpha \frac{\partial E_\alpha}{\partial \mathbf{B}}. \tag{1.7}$$

In more complex systems, the E_α may depend on several variables. For example, the energy levels of a diamond crystal depend not only on the crystal's volume, but also on its shape: you have to do work to shear it at constant volume. By analogy with equation (1.4) there is an analogue of pressure associated with each of the variables upon which the energy levels depend. Below we shall focus on the case in which the energy levels depend on only one parameter, which we shall call V, and use the symbol P for the associated variable. Our formulae can be readily adapted to other physical situations by replacing (P, V) with $(-\tau, l)$, $(\mathbf{M}, \mathbf{B})$, or a sum of such pairs of variables.

We shall see below that the system's temperature and entropy depend on the probabilities p_α, and we now ask what the values of these should be.

2 The principle of maximum entropy

Many practical problems, both in physics and in many other branches of life, such as bookmaking, image-processing and business, can be reduced to the determination of probabilities given certain information. It turns out that there is just one consistent way doing this – to

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[1] In these notes an object inside curly brackets, such as $\{p_i\}$ means 'the set of p_is'.

maximize the 'entropy' of the probability distribution. The American physicist, J.W. Gibbs was the first to determine probability distributions in this way, but he offered no satisfactory explanation of why it was the correct procedure, perhaps because illness and death forced him to cut short his book on statistical mechanics. Hence it was left to Shannon, who was interested in communication theory, to give a clear account of entropy maximization in 1948. Many physicists have still not grasped that entropy maximization lies at the heart of statistical mechanics and is a general principle of logical deduction, more basic than any physical application.

Consider some event that can have n different outcomes $x_1, \dots, x_n$. The event might be the throwing of a die, and x might the number obtained ($x_1 = 1$, etc). We want to assign probabilities to each possible outcome $p_1, \dots, p_n$ that reflect our knowledge about the event, *and nothing more*. If we know nothing about the die, we will argue that every outcome is equally likely, and set $p_i = \frac{1}{6}$ for all i. But we might know more; for example, we might know that the average value obtained over 10^6 throws is 3.667, which differs significantly from the value 3.5 expected of an unbiased die. What p_i should we then choose? If $p_1 = \frac{1}{3}$, $p_4 = \frac{1}{3}$, $p_6 = \frac{1}{3}$ and every other $p_i = 0$ we would have $\langle x \rangle = 11/3$ as required. But it doesn't seem likely that the slight difference between the mean value of x and 3.5 arises because the die never lands on 2 or 3 or 5; it is much more probable that 4, 5 and 6 come up just a bit more often than 1, 2 or 3. We need a rational way of choosing p_i that reflect the knowledge that we do have ($\langle x \rangle = 3.667$) without making unjustified assumptions (such as that 2 won't come up).

To achieve this goal we look for a measure $S(p_1, \dots, p_n)$ of the uncertainty, or 'missing information', associated with a probability distribution and maximize this by varying the p_i subject to whatever data we have (in the case of the die $\langle x \rangle = 3.667$). We require that S have the following properties:

- S must be a continuous, symmetric function of the p_i;
- S should be largest when every outcome is equally likely, i.e., when $p_i = 1/n$ for all i. We define
  $$S(\tfrac{1}{n}, \dots, \tfrac{1}{n}) = S_n \tag{2.1}$$
  and require that $S_{n+1} > S_n$ (more possibilities implies more uncertainty).
- S shall be consistent in the sense that it yields the same uncertainty when there are different ways of enumerating the possible outcomes of the event.

To grasp the essence of the last requirement, consider an experiment with three possible outcomes x_1, x_2 and x_3 to which we assign probabilities p_1, p_2 and p_3, yielding an uncertainty $S(p_1, p_2, p_3)$. We could group the last two outcomes together and assign a probability $p_{23} = p_2 + p_3$ to getting x_{23} (i.e., x_2 *or* x_3), giving uncertainty $S(p_1, p_{23})$. To this uncertainty we have to add that associated with resolving the outcome x_{23} into either x_2 or x_3. The probability that we will have to resolve this uncertainty is p_{23}, and the probability of getting x_2 given that we have x_{23} is p_2/p_{23}, so we argue that

$$S(p_1, p_2, p_3) = S(p_1, p_{23}) + p_{23} S\Big(\frac{p_2}{p_{23}}, \frac{p_3}{p_{23}}\Big) \tag{2.2}$$

This equation is readily generalized: we have n possible outcomes $x_1, \dots, x_n$ with probabilities $p_1, \dots, p_n$. We gather the outcomes into r groups and let y_1 be the outcome in which one of $x_1, \dots, x_{k_1}$ was obtained, y_2 the outcome in which one of $x_{k_1+1} \dots, x_{k_2}$ was obtained etc, and let w_i denote the probability of the outcome y_i. Then since the probability that we get x_1 given that we have already obtained y_1 is p_1/w_1, we have

$$\begin{aligned} S(p_1, \dots, p_n) = S(w_1, \dots, w_r) + w_1 S(p_1/w_1, \dots, p_{k_1}/w_1) + \\ \dots + w_r S(p_{n-k_r}/w_r, \dots, p_n/w_r). \end{aligned} \tag{2.3}$$

Since S is a continuous function of its arguments, it suffices to evaluate it for rational values of the arguments. So we assume that $p_i = n_i/N$, where $\sum_i n_i = N$ by the requirement that the probabilities sum to unity. Consider a system in which there are N equally likely outcomes, and from these form n groups, with n_i possibilities in the ith group. Then the probability of the group is p_i and the probability of getting any possibility in the ith group given that the ith group has come up, is $1/n_i$. Hence applying (2.3) to the whole system we find

$$S(1/N,\dots,1/N) = S(p_1,\dots,p_n) + \sum_i^n p_i S(1/n_i,\dots,1/n_i) \tag{2.4}$$

or with (2.1)

$$S(p_1,\dots,p_n) = S_N - \sum_i^n p_i S_{n_i} \qquad \Big(N = \sum_i^n n_i\Big). \tag{2.5}$$

This equation relates S evaluated on a general argument list to the values that S takes when all its arguments are equal. Setting all the $n_i = m$ we obtain a relation that involves only S_n:

$$S_n = S_{nm} - S_m. \tag{2.6}$$

This functional equation is solved by $S_n = K \ln n$, where K is an arbitrary constant. In fact, one may show (Appendix A) that this is the only monotone solution of (2.6). We set $K = k_\mathrm{B}$ (Boltzmann's constant) and conclude from (2.5) that (up to a multiplicative constant) the unique measure of uncertainty is

$$\begin{aligned} S(p_1,\dots,p_n) &= k_\mathrm{B}\ln N - k_\mathrm{B}\sum_i^n p_i \ln n_i = -k_\mathrm{B}\sum_i p_i(\ln n_i - \ln N) \\ &= -k_\mathrm{B}\sum_i p_i \ln p_i. \end{aligned} \tag{2.7}$$

A vast number of practical problems can be solved by applying the principle that the probabilities of outcomes should be chosen so that this function S has the largest value that is compatible with whatever prior information we may have about the probabilities.

3 The canonical distribution

We now consider the situation in which there are just two constraints on the probabilities p_α:

$$\sum_\alpha p_\alpha = 1 \quad ; \quad \sum_\alpha p_\alpha E_\alpha = U \tag{3.1}$$

The first of these constraints simply states that on measurement of the energy, the system would be found to be in *some* state $|\alpha\rangle$, and the second condition states that the system has internal energy U. We use the method of Lagrange multipliers to maximize

$$S/k_\mathrm{B} = -\sum_\alpha p_\alpha \ln p_\alpha \tag{3.2}$$

subject to these constraints. Thus we multiply the left side of each constraint equation by a Lagrange multiplier (λ or β) and subtract it from S/k_B before varying each p_α. The Lagrange multipliers allow us to equate the coefficient of $\mathrm{d}p_\alpha$ to zero for every α. In this way we find

$$0 = -(\ln p_\alpha + 1) - \lambda - \beta E_\alpha. \tag{3.3}$$

Solving for p_α we have

$$p_\alpha = \frac{\mathrm{e}^{-\beta E_\alpha}}{Z} \quad \text{where} \quad Z \equiv \mathrm{e}^{1+\lambda} \tag{3.4}$$

Inserting this solution into the first of the constraints (3.1), we see that

$$Z = \sum_\alpha \mathrm{e}^{-\beta E_\alpha}. \tag{3.5}$$

Z is called the **partition function** – we shall find that it plays a central role in statistical mechanics.

Exercise (1):

Use the principle of maximum entropy to show that the biased die described above should be assigned probabilities

$$p_k = \frac{1-\mathrm{e}^{-\beta}}{1-\mathrm{e}^{-6\beta}}\,\mathrm{e}^{-(k-1)\beta},$$

where β is the solution of

$$3.667 = 1 - \frac{6}{\mathrm{e}^{6\beta}-1} + \frac{1}{\mathrm{e}^{\beta}-1}.$$

[The probabilities p_1 to p_6 are 0.144 0.152 0.161 0.171 0.181 0.191.]

If our system is large enough for its energy levels to be treated as a continuum, we may write

$$Z = \int \mathrm{d}E\, g(E)\mathrm{e}^{-\beta E}. \tag{3.6}$$

We now hypothesize that the quantity S that is defined by equation (3.2) is the thermodynamic entropy. When we use (3.4) to eliminate $\ln p_\alpha$ from (3.2), we get

$$\begin{aligned} S &= k_\mathrm{B}\sum_\alpha p_\alpha(\beta E_\alpha + \ln Z) = k_\mathrm{B}\beta U + k_\mathrm{B}\ln Z \\ \Rightarrow U &= \frac{S}{k_\mathrm{B}\beta} - \beta^{-1}\ln Z. \end{aligned} \tag{3.7}$$

In thermodynamics the definition of the Helmholtz free energy F reads

$$U = TS + F. \tag{3.8}$$

If equations (3.7) and (3.8) are to be the same, we must have

$$\beta = \frac{1}{k_\mathrm{B}T} \quad \text{and} \quad F = -k_\mathrm{B}T\ln Z. \tag{3.9}$$

These two equations are of fundamental importance. For future reference we note that the second equation can be written

$$\ln Z = -\beta F, \tag{3.10}$$

so (3.4) yields

$$\ln p_\alpha = \beta(F - E_\alpha). \tag{3.11}$$

Consider the effect on S of changing the probabilities p_α. Bearing in mind the first of equations (3.1), we have from (3.2) and (3.11) that

$$\mathrm{d}S = -k_\mathrm{B}\sum_\alpha \mathrm{d}p_\alpha \ln p_\alpha = -k_\mathrm{B}\beta\sum_\alpha \mathrm{d}p_\alpha(F - E_\alpha) = k_\mathrm{B}\beta\sum_\alpha E_\alpha \mathrm{d}p_\alpha. \tag{3.12}$$

Consider finally the change in U under an arbitrary variation in V and the p_α:

$$\begin{aligned} \mathrm{d}U &= \sum_\alpha \Big(E_\alpha \mathrm{d}p_\alpha + \frac{\partial E_\alpha}{\partial V}p_\alpha \mathrm{d}V\Big) \\ &= T\mathrm{d}S - P\mathrm{d}V, \end{aligned} \tag{3.13}$$

where we have used (1.4) and (3.12). Thus our hypothesis that S is the thermodynamic entropy is vindicated in that it enables us to recover the basic equations of thermodynamics.

In practical calculations the most efficient procedure is to calculate Z first, which immediately yields F from (3.9). Then we have S and P from

$$S = -\Big(\frac{\partial F}{\partial T}\Big)_V \quad ; \quad P = -\Big(\frac{\partial F}{\partial V}\Big)_T. \tag{3.14}$$

U then follows immediately from (3.8).

3.0.1 $\ln Z$ *as a generating function* We have just seen that knowledge of Z enables us to calculate many of the thermal averages of thermodynamics without explicitly recovering the p_α. Actually, by differentiating $\ln Z$ w.r.t. $-\beta$ we can recover other useful quantities. The first derivative is

$$-\frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z}\sum_\alpha E_\alpha \mathrm{e}^{-\beta E_\alpha} = \langle E\rangle = U. \tag{3.15}$$

Differentiating again we have

$$\begin{aligned}\frac{\partial^2 \ln Z}{\partial \beta^2} &= \frac{1}{Z}\sum_\alpha E_\alpha^2 \mathrm{e}^{-\beta E_\alpha} - \frac{1}{Z^2}\sum_\alpha E_\alpha \mathrm{e}^{-\beta E_\alpha}\sum_\gamma E_\gamma \mathrm{e}^{-\beta E_\gamma}\\ &= \langle E^2\rangle - \langle E\rangle^2 \equiv (\Delta E)^2\end{aligned} \tag{3.16}$$

Thus the first derivative of $\ln Z$ is the expectation value of the energy, which we have identified with the internal energy U, while the second derivative is the mean-square variation $(\Delta E)^2$ of the energy. The third derivative would give an interesting third moment of E (try it!) and so on.

The energy of a body in thermal equilibrium with a heat bath at temperature $T = 1/k_\mathrm{B}\beta$ fluctuates because equilibrium is established by exchanging energy with the heat bath. In as much as we expect the internal energy of a thermodynamic system to be well defined, we expect $(\Delta E) \ll \langle E\rangle$. Below we shall check that this is so for some specimen systems.

The specific heat at constant volume is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = -\frac{\beta}{T}\frac{\partial U}{\partial \beta} = \frac{\beta}{T}\frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{(\Delta E)^2}{k_\mathrm{B}T^2}. \tag{3.17}$$

Thus, the mean-square fluctuations in energy are proportional to the specific heat. The key point is that the r.m.s. energy fluctuation is the geometric mean of $k_\mathrm{B}T$, which is small, and $C_V T$, which is generally of order U. During a phase change, C_V may become very large (even formally infinite) and fluctuations in E may be macroscopic in size.

Exercise (2):

Use equations (3.7) and (3.17) to show that $C_V = -\beta(\partial S/\partial\beta)$ and explain the significance of this result in terms of the usual thermodynamic definition of entropy.

3.0.2 Linear response theorem In the case of a magnetic system there will be a term in E_α that is proportional to the externally applied magnetic field B: that is, E_α is of the form

$$E_\alpha = \epsilon_\alpha - Bm_\alpha \quad\Rightarrow\quad Z = \sum_\alpha \mathrm{e}^{-\beta(\epsilon_\alpha - Bm_\alpha)}, \tag{3.18}$$

where ϵ_α is the contribution to the energy of the state $|\alpha\rangle$ from internal interactions and m_α is the dipole moment of $|\alpha\rangle$. Differentiating $\ln Z$ w.r.t. B and using (3.4) we see that

$$M \equiv \langle m_\alpha\rangle = \frac{1}{\beta}\frac{\partial \ln Z}{\partial B}. \tag{3.19}$$

Differentiating again we have

$$\chi \equiv \frac{\partial M}{\partial B} = \beta\big(\langle m_\alpha^2\rangle - \langle m_\alpha\rangle^2\big) \tag{3.20}$$

Thus the susceptibility χ is proportional to the mean-square fluctuation in the magnetization. A similar proportionality holds for any system between the coefficient of the linear response of a system to an external stimulus such as B and the amplitude of the fluctuations in the response. This result is known as the **linear response theorem**. One can understand it physically by considering that the fluctuations in m_α are responses of the system to random stimuli from the heat bath with which the system is in thermal contact. The more rapidly the systems responds to a given stimulus, the larger the resulting fluctuations are going to be.

3.0.3 Composite systems The system under study sometimes consists of two parts that are mutually independent in the sense that the eigenstates of the system's Hamiltonian are simply products $|\alpha\gamma\rangle = |\alpha\rangle|\gamma\rangle$ of eigenstates of the Hamiltonians H_1 and H_2 of the parts, with eigenvalues $E_{\alpha\gamma} = E^{(1)}_\alpha + E^{(2)}_\beta$ that are sums of the corresponding eigenvalues for the parts. On calculating the partition function of the whole system we find

$$\begin{aligned} Z &= \sum_{\text{states } |\alpha\gamma\rangle} \mathrm{e}^{-\beta E_{\alpha\gamma}} = \sum_{\alpha,\gamma} \mathrm{e}^{-\beta(E^{(1)}_\alpha + E^{(2)}_\gamma)} \\ &= Z_1 Z_2 . \end{aligned} \tag{3.21}$$

Thus the partition function of the composite system is simply the product of the partition functions of its component parts and the probability $p_{\alpha\gamma}$ that the whole is in the state $|\alpha\gamma\rangle = |\alpha\rangle|\gamma\rangle$ is $p_{\alpha\gamma} = p^{(1)}_\alpha p^{(2)}_\gamma$. By induction it immediately follows that the partition function of a system of N independent parts is the product of the partition functions of the parts. We have seen that most thermodynamic quantities depend on $\ln Z$, so these will be the sum of the corresponding quantities for the component parts: in the language of thermodynamics, quantities depending on $\ln Z$ will be *extensive*.

3.1 Spin-half paramagnet

We consider an array of N spin-half dipoles in a uniform magnetic field $\mathbf{B}$. Each dipole has two stationary states $|+\rangle$ and $|-\rangle$, with energies $\pm\mu B$, where μ is the magnetic moment of a dipole. Consequently, the partition function of a single dipole is

$$Z^{(1)} = \mathrm{e}^{-\beta\mu B} + \mathrm{e}^{\beta\mu B} = 2\cosh(\beta\mu B). \tag{3.22}$$

From (3.21) it now follows that the partition function of the array is

$$Z = 2^N \cosh^N(\beta\mu B) \quad \Rightarrow \quad \ln Z = N\ln[\cosh(\beta\mu B)] + \text{constant}. \tag{3.23}$$

With (3.15) and (3.16) we have

$$U = \langle E\rangle = -N\mu B\tanh(\beta\mu B) \quad ; \quad (\Delta E)^2 = N(\mu B)^2\,\mathrm{sech}^2(\beta\mu B). \tag{3.24}$$

At low temperatures, β is very large and the tanh will be $\simeq -1$ for $\mu B < 0$ and $\simeq +1$ for $\mu B > 0$. Consequently, $U \simeq -N|\mu B|$ regardless of the sign of μB. As regards the fluctuations in E, we have

$$\frac{|\Delta E|}{U} = \frac{1}{\sqrt{N}|\sinh(\beta\mu B)|}, \tag{3.25}$$

which is small if N is large provided $\beta\mu B \neq 0$.

From (3.17) the specific heat is

$$C_V = Nk_{\mathrm{B}}(\beta\mu B)^2\,\mathrm{sech}^2(\beta\mu B). \tag{3.26}$$

This is small unless $|\beta\mu B|$ is small, when it is $\sim Nk_{\mathrm{B}}(\beta\mu B)^2$. At low temperatures (large $\beta\mu B$) the dipoles are all aligned with the field and increasing the temperature a little does not induce a significant number to increase their energy by aligning against the field. At high temperatures, nearly equal numbers of dipole are aligned parallel and antiparallel to $\mathbf{B}$, so again increasing the temperature makes little difference to U. The specific heat peaks when $k_{\mathrm{B}}T \sim \mu B$, when increasing T allows significant numbers of extra dipoles to align antiparallel to the field.

We have $F = -k_{\mathrm{B}}TN\ln[\cosh(\beta\mu B)]$ and

$$M = -\left(\frac{\partial F}{\partial B}\right)_T = \mu N\tanh(\beta\mu B). \tag{3.27}$$

When $|\beta\mu B| \gg 1$, $\tanh(\beta\mu B) \simeq \pm 1$, so $M = \pm N\mu$ because the dipoles are nearly all aligned with $\mathbf{B}$. When $|\beta\mu B| \lesssim 1$, $M \simeq N\mu(\beta\mu B)$ is proportional to B and we have a constant polarizability $\chi \equiv \partial M/\partial B = \beta N\mu^2$. Notice the quadratic dependence of χ on the dipole moment μ: one power of μ arises because the propensity of the dipoles to align is proportional to μ, and the other power arises because the magnetization generated by an aligned dipole is proportional to μ.

Exercise (3):

Obtain (3.27) from $M = -\partial U/\partial B$ [cf. (1.7)].

We have seen that for N large E will lie in a narrow range around $U = \langle E\rangle$. It is important to understand how this fact can be reconciled with the fact that the probability that any given state $|\alpha\rangle$ is occupied declines exponentially with E_α, so at any temperature, the ground state is the one most likely to be occupied; yet if you measure the energy, you are almost certain to get a value U that at high T will significantly exceed the ground-state energy. This apparent paradox arises by competition between the density of states, $g(E)$, which increases very strongly with E, and the Boltzmann factor $\mathrm{e}^{-\beta E}$, which eventually swamps its growth. Let's see how this works out for the spin-half paramagnet.

Let there be n_a dipoles aligned antiparallel to $\mathbf{B}$ and $N - n_a$ parallel. Then the energy is

$$E = \mu B(2n_a - N) \quad \Rightarrow \quad n_a = \tfrac{1}{2}\Big(\frac{E}{\mu B} + N\Big) = \frac{E - E_0}{2\mu B}, \tag{3.28}$$

where $E_0 = -N\mu B$ is the ground-state energy. Thus n_a is a dimensionless measure of the system's excitation energy. The number of states at a given energy is the number of ways in which n_a locations for antiparallel dipoles can be chosen from N locations, i.e., $n_s = N!/[n_a!(N-n_a)!]$. When n_a is increased by 1, E increases by $2\mu B$. Hence, the density of states is

$$\begin{aligned} g(E_0 + 2\mu B n_a) &= \frac{n_s}{2\mu B} = \frac{N!}{2\mu B n_a![N - n_a]!} \\ &= \frac{1}{2\mu B}\frac{N}{1} \times \frac{N-1}{2} \times \cdots \times \frac{N - n_a + 1}{n_a}, \end{aligned} \tag{3.29}$$

so on increasing n_a by one, $\ln g$ increases by $\ln[(N - n_a + 1)/n_a] \simeq \ln N/n_a$ for $n_a \ll N$. On the other hand, $\ln\left(\mathrm{e}^{-\beta E}\right)$ decreases by $2\beta\mu B$ as n_a increases, so the peak in the product $g\mathrm{e}^{-\beta E}$ occurs when $n_a \simeq N\mathrm{e}^{-2\beta\mu B}$ and $E - E_0 \simeq 2N\mu B\mathrm{e}^{-2\beta\mu B}$. From (3.24) we have

$$U - E_0 = N\mu B[1 - \tanh(\beta\mu B)] \simeq 2N\mu B\mathrm{e}^{-2\beta\mu B} \tag{3.30}$$

in agreement with prediction. The magnetization starts to saturate when $\beta\mu B \simeq 1$ and at this point the probability p_α for a state with $E_\alpha = U$ is smaller than the probability of the ground state by a factor

$$\frac{p_\alpha(E_\alpha = U)}{p_\alpha(E_\alpha = E_0)} = \exp(-2N\beta\mu B\mathrm{e}^{-2}) \sim \mathrm{e}^{-10^{24}} < 10^{-10^{23}}. \tag{3.31}$$

Yet states with this incredibly small probability dominate Z because they are so extraordinarily numerous.

3.2 Ideal Gases

We now apply the canonical distribution to ideal gases. Undergraduate courses in quantum mechanics concentrate on non-relativistic, single-particle quantum mechanics. This is fundamentally absurd since we are either interested in large numbers of interacting non-relativistic particles (for example the electrons in a metal, or the atoms in a crystal) or we are interested in a small number of ultra-relativistic particles (as in an accelerator). You might guess that handling the dynamics of 10^{24} particles is hard (we're making a stab at it right now), but that doing relativistic quantum mechanics shouldn't be hard – once you're used to thinking in terms of events, relativistic mechanics isn't any harder than the Newtonian kind; in fact Lorentzian covariance is more easily exploited than is Galilean invariance. The reason we don't teach relativistic quantum mechanics to undergraduates is that there is no such mechanics for single particles! To introduce quantum mechanics into relativity, you have to revolutionize your whole world-view and recognize that the Universe isn't made up of particles, but of fields. A particle is just an excitation of a field. One of the wonderful things about statistical mechanics is that it discovered this vital fact more than a generation before high-energy physics did, and it made the discovery through experiments at low temperatures, i.e., very low energies.

We're going to discuss the statistical mechanics of an 'ideal gas'. The system is a box full of a quantum field. Excitations of the field might be photons, or neutrinos, or helium atoms, or lithium atoms, whatever. But the physical reality is not a box full of particles, but a box full of quantum field.[2]

The field in the box has normal modes in which $\psi \sim A_{\mathbf{k}} \mathrm{e}^{\mathrm{i}\mathbf{k}\cdot\mathbf{x}}$. The wavevector $\mathbf{k}$ of the mode determines the momentum of the particles through $\mathbf{p} = \hbar\mathbf{k}$ and the amplitude $A_{\mathbf{k}}$ of the mode determines how many particles with this momentum are present – if the field has half-integer spin (fermionic) there can be 0 or 1 particles. If the field has integer spin (bosonic) there can be $0, 1, 2, \dots$ particles with any momentum $\mathbf{p}$. Let i enumerate the normal modes of the box and let the energy of the ith normal mode be $\epsilon_i = \zeta_i + n_i E_i$, where ζ_i is the zero-point energy of the mode and E_i is the spacing of the mode's energy levels. (From the theory of a harmonic oscillator we expect $\zeta_i = E_i/2$.) Then the partition function of the box is

$$Z = \sum_{\{n_i\}} \mathrm{e}^{-\beta\sum_i(\zeta_i + n_i E_i)} = \prod_i \mathrm{e}^{-\beta\zeta_i} \sum_{\{n_i\}} \prod_i z_i^{n_i} \quad \text{where} \quad z_i \equiv \mathrm{e}^{-\beta E_i}. \tag{3.32}$$

We have seen that thermodynamic quantities depend on $\ln Z$, to which the zero-point energies of the modes contribute a term

$$\Delta \ln Z = -\beta \sum_i \zeta_i. \tag{3.33}$$

The corresponding contribution to the internal energy is

$$\Delta U = -\frac{\partial}{\partial\beta}\Delta \ln Z = \sum_i \zeta_i, \tag{3.34}$$

which does not depend on temperature. By equation (3.7) there is no contribution from the zero-point energies to S, while equation (3.8) implies that the contribution to F is the same as that to U. Under most circumstances the contribution (3.34) to U and F are not physically significant,[3] and we shall ignore them in the following by taking the partition function to be

$$Z = \sum_{\{n_i\}} \prod_i z_i^{n_i} \quad \text{where} \quad z_i \equiv \mathrm{e}^{-\beta E_i} \tag{3.35}$$

It is easy to do the sum over the number sets $\{n_i\}$ in (3.35) so long as the only restrictions on the n_i is that inherent in the field being bosonic or fermionic. The key step is to recognize that

$$Z = \sum_{\{n_i\}} \prod_i z_i^{n_i} = \prod_i \Big(\sum_{n=0,\dots} z_i^n \Big) = \begin{cases} \prod_i (1 + z_i) & \text{for fermions,} \\ \prod_i (1 - z_i)^{-1} & \text{for bosons,} \end{cases} \tag{3.36}$$

---

[2] Some will find this an eccentric position: is there really a quantum field for lithium atoms? Two replies are effective: (i) in recent experiments on Bose-Einstein condensates of Li and other atoms, the fundamental mode of the Li field in an atomic trap is manifest; (ii) at a deeper level a Li atom is a complex non-linear interaction of the quark, electron, photon and gluon fields. These fields are mildly relativistic even if the Li atom is stationary. Adding a Li atom involves increasing the number of excitations of the quark etc fields in well defined amounts, so the number of Li atoms is subject to the rules that govern excitations of relativistic fields. Z for a Li-atom trap can be considered to be a sum over carefully chosen states of the quark etc fields.

[3] ΔU will be physically manifest if the ζ_i depend on some parameter. When the electron/positron field is bounded by two grounded capacitor plates, the ζ_i are functions of the distance d between the plates, so $\Delta U(d)$. If fact, ΔU decreases with d, so the plates attract one another. This attraction is called the **Casimir effect**. Since the sum over modes should in (3.34) should be continued at least up to modes with wavelengths comparable to the Planck length $(G\hbar/c^3)^{1/2}$, ΔU should be large. An important current problem is why ΔU does not manifest itself as a cosmological constant ~ 120 orders of magnitude larger than that measured experimentally.

which implies that

$$\ln Z = \begin{cases} \displaystyle\sum_i \ln(1+z_i) & \text{for fermions,} \\ \displaystyle -\sum_i \ln(1-z_i) & \text{for bosons.} \end{cases} \tag{3.37}$$

The mean number of particles in the ith mode is

$$\langle n_i \rangle = -\frac{1}{\beta}\frac{\partial}{\partial E_i}\ln Z = \begin{cases} (\mathrm{e}^{\beta E_i}+1)^{-1} & \text{for fermions,} \\ (\mathrm{e}^{\beta E_i}-1)^{-1} & \text{for bosons.} \end{cases} \tag{3.38}$$

The internal energy of the box is

$$U = -\frac{\partial \ln Z}{\partial \beta} = \sum_i \langle n_i \rangle E_i. \tag{3.39}$$

By (3.14) all the thermodynamic variables are obtainable from

$$F = \mp k_{\mathrm{B}} T \sum_i \ln(1 \pm z_i) \text{ (upper signs for fermions)} \tag{3.40}$$

To proceed further one has to specify the E_i. Black-body radiation is a simple case: then $E_i = \hbar\omega_i = \hbar k_i c$. In evaluating the sums we argue that in thermodynamic limit the system (box) is very big, so its levels E_i form an effective continuum. Then a negligible fraction of any sum comes from the lowest few modes. (This statement would be false if the side length L of the box was such that $\beta\hbar 2\pi c/L \gtrsim 1$.) It is simplest to impose periodic boundary conditions on ψ at the walls of the box $[\psi(x+L,y,z) = \psi(x,y,z)]$, which implies that $k_i = 2m\pi/L$, where m is an integer. Then there is one allowed value of $\mathbf{k}$ in the k-space volume $(\Delta k)^3 = (2\pi/L)^3 = (2\pi)^3/V$, and the density of modes is given by

$$\text{no. of modes} = \text{spin factor} \times V\frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} = 2V\frac{4\pi k^2 \mathrm{d}k}{(2\pi)^3} \quad \text{(photons)} \tag{3.41}$$

Hence we find for the free energy density of black-body radiation

$$F/V = \frac{k_{\mathrm{B}}T}{\pi^2}\int_0^\infty \mathrm{d}k\, k^2 \ln(1-\mathrm{e}^{-\beta\hbar k c}) = \frac{(k_{\mathrm{B}}T)^4}{(\hbar c)^3\pi^2}\int_0^\infty \mathrm{d}x\, x^2 \ln(1-\mathrm{e}^{-x}). \tag{3.42}$$

We integrate by parts to find

$$F/V = -\frac{(k_{\mathrm{B}}T)^4}{3(\hbar c)^3\pi^2}\int \mathrm{d}x\,\frac{x^3}{\mathrm{e}^x - 1} = -\frac{(k_{\mathrm{B}}T)^4\pi^2}{45(\hbar c)^3}, \tag{3.43}$$

where we have used the fact that the integral equals $\pi^4/15$. From (3.14) and $U = F + TS$ we find that the other thermodynamic variables are

$$S/V = -4\frac{F/V}{T} \quad \Rightarrow \quad U/V = -3F/V; \quad P = -F/V = \tfrac{1}{3}U/V. \tag{3.44}$$

It is interesting to compare this result with that for a population of zero rest-mass neutrinos. The spin factor in (3.42) is now unity, so from the free-energy of fermions we have

$$F/V = -\frac{(k_{\mathrm{B}}T)^4}{6(\hbar c)^3\pi^2}\int_0^\infty \mathrm{d}x\,\frac{x^3}{\mathrm{e}^x + 1}. \tag{3.45}$$

where the integral evaluates to $-3!\sum_1^\infty(-)^n/n^4 = 5.683$. Since this expression differs from (3.43) only in the numerical factor (smaller for fermions by a factor 0.4375), the relations (3.44) between the thermodynamic variables apply also to zero rest-mass fermions.

3.2.1 Case of a specified number of particles We may know how many particles we have in our box – this would be case if the particles were electrons in a lump of metal, or helium atoms in a dewar. The partition function (3.37) is too large because it includes states in which the $\sum_i n_i$ takes all values, and we want to sum $\mathrm{e}^{-\beta E_\alpha}$ only over states for which $\sum_i n_i = N$.

Let ζ be a complex variable and consider the function

$$\begin{aligned} f(\zeta) &= \sum_{\{n_i\}} \prod_i \zeta^{n_i} \mathrm{e}^{-\beta n_i E_i} \\ &= \prod_i (1 \pm \zeta \mathrm{e}^{-\beta E_i})^{\pm 1}. \quad (+ \text{ for fermions}) \end{aligned} \tag{3.46}$$

For $\zeta = 1$ this coincides with our unrestricted sum (3.36). More generally it is a power series in ζ, with one factor of ζ for each particle. Hence, the coefficient of ζ^N is precisely the restricted sum we wish to evaluate.

One of Cauchy's theorems states that if $f(\zeta)$ is a function that is analytic in the neighbourhood of the origin, then the contour integral

$$Z_N = \frac{1}{2\pi \mathrm{i}} \oint \frac{\mathrm{d}\zeta}{\zeta^{N+1}} f(\zeta) \tag{3.47}$$

yields the coefficient of ζ^N in the expansion of f in positive and negative powers of ζ. Here the contour of integration goes around the origin so as to include the singularity at the origin (due to the factor $\zeta^{-(N+1)}$) and no other. Hence, our problem has been reduced to doing a contour integral.

We evaluate the integral using a technique called "the method of steepest descent", which is approximate for finite N but becomes exact in the thermodynamic limit $N \to \infty$. In this method we write our integral in the form $\oint \mathrm{d}\zeta \, \mathrm{e}^{g(\zeta)}$ and approximate it by a phase factor times $\mathrm{e}^g \sqrt{2\pi/|g''|}$ evaluated at a stationary point of g (see Appendix B). In our application the function g is

$$g(\zeta) = -(N+1)\ln\zeta \pm \sum_i \ln(1 \pm \zeta \mathrm{e}^{-\beta E_i}) \quad (+ \text{ for fermions}) \tag{3.48}$$

Differentiating we find

$$\begin{aligned} g'(\zeta) &= -\frac{N+1}{\zeta} + \sum_i \frac{\mathrm{e}^{-\beta E_i}}{1 \pm \zeta \mathrm{e}^{-\beta E_i}} \\ g''(\zeta) &= \frac{N+1}{\zeta^2} \mp \sum_i \frac{1}{(\mathrm{e}^{\beta E_i} \pm \zeta)^2} \end{aligned} \tag{3.49}$$

For small real, positive ζ, the first term in g' dominates and $g' < 0$. Sufficiently far from the origin, the sum term dominates because there are arbitrarily many modes (and in the case of bosons the first denominator may become small). Hence at some distance from the origin $g' > 0$ and g has a stationary point when

$$0 = -\frac{N+1}{\zeta} + \sum_i \frac{\mathrm{e}^{-\beta E_i}}{1 \pm \zeta \mathrm{e}^{-\beta E_i}} \tag{3.50}$$

Taking logs we then find with (3.47) that

$$\ln Z_N \simeq -(N+1)\ln\zeta \pm \sum_i \ln(1 \pm \zeta \mathrm{e}^{-\beta E_i}) - \tfrac{1}{2}\ln(2\pi g'') \tag{3.51}$$

Now we allow N to increase as we approach the thermodynamic limit. Eq. (3.49) shows that the value of g'' at the stationary point of g grows with N so the method of steepest descent

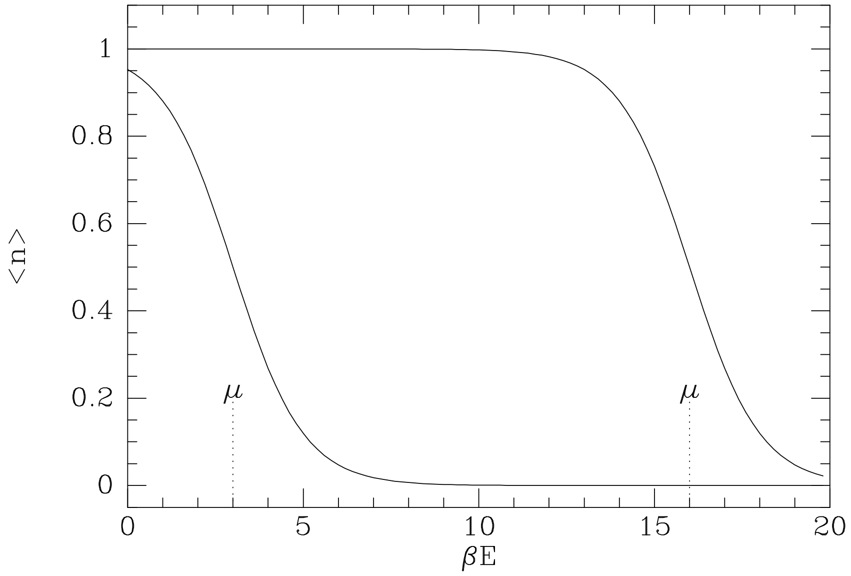

Figure 1 $\langle n_i \rangle$ for a gas of Fermions for two values of E_F.

becomes ever more accurate. Moreover, in (3.51) the first term and the sum grow as N, while the term involving g'' grows only as $\ln N$. Therefore we may neglect the latter and write finally

$$\ln Z_N = -N\ln\zeta \pm \sum_i \ln(1 \pm \zeta e^{-\beta E_i}), \quad \text{(macroscopic } N) \tag{3.52a}$$

where from (3.49) ζ is the number for which

$$N = \sum_i \frac{1}{\zeta^{-1}e^{\beta E_i} \pm 1}. \tag{3.52b}$$

To make contact with thermodynamics, we introduce a new variable μ that is defined by $\zeta = e^{\beta\mu}$. Then we have

$$\ln Z_N = -N\beta\mu \pm \sum_i \ln(1 \pm e^{-\beta(E_i-\mu)}) \quad ; \quad N = \sum_i \frac{1}{e^{\beta(E_i-\mu)} \pm 1}. \tag{3.53}$$

The terms in the sum for N are the $\langle n_i \rangle$, as one can show by evaluating $\langle n_i \rangle = -\beta^{-1}\partial \ln Z_N/\partial E_i$, bearing in mind that through (3.53) μ is a function of the E_i. We have

$$\frac{\partial \ln Z_N}{\partial E_i} = -N\beta\frac{\partial\mu}{\partial E_i} - \beta\sum_j \frac{\delta_{ij} - \partial\mu/\partial E_i}{e^{\beta(E_j-\mu)} \pm 1} \tag{3.54}$$

By second of equations (3.53), the coefficient of $\partial\mu/\partial E_i$ vanishes, so

$$\langle n_i \rangle = \frac{1}{e^{\beta(E_i-\mu)} \pm 1} \quad \text{(upper sign for fermions).} \tag{3.55}$$

In the case of a gas of Fermions, $\langle n_i \rangle \simeq 1$ for $E_i < \mu$ and $\langle n_i \rangle \sim e^{-\beta(E_i-\mu)}$ for $E_i \gg \mu$ (see Fig. 1).

In the case of a gas of bosons, $\langle n_i \rangle$ becomes very large as E_i approaches μ. Since there can be no upper bound on E_i and it is clear physically that $\langle n_i \rangle \le N$, we infer that for bosons

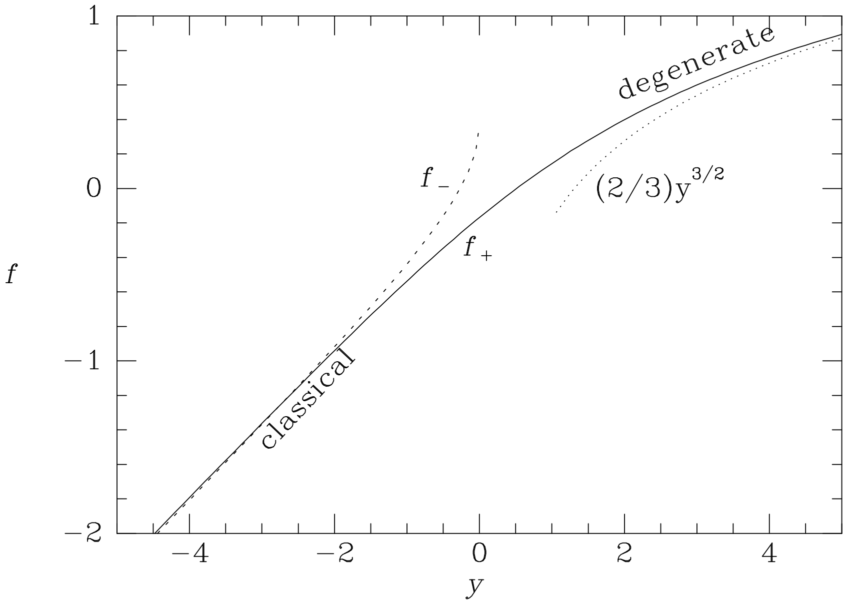

Figure 2 The function $f_\pm$ defined in eq. (3.56). At large negative y, $f \sim e^y$ for both bosons and fermions. As $y \to 0$ the bosonic function f_- tends to 3.28. At large y the fermionic function, f_+, asymptotes to $f = \frac{2}{3}y^{3/2}$ that is shown dotted.

$\mu < E_0$, the energy spacing of the fundamental mode. For $E_i \gg \mu$ we have $\langle n_i \rangle \sim e^{-\beta(E_i-\mu)}$ as in the case of Fermions.

Boltzmann believed that the number of molecules in the box with energy E was $\propto e^{-\beta E}$ times the phase-space volume associated with energy E, $\Omega(E)\mathrm{d}E$. This proposition is consistent with the limiting forms of $\langle n_i \rangle$ at $E \gg \mu$ providing the number of states at energy E, $g(E)\mathrm{d}E = \Omega(E)\mathrm{d}E$. This is in fact the case.

We now evaluate the sum over modes by assuming that we are working in the thermodynamic limit of a large box, so the modes form a continuum. We assume that our particles are non-relativistic,[4] have mass m and two spin states. Then the density of modes is given by (3.41), and we have $E_i = (\hbar k)^2/2m$, so (3.53) becomes

$$\begin{aligned} N/V &= \frac{1}{\pi^2}\int \mathrm{d}k\, \frac{k^2}{e^{\beta(E_i-\mu)} \pm 1} = \frac{m^{3/2}}{\pi^2\hbar^3}\int_0^\infty \mathrm{d}E\, \frac{\sqrt{2E}}{e^{\beta(E-\mu)} \pm 1} \\ &= \frac{(2mk_\mathrm{B}T)^{3/2}}{2\pi^2\hbar^3} f_\pm(\beta\mu) \quad \text{where} \quad f_\pm(y) \equiv \int_0^\infty \mathrm{d}x \frac{\sqrt{x}}{e^{x-y} \pm 1}. \end{aligned} \tag{3.56}$$

Figure 2 shows $f_\pm$.

N/V is a monotonic increasing function of μ because for both fermions (upper sign) and bosons, increasing μ makes the denominator of the integrand smaller at any E. In the case of fermions there is no upper bound on μ, and N/V can be made as large as we please. In the limit of large N/V, $f(y) \sim y^{3/2}$ so $N/V \sim k_\mathrm{B}Tf(\beta\mu) \sim \mu^{3/2}$, and μ becomes independent of T. Quantitatively, μ tends to the **Fermi energy**

$$E_F = \frac{(3\pi^2)^{2/3}\hbar^2}{2m}\left(\frac{N}{V}\right)^{2/3}. \tag{3.57}$$

---

[4] In the relativistic case, pair creation will ensure that N fluctuates rather than being fixed.

3.2.2 Bose–Einstein condensation In the bosonic case, we have seen that the largest allowed value of μ is zero, so there is a largest permitted value of N/V, namely

$$N_{\rm max}/V = \frac{(mk_{\rm B}T)^{3/2}}{\pi^2\hbar^3} f_-(0) = 3.28\frac{(mk_{\rm B}T)^{3/2}}{\pi^2\hbar^3}. \tag{3.58}$$

How are we to understand this? At large T, $N_{\rm max}$ is large, so let's stuff a good number of bosons into our box at a high enough T for this number to be permitted by (3.58). Now let's cool the box. As T drops to the critical value

$$T_c = \frac{2.08\hbar^2}{k_{\rm B}m}(N/V)^{2/3} \tag{3.59}$$

$\mu \to 0$ and $N_{\rm max} \to N$. What happens when T drops below T_c? A macroscopic number of particles crowds into the fundamental mode, and the approximation we have implicitly made, that $\langle n_i \rangle$ is a continuous function of E_i breaks down. In fact, at $T < T_c$ the number N_0 in the fundamental mode is given by

$$N_0(T) = N - N_{\rm max}(T). \tag{3.60}$$

This crowding of particles into the fundamental mode is called **Bose–Einstein condensation**.

Exercise (4):

Show that at T_c, $L/\lambda = 0.997$, where λ is the de Broglie wavelength associated with T_c and $L^3 = V/N$ is the mean interparticle separation.

The condensation occurs only at low temperatures and high particle densities, which are precisely the conditions under which inter-particle forces, which we have neglected, are important. The lowest temperatures on Earth are attained in atomic traps ($T \sim 1\,\mu$K), and in these condensation can be observed at densities low enough ($n \sim 10^{20}\,{\rm m}^{-3}$) that inter-particle forces do not lead to the formation of clusters of particles within the lifetime of experiments. Consequently, condensates that are well described by our simple theory can be studied. For an accessible introduction to this very active field, see Burnett et al., *Physics Today*, Dec 1999, p. 37.

Above about 2 K liquid ^{4}He is a normal viscous liquid, called **He I**. But when ^{4}He is cooled through about 2 K (the exact temperature depends on the pressure), a 'superfluid' component starts to form in the liquid; that is, below $\approx$ 2 K the liquid appears to contain a component that flows without viscosity. This zero-viscosity component coexists with ordinary, viscous ^{4}He rather as water coexists with steam.[5] The lower the temperature, the greater the proportion of ^{4}He that is in the superfluid condensate [cf (3.60)]. ^{4}He that contains some of the superfluid condensate is called **He II**.

The superfluid condensate in He II is made up of ^{4}He atoms with momenta so small that their de Broglie wavelengths are macroscopic in size. These delocalized atoms move coherently and are insensible of the small-scale structures which dominate the scattering of normal, thermally excited helium atoms, for the same reason that infrared radiation passes unscattered through a cloud of small water droplets.

In 1911 Kamerlingh Onnes discovered that mercury lost all trace of electrical resistivity when cooled through about 4.2 K. Many other materials have subsequently been found to become such **superconductors** at low temperatures, and in recent years this phenomenon has become of considerable technological importance. The standard BCS theory of superconductivity has it that at low temperatures electrons with oppositely aligned spins form **Cooper pairs** by exchanging phonons. Each Cooper pair is a charged, spin-zero particle. Since Cooper pairs are bound by phonons, which by electronic standards are slow-moving beasts, they form with near-zero momentum. Consequently, as soon as significant numbers of Cooper pairs are present, they constitute a Bose condensate, which is in some ways analogous to He II. Since this Bose condensate is charged and can flow without viscosity, all trace of electrical resistance vanishes when the condensate forms.

[5] The analogy is inexact—in particular, no latent heat is involved in the passage of He atoms in and out of the condensate.

3.2.3 Degenerate matter To derive the equation of state of degenerate matter we use (3.53) to evaluate $\ln Z_N$ in the limit of a continuum of energy levels. The calculation is closely analogous to that of (3.56):

$$F = -k_{\rm B}T\Big(- N\beta\mu + \frac{m^{3/2}V}{\pi^2\hbar^3}\int_0^\infty {\rm d}E\sqrt{2E}\,\ln[1+{\rm e}^{-\beta(E-\mu)}]\Big) \tag{3.61}$$

The integral is dominated by the portion at $E < \mu$ in which we can approximate $\ln(1+{\rm e}^{-\beta(E-\mu)})$ by $\beta(\mu - E)$, so we have

$$F \simeq N\mu - \frac{m^{3/2}V}{\pi^2\hbar^3}\int_0^\mu {\rm d}E\,\sqrt{2E}(\mu - E) = N\mu - \frac{m^{3/2}V(2\mu)^{5/2}}{15\pi^2\hbar^3}. \tag{3.62}$$

From (3.56) and Fig. 2, in the degenerate limit N/V is

$$\frac{N}{V} = \frac{(2m\mu)^{3/2}}{3\pi^2\hbar^3}. \tag{3.63}$$

Substituting this into (3.62) we find

$$F = \tfrac{3}{5}N\mu \quad\Rightarrow\quad P = -\frac{\partial F}{\partial V} = -\tfrac{3}{5}N\frac{\partial\mu}{\partial V}. \tag{3.64}$$

Taking logs and differentiating (3.63) w.r.t. V we find that $\partial\mu/\partial V = -\frac{2}{3}\mu/V$, so

$$P = \tfrac{2}{5}\frac{N\mu}{V} = \tfrac{2}{5}\Big(\frac{3\pi^2\hbar^3}{(2m)^{3/2}}\Big)^{2/3}\Big(\frac{N}{V}\Big)^{5/3} = \frac{(3\pi^2)^{2/3}\hbar^2}{5m}\Big(\frac{N}{V}\Big)^{5/3}. \tag{3.65}$$

Thus, for a degenerate gas $PV^\gamma = $ const, where $\gamma = \frac{5}{3}$, just as for any other ideal monotonic gas; but γ is not now the ratio of the principal specific heats.

Let's apply these results to white dwarf and neutron stars, in which the thermal energy density is dominated by degenerate electrons and neutrons, respectively. Since F is independent of T, $S = -\partial F/\partial T = 0$ and $U = F$. The gravitational potential energy E_G of a star of mass M and radius R is $\sim -2GM^2/5R$. Its equilibrium radius is that at which $\partial E_G/\partial R = -\partial U/\partial R$. Now

$$\frac{\partial U}{\partial R} = \frac{\partial F}{\partial R} = \frac{\partial F}{\partial V}\frac{\partial V}{\partial R} = -P4\pi R^2, \tag{3.66}$$

so the equilibrium radius is that at which

$$\tfrac{2}{5}\frac{GM^2}{R^2} \simeq 4\pi R^2 P \quad\Rightarrow\quad 4\pi R^4 P \simeq \tfrac{2}{5}GM^2. \tag{3.67}$$

We now use (3.65) to eliminate P and put $M = Nm_H$ to find

$$R \simeq \frac{3^{5/3}(3\pi/4)^{2/3}\hbar^2}{2Gm_H^2 m}N^{-1/3} = 1.96\times10^{23}\frac{m_H}{N^{1/3}m}\ {\rm m}. \tag{3.68}$$

In a neutron star with $M \simeq {\rm M}_\odot = 2\times10^{30}\,{\rm kg}$, $N^{1/3} \sim 10^{19}$, so $R \sim 20\,{\rm km}$. The radius of a white dwarf of the same mass should be larger by $m_H/m_{\rm e} \sim 1800$, and thus be $\sim 40\,000\,{\rm km}$. An important feature of (3.68) is the prediction that more massive stars have smaller radii. This clearly implies that the Fermi energy rises with N. From (3.57) we have that $E_F \sim (N/V)^{2/3}/m \sim 1/(R^2 m) \sim m$, since we have seen that $R \sim m^{-1}$. It turns out that as $M \to 1.4\,{\rm M}_\odot$, $E_F \to mc^2$ for both white dwarfs and neutron stars. Our calculations are invalid in this limit (because we adopted $E_i = \hbar^2k^2/2m$ rather than $E_i = c\sqrt{m^2c^2 - \hbar^2k^2}\,$). When relativistic formulae are used, one finds that no equilibrium is possible for M larger than a limit $\sim 1.4\,{\rm M}_\odot$ that is known as the **Chandrasekhar mass**.

4 The Grand Canonical Distribution

An earthed conductor is free to exchange electrons with a large reservoir, so the number of electrons in it will fluctuate thermally. Similarly, an iceberg that floats in water at 0°C can exchange water molecules with the ocean, so the number of water molecules in the iceberg will fluctuate. So let's apply the principle of maximum entropy to the case in which we add to the constraints (3.1) the constraint

$$\sum_\alpha p_\alpha n_\alpha = \langle N\rangle. \tag{4.1}$$

Let the Lagrange multipliers used to apply this constraint on the p_α be denoted γ. Then by analogy with (3.3) extremization of S/k_B yields

$$0 = -(\ln p_\alpha + 1) - \lambda - \beta E_\alpha - \gamma n_\alpha \tag{4.2}$$

and solving for p_α we have

$$p_\alpha = \frac{\mathrm{e}^{-\beta E_\alpha - \gamma n_\alpha}}{\mathcal{Z}}, \tag{4.3}$$

where from $\sum_\alpha p_\alpha = 1$ we have

$$\mathcal{Z} = \sum_\alpha \mathrm{e}^{-\beta E_\alpha - \gamma n_\alpha}. \tag{4.4}$$

$\mathcal{Z}$ is the **grand-canonical partition function**. We discover its physical interpretation by evaluating the entropy of the probability distribution (4.3):

$$\begin{aligned} S/k_\mathrm{B} &= -\sum_\alpha p_\alpha \ln p_\alpha = \sum_\alpha p_\alpha(\beta E_\alpha + \gamma n_\alpha) + \ln \mathcal{Z} \\ &= \beta U + \gamma\langle N\rangle + \ln\mathcal{Z} \\ \Rightarrow \quad & U - TS + k_\mathrm{B}T\ln\mathcal{Z} = -\gamma k_\mathrm{B}T\langle N\rangle. \end{aligned} \tag{4.5}$$

To proceed further we need to recall the form taken by the laws of thermodynamics for systems of variable mass. Thermodynamics is concerned with **extensive systems**: if you double the size of the system you double its volume, entropy, and energies (internal, Helmholtz and Gibbs).[6] Mathematically, in thermodynamics we are concerned with systems for which

$$\begin{gathered} S_2 = 2S_1 \quad ; \quad V_2 = 2V_1 \quad ; \quad U_2 = U(S_2, V_2) = 2U(S_1, V_1) = 2U(S_2/2, V_2/2) \\ F_2 = F(T, V_2) = 2F(T, V_2/2) \quad ; \quad G(T_2, P_2) = 2G(T_1, P_1) \end{gathered} \tag{4.6}$$

These relations show that G is the simplest energy to work with when the size of the system is variable, because it is straightforwardly proportional to the amount of stuff in the system. We define the **chemical potential** $\mu = G/\langle N\rangle$ to be the free energy of the system when it is reduced to a single particle, and have

$$G = U - TS + PV = \mu(T,P)\langle N\rangle. \tag{4.7}$$

Comparing this with (4.5), we see that the equations will be identical providing

$$PV = k_\mathrm{B}T\ln\mathcal{Z} \quad ; \quad \mu = -\gamma k_\mathrm{B}T. \tag{4.8}$$

With the second of these equations, we have

$$p_\alpha = \frac{1}{\mathcal{Z}}\mathrm{e}^{-\beta(E_\alpha - \mu n_\alpha)}. \tag{4.9}$$

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[6] Real systems are usually not quite extensive: double the mass of a water droplet and you don't quite double its internal energy because surface tension (a source of positive internal energy) is less important in the larger drop than it was in the smaller.

By analogy with (3.9) we define a new thermodynamic potential

$$\Phi = -k_{\mathrm{B}}T\ln\mathcal{Z} = -PV, \tag{4.10}$$

where we have used (4.8). Now $\Phi = -PV = F - G = F - \mu\langle N\rangle$, so[7]

$$\begin{aligned} \mathrm{d}\Phi &= \mathrm{d}F - \mathrm{d}\mu\langle N\rangle - \mu\mathrm{d}\langle N\rangle = (-S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}\langle N\rangle) - \mathrm{d}\mu\langle N\rangle - \mu\mathrm{d}\langle N\rangle \\ &= -S\mathrm{d}T - P\mathrm{d}V - \langle N\rangle\mathrm{d}\mu. \end{aligned} \tag{4.11}$$

It follows that

$$S = -\Big(\frac{\partial\Phi}{\partial T}\Big)_{V,\mu} \quad ; \quad P = -\Big(\frac{\partial\Phi}{\partial V}\Big)_{T,\mu} \quad ; \quad \langle N\rangle = -\Big(\frac{\partial\Phi}{\partial\mu}\Big)_{T,V}. \tag{4.12}$$

Equations (4.10) and (4.12) enable us to obtain any required thermodynamic quantity once we know $\mathcal{Z}(\beta,\mu,V)$.

Exercise (5):

Express the derivatives in (4.12) in terms of the p_α and check that these expressions make physical sense.

4.1 Application to a perfect gas

We can easily evaluate $\mathcal{Z}$ for a box full of ideal gas: we have $E_\alpha = \sum_i(\zeta_i + n_iE_i)$, where i enumerates the modes of the box, and $n_\alpha = \sum_i n_i$, so

$$\mathcal{Z} = \sum_{\{n_i\}}\exp\Big[-\beta\Big(\sum_i(\zeta_i + n_iE_i) - \mu\sum_i n_i\Big)\Big]. \tag{4.13}$$

As in our evaluation of Z we neglect the ζ_i and then with $z_i \equiv \mathrm{e}^{-\beta(E_i-\mu)}$ we have

$$\mathcal{Z} = \sum_{\{n_i\}}\prod_i z_i^{n_i} = \prod_i\sum_{n_i=0,1,\dots} z_i^{n_i} = \begin{cases}\prod_i(1+z_i) & \text{(fermions)},\\ \prod_i(1-z_i)^{-1} & \text{(bosons)}.\end{cases} \tag{4.14}$$

It follows that

$$\ln\mathcal{Z} = \pm\sum_i\ln(1\pm\mathrm{e}^{-\beta(E_i-\mu)}) \tag{4.15}$$

From (4.13) it is clear that we can obtain $\langle n_i\rangle$, the expected number of excitations (particles) in the ith mode by differentiating $\ln\mathcal{Z}$ w.r.t. E_i:

$$\langle n_i\rangle = -\frac{1}{\beta}\frac{\partial\ln\mathcal{Z}}{\partial E_i} = \frac{1}{\mathrm{e}^{\beta(E_i-\mu)}\pm 1} \quad \text{(upper sign for fermions)}. \tag{4.16}$$

This result is identical to equation (3.54). It applies to a different physical problem, however: eq. (3.54) applies when the number of particles is fixed at N (hence to the electrons in an isolated conductor), while (4.16) applies when the number of particles is fluctuating thermally, and only its expectation value is equal to $\langle N\rangle$ (hence to the electrons in a grounded conductor). For very large $\langle N\rangle$ one might expect the fluctuations in N to be much smaller than $\langle N\rangle$, and might not be surprised that $\langle n_i\rangle$ is identical in the two cases. We have not, however, assumed

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[7] When the system size can vary we have $\mathrm{d}G = \langle N\rangle\mathrm{d}\mu + \mu\mathrm{d}\langle N\rangle = -S\mathrm{d}T + V\mathrm{d}P + \mu\mathrm{d}\langle N\rangle$, so $\mathrm{d}F = \mathrm{d}(G-PV) = -S\mathrm{d}T - P\mathrm{d}V + \mu\mathrm{d}\langle N\rangle$ and $\mathrm{d}U = \mathrm{d}(F+TS) = T\mathrm{d}S - P\mathrm{d}V + \mu\mathrm{d}\langle N\rangle$.

that $\langle N\rangle$ is large in deriving these results. Moreover, by differentiating $\ln\mathcal{Z}$ w.r.t. μ we can obtain an expression for the fluctuations in N and show that they may be non-negligible:

$$\begin{aligned}\langle N\rangle &= \frac{1}{\beta}\frac{\partial\ln Z}{\partial\mu} = \sum_i \frac{1}{\mathrm{e}^{\beta(E_i-\mu)}\pm 1}\\ \Rightarrow\quad \langle(\Delta N)^2\rangle &= \frac{1}{\beta^2}\frac{\partial^2\ln\mathcal{Z}}{\partial\mu^2}\\ &= \sum_i \frac{\mathrm{e}^{\beta(E_i-\mu)}}{(\mathrm{e}^{\beta(E_i-\mu)}\pm 1)^2} = \sum_i \langle n_i\rangle^2\mathrm{e}^{\beta(E_i-\mu)}.\end{aligned} \tag{4.17}$$

In the classical regime, $\mathrm{e}^{\beta(E_i-\mu)} \sim \langle n_i\rangle^{-1}$ and we have $\langle(\Delta N)^2\rangle \simeq \langle N\rangle$ as we might naively expect from Poisson statistics. If a Bose condensate is present, the first term in the sum for $\langle(\Delta N)^2\rangle$ is the square of the number of particles expected in the fundamental mode, which is macroscopically large, so $\langle(\Delta N)^2\rangle$ is non-negligible.[8] In these circumstances the agreement between (3.54) and (4.16) is remarkable.

4.2 Application to an $e_\pm$ plasma

If you heat matter to temperatures $\gtrsim 10^9$ K, the thermal energies of particles attain values at which the creation of electron-positron pairs becomes a non-negligible process. Let's adapt the grand-canonical formalism to this case. Now we don't wish to constrain the number of electrons present n_α, but the difference $n_\alpha - m_\alpha$ between the number of electrons and positrons in the box (this should be equal to the number of electrons present when the box was cold). Consequently, we replace (4.1) by

$$\sum_\alpha (n_\alpha - m_\alpha) = \langle N\rangle. \tag{4.18}$$

It is easy to see that (4.4) then becomes

$$\mathcal{Z} = \sum_\alpha \mathrm{e}^{-\beta E_\alpha - \gamma(n_\alpha - m_\alpha)} \tag{4.19}$$

We have $E_\alpha = \sum_i (n_i + m_i)E_i$, $n_\alpha = \sum_i n_i$ and $m_\alpha = \sum_i m_i$, where the sums are as usual over normal modes and n_i and m_i are the number of electrons and positrons with energy E_i. Hence, (4.13) is replaced by

$$\mathcal{Z} = \sum_{\{n_i,m_i\}} \exp\Big[-\beta\Big(\sum_i [n_i(E_i-\mu) + m_i(E_i+\mu)]\Big)\Big]. \tag{4.20}$$

Here we have replaced γ by $-\beta\mu$ as before. Notice that the first occurrence of μ in (4.20) is the chemical potential of the electrons, and the second is minus the chemical potential of the positrons; that is, we are asserting that the chemical potential of the positrons is minus that of the electrons. This is an incidence of the general rule that when species $A + B + \cdots$ react together to produce species $a + b + \cdots$, the sum of the chemical potentials on the left (here the chemical potentials of an electron and a positron) has to equal the sum of the chemical potentials on the right (here two photons). Finally for the electron-positron system (4.14) becomes

$$\mathcal{Z} = \prod_i (1 + \mathrm{e}^{-\beta(E_i-\mu)})(1 + \mathrm{e}^{-\beta(E_i+\mu)}), \tag{4.21}$$

which is simply the product of the partition functions of a box full of electrons, with that of a box full of positrons, with the positron chemical potential minus that of the electrons. To proceed further we set

$$E_i = mc^2\Big(1 + \frac{\hbar^2 k^2}{2m^2c^2} + \cdots\Big) \tag{4.22}$$

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[8] For a degenerate Fermi gas, $\mathrm{e}^{\beta(E_i-\mu)} \ll \langle n_i\rangle$, so $\langle(\Delta N)^2\rangle$ is negligible.

and use (4.16) to sum $\langle n_i \rangle$ over normal modes. The expression we obtain is just the first equality of (3.56) with $E_i(k)$ given by (4.22), and the second equality of (3.56) with μ replaced by $\pm\mu - mc^2$ (upper sign electrons). Thus the electron and positron densities are

$$N_{\mp}/V = \frac{m^{3/2}}{\pi^2\hbar^3}\int_0^\infty \mathrm{d}\epsilon\,\frac{\sqrt{2\epsilon}}{\mathrm{e}^{\beta(\epsilon+mc^2\mp\mu)}+1} = \frac{(2mk_\mathrm{B}T)^{3/2}}{2\pi^2\hbar^3}f_+[\beta(\pm\mu - mc^2)]. \tag{4.23}$$

The value of μ is now determined from

$$\langle N\rangle = N_- - N_+ = \frac{(2mk_\mathrm{B}T)^{3/2}V}{2\pi^2\hbar^3}\{f_+[\beta(\mu - mc^2)] - f_+[\beta(-\mu - mc^2)]\}. \tag{4.24}$$

The case of greatest interest is that in which the electrons are degenerate $[f_+(y) \simeq \frac{2}{3}y^{3/2}]$, and the positrons are in the classical limit $[f_+(y) \simeq \frac{1}{2}\sqrt{\pi}\mathrm{e}^y]$. Then

$$\frac{N_+}{N_-} = \frac{f_+[\beta(-\mu - mc^2)]}{f_+[\beta(\mu - mc^2)]} = \frac{3\sqrt{\pi}\mathrm{e}^{-\beta(\mu+mc^2)}}{4[\beta(\mu - mc^2)]^{3/2}}. \tag{4.25}$$

We have seen that in a white dwarf $\mu \sim mc^2$ when rest-mass energy is neglected, or $\mu \simeq 2mc^2$ when it's included, so (4.25) shows that the positron density is small until $k_\mathrm{B}T \gtrsim 3mc^2$, as one might naively expect.

5 The Microcanonical distribution

We have seen that unless C_V is anomalously large, the fluctuations in E are $\sim \sqrt{k_\mathrm{B}TU}$, so they become negligible in the thermodynamic limit ($U \to \infty$). This result implies that the partition function is dominated by terms with energies in a very narrow band in E. Let's investigate the approximation in which we assume that the only states that are occupied are those with $E = U$. If there are $\Omega(U)$ such states, our approximate value of the partition function is

$$Z = \Omega(U)\mathrm{e}^{-\beta U} \tag{5.1}$$

In this approximation

$$p_\alpha = \begin{cases} 0 & \text{for } E_\alpha \neq U, \\ 1/\Omega & \text{for } E_\alpha = U. \end{cases}$$

Consequently, the entropy is

$$S = -k_\mathrm{B}\sum_\alpha p_\alpha \ln p_\alpha = k_\mathrm{B}\ln\Omega. \tag{5.2}$$

The probability distribution (5.2) and its consequences are called the **microcanonical distribution**.

In calculations based on the canonical and grand-canonical distributions, one tends to consider T (or β) to be given, and U to be something that one determines from it through Z. When working with the microcanonical distribution one regards U as given since Ω is a function of U and by (5.2) S is a function of Ω. To find the value of β that matches the given U we argue from $\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V$ that

$$\beta = \left(\frac{\partial S/k_\mathrm{B}}{\partial U}\right)_V = \frac{\partial \ln\Omega}{\partial U}. \tag{5.3}$$

We find the pressure from

$$P = T\left(\frac{\partial S}{\partial V}\right)_U. \tag{5.4}$$

Exercise (6):

Show that $F = -k_\mathrm{B}T\ln Z$, with Z from (5.1) yields the same expression for F as $F = U - TS$ with S from (5.2).

5.1 Dynamics of a rubber band

As an instructive application of the microcanonical distribution, consider a simple model of a rubber band. We imagine the band to consist of N links of length l joined end to end. Let the band be laid along the x-axis with one end at the origin, and the other at $x = L > 0$. Some links point towards increasing x, and some towards decreasing x. Let there be n_+ pointing to increasing x and n_- pointing towards decreasing x, where $n_+ + n_- = N$. Since the ends are distance L apart, we have $n_+ - n_- = L/l$. A 'state' of the band consists of a particular arrangement of forward- and backward-pointing links. There are

$$\Omega = \frac{N!}{n_+!n_-!} = \frac{N!}{[\frac{1}{2}(N+L/l)]![\frac{1}{2}(N-L/l)]!} \tag{5.5}$$

ways of arranging the required number of forward- and backward-pointing links, so with Stirling's approximation and $y \equiv L/l$, the band's entropy is

$$\begin{aligned} S/k_\mathrm{B} = \ln\Omega &\simeq N(\ln N + 1) - \tfrac{1}{2}(N+y)\{\ln[\tfrac{1}{2}(N+y)] + 1\} \\ &\qquad - \tfrac{1}{2}(N-y)\{\ln[\tfrac{1}{2}(N-y)] + 1\} \\ &= N\ln N - \tfrac{1}{2}(N+y)\ln(N+y) - \tfrac{1}{2}(N-y)\ln(N-y) + N\ln 2. \end{aligned} \tag{5.6}$$

Differentiating w.r.t. y we find

$$\frac{\partial S/k_\mathrm{B}}{\partial y} = -\tfrac{1}{2}\ln(N+y) + \tfrac{1}{2}\ln(N-y) = -\tfrac{1}{2}\ln\left(\frac{N+y}{N-y}\right). \tag{5.7}$$

According to the equation analogous to (5.4) for a system under tension, the tension in the band is

$$\begin{aligned} \tau = -T\left(\frac{\partial S}{\partial L}\right)_U &= \frac{k_\mathrm{B}T}{2l}\ln\left(\frac{N+y}{N-y}\right) \\ &= \frac{k_\mathrm{B}T}{l}[\epsilon + \mathrm{O}(\epsilon^3)] \qquad \text{where} \qquad \epsilon \equiv \frac{y}{N} = \frac{L}{Nl}, \end{aligned} \tag{5.8}$$

in accordance with Hookes law. Unfortunately, for this system one cannot use (5.3) to relate the internal energy to the temperature, because it is impossible to vary S at fixed y.

5.2 Fluctuations

The density within a fluid in thermal equilibrium fluctuates—the blue of a clear sky arises through the scattering of blue light off just such fluctuations in the density of the atmosphere. Imagine that you are using an optical laser to measure these fluctuations. Light is scattered by fluctuations in the density $\rho(\mathbf{x})$, so you seek the probability functional[9] $P[\delta\rho]$ that will return the probability associated with any given form $\delta\rho(\mathbf{x})$ of the difference between the density and its mean value. Since one cannot see atoms with visible light, you argue that P should not involve details of the structure and disposition of individual gas molecules, but should be expressible in terms of macroscopic, phenomenological parameters such as the temperature $T(\mathbf{x})$, compressibility $\kappa_T(\mathbf{x})$, or whatever, averaged within volumes large compared with the wavelength of visible light—volumes which contain hundreds of millions of atoms. Correspondingly, $\delta\rho(\mathbf{x})$ is to be interpreted as the mean density within a volume of this type centred on $\mathbf{x}$.

Einstein offered an early solution to this problem of finding the probability functional $P[\delta\rho]$. He argued that the probability P of a macroscopic configuration is proportional to the phase-space volume Ω compatible with it. Equation (5.2) enables us to connect this to the entropy S of the density field $\delta\rho$:

$$P[\delta\rho] \propto \Omega = \mathrm{e}^{S/k_B}, \tag{5.9}$$

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[9] A function $f(x)$ is a number that depends on a number. A functional $P[f]$ is a number that depends on a whole function. It is conventional to enclose the argument of a functional in square brackets. Often the function is given a dummy argument as well for clarity thus: $P[f(\mathbf{x})]$.

To find $S[\delta\rho]$ one imagines starting with the mean density distribution $\delta\rho = 0$ and changing the energy and specific volume of each fluid element until the desired form $\delta\rho(\mathbf{x})$ has been set up. Let lower-case letters u, v, etc., denote internal energy, volume, etc. per unit mass. Then from $T\mathrm{d}S = \mathrm{d}U + P\mathrm{d}V$ we have that on setting up $\delta\rho(\mathbf{x})$ the net entropy changes by

$$\Delta S = \int \mathrm{d}^3\mathbf{x}\,\rho(\mathbf{x}) \int_0^1 \mathrm{d}\alpha\,\delta s(\mathbf{x}) = \int \mathrm{d}^3\mathbf{x}\,\rho(\mathbf{x}) \int_0^1 \frac{\mathrm{d}\alpha}{T}[\delta u + P\delta v]_{\mathbf{x}}, \tag{5.10}$$

where α parameterizes the various stages through which we deform the fluid to over-density $\delta\rho$. Since the whole system is to be regarded as a microcanonical ensemble, the total energy $U = \int \mathrm{d}^3\mathbf{x}\,\rho u$ and the total volume are constant during the deformation parameterized by α. So if $T(\mathbf{x})$ and $P(\mathbf{x})$ were constant, the right-hand side of (5.10) would vanish. So we write

$$T(\mathbf{x},\alpha) \simeq T(\mathbf{x},0) + \alpha\delta T; \quad P(\mathbf{x},\alpha) \simeq P(\mathbf{x},0) + \alpha\delta P \tag{5.11}$$

and have to second order in δ

$$\begin{aligned}\Delta S &= \int \mathrm{d}^3\mathbf{x}\,\rho(\mathbf{x})\tfrac{1}{2}\Big[-\frac{\delta T(\delta u + P\delta v)}{T^2} + \frac{\delta P\delta v}{T}\Big]_{\mathbf{x}} \\ &= \int \mathrm{d}^3\mathbf{x}\,\rho(\mathbf{x})\tfrac{1}{2}\Big[-\frac{\delta T\delta s}{T} + \frac{\delta P\delta v}{T}\Big]_{\mathbf{x}}.\end{aligned} \tag{5.12}$$

When we now eliminate δs and δP through

$$\delta s = \Big(\frac{\partial s}{\partial T}\Big)_v \delta T + \Big(\frac{\partial s}{\partial v}\Big)_T \delta v \quad \text{and} \quad \delta P = \Big(\frac{\partial P}{\partial T}\Big)_v \delta T + \Big(\frac{\partial P}{\partial v}\Big)_T \delta v, \tag{5.13}$$

a Maxwell relation enables us to cancel the terms proportional to $\delta T\delta v$, and we have

$$\begin{aligned}\Delta S &= -\int \mathrm{d}^3\mathbf{x}\,\frac{\rho}{2T}\Big[\frac{C_v}{T}(\delta T)^2 + \frac{1}{\kappa_T v}(\delta v)^2\Big] \\ &= -\int \mathrm{d}^3\mathbf{x}\,\tfrac{1}{2}\Big[\rho C_v\Big(\frac{\delta T}{T}\Big)^2 + \frac{1}{T\kappa_T}\Big(\frac{\delta\rho}{\rho}\Big)^2\Big].\end{aligned} \tag{5.14}$$

This equation expresses the change in the overall entropy as a function of the magnitude of fluctuations in the local temperature and density. Substituting this into equation (5.9) we obtain a probability functional $P[\delta\rho, \delta T]$. To obtain the desired functional $P[\delta\rho]$ we must sum $P[\delta\rho, \delta T]$ over all configurations in which $\delta\rho(\mathbf{x})$ has a particular form; in other words, we have to integrate $P[\delta\rho, \delta T]$ over all possible forms of $\delta T(\mathbf{x})$. This integration merely generates a constant that is independent of $\delta\rho(\mathbf{x})$. Hence Einstein's final probability functional is

$$P[\delta\rho] \propto \exp\Big[-\frac{\beta}{2\kappa_T}\int \mathrm{d}^3\mathbf{x}\,\big(\delta\rho(\mathbf{x})/\rho\big)^2\Big]. \tag{5.15}$$

According to this formula, density fluctuations have a Gaussian distribution with variance proportional to the isothermal compressibility κ_T. This diverges at the critical point $T = T_c$, so the fluctuations also diverge there giving rise to the phenomenon of 'critical opalescence'.

5.3 General remarks

You have seen many examples of the microcanonical distribution in the Part A course, so I won't repeat them here. Notice that the philosophical role of the microcanonical distribution in the Part A course is entirely different to that here: there it is the axiomatic starting point for statistical mechanics, and the canonical distribution is derived from it by the method of 'ensembles' in which one imagines a dynamical system, or ensemble, that is made of a large number of copies of the system of experimental interest. When one fixes the energy of the ensemble and assumes that it obeys the microcanonical distribution, one can deduce that each copy obeys the canonical distribution.

The approach taken here is that entropy maximization provides the only secure foundation for statistical mechanics. The canonical and grand canonical distributions follow trivially from it. The microcanonical distribution is a crude approximation to the canonical one in that the p_α are not well approximated by (5.2). Despite this, these p_α do give accurate results for *most* macroscopically measurable thermal averages.

6 Strongly interacting systems

The models we have been discussing are of limited interest because they omit a key aspect of real systems: inter-molecular forces. Such forces make for much richer thermodynamic behaviour, and it is very interesting to understand how complex thermodynamics of the bulk emerges from simple microscopic interactions. Understanding this question also provides insights into related economic and social phenomena.

6.1 Models

We discuss models of a magnetic material, a non-ideal gas and a binary alloy that all have the same mathematical structure. The dimensionality of the system proves to have a profound influence on the thermodynamics, so we introduce a parameter $d = 1, 2, 3$ that gives the dimensionality of the system: $d = 1$ implies a linear chain of sites, $d = 2$ a planar array of sites, etc.

6.1.1 The Ising model Far and away the most influential model of a system with strong interactions is the **Ising model**. It was first solved by E. Ising in 1925, who treated the case $d = 1$. In 1944 Onsager (1903–1976) solved the model for $d = 2$ in the absence of an externally applied magnetic field and showed that at its phase transition the model differed significantly from the predictions of 'Landau theory', which had until then been thought correct. An exact solution for the $d = 2$ model in non-zero external field appeared only in 1989.[10] Despite decades of intensive effort, we still have no exact solution for the $d = 3$ model even in the absence of magnetic field.

The lattice is cubic, and associated with each point of the lattice is a number s that is either 1 or -1. The system's Hamiltonian is

$$H = \tfrac{1}{2}\sum_{ij} \mathcal{J}_{ij} s_i s_j - B \sum_i s_i, \tag{6.1}$$

where B is an externally imposed field, the subscripts label lattice sites, and $\mathcal{J}_{ij}$ is defined such that

$$\mathcal{J}_{ij} = \begin{cases} \mathcal{J}, & i \text{ and } j \text{ neighbouring sites,} \\ 0, & \text{otherwise.} \end{cases} \tag{6.2}$$

The model's partition function can now be written

$$Z_{\text{Ising}} = \sum_{\{s_i\}} \exp\left[\beta\Big(B\sum_i s_i - \tfrac{1}{2}\sum_{ij} \mathcal{J}_{ij} s_i s_j\Big)\right], \tag{6.3}$$

where $\{s_i\}$ indicates that the sum should be extended over all possible assignments of ±1 to lattice sites. The physical picture is of an array of magnets that are obliged to be either parallel or anti-parallel to a uniform magnetic field $\mathbf{B}$.

Note:

> It is tempting to replace the magnets by spin-half dipoles and to associate $\hbar s_i/2$ with the eigenvalues of the spin-half operator $\mathbf{s}$. This is erroneous, however. The interaction Hamiltonian of two spin-half dipoles is $(4\mathcal{J}/\hbar^2)\mathbf{s}_i \cdot \mathbf{s}_j$, and if $\mathbf{S} \equiv \mathbf{s}_i + \mathbf{s}_j$ is the spin operator for the pair of atoms, it is easy to show that $\mathbf{s}_i \cdot \mathbf{s}_j = \frac{1}{2}(S^2 - s_i^2 - s_j^2)$. The eigenvalues of S^2 are 0 (non-degenerate) and $2\hbar^2$ (3-fold degenerate), and $s^2 = \frac{3}{4}\hbar^2$. Hence the partition function for a pair of spin-half dipoles is $Z = \mathrm{e}^{3\beta\mathcal{J}} + 3\mathrm{e}^{-\beta\mathcal{J}}$, which differs significantly from that of an Ising chain of two dipoles, $Z = 2\mathrm{e}^{\beta\mathcal{J}} + 2\mathrm{e}^{-\beta\mathcal{J}}$.

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[10] Zamalodchikov, *Int. J. Mod. Phys.*, **A4**, 4235.

If in equation (6.2) we set $\mathcal{J} < 0$, neighbouring spins try to align parallel to one another and parallel to **B**—the model is a ferromagnet. If we set $\mathcal{J} > 0$, neighbouring spins try to align anti-parallel to one another and (6.3) becomes the partition function of an anti-ferromagnet. One may show that the thermodynamic properties of an anti-ferromagnetic system are identical with those of the corresponding ferromagnetic system.

6.1.2 The lattice gas The Ising model turns out to be mathematically equivalent to the following highly stylized model of a non-ideal gas.

We divide the d-dimensional space occupied by the gas up into cells of just the same size as an individual molecule. Each molecule is obliged to occupy a single cell, and no cell may contain more than one molecule. Since the gas is non-ideal, molecules attract each other and the energy of the gas is lower when molecules are in adjacent cells than when each lives in glorious isolation. We model this state of affairs by changing the energy of the gas by $4\mathcal{J} < 0$ for every pair of molecules in adjacent cells. Let e_i be zero if the cell i is vacant and one otherwise. Then inter-molecular attraction changes the system's energy by

$$2\sum_{ij}\mathcal{J}_{ij}e_ie_j, \tag{6.4}$$

where $\mathcal{J}_{ij}$ is defined by equation (6.2). With these definitions, the grand partition function of the gas is

$$\mathcal{Z} = \sum_{\{e_i\}}\exp\Big(\beta\mu\sum_i e_i - 2\beta\sum_{ij}\mathcal{J}_{ij}e_ie_j\Big), \tag{6.5}$$

where μ is the chemical potential of the gas and $\{e_i\}$ indicates that the sum should be extended over all possible assignments of zeros and ones to the cells.

The grand partition function (6.5) of the lattice gas is fundamentally identical with the partition function (6.3) of the Ising model. We show this by eliminating the e_i in favour of the variables s_i defined by

$$s_i \equiv 2e_i - 1. \tag{6.6}$$

In terms of the s_i equation (6.5) reads

$$\mathcal{Z} = \sum_{\{s_i\}}\exp\Big[\beta\Big((\tfrac{1}{2}\mu - z\mathcal{J})\sum_i s_i - \tfrac{1}{2}\sum_{ij}\mathcal{J}_{ij}s_is_j\Big) + \beta N(\tfrac{1}{2}\mu - z\mathcal{J})\Big], \tag{6.7}$$

where N is the total number of cells and we have assumed that each cell has z nearest neighbours. (z is known as the **coordination number**. On a d-dimensional cubic lattice $z = 2d$.) Apart from the multiplicative factor $\exp\big[\beta N(\frac{1}{2}\mu - z\mathcal{J})\big]$, (6.7) is identical with equation (6.3) for the partition function of the Ising model when $B = \frac{1}{2}\mu - z\mathcal{J}$.

6.1.3 β-brass β-brass is an alloy consisting of equal numbers of copper and zinc atoms. At $T = 0$ the alloy consists of two interpenetrating cubic lattices, one of copper and one of zinc atoms, arranged such that each copper atom is surrounded by eight zinc atoms, and *vice versa* for each zinc atom. As the temperature is raised, more and more copper atoms stray onto the zinc sub-lattice and *vice versa*, until at 739 K the division into two distinct sub-lattices breaks down altogether; above 739 K both sub-lattices contain equal numbers of each kind of atom (see Figure 3). This system can be represented by the Ising model as follows.

At low temperatures the system is ordered because it is energetically preferable for unlike atoms to be nearest neighbours rather than like atoms. Suppose the system's energy is lowered by an amount $\mathcal{J}$ for every bond between unlike atoms on adjacent sites, and raised by $\mathcal{J}'$ for every bond between like atoms on adjacent sites. By a suitable choice of the arbitrary zero point of the energy scale we can ensure that $\mathcal{J} = \mathcal{J}'$.

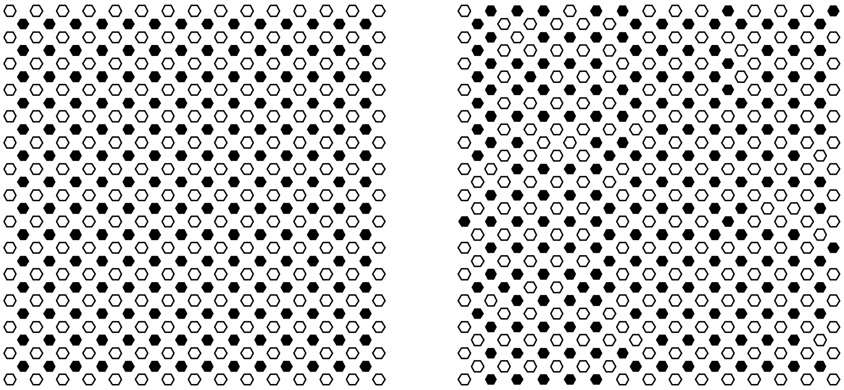

Figure 3 Projection of a slice through the lattice of β-brass, well below (left) and near (right) the critical temperature.

Now we set the order parameter on the i^{th} site s_i to $+1$ if the site is occupied by a copper atom and to -1 if it is occupied by a zinc atom. Then the system's partition function becomes

$$Z = \sum_{\{s_i\}} \exp\Big(-\tfrac{1}{2}\beta \sum_{ij} \mathcal{J}_{ij} s_i s_j \Big), \tag{6.8}$$

which is identical with equation (6.3) for the Ising model's partition function in the case $B = 0$.

6.2 Evaluating Z_{Ising}

We have a chain of N dipoles, s_i, that interact only with their neighbours on each side. To keep everything symmetrical, we assume that the chain is wrapped round on itself to form a ring. So dipole 0 interacts with dipoles 1 and $N-1$ and we consider that $s_N \equiv s_0$. We consider first the case $B = 0$. The partition function of the system is

$$Z = \sum_{\{s_i\}} \exp\Big[-\beta\mathcal{J} \sum_{i=0}^{N-1} s_i s_{i+1} \Big] = \sum_{\{s_i\}} \prod_{i=0}^{N-1} \exp\Big[-\beta\mathcal{J} s_i s_{i+1} \Big]. \tag{6.9}$$

Now consider the expression for the Nth power of a 2×2 matrix $T_{\sigma\tau}$, where the indices σ, τ take the values ± 1:

$$\big(T^N\big)_{\alpha\omega} = \sum_{\beta,\gamma,\ldots=\pm 1} T_{\alpha\beta} T_{\beta\gamma} \times \cdots \times T_{\zeta\omega} \tag{6.10}$$

The trace of this Nth power will be identical with the right side of (6.9) if we define the **transfer matrix** to be

$$T_{\sigma\tau} \equiv \exp\Big[-\beta\mathcal{J}\sigma\tau \Big] = \begin{pmatrix} \mathrm{e}^{-\beta\mathcal{J}} & \mathrm{e}^{\beta\mathcal{J}} \\ \mathrm{e}^{\beta\mathcal{J}} & \mathrm{e}^{-\beta\mathcal{J}} \end{pmatrix}. \tag{6.11}$$

Now (6.9) becomes simply

$$Z = \operatorname{Tr} \mathbf{T}^N. \tag{6.12}$$

In this expression each of the matrix products involved in raising $\mathbf{T}$ to the N^{th} power introduces one of the sums in (6.9) over the possible values of a spin.

In the limit of large N the trace of $\mathbf{T}^N$ is easily calculated. The trace is invariant under orthogonal transformations of $\mathbf{T}$, and since $\mathbf{T}$ is symmetric and positive it has real, positive eigenvalues and can be diagonalized by such a transformation. In the frame in which $\mathbf{T}$ is diagonal, $\mathbf{T}^N$ is also diagonal, consisting of $\mathbf{T}$'s eigenvalues to the power N. Thus if we denote $\mathbf{T}$'s eigenvalues in order of decreasing magnitude by λ_0, λ_1, then

$$\begin{aligned}\lim_{N\to\infty}\frac{1}{N}\ln\left(\operatorname{Tr}\mathbf{T}^N\right) &= \lim_{N\to\infty}\frac{1}{N}\ln\left\{\lambda_0^N\left[1+(\lambda_1/\lambda_0)^N\right]\right\}\\ &= \ln\lambda_0,\end{aligned} \tag{6.13}$$

where λ_0 is $\mathbf{T}$'s larger eigenvalue, which is easily shown to be $2\cosh(\beta\mathcal{J})$. Thus the ring's partition function and Helmholtz free energy per site are

$$Z = 2^N\cosh^N(\beta\mathcal{J}) \quad\text{and}\quad f = -\frac{1}{\beta}\ln[2\cosh(\beta\mathcal{J})]. \tag{6.14}$$

The internal energy per site, $\mathrm{d}(\beta f)/\mathrm{d}\beta$, is

$$u = \mathcal{J}\tanh(\beta\mathcal{J}), \tag{6.15}$$

which is a perfectly smooth function of β. So this system has no specific heat anomaly such as that which usually occurs at the Curie point of a ferromagnetic material.

We can generalize the definition (6.11) of the transfer matrix to the case of non-zero $\mathbf{B}$:

$$T_{\sigma\tau} = \exp\left[-\beta\mathcal{J}\sigma\tau + \tfrac{1}{2}\beta\mu B(\sigma+\tau)\right] = \begin{pmatrix}\mathrm{e}^{-\beta(\mathcal{J}-B)} & \mathrm{e}^{\beta\mathcal{J}}\\ \mathrm{e}^{\beta\mathcal{J}} & \mathrm{e}^{-\beta(\mathcal{J}+B)}\end{pmatrix}. \tag{6.16}$$

$\mathbf{T}$ is still symmetrical in its indices and we still have $Z = \operatorname{Tr}\mathbf{T}^N$. The larger eigenvalue of $\mathbf{T}$ is

$$\lambda_0 = \mathrm{e}^{-\beta\mathcal{J}}\left[\cosh\beta B + \sqrt{\cosh^2\beta B + (\mathrm{e}^{4\beta\mathcal{J}}-1)}\right], \tag{6.17}$$

so in the presence of a magnetic field the free energy per site is

$$f = \mathcal{J} - \frac{1}{\beta}\ln\left[\cosh\beta B + \sqrt{\cosh^2\beta B + (\mathrm{e}^{4\beta\mathcal{J}}-1)}\right]. \tag{6.18}$$

Differentiating with respect to B we obtain the average of s:

$$\begin{aligned}\langle s\rangle &= -\left(\frac{\partial f}{\partial B}\right)_T\\ &= \frac{\sinh\beta B}{\sqrt{\cosh^2\beta B + (\mathrm{e}^{4\beta\mathcal{J}}-1)}}.\end{aligned} \tag{6.19}$$

No matter what the value of β or the sign of $\mathcal{J}$, $\langle s\rangle \to 0$ as $B \to 0$. Thus the system never becomes a ferromagnet. Evidently this simply solved system does not exhibit a phase change.

It is not difficult to understand why the Ising ring never makes the transition to a ferromagnetic state. Suppose that it did and that we examined the system with $\mathcal{J} < 0$ at a very low temperature, when the great majority of the spins would be aligned. We consider how the entropy of the Universe would change if the spins in some section of the ring decided to flip over. The ring's energy would usually go up by $-4\mathcal{J}$, so the entropy of the rest of the Universe, whence the energy came, would drop by $-4\mathcal{J}/T$. But the beginning and end of the flipped section can be placed in N^2 different places. So the entropy of the ring goes up by $2k_B\ln N$. Hence for sufficiently large N, flipping a section of the ring, even a large section, will always produce a net entropy gain no matter how low the ring's temperature.

In 1944 Onsager showed that the $d = 2$ Ising model does spontaneously magnetize. It is instructive to see whether an extension of the argument we have just given enables us to anticipate this result. The energy required to flip a section of the Ising ring is independent of the length of the section. In higher dimensions the 'surface energy' of a flipped block of spins increases with the number of spins in the block. The minimum energy for a block containing a given number M of spins is achieved when the block is a d-sphere: if a is the lattice spacing and r the radius of the block, it is for $d = 2$

$$-2\mathcal{J} \times \frac{2\pi r}{a} = -4\mathcal{J}\sqrt{\pi M}.$$

For $d = 3$ the corresponding number is $-2\mathcal{J}(36\pi M^2)^{1/3}$—the energetic cost of flipping a block rises more sharply with the block's size the bigger d is. The gain in the system's entropy is harder to calculate. The centre of the block can be located at any of N sites, which gives us a straight entropy gain $k_B \ln N$. If the block had to be spherical, we could immediately conclude that flipping blocks with M comparable with N must lead to a net entropy decrease since the entropy cost of the energy, which is $\propto \beta M^p$ with $p = \frac{1}{2}$ or $\frac{2}{3}$, can be offset by an entropy gain $\propto \ln N$ only for $M \ll N$. However, the block doesn't need to be spherical, so we should consider the number of ways $n_{\rm wrap}$ in which a boundary of given area can be wrapped around the centre. This is a hard problem, but one can see that $n_{\rm wrap}$ must increase very rapidly with M if $\ln(n_{\rm wrap})$ is going to overwhelm M^p and prevent the system settling to an ordered state at sufficiently low temperature. Hence it is not *a priori* unlikely that the $d = 2$ Ising model can spontaneously magnetize.

7 Mean-field theory

Consider the d-dimensional Ising model in a uniform external magnetic field B. We write down the thermal average of a certain spin s_i given that the spins of its neighbours are constrained to take particular values:

$$\begin{aligned}\langle s_i\rangle &= \frac{\exp\Big[-\beta\big(\sum_j \mathcal{J}_{ij}s_j - B\big)\Big] - \exp\Big[\beta\big(\sum_j \mathcal{J}_{ij}s_j - B\big)\Big]}{\exp\Big[-\beta\big(\sum_j \mathcal{J}_{ij}s_j - B\big)\Big] + \exp\Big[\beta\big(\sum_j \mathcal{J}_{ij}s_j - B\big)\Big]} \\ &= -\tanh\Big[\beta\big(\sum_j \mathcal{J}_{ij}s_j - B\big)\Big].\end{aligned} \tag{7.1}$$

Here, $\mathcal{J}_{ij}$ arises rather than $\frac{1}{2}\mathcal{J}_{ij}$ because each pair of sites is counted twice in the sum over i and j of (6.1). To get the true value of $\langle s_i\rangle$ we must now average over all the values that the neighbouring spins $\{s_j\}$ can take. The correct weights of these spin configurations involve the interaction of the neighbouring spins with *their* neighbours, and so on. In order to break into this ladder of successively more complicated equations for the thermal averages of more and more distant spins, we make a simple approximation. We see that the quantity $B - \sum_j \mathcal{J}_{ij}s_j$ acts in (7.1) just like an effective magnetic field at site i; our approximation will be to replace this field by its mean value $B - \sum_j \mathcal{J}_{ij}\langle s_j\rangle$. This is the origin of the name mean-field theory. Equation (7.1) then becomes

$$\langle s_i\rangle = -\tanh\Big[\beta\big(\sum_j \mathcal{J}_{ij}\langle s_j\rangle - B\big)\Big]. \tag{7.2}$$

We assume that $\mathcal{J}_{ij}$ is given by (6.2) with $\mathcal{J} < 0$, so that the model has a tendency for spins to align, and put $\epsilon = -\mathcal{J}$. Since the system is translationally invariant, we do not expect the average $\langle s_i\rangle$ of a spin to vary from site to site—it will be everywhere equal to the specific magnetization m. Equation (7.2) now becomes

$$m = \tanh[\beta(z\epsilon m + B)], \tag{7.3}$$

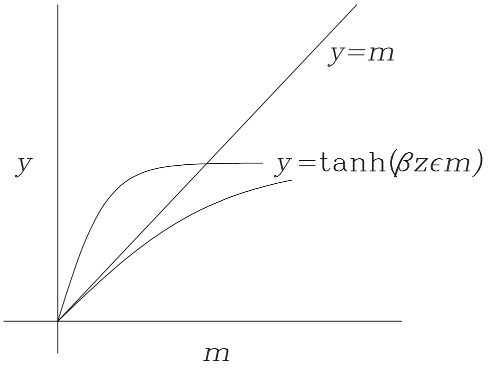

Figure 4 Graphical solution of the mean-field equation (7.3) for the Ising model.

where z is the number of nearest neighbours (the coordination number).

A graphical solution of (7.3) with $B = 0$ is shown in Fig. 4. For small $z\beta\epsilon$, (7.3) has no non-zero solution for m. However, as $z\beta\epsilon$ increases, a solution with non-zero m appears. The critical value β_c of β at which a non-zero average value of the total spin becomes possible is given by

$$z\beta_c\epsilon = 1. \tag{7.4}$$

Equation (7.4) predicts that β_c should depend on the geometry of the model only through the coordination number z and that it is finite for all $z \neq 0$. We know, however, that spatial dimensionality is crucial in determining the behaviour of the model. In particular, we saw that the one-dimensional Ising model has no ordered phase. In two and three dimensions mean-field theory is more successful; equation (7.4) correctly predicts that there will be a transition to non-zero magnetization, and the mean-field value for the transition temperatures on square and cubic lattices ($\beta_c\epsilon = 0.25$ for $d = 2$ and 0.133 for $d = 3$) are at least of the same order of magnitude as the true values, $\beta_c\epsilon = 0.4407$ for $d = 2$ from Onsager's work and $\beta_c = 0.222$ for $d = 3$ from numerical simulations. In every case mean-field theory has underestimated β_c and therefore overestimated T_c. This is a general property of mean-field theory.

7.1 Mean-field theory of the non-ideal gas

Let's apply mean-field theory to a non-degenerate non-ideal gas. Since the gas is non-degenerate, we can work in the classical picture, in which the gas has $2N$ phase-space coordinates, namely the coordinates $\mathbf{x}_i$ and momenta $\mathbf{p}_i$ of the $i = 1, \ldots, N$ molecules. The molecules interact with each other through some potential $\Phi(\{\mathbf{x}_i\})$, so the partition function is

$$Z = \int \mathrm{d}^3\mathbf{p}_1\mathrm{d}^3\mathbf{x}_1 \ldots \mathrm{d}^3\mathbf{p}_N\mathrm{d}^3\mathbf{x}_N \, \exp\Big\{-\beta\Big[\sum_i \frac{p_i^2}{2m} + \Phi(\{\mathbf{x}_i\})\Big]\Big\}. \tag{7.5}$$

The mean-field theory of this gas consists in supposing that the effect on each particle of all the others can be represented by an effective single-particle potential $\phi(\mathbf{x})$ in which all the molecules may be assumed to move. The total potential energy then decomposes into a sum of terms, one for each particle:

$$\Phi(\{\mathbf{x}_i\}) \approx \sum_i \phi(\mathbf{x}_i). \tag{7.6}$$

The integral in (7.5) now factorizes and we obtain

$$Z = \left[\int \mathrm{d}^3\mathbf{p}\mathrm{d}^3\mathbf{x} \, \exp\left\{-\beta[p^2/2m + \phi(\mathbf{x})]\right\}\right]^N . \tag{7.7}$$

The momentum and position integrals now separate. The momentum integral will contribute a volume-independent term to the free energy and we can therefore neglect it for the purpose of calculating the pressure exerted by the gas.

The optimum form of the function $\phi(\mathbf{x})$ will depend on the original potential Φ. For the purposes of the present calculation, however, let us assume a particular simple form for it; let us suppose that it excludes each molecule from some volume V_{ex} of space by means of an infinite potential barrier (in order to model the 'hard-core repulsion' of the other molecules) and takes some finite value u elsewhere (which will be negative because of the long-range attractive forces acting between molecules). Therefore, to within a volume-independent factor coming from the momentum integration in (7.7),

$$Z = \left[(V - V_{\mathrm{ex}})\mathrm{e}^{-\beta u}\right]^N . \tag{7.8}$$

The free energy is then

$$F = -Nk_BT[\ln(V - V_{\mathrm{ex}}) - \beta u]. \tag{7.9}$$

The pressure may be found by differentiating with respect to volume at constant temperature:

$$p = -\Big(\frac{\partial F}{\partial V}\Big)_T = \frac{Nk_BT}{V - V_{\mathrm{ex}}} - N\Big(\frac{\partial u}{\partial V}\Big)_T. \tag{7.10}$$

Recalling that u was supposed to originate from the attraction of a given molecule for all the others outside the excluded-volume region, it is clear that u should be proportional to the density of molecules in the gas, $u \propto N/V$. Presumably the excluded volume itself will be proportional to N. If we choose the constants of proportionality so that

$$u = -\frac{a}{N_A^2}\frac{N}{V}, \qquad\qquad V_{\mathrm{ex}} = \frac{b}{N_A}N, \tag{7.11}$$

where N_A is Avogadro's constant, then (7.10) becomes

$$p = \frac{Nk_BT}{V - bn} - \frac{an^2}{V^2}, \tag{7.12}$$

where $n = N/N_A$ is the number of moles of gas in our sample. Equation (7.12) is nothing but the van der Waals equation of state.

Appendix A Solving (2.6)

Let $s(n) \equiv S_n$. Then eq. (2.6) is easily extended to

$$s(mnr\cdots) = s(n) + s(m) + s(r) + \cdots, \tag{A.1}$$

so with $n = m = r = \cdots$ we conclude that

$$s(n^k) = ks(n). \tag{A.2}$$

Now let u, v be any two integers bigger than 1. Then for arbitrarily large n we can find m s.t.

$$\frac{m}{n} \le \frac{\ln v}{\ln u} < \frac{m+1}{n} \quad \Rightarrow \quad u^m \le v^n < u^{m+1}. \tag{A.3}$$

Since s is monotone increasing,

$$\begin{aligned} s(u^m) \le s(v^n) < s(u^{m+1}) \quad &\Rightarrow \quad ms(u) \le ns(v) < (m+1)s(u) \\ \Rightarrow \quad \frac{m}{n} \le \frac{s(v)}{s(u)} < \frac{m+1}{n}. & \end{aligned} \tag{A.4}$$

Comparing (A.3) with (A.4) we see that

$$\left|\frac{s(v)}{s(u)} - \frac{\ln v}{\ln u}\right| \le \frac{1}{n} \quad \Rightarrow \quad \left|\frac{s(v)}{\ln v} - \frac{s(u)}{\ln u}\right| \le \epsilon, \tag{A.5}$$

where $\epsilon = s(u)/(n\ln v)$ is arbitrary small. Thus we have shown that $s(v) \propto \ln v$.

Appendix B The method of steepest descent

Suppose one wishes to evaluate a contour integral of the form

$$I \equiv \int_\gamma \mathrm{d}z\, \mathrm{e}^g, \tag{B.1}$$

where γ is some contour in the complex plane and $g(z)$ is an analytic function of z. Then one can obtain an approximate value for I as follows.

The modulus of the integrand is largest at the point z_s at which $u(z) \equiv \Re\mathrm{e}(g)$ peaks. At this point $\partial u/\partial x = \partial u/\partial y = 0$, where $z = x + \mathrm{i}y$, so by the Cauchy-Riemann conditions, at z_s, $v(z) \equiv \Im\mathrm{m}(g)$ also has vanishing derivatives with respect to x and y. So at z_s, $\mathrm{d}g/\mathrm{d}z = 0$. Consequently, g's Taylor series about z_s reads:

$$g(z) = g(z_s) + \tfrac{1}{2!}g''(z_s)(z - z_s)^2 + \cdots. \tag{B.2}$$

We write $g''(z_s) = -2a\mathrm{e}^{\mathrm{i}\phi}$ and $z - z_s = \epsilon \mathrm{e}^{-\mathrm{i}\phi'/2}$, where $a > 0$, ϵ, ϕ and ϕ' are all real numbers. Then

$$g(z) \simeq g(z_s) - a\mathrm{e}^{\mathrm{i}(\phi-\phi')}\epsilon^2 \tag{B.3}$$

Now we deform the original contour of integration γ until it passes through z_s along the line $\phi' = \phi$. The contribution to the integral I from points near z_s can now be written

$$I' \equiv \mathrm{e}^{-\mathrm{i}\phi/2}\mathrm{e}^{g(z_s)} \int_{\text{small } \epsilon} \mathrm{d}\epsilon\, \mathrm{e}^{-a\epsilon^2}. \tag{B.4}$$

Although the Taylor expansion on which this expression is based is valid only for sufficiently small ϵ, the Gaussian nature of the integrand of (B.4) allows us to extend the limits of integration to $\pm\infty$ without appreciable error. Thus from the usual Gaussian integral we have

$$I' \simeq \mathrm{e}^{-\mathrm{i}\phi/2}\mathrm{e}^{g(z_s)}\sqrt{\pi/a}. \tag{B.5}$$

The method of steepest descent consists in equating I with the contribution I' from the neighbourhood of z_s:

$$\int_\gamma \mathrm{d}z\, \mathrm{e}^g \simeq \mathrm{e}^{\mathrm{i}\theta}\mathrm{e}^{g(z_s)}\sqrt{\frac{2\pi}{|g''(z_s)|}} \quad \text{where} \quad \theta \equiv -\tfrac{1}{2}\arg[-g''(z_s)]. \tag{B.6}$$

If we deform our contour so that is passes through the stationary point of g along the line $\phi' = \phi \pm \pi$, the integrand has a *minimum* at the stationary point because it is then proportional to e^{ϵ^2}. Thus the stationary point is a saddle point of the integrand. When we used the method of steepest descent to evaluate Z_N for an ideal gas, we located the stationary point as a minimum of the integrand along the real axis, and chose a contour that crosses the stationary point at right angles to the real axis, thus perceiving it as a maximum.