MAU34406 - Statistical Physics II
Brief Notes

Liam Kavanagh
B.A. Theoretical Physics

Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906 by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics. Perhaps it will be wise to approach the subject cautiously.

David Goodstein, “States of Matter”, 1975

1 Quantum Statistical Physics

1.1 Quantum Harmonic Oscillators

The discussions in Statistical Physics I consisted primarily of classical, continuous systems and their thermodynamic properties. A more realistic treatment of different systems is of course quantum mechanical, where properties such as energies of a system are quantised. As an introductory example, we discuss the statistical treatment of the Harmonic Oscillator. Specifically, a system of N distinguishable, non-interacting harmonic oscillators (i.e. the Hamiltonian has no interaction potential).

The Canonical Partition Function $Z(T, V, N)$[1] is generally

$$Z(T,V,N) = \sum_{\underline{n}} e^{-\beta E_{\underline{n}}}$$

where here $E_{\underline{n}}$ is the total energy corresponding to a particular microstate $\underline{n}$. Each of these microstates has N particles (harmonic oscillators) and our quantum mechanical treatment of the harmonic oscillator gives the energy of a single harmonic oscillator to be $E_i = (n_i + \frac{1}{2})\hbar\omega_i$, where n_i is the energy level occupied by the i^{th} particle, with frequency ω_i. n_i can take any positive integer value, depending on the constraints of the system. Thus, the total energy of this microstate will be the sum of the energies of the individual constituent particles;

$$E_{\underline{n}} = \sum_{i=1}^{N} (n_i + \frac{1}{2})\hbar\omega_i := \sum_{i=1}^{N} \varepsilon_i(n_i).$$

Thus, the partition function is the sum of all of these possible microstates

$$Z(T,V,N) = \sum_{\underline{n}} e^{-\beta \sum\limits_{i=1}^{N}(n_i+\frac{1}{2})\hbar\omega_i} = \sum_{\underline{n}} e^{-\beta \sum\limits_{i=1}^{N}\varepsilon_i(n_i)}.$$

Breaking up this exponential using the usual rule $e^{a+b} = e^a \cdot e^b$, we get

$$Z(T,V,N) = \sum_{\underline{n}=\{n_1,\dots n_N\}} e^{-\beta\varepsilon_1(n_1)} \cdots e^{-\beta\varepsilon_N(n_N)} = \sum_{n_1} e^{-\beta\varepsilon_1(n_1)} \cdots \sum_{n_N} e^{-\beta\varepsilon_N(n_N)} = \prod_{i=1}^{N} \sum_{n_i} e^{-\beta\varepsilon_i(n_i)}.$$

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[1] The letter Z is used in reference to the German “Zustandssumme”, or “sum over states”, as the partition function characterises how probabilities are distributed over individual microstates.

So, we see that the canonical partition function of the total system of N harmonic oscillators is just the product of the partition functions of N single harmonic oscillators. This makes sense, as each of the N particles are independent and non-interacting.

$$Z(T,V,N) = \prod_{i=1}^{N} \left(\sum_{n_i} e^{-\beta\varepsilon_i(n_i)} \right) = \prod_{i=1}^{N} \zeta_i .$$

We can now consider the partition function of a single harmonic oscillator, safe in the knowledge that the total system can be recovered by simply multiplying them all together. Writing out the energy explicitly, we find that the individual partition functions look like

$$\zeta_i = \sum_{n_i=0}^{\infty} e^{-\frac{1}{2}\beta\hbar\omega_i} e^{-\beta\hbar\omega_i n_i} = e^{-\frac{1}{2}\beta\hbar\omega_i} \sum_{n_i}^{\infty} e^{-(\beta\hbar\omega_i)n_i},$$

which is a geometric series. Hence, the single partition function can be written as

$$\zeta_i = e^{-\frac{1}{2}\beta\hbar\omega_i} \frac{1}{1-e^{-\beta\hbar\omega_i}}$$

and thus the total partition function is

$$Z(T,V,N) = \prod_{i=1}^{N} \frac{e^{-\frac{1}{2}\beta\hbar\omega_i}}{1-e^{-\beta\hbar\omega_i}} = \frac{1}{2^N} \prod_{i=1}^{N} \frac{1}{\sinh\left(\frac{1}{2}\beta\hbar\omega_i\right)} .$$

We can now compute some thermodynamic quantities, like the Helmholtz free energy $\mathcal{F}$, the total energy $\langle E \rangle$, the heat capacity C_V.

$$\mathcal{F} = kT \ln Z = kT \sum_{i=1}^{N} \ln[2\sinh\left(\frac{1}{2}\beta\hbar\omega_i\right)] = kT \sum_{i=1}^{N} \left[\frac{1}{2}\beta\hbar\omega_i + \sum_{i=1}^{N} \ln\left(1-e^{-\beta\hbar\omega_i}\right) \right],$$

$$\langle E \rangle = -\frac{\partial}{\partial\beta} \ln Z = \sum_{i=1}^{N} \frac{1}{2}\hbar\omega_i + \sum_{i=1}^{N} \frac{\hbar\omega_i}{e^{\beta\hbar\omega_i}-1},$$

$$C_V = \left(\frac{\partial\langle E \rangle}{\partial T} \right)_V = k \sum_{i=1}^{N} \frac{(\beta\hbar\omega_i)^2 e^{\beta\hbar\omega_i}}{(e^{\beta\hbar\omega_i}-1)^2} .$$

These results are nice-ish, but still rather ugly with all these sums everywhere. We can go further if we assume that all the oscillators have the same frequency[2], i.e. $\omega_i = \omega$. In this case,

$$Z(T,V,N) = \left[2\sinh\left(\tfrac{1}{2}\beta\hbar\omega\right)\right]^{-N},$$

$$\mathcal{F} = \frac{N}{2}\hbar\omega + NkT\ln\left(1-e^{-\beta\hbar\omega}\right),$$

$$\langle E \rangle = \frac{N}{2}\hbar\omega + \frac{N\hbar\omega}{e^{\beta\hbar\omega}-1},$$

$$\mathcal{S} = -\frac{\partial\mathcal{F}}{\partial T} = kN \left[\frac{\beta\hbar\omega}{e^{-\beta\hbar\omega}-1} - \ln\left(1-e^{-\beta\hbar\omega}\right) \right],$$

$$C_V = \frac{kN\beta\hbar\omega e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2} .$$

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[2] This is not completely unreasonable, and is in fact the approximation that Einstein made in 1907 in an attempt to characterise the heat capacity of solids. It gives reasonable results at high temperatures, however the approximation fails at low temperatures, as we'll see.

We can see that as $T \to 0$, or equivalently as $\frac{1}{kT} = \beta \to \infty$, the heat capacity C_V vanishes exponentially fast. This is contrary to experimental results which show that the heat capacity changes with the cube of the temperature. The issue arises in assuming the frequencies are all identical. An alternative model was formulated in 1912 by Peter Debye by thinking of the vibrational (kinetic) frequencies as sound waves - or "phonons"[3] - propagating through the solid.

1.2 Debye's Kinetic Theory of Solids

In 1912, building on Einstein's work on a kinetic theory of solids, Peter Debye proposed the Debye model for the specific heat of a system. He considered heat as the propagation of phonons (waves) through the solid. The wave energy is transferred by the particles in the solid, atoms, which would imply that their wavelength could not be shorter than the atomic spacing of the material. This gives an upper bound on the frequency of the phonons, called the Debye frequency ω_D. He also assumed that the distribution of frequencies was continuous, described by a density of states

$$g(\omega) = \sum_{i=1}^{3N} \delta(\omega - \omega_i),$$

where the continuous delta function picks out the discrete frequencies ω_i of each particle from the continuous parameter ω. Note the sum running from $i = 1$ to $3N$. This is because we are now treating the system in three dimensional space, where each of N particles has three spatial components. Each particle can vibrate in three directions: one longitudinal and two transverse, known as "modes". Assuming these are all equal, we can write the frequency density of states as

$$g(\omega) = 3\sum_{i=1}^{N} \delta(\omega - \omega_i).$$

If we treat the system as a large box of side length L with the phonons as plane waves, we know the frequency solutions are

$$\omega_i = v_s \frac{2\pi}{L}(n_x^2 + n_y^2 + n_z^2)^{1/2}$$

where $n_{x,y,z}$ are the components of the phonon plane wave wavevector $\vec{k}$ and v_s is the wave speed. This is the classic "particle in a box" example of Quantum Mechanics. The density of states is now

$$g(\omega) = 3 \sum_{n_x,n_y,n_z} \delta(\omega - \omega_{n_x,n_y,n_z}).$$

Considering we are summing over a delta function, we can substitute the sum for an integral over the three integer components n_x, n_y, n_z to get

$$g(\omega) = 3\int_{-\infty}^{\infty} dn_x dn_y dn_z \delta(\omega - \frac{2\pi v_s}{L}(n_x^2 + n_y^2 + n_z^2)^{1/2}).$$

Letting $\hat{\omega}_{x,y,z} = \frac{2\pi v_s}{L} n_{x,y,z}$, this integral becomes

$$g(\omega) = \frac{3L^3}{(2\pi)^3 v_s^3} \int d\hat{\omega}_x d\hat{\omega}_y d\hat{\omega}_z \delta(\omega - |\hat{\omega}_{x,y,z}|).$$

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[3] The name "phonon", from the Greek *φωνή* (phonē) meaning "sound" is attributed to Igor Tamm (1895-1971), a very influential figure in theoretical particle physics. He won the 1958 Nobel Prize in Physics along with Pavel Cherenkov and Ilya Frank for the discovery and study of Cherenkov radiation. He also, along with Semen Altshuller (unfortunate name), postulated in 1934 that neutrons have a non-zero magnetic moment, which would imply that neutrons are not elementary particles (spoiler alert: they aren't).

Letting $\hat{\omega} = \sqrt{|\hat{\omega}_{x,y,z}|}$ and moving to spherical coordinates, we get

$$g(\omega) = \frac{3L^3}{(2\pi)^3 v_s^3}(4\pi)\int_0^\infty d\hat{\omega}\hat{\omega}^2\delta(\omega - \hat{\omega}) = \frac{3(4\pi)V}{(2\pi)^3 v_s^3}\omega^2,$$

where we have let $V = L^3$ be the volume of the box. Since ω_D is the maximum frequency, all $3N$ frequency modes must sit in the interval $[0, \omega_D]$. Thus,

$$3N = \int_0^{\omega_D} g(\omega)d\omega = \frac{3(4\pi)V}{(2\pi)^3 v_s^3}\int_0^{\omega_D}\omega^2 d\omega = \frac{4\pi V}{(2\pi)^3 v_s^3}\omega_D^3.$$

Thus, we have the maximum frequency characterised by

$$\omega_D^3 = \frac{6N\pi^2 v_s^3}{V}.$$

The density of states can now be written in terms of the Debye frequency as

$$g(\omega) = \frac{9N}{\omega_D^3}\omega^2.$$

Recall the expression we had for the heat capacity

$$C_V = k\sum_{i=1}^N \frac{(\beta\hbar\omega_i)^2 e^{\beta\hbar\omega_i}}{(e^{\beta\hbar\omega_i} - 1)^2}.$$

Instead of the sum over the discrete frequencies ω_i, we can write this instead as an integral over the continuous parameter ω, modulated by our density of states $g(\omega)$ to pick out the frequency values we want. Thus,

$$C_V = k\int_0^{\omega_D} d\omega g(\omega)\frac{(\beta\hbar\omega)^2 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} = \frac{9Nk}{\omega_D^3}\frac{1}{(\beta\hbar)^3}\int_0^{x_D} dx\frac{x^4 e^x}{(e^x - 1)^2},$$

where we have made the substitution $x = \beta\hbar\omega$ such that $x_D = \beta\hbar\omega_D$. Defining the Debye temperature as $\theta_D = \frac{\hbar\omega_D}{k}$, we can write this as

$$C_V = 9Nk\left(\frac{T}{\theta_D}\right)^3\int_0^{x_D} dx\frac{x^4 e^x}{(e^x - 1)^2}.$$

In the small T limit, i.e. $T \to 0$, then $x_D \to \infty$ and this integral can be approximated as an improper integral

$$C_V \simeq 9Nk\left(\frac{T}{\theta_D}\right)^3\int_0^{x_D} dx\frac{x^4 e^x}{(e^x - 1)^2} \overset{IBP}{=} \underbrace{9Nk\left(\frac{T}{\theta_D}\right)^3 \left.\frac{-x^4}{e^x - 1}\right|_0^\infty}_{=0} + 36Nk\left(\frac{T}{\theta_D}\right)^3\int_0^{\omega_D} dx\frac{x^3}{e^x - 1}.$$

We can see that if this integral is convergent, it will yield a number independent of the temperature. So, the low-temperature behaviour of the heat capacity is

$$C_V \sim T^3$$

which corresponds exactly with the experimental result that the heat capacity changes with the cube of the temperature as $T \to 0$. The exact result, found by expressing the integrand in terms of a geometric series, is

$$C_V \underset{T\to 0}{=} \frac{12\pi^4}{5}Nk\left(\frac{T}{\theta_D}\right)^3.$$

In the high temperature limit, $x << 1$ and we can approximate the integrand

$$\frac{x^4 e^x}{(e^x-1)^2} \simeq \frac{x^4(1+x+...)}{(x+...)^2} \simeq \frac{x^4}{x^2} = x^2.$$

Thus, the heat capacity for high temperatures is

$$C_V \simeq 9Nk\left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} dx x^2 = 9Nk\left(\frac{T}{\theta_D}\right)^3 \frac{1}{3}\left(\frac{\theta_D}{T}\right)^3 = 3Nk,$$

which is exactly the classical Dulong-Petit law.

1.3 Single Particle Density of States

Our density of states $g(\omega)$, derived in **1.2**, is rather general in the form

$$g(k) = \frac{V}{(2\pi)^3} 4\pi k^2,$$

where k is the magnitude of the wavevector $\vec{k}$ of a plane wave in the solid. It comes directly from the "particle in a box" system and we used it in our derivation of the phonon density of states, where we immediately substituted for $k = (n_x^2 + n_y^2 + n_z^2)^{1/2}$ and subsequently for the frequency. If we consider a range $k, k+dk$, the quantity $g(k)dk$ represents a single particle density of states. For greater clarity later, as well as consistency of notation with Statistical Physics I, we will call this single particle density of states

$$g(k)dk = \mathcal{W}(1,k).$$

We've somewhat skimmed over the problem so far, as we've been mainly looking at the temperature dependence of heat capacity, but generally we want to be able to express thermodynamic quantities in terms of energy. To find the density of states in terms of other quantities like energy, we need to define dispersion relations between the frequency and these quantities. For relativistic photons, the momentum and energy are given by

$$p := |\vec{p}| = \hbar k = \frac{\hbar\omega}{c}, \quad \varepsilon = pc = \hbar\omega,$$

so we have

$$\mathcal{W}(1,p) = (\text{deg.})\frac{4\pi V}{(2\pi\hbar)^3} p^2 dp,$$

where (deg.) is the degeneracy of the states. Remember in the case of phonons there were three modes for each particle, so each of these three modes contributes to the density of states as the same particle. In the case of photons, they can be polarised in two transverse directions, so their degeneracy is 2.

Expressing this in terms of frequency, we get

$$\mathcal{W}(1,\omega) = (\text{deg.})\frac{4\pi V}{(2\pi c)^3} \omega^2 d\omega,$$

which for a degeneracy of 3 and velocity $c = v_s$, would be exactly our expression for the density of states for phonons from before[4]. In terms of the energy, we have

$$\mathcal{W}(1,\varepsilon) = (\text{deg.})\frac{4\pi V}{(2\pi\hbar c)^3} \varepsilon^2 d\varepsilon.$$

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[4] The linear dispersion relations for photons and phonons are very similar. One difference is in the degeneracy of the two types of particles. While photons can only be polarised in the two transverse directions, giving a degeneracy of 2, phonons can also be polarised in the longitudinal direction, giving them a degeneracy of 3. As well, generally the velocity of a phonon is dependent on the type of material and also on the direction of propagation. Usually the longitudinal velocity is not equal to the transverse velocities, so an average velocity is used, defined by $\frac{3}{v_s^3} = \frac{1}{v_{\text{long}}^3} + \frac{2}{v_{\text{trans}}^3}$, which is what was used in the derivation in **1.2**.

For non-relativistic massive particles, e.g. electrons, we generally have the dispersion relation

$$p = \sqrt{2m\varepsilon} = \hbar k$$

and, with the degeneracy given by $2s+1$ for the spins of the particles, the density of states is

$$\mathcal{W}(1,\varepsilon) = (2s+1)\frac{V}{(2\pi)^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon^{1/2}.$$

2 Ideal Decoupled Systems of Identical Particles

2.1 Why We Have More Than One Ensemble

Going back to our quantum harmonic oscillators, the equation for the canonical partition function is actually more general if we don't specify the form of the energies. We also had an expression for the total energy which was essentially just the sum of the energies of the individual components.

$$E = \sum_{i=1}^{N} \varepsilon_i(n_i).$$

This equation is fine if we can distinguish each particle in order to count the total energy. If we consider systems of identical particles, however, then we cannot count the energies of each. Instead, we count how many particles there are in each energy state and add those up to get

$$E = \sum_i n_i \varepsilon_i.$$

However, we need the constraint that the total of the occupation numbers n_i (the number of particles in the state with energy ε_i) must be equal to the total number of particles N, since every particle has to be in some state. So, we have the constraint

$$\sum_i n_i = N.$$

The canonical partition function is then

$$Z = \sum_{n_1,\ldots,n_N} e^{-\beta \sum\limits_i n_i\varepsilon_i} \delta_{\sum n_i, N},$$

where the Kronecker delta picks out those sums whose occupation numbers sum to N. This problem is more difficult to solve than the case of distinguishable particles and harmonic oscillators. Wouldn't it be nice if we didn't need to bother with that constraint of having a fixed particle number N... Aha! We know how to deal with those kind of systems. We use the Grand Canonical Ensemble, where the fixed parameters are volume V, temperature T, and chemical potential μ. The total energy and total number of particles can be anything we want. Now we don't need the constraint $\sum n_i = N$, because N isn't fixed. We can continue, pleased with ourselves for such an ingenious solution.

The grand canonical partition function is given in terms of the canonical partition function as

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

Substituting for Z, we get

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{\{n_i\}} e^{-\beta\sum\limits_i n_i\varepsilon_i} \delta_{\sum n_i, N} = \sum_{\{n_i\}} e^{-\beta\sum\limits_i n_i\varepsilon_i} \sum_{N=0}^{\infty} e^{\beta\mu N} \delta_{\sum n_i, N}.$$

Noting that the delta function now simply changes N into a sum over n_i, we can write this as

$$\mathcal{Z} = \sum_{\{n_i\}} e^{-\beta \sum\limits_i n_i \varepsilon_i} e^{\beta\mu \sum\limits_i n_i} = \sum_{\{n_i\}} e^{-\beta \sum\limits_i n_i(\varepsilon_i - \mu)}.$$

Breaking up the sum into sums over individual occupation numbers, we have

$$\mathcal{Z} = \sum_{\{n_i\}} e^{-\beta n_1(\varepsilon_1-\mu)} \cdot e^{-\beta n_2(\varepsilon_2-\mu)} \ldots = \prod_{i=1}^{n_{i_k}} \Big(\sum_{n_{i_k}} e^{-\beta n_i(\varepsilon_i-\mu)} \Big) = \prod_i \xi_i,$$

where ξ_i is the grand canonical partition function for a single state. We now need to distinguish two separate cases in order to continue.

1. A single energy level can be occupied by several particles such that

   $$n_i = 0, 1, 2, \ldots\ .$$

   This corresponds physically to particles with integer spin, which follow Bose-Einstein statistics.

2. A single energy level can be occupied by at most one single particle, in which case

   $$n_i = 0, 1.$$

   This condition is essentially the Pauli exclusion principle and corresponds to particles with half-integer spin, which follow Fermi-Dirac statistics.

In case 1, the grand canonical partition function of a single state runs over all the positive integers, corresponding to any number of particles being in that state;

$$\xi_i = \sum_{n_i=0}^{\infty} e^{-\beta n_i(\varepsilon_i-\mu)}.$$

For $\varepsilon_i - \mu > 0$, this sum is a geometric series, which can be expressed in the closed form

$$\xi_i^{BE} = \frac{1}{1 - e^{-\beta(\varepsilon_i-\mu)}}.$$

In case 2, the partition function no longer has an infinite sum, rather it has only two terms, corresponding to an occupation number of 0 or an occupation number of 1 (the state being empty or filled);

$$\xi_i^{FD} = \sum_{n_i=0}^{1} e^{-\beta n_i(\varepsilon_i-\mu)} = e^{-\beta(0)(\varepsilon_i-\mu)} + e^{-\beta(1)(\varepsilon-\mu)} = 1 + e^{-\beta(\varepsilon_i-\mu)}.$$

So, we have our two cases

$$\mathcal{Z}(T,V,\mu) = \begin{cases} \prod\limits_i \dfrac{1}{1-e^{-\beta(\varepsilon_i-\mu)}}, & \text{Bose-Einstein} \\ \prod\limits_i 1 + e^{-\beta(\varepsilon_i-\mu)}, & \text{Fermi-Dirac} \end{cases}.$$

The grand canonical potential, from which we can find all the usual thermodynamic quantities, is given by

$$\mathcal{J} = -kT \ln \mathcal{Z} = \begin{cases} kT \sum\limits_i \ln\big(1 - e^{-\beta(\varepsilon_i-\mu)}\big), & \text{Bose-Einstein} \\ -kT \sum\limits_i \ln\big(1 + e^{-\beta(\varepsilon_i-\mu)}\big), & \text{Fermi-Dirac} \end{cases}.$$

We can write this in a slightly nicer form as

$$\mathcal{J}_{\pm} = \pm kT \sum_i \ln\Big(1 \mp e^{-\beta(\varepsilon_i - \mu)}\Big),$$

where $(+)$ corresponds to Bosons and Bose-Einstein statistics and $(-)$ corresponds to Fermions and Fermi-Dirac statistics. We can, to ease computations, introduce the so-called "fugacity" (also called "activity"), $z = e^{\beta\mu}$, so the grand canonical potential becomes

$$\mathcal{J} = \pm kT \sum_i \ln\big(1 \mp z e^{-\beta\varepsilon_i}\big).$$

The average value of the occupation numbers can also be found to be the Bose-Einstein and Fermi-Dirac distributions;

$$\langle n_i \rangle = z\frac{\partial}{\partial z}\ln \xi_i = \frac{1}{e^{\beta(\varepsilon_i-\mu)} \mp 1}.$$

2.2 Bosonic Systems

We now want to consider specifically the case of free Bosonic systems, where

$$\ln \mathcal{Z} = -\sum_i \ln\big(1 - z e^{-\beta\varepsilon_i}\big).$$

We can express this sum as an integral by once again employing a density of states,

$$\mathcal{W}(\varepsilon) = \delta(\varepsilon) + \sum_{i\neq 0}^{\infty} \delta(\varepsilon - \varepsilon_i) \implies \ln \mathcal{Z} = -\int_0^{\infty} d\varepsilon \mathcal{W}(\varepsilon)\ln\big(1 - z e^{-\beta\varepsilon}\big).$$

Notice that we have separated the ground state contribution to the density of states. This is because, if one looks at the average occupation number for the ground state ($\varepsilon_0 = 0$), as $\mu \to 0$, the expression blows up. It must therefore be treated separately.

Taking the system to be in a box of side L, [5] the energy levels are $\frac{\hbar^2 k^2}{2m} = \frac{\hbar^2 n^2 \pi^2}{2mL^2} = \varepsilon_n, n \in \mathbb{Z}$. Thus, we have

$$\mathcal{W}(\varepsilon) = \delta(\varepsilon) + g_s \int_{-\infty}^{\infty} d^3\vec{n}\delta(\varepsilon - \frac{\hbar^2 n^2 \pi^2}{2mL^2}),$$

where we have included a factor $g_s = (2s+1)$, the spin degeneracy[6]. Substituting for $x = \frac{\hbar^2 n^2 \pi^2}{2mL}$ and moving to spherical coordinates where we get a factor of 4π, we get

$$\mathcal{W}(\varepsilon) = \delta(\varepsilon) + g_s 4\pi \frac{mL^2}{\hbar^2\pi^2}\frac{\sqrt{2m}L}{\hbar\pi}\int_0^{\infty} dx x^{1/2}\delta(\varepsilon - x).$$

Expressing in terms of the volume $V = L^3$, we get our final expression

$$\mathcal{W}(\varepsilon) = \delta(\varepsilon) + g_s\frac{2\pi V(2m)^{3/2}}{\pi^3\hbar^3}\varepsilon^{1/2}.$$

Substituting this expression into the grand canonical partition function,

$$\ln \mathcal{Z} = -\int_0^{\infty} d\varepsilon\delta(\varepsilon)\ln\big(1 - z e^{-\beta\varepsilon}\big) - g_s\frac{2\pi V(2m)^{3/2}}{\pi^3\hbar^3}\int_0^{\infty} d\varepsilon\varepsilon^{1/2}\ln\big(1 - z e^{-\beta\varepsilon}\big).$$

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[5] This is a relatively acceptable approximation, as we will take the volume $V = L^3 \to \infty$ in the thermodynamic limit.

[6] Not to be confused with the electron spin g-factor.

Computing this latter integral is somewhat non-trivial, but can be done by expressing the logarithm as an infinite sum. Namely,

$$\int_0^\infty d\varepsilon \varepsilon^{1/2} \ln\bigl(1 - ze^{-\beta\varepsilon}\bigr) = \sum_{l=1}^\infty \int_0^\infty d\varepsilon \varepsilon^{1/2} \frac{(-1)(ze^{-\beta\varepsilon})^l}{l} = \sum_{l=1}^\infty \frac{(-1)z^l}{l} \int_0^\infty d\varepsilon \varepsilon^{1/2} e^{-\beta\varepsilon l}.$$

Substituting $x = \beta\varepsilon l$ and recognising the definition of the Gamma function, we have

$$\sum_{l=1}^\infty \frac{(-1)z^l}{l^{5/2}} \beta^{-3/2} \int_0^\infty dx x^{1/2} e^x = -\beta^{-3/2}\Gamma(\tfrac{3}{2}) \sum_{l=1}^\infty \frac{z^l}{l^{5/2}}.$$

Defining the polylogarithm function[7] as

$$\mathrm{Li}_s(z) := \sum_{l=1}^\infty \frac{z^l}{l^s},$$

we have our total expression

$$\ln \mathcal{Z} = -\ln(1-z) + g_s V \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} \mathrm{Li}_{\frac{5}{2}}(z).$$

Using the identity $z\dfrac{d}{dz}\mathrm{Li}_s(z) = \mathrm{Li}_{s-1}(z)$, we can find

$$\langle N \rangle = z\frac{\partial \ln \mathcal{Z}}{\partial z} = \frac{z}{1-z} + g_s V \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} \mathrm{Li}_{\frac{3}{2}}(z),$$

$$\langle E \rangle = \mu \langle N \rangle - \frac{\partial}{\partial\beta} \ln \mathcal{Z} = \frac{3}{2\beta} g_s V \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} \mathrm{Li}_{\frac{5}{2}}(z).$$

The average occupation number of the ground state (i.e. the average number of particles in the lowest energy state) is

$$\langle n_0 \rangle = \frac{z}{1-z},$$

and the remainder is that of the excited states

$$\langle n_{\mathrm{exc}} \rangle = g_s V \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} \mathrm{Li}_{\frac{3}{2}}(z).$$

We can see from the second equation that $\langle n_{\mathrm{exc}} \rangle \propto T^{3/2}$, so as $T \to 0$, the number of occupied states above the ground state is bounded. We can also rewrite the first equation to get

$$z = e^{\beta\mu} = \frac{\langle n_0 \rangle}{1 + \langle n_0 \rangle} \implies \mu(T) = -kT \ln\biggl(1 + \frac{1}{\langle n_0 \rangle}\biggr).$$

So, we see that μ is negative, until we take $T \to 0$ and $\langle N \rangle = \langle n_0 \rangle + \langle n_{\mathrm{exc}} \rangle \to \infty$ (the thermodynamic limit), where $\mu \to 0$. This implies that $z \leq 1$, where $z \to 1$ as $T \to 0$ in the thermodynamic limit.

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[7] Also known as Jonquière's function. Some useful identities of polylogarithms are:

$$\mathrm{Li}_{s-1}(z) = z\frac{d}{dz}\mathrm{Li}_s(z), \quad \mathrm{Li}_{s+1}(z) = \int_0^z dx \frac{\mathrm{Li}_s(x)}{x}, \quad \mathrm{Li}_s(z) = \frac{1}{\Gamma(s)} \int_0^\infty dt \frac{t^{s-1}}{e^t/z - 1},$$

$$\mathrm{Li}_s(-z) + \mathrm{Li}_s(z) = 2^{1-s}\left[\mathrm{Li}_s(z)\right]^2, \quad \mathrm{Li}_s(1) = \zeta(s), \quad \mathrm{Li}_1(z) = -\ln(1-z).$$

Thus, we know that the polylogarithm in $\langle n_{\text{exc}} \rangle$ is bounded by $\text{Li}_{\frac{3}{2}}(1) = \zeta(\frac{3}{2}) \simeq 2.612$, giving us a bound on the average number of excited states

$$\langle n_{\text{exc}} \rangle \leq n_{\text{exc}}^{\text{max}} = g_s V \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} \text{Li}_{\frac{3}{2}}(1).$$

Rearranging this equation defines for us a critical temperature T_c such that below this temperature, the occupancy of the ground state actually begins to increase because all of the excited states are full. Obviously we also require $N > n_{\text{exc}}^{\text{max}}$.

$$T_c := \frac{h^2}{2\pi m k} \left(\frac{N}{g_s V} \frac{1}{\text{Li}_{\frac{3}{2}}(1)} \right)^{2/3}.$$

Thus, for a given N, there is a critical temperature T_c such that iff $T < T_c$, the phenomenon of Bose-Einstein consendation will occur and the occupancy of the ground state will increase. For $T << T_c$, a significant number of Bosons will occupy the ground state, $\varepsilon = 0$.

2.3 Fermionic Systems

Cast your mind, now, far back to before we split off into the Bosonic case. We also had the case for Fermions, governed by

$$\ln \mathcal{Z} = \sum_i \ln\bigl(1 + z e^{-\beta \varepsilon_i}\bigr).$$

In a very similar way to the Bosonic case, we can express this sum as an integral over a density of states to get

$$\ln \mathcal{Z} = \ln(1 + z) + g_s \frac{2\pi V (2m)^{3/2}}{\pi^3 \hbar^3} \int_0^\infty d\varepsilon \varepsilon^{1/2} \ln\bigl(1 + z e^{-\beta \varepsilon}\bigr).$$

Integrating this expression by parts, with $x = \beta \varepsilon$, we have

$$\ln \mathcal{Z} = \ln(1 + z) + g_s V \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} \int_0^\infty dx \frac{x^{3/2}}{e^x / z + 1}.$$

Recalling the integral definition of the Logarithm (see footnote 7, pg. 9), we have

$$\ln \mathcal{Z} = \ln(1 + z) - g_s V \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} \text{Li}_{\frac{5}{2}}(-z).$$

We can also compute the quantities in the same way as for Bosonic systems

$$\langle N \rangle = \frac{z}{z + 1} - g_s V \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} \text{Li}_{\frac{3}{2}}(-z),$$

$$\langle E \rangle = \frac{3}{2\beta} g_s V \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} \text{Li}_{\frac{5}{2}}(-z) = \frac{3}{2} k \langle N \rangle T \frac{\text{Li}_{\frac{5}{2}}(-z)}{\text{Li}_{\frac{3}{2}}(-z)}.$$

Notice that for $z >> 1$, $\frac{z}{z+1} < 1$ is always true. Thus, in the thermodynamic limit we can neglect the ground state contribution to $\ln \mathcal{Z}$. We can also see that for $z << 1$, the polylogarithms in the energy are approximately equal and we recover the classical result

$$\langle E \rangle = \frac{3}{2} k N T.$$

If we consider $T \to 0$ and $z >> 1$, we can approximate the behaviour of the polylogarithm for large z to leading order as

$$\text{Li}_{\frac{5}{2}}(-z) \simeq \frac{(\ln z)^{3/2}}{\Gamma(\frac{5}{2})}.$$

Thus, taking our expression for $\langle N\rangle$ and remembering that we can neglect the ground state contribution, we have for low T

$$N = g_s V \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} \frac{(\ln z)^{3/2}}{\Gamma(\frac{5}{2})}.$$

However, $z = e^{\beta\mu}$, so $\ln z = \beta\mu$. Thus, we have

$$\mu(T\to 0) = \frac{h^2}{2\pi m}\left(\frac{\Gamma(\frac{5}{2})N}{g_s V}\right)^{2/3} := \mu_0,$$

which we note is independent of the temperature. Let's use this fact in the expression for the occupancy of single states, namely

$$\langle n\rangle = \frac{1}{1+e^{\beta(\varepsilon-\mu)}}.$$

As $T\to 0$, if $\varepsilon-\mu_0 > 0$, then the denominator will get large and $\langle n\rangle \to 0$. If $\varepsilon - \mu_0 < 0$, then the exponential term will vanish and $\langle n\rangle = 1$. Thus, the chemical potential at $T=0$ defines a "cutoff point" where all states below a certain threshold are filled, and all those above are empty! We call this energy cutoff the Fermi energy, $\varepsilon_F := \mu_0$. We can write N in terms of the Fermi energy by considering the integral counting up all the states

$$N = \int_0^\infty d\varepsilon \mathcal{W}(1,\varepsilon)\left\langle n_\varepsilon\right\rangle,$$

however for $\varepsilon > \varepsilon_F$, $\langle n_\varepsilon\rangle = 0$ and for $\varepsilon \le \varepsilon_F$, $\langle n_\varepsilon\rangle = 1$. Thus, we have

$$N = \int_0^{\varepsilon_F} d\varepsilon \mathcal{W}(1,\varepsilon) = g_s V \frac{4\pi}{3}\left(\frac{2m}{h^2}\right)^{3/2} \varepsilon_F^{3/2}.$$

Similarly, for the energy as $T\to 0$

$$\langle E\rangle = \int_0^{\varepsilon_F} d\varepsilon \mathcal{W}(1,\varepsilon)\varepsilon = \frac{3}{5}N\varepsilon_F.$$

Notice how even at $T=0$ the energy is non-zero. This is because, unline Bose-Einstein condensates, the particles cannot all occupy the same state due to Pauli's exclusion principle. Instead, they pile up on top of each other and still exist as a Fermi gas.

3 Statistics of Paramagnetism

3.1 Classical Treatment

We now want to consider magnetic systems. Specifically, a system of N magnetic dipoles (think tiny bar magnets) with total magnetic moment $\vec{\tilde{\mu}}$ in an applied external magnetic field $\vec{H}$. The application of the magnetic field induces a torque on the dipoles which tends to align them in a particular direction, however these particles also have thermal fluctuations which means they're not always perfectly aligned, especially at high temperatures.

As $T\to 0$, these thermal fluctuations vanish and its possible to obtain a state where all the dipoles are oriented the same way. As $T\to\infty$ however, the thermal excitations of the particles dominates and there is total disorder in the directions of the magnetic moments. At intermediate temperatures, the system is governed by the quantity $\frac{\tilde{\mu}H}{kT}$, which you will notice is similar to the expression governing Bosonic and Fermionic systems, $\frac{\hbar\omega}{kT}$. We will also see many correspondences between different quantities in the canonical ensemble.

The Hamiltonian for the system, i.e. the total energy, is

$$E = \sum_{i=1}^{N} E_i = -\sum_{i=1}^{N} \vec{\widetilde{\mu}} \cdot \vec{H} = -\widetilde{\mu} H \sum_{i=1}^{N} \cos\theta_i,$$

where θ_i is the angle between the i^{th} particle's magnetic moment $\vec{\widetilde{\mu}}_i$ and the magnetic field $\vec{H}$ (the usual dot product definition). Note that we have assumed the magnitudes of the magnetic moments to be equal, and that the particles are completely localised (no kinetic energy from momentum). Because the particles are decoupled, the canonical partition function can be expressed in terms of the partiton functions of individual particles, so

$$Z(T, V, N) = \prod_{i=1}^{N} \zeta_i = \prod_{i=1}^{N} \sum_{(\theta_i, \phi)} e^{\beta \widetilde{\mu} H \cos\theta_i}$$

where (θ_i, ϕ) parametrise the angular directions of the magnetic moment in 3D space. This problem was solved by Langevin[8] in 1905 by replacing (read: approximating) the sum as an integral over the solid angles (θ_i, ϕ), since the dipoles are assumed to be freely orientable and spherically symmetric. Thus,

$$\zeta_i = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta_i e^{\beta \widetilde{\mu} H \cos\theta_i} \sin\theta_i = \frac{4\pi}{\beta \widetilde{\mu} H} \sinh(\beta \widetilde{\mu} H).$$

We can define the total average magnetisation $\langle M \rangle$ as the average value of the magnetic moments $\langle \widetilde{\mu} \cos\theta \rangle$ to get

$$\langle M \rangle := \langle \widetilde{\mu} \cos\theta \rangle = \frac{\sum \widetilde{\mu} \cos\theta e^{\beta \widetilde{\mu} H \cos\theta}}{\sum e^{\beta \widetilde{\mu} H \cos\theta}} = \frac{1}{\zeta} \frac{\partial}{\partial H} \frac{\zeta}{\beta} = \frac{\partial}{\partial H} \big[kT \ln\zeta \big].$$

However, recall that the canonical partition function of the total system is simply the product of the N single particle partition functions. Thus,

$$kT \ln\zeta = kT \ln Z^{1/N} = \frac{1}{N} kT \ln Z = -\frac{1}{N} \mathcal{F},$$

where $\mathcal{F} = -kT \ln Z$ is the Helmholtz free energy. Thus, we have the total average magnetisation

$$\langle M \rangle = -\frac{1}{N} \left(\frac{\partial \mathcal{F}}{\partial H} \right)_T .$$

Using our solution for the single particle canonical partition function, ξ, we can find an explicit expression for the magnetisation,

$$\langle M \rangle = kT \frac{\partial}{\partial H} \big[\ln\left(4\pi \sinh(\beta \widetilde{\mu} H)\right) - \ln\left(\beta \widetilde{\mu} H\right) \big] = -\frac{!}{\beta H} + \widetilde{\mu} \coth(\beta \widetilde{\mu} H) := \widetilde{\mu} \mathcal{L}(\beta \widetilde{\mu} H)$$

where $\mathcal{L}(x) = \coth(x) - \frac{1}{x}$ is the Langevin function. The quantity $x := \beta \widetilde{\mu} H = \dfrac{\widetilde{\mu} H}{kT}$ denotes the relative strength of the magnetic potential energy to the thermal energy. Note that when $x >> 1$, $L(x) \simeq 1$ and $M \simeq \widetilde{\mu}$. The system acquires a state of magnetic saturation. Alternatively, when $x << 1$, $L(x) \simeq \frac{x}{3} - \frac{x^3}{45} + ...$ and $M \simeq \frac{\widetilde{\mu}^2 H}{3kT}$.

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[8] Paul Langevin (1872-1946) is a very interesting character and has made numerous contributions to Physics and Mathematics. He studied under J. J. Thomson in the famous Cavendish Laboratory and later was a PhD student of Pierre Curie. He was a strong supporter of Einstein's work on relativity and came up with the concept of the Twin Paradox. He was a thesis advisor to both Léon Brillouin and Louis de Broglie.

This also leads to the the isothermal "magnetic suceptibility", another useful quantity[9]:

$$\chi_T := \left(\frac{\partial\langle M\rangle}{\partial H}\right)_T = -\frac{1}{N}\left(\frac{\partial^2\mathcal{F}}{\partial H^2}\right)_T,$$

which is a measure of how much a material will become magnetised when an external field is applied. For $x >> 1$ (large T or small H), we have

$$\chi_T \simeq \frac{\widetilde{\mu}^2}{3kT} := \frac{C}{T}$$

where $C = \frac{\widetilde{\mu}^2}{3k}$ is the Curie constant. This result is known as the Curie Law of Paramagnetism, which is a classical result. We can see from the derivation of this law that a large temperature or weak magnetic field is required. A more accurate treatment is one employing Quantum Mechanics so that we can attempt to describe the low-temperature limit.

3.2 Quantum Mechanical Treatment

The primary difference between the classical and quantum approaches is the quantisation of the magnetic moments. Namely, we now have

$$\vec{\widetilde{\mu}} = \frac{ge}{2mc}\vec{L}$$

where $\vec{L}$ is the angular momentum (angular or spin intrinsic, or both) of the particle (we are now explicitly taking the particles to be electrons) and g is the gyromagnetic ratio or Landé g-factor. The values the angular momentum can take are the discrete eigenvalues $l = \sqrt{j(j+1)}\hbar$. If the electron's angular momentum is purely due to intrinsic spin, $g = 2.0023... \simeq 2$ and if it is purely due to orbital motion, $g = 1$. The explicit expression is

$$g = \frac{3}{2} + \frac{s(s+1) - l(l+1)}{2j(j+1)}$$

The equation for the magnetic moment is generally written instead as

$$\widetilde{\mu}^2 = g^2\mu_B^2 j(j+1)$$

where $\mu_B = \frac{e\hbar}{2mc}$ is the Bohr magneton, a convenient unit for these interactions. If we consider completely localised electrons (free electrons e.g. in conductors must be treated differently) with the magnetic field in the z direction, then we have

$$M = -\vec{\widetilde{\mu}} \cdot \vec{H} = -\widetilde{\mu}_z H_z = -g\mu_B m H$$

where the integer values $m = -j, -j+1, ..., j-1, j$ are the eigenvalues of L_z, the z component of the angular momentum. The number of allowed orientations of the magnetic moment is $2j+1$. The canonical partiton function for a single particle is thus

$$\zeta(T,V) = \sum_{m=-j}^{j} e^{\beta g m H \mu_B} = \sum_{m=-j}^{j} e^{mx/j}$$

---

[9] This measure of a material's response to a magnetic field actually has numerous uses. It is used is the geosciences to measure thermoremanant magnetisation (TRM) in rocks, which is how we can map the evolution of the Earth's magnetic field, including the numerous times the planet's magnetic field has flipped. It can also tell us about the history of magnetic fields of other planets, like Mars. One of the most important uses however is in Susceptibility Weighted Imaging (SWI), which is used in MRI sequencing to compare and contrast different structures by exploiting differences in the magnetic suceptibility of various tissues. It can identify strokes, calcium deposits, brain haemorrharing, and is even accurate enough to classify tumours by measuring the growth rates of cancerous cells.

where we have let $x = \beta g\mu_B jH$. So,

$$\zeta(T,V) = e^{-x}\left(\frac{e^{\frac{2j+1}{j}x}-1}{e^{x/j}-1}\right) = \frac{\sinh\!\left(\frac{2j+1}{2j}x\right)}{\sinh\!\left(\frac{x}{2j}\right)}.$$

We now have the average magnetism, as before,

$$\langle M\rangle = \frac{1}{\beta}\frac{\partial}{\partial H}\ln\zeta = g\mu_B j\left[(1+\tfrac{1}{2j})\coth\!\Big(x(1+\tfrac{1}{2j})\Big) - \frac{1}{2j}\coth\!\Big(\tfrac{x}{2j}\Big)\right].$$

The term in the square brackets is known as the Brillouin function of order j, $B_j(x)$. When the magnetic field is strong, i.e. $H >> 1$, and/or the temperature is low, $T << 1$, we have $x >> 1$ and $B_j(x) \approx 1$ for all j. This is magnetic saturation. On the other hand, for $T >> 1$ or $H << 1$, we have $x << 1$ and

$$B_j(x) \simeq \frac{1}{3}(1+\frac{1}{j})x + ...$$

which yields

$$\langle M\rangle \simeq \frac{g^2\mu_B^2}{2kT}j(j+1)H$$

and thus we have

$$\chi_T = \frac{\partial\langle M\rangle}{\partial H} \simeq \frac{g^2\mu_B^2 j(j+1)}{3kT}.$$

We can see that even in the high temperature limit, we require the discrete levels of Quatntum Physics! If we take $j\to\infty$ while simultaneously $g\to 0$ and insisting that $\widetilde{\mu}$ remains constant, we recover the classical limit where we have a continuum of states and $\widetilde{\mu}$ can have continuous values. Indeed, we find that in this limit

$$B_j(x) \underset{j\to\infty}{\simeq} \underbrace{g\mu_B j}_{\widetilde{\mu}}\underbrace{\left[\coth(x) - \tfrac{1}{x}\right]}_{\mathcal{L}(x)}.$$

Note that the Curie constant is now a different value, but this improved approximation agrees very well with experimental results.

3.3 Spin-$\frac{1}{2}$ Particles

We now want to consider the specific case of electrons, particles with spin $\frac{1}{2}$, and no orbital angular momentum. In this case, we have $g \simeq 2$ and $j = \frac{1}{2}$, giving us $2j+1 = 2$ possible orientations of the magnetic moment. The possible energies for each dipole are, noting that $gj \simeq 1$,

$$\varepsilon_i = \begin{cases} -\mu_B H = -\varepsilon_0 \\ +\mu_B H = +\varepsilon_0 \end{cases}.$$

Substituting this into our previous results, we find

$$Z(T,V,N) = \zeta^N = \left(\frac{\sinh(2x)}{\sinh(x)}\right)^N = (2\cosh(x))^N = (2\cosh(\beta\varepsilon_0))^N,$$

since $x = \beta\mu_B H = \beta\varepsilon_0$. The thermodynamic properties can be computed as normal:

$$\mathcal{F} = -kT\ln\mathcal{Z} = -NkT\ln(2\cosh(\beta\varepsilon_0)),$$

$$\mathcal{S} = -\left(\frac{\partial\mathcal{F}}{\partial T}\right)_H = Nk\left[\ln\left(2\cosh(\beta\varepsilon_0)\right) - \beta\varepsilon_0\tanh(\beta\varepsilon_0)\right],$$

$$\langle E\rangle = \mathcal{F} + T\mathcal{S} = -N\varepsilon_0\tanh(\beta\varepsilon_0),$$

$$\langle M\rangle = -\frac{1}{N}\left(\frac{\partial \mathcal{F}}{\partial H}\right)_T = \mu_B \tanh(\beta\varepsilon_0),$$

$$C_V = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_H = \frac{Nk\beta^2\varepsilon_0^2}{\cosh^2(\beta\varepsilon_0)}.$$

Note from this that $\langle E\rangle = -N\langle M\rangle H$, as we expect. Considering the entropy $\mathcal{S}$ as $T \to \infty$, we have

$$\mathcal{S} \simeq Nk\left[\ln(2) - \frac{\varepsilon_0^2}{(kT)^2}\right] \simeq Nk\ln(2).$$

In the other limit, $T \to 0$, we find

$$\mathcal{S} \simeq Nk\left[\ln\!\left(e^{\beta\varepsilon_0}\right) - \beta\varepsilon_0\right] \simeq 0.$$

Let's look at these results more carefully. Remember that in the thermodynamic limit, the entropy can be calculated equivalently in the microcanonical ensemble, where

$$\mathcal{S} = k\ln\Omega = \begin{cases} Nk\ln(2) = k\ln\!\left(2^N\right), & T \to \infty \\ 0 = k\ln(1), & T \to 0 \end{cases}.$$

So, it looks as if the number of microstates of the system is

$$\Omega(E,V,N) = \begin{cases} 2^N, & T \to \infty \ (kT >> \varepsilon_0) \\ 1, & T \to 0 \ (kT << \varepsilon_0) \end{cases}.$$

We see that at high temperatures, the orientation of the dipoles is random (complete disorder), so all microstates are equally likely and are equal in number to 2^N, two possibilities for each particle.

At very low temperatures, there is only one microstate and $\langle E\rangle \to -N\varepsilon_0$, corresponding to all of the dipoles being in their lowest state and aligned in the direction of the magnetic field (complete order). We can also see that the heat capacity C_V takes its maximum value for $\varepsilon_0 \simeq kT$. This is known as the Schottky anomaly[10], since heat capacities usually increase with temperature.

We can see a very peculiar result here, by rearranging the energy expression for temperature. We find

$$\frac{1}{T} = \frac{k}{\varepsilon_0}\ln\left[\frac{1 - \frac{\langle E\rangle}{N\varepsilon_0}}{1 + \frac{\langle E\rangle}{N\varepsilon_0}}\right].$$

We see that when $\langle E\rangle > 0$, the temperature of the system is negative! This is actually an observable phenomenon in systems that have an upper limit on the amount of energy the system can hold. In a physical sense, negative temperatures refer to the fact that heat will always flow to an area of positive temperature. In that sense, negative temperatures are "hot".

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[10] Named after Walter H. Schottky, yet another underrated physicist. The majority of his research focused on semiconductor devices and his contributions to the field of semiconductor physics are vast and significant. He invented the Schottky diode, which is formed from the junction of a semiconductor and a metal, with the metal acting as the p-type conductor. The junction voltage of these diodes is lower than that of Silicon and Germanium, making them preferable in efficiency-sensitive applications. The charge states in Schottky diodes are highly susceptible to applied electric fields, making them useful in loading and unloading single electrons into quantum wells and quantum dots.

4 One-Dimensional Spin Chains

4.1 The Ising Model

Continuing on from the previous topic, we consider magnetic dipoles with two possible values, ±1, where neighbouring dipoles can interact weakly with their neighbours to influence the direction of their spin. If we consider the dipoles in a one-dimensional lattice, or chain, this is known as the 1D Ising Model. Writing the spin of each particle as $\sigma_i = \pm 1$, the Hamiltonian of the system is

$$\mathcal{H} = -\sum_{i,j}^{N} J_{ij}\sigma_i\sigma_j - \mu\sum_{i=1}^{N} H_i\sigma_i.$$

J_{ij} represents the strength of the interaction between the i^{th} and j^{th} dipoles. If $J_{ij} > 0$, the system is ferromagnetic, if $J_{ij} < 0$, it is anti-ferromagnetic, and if $J_{ij} =$, the system is non-interacting (which is our previous discussion). We first want to discuss "nearest-neighbour" interactions, where $J_{ij} = J > 0$ for $j = i + 1$ and 0 otherwise. Thus, we have

$$\mathcal{H} = -J\sum_{i=1}^{N-1} \sigma_i\sigma_{i+1} - \mu\sum_{i=1}^{N} H_i\sigma_i.$$

We want to first consider the case of no magnetic field ($H_i = 0$) and free boundary conditions. We have the canonical partition function

$$Z = \sum_{\{\sigma_i\}} e^{\beta J \sum\limits_{i=1}^{N-1} \sigma_i\sigma_{i+1}} = \sum_{\sigma_1}\cdots\sum_{\sigma_N} e^{\beta J \sum\limits_{i=1}^{N-1} \sigma_i\sigma_{i+1}}.$$

Letting $\eta_i = \sigma_i\sigma_{i+1}$ such that $\eta_i = +1$ for $\sigma_i = \sigma_{i+1}$ and $\eta_i = -1$ for $\sigma_i \neq \sigma_{i+1}$, we have

$$Z = \sum_{\sigma_1}\sum_{\eta_1}\cdots\sum_{\eta_{N-1}} e^{\beta J(\eta_1 + \cdots \eta_{N-1})} = \sum_{\sigma_i = \pm 1}\left(\sum_{\eta = \pm 1} e^{\beta J\eta}\right)^{N-1} = 2^N\big[\cosh(\beta J)\big]^{N-1}.$$

We could consider another case, where the one-dimensional chain is in a loop, whereby we have $\sigma_{N+1} = \sigma_1$, and we still have $H_i = 0$. In this case,

$$\mathcal{H} = -J\sum_{i=1}^{N-1} \sigma_i\sigma_{i+1} - J\sigma_N\sigma_1.$$

We have the same expression as before with the exception of an added term

$$Z = \sum_{\sigma_1}\cdots\sum_{\sigma_N} e^{\beta J \sum\limits_{i=1}^{N-1} \sigma_i\sigma_{i+1}} e^{\beta J\sigma_N\sigma_1}.$$

If we want to perform the same substitution for η, we need to write $\sigma_N\sigma_1$ in terms of that notation. Notice however that since $\sigma_i^2 = 1$,

$$\sigma_N\sigma_1 = (\sigma_1\sigma_2)(\sigma_2\sigma_3)(\sigma_3\sigma_4)\cdots(\sigma_{N-2}\sigma_{N-1})(\sigma_{N-1}\sigma_N).$$

Thus, we have $\sigma_N\sigma_1 = \eta_1\cdots\eta_{N-1}$ and we get

$$Z = \sum_{\sigma_1}\sum_{\eta_1}\cdots\sum_{\eta_{N-1}} e^{\beta J(\eta_1 + \ldots + \eta_{N-1}) + \beta J\eta_1\cdots\eta_{N-1}} = \sum_{\sigma_1}\sum_{\alpha=0}^{\infty}\frac{(\beta J)^\alpha}{\alpha!}\left(\sum_{\eta=\pm 1}\eta^\alpha e^{\beta J\eta}\right)^{N-1}.$$

Breaking this up into odd and even terms in α, we get the final result

$$Z = \left[2\cosh(\beta J)\right]^N + \left[2\sinh(\beta J)\right]^N.$$

We can also consider the case where there is a magnetic field ($H_i = H \neq 0$) with periodic boundary conditions. We have to treat this somewhat differently. We have

$$Z = \sum_{\sigma_1} \cdots \sum_{\sigma_N} e^{\frac{1}{2}\beta H(\sigma_1+\sigma_2)+\beta J\sigma_1\sigma_2} \cdots e^{\frac{1}{2}\beta H(\sigma_N+\sigma_1)+\beta J\sigma_N\sigma_1}.$$

We consider each factor as an element of a "transfer matrix", e.g.

$$\mathcal{T}_{\sigma_1\sigma_2} := e^{\frac{1}{2}\beta H(\sigma_1+\sigma_2)+\beta J\sigma_1\sigma_2} = \begin{bmatrix} e^{\beta H+\beta J} & e^{-\beta J} \\ e^{-\beta J} & e^{-\beta H+\beta J} \end{bmatrix}.$$

Thus, we have

$$Z = \sum_{\sigma_1} \cdots \sum_{\sigma_N} \mathcal{T}_{\sigma_1\sigma_2} \cdots \mathcal{T}_{\sigma_N\sigma_1} = \sum_{\sigma_1} (\mathcal{T}^N)_{\sigma_1\sigma_1}$$

So, we can write the partition function as the trace of the transfer matrix

$$Z = \mathrm{Tr}(\mathcal{T}^N).$$

We can compute $\mathcal{T}^N$ by diagonalising the matrix. It is real and symmetric, so $\mathcal{T}_{\text{diag}} = \mathcal{O}^T\mathcal{T}\mathcal{O}$ for a real orthonormal matrix $\mathcal{O}$. Thus, $\mathrm{Tr}(\mathcal{T}^N) = \lambda_1^N + \lambda_2^N$ for eigenvalues $\lambda_{1,2}$ of $\mathcal{T}$.

For $\lambda_1 \neq \lambda_2$ and $\lambda_1 > \lambda_2$, we have

$$Z = \lambda_1^N \left(1 + \left(\frac{\lambda_2}{\lambda_1}\right)^N\right)^N$$

However, since $\frac{\lambda_2}{\lambda_1} < 1$, as $N \to \infty$, we will have

$$Z = \lambda_1^N + \mathcal{O}(e^{-N\ln(\lambda_2/\lambda_1)}).$$

So, in the thermodynamic limit, only the largest eigenvalue contributes. A concrete value for Z can be found by computing the eigenvalues of $\mathcal{T}$, which are

$$\lambda_{1,2} = \frac{1}{2}\left[2e^{\beta J}\cosh(\beta H) \pm \sqrt{4e^{2\beta J}\cosh^2(\beta H) - 8\sinh(2\beta J)}\right].$$

As the positive solution is the larger, we have in the thermodynamic limit

$$\mathcal{F} = -NkT\ln\lambda_1 = -NJ - NkT\ln\left[\cosh(\beta H) + \sqrt{\sinh^2(\beta H) + e^{-4\beta J}}\right].$$

Looking at the case where $T \to 0$ (or $J \to \infty$), we have

$$\lambda_1 \simeq e^{\beta J}(\cosh(\beta H) + \sqrt{\sinh^2(\beta H)}(1 + \mathcal{O}(e^{-4\beta J})) = e^{betaJ}(\cosh(\beta H) + |\sinh(\beta H)|).$$

Thus, we see that $\lambda_1 \simeq e^{\beta J} + |\beta H|$ and so

$$\mathcal{F} \simeq -NkT(\beta J + |\beta H|) = -NJ - N|H|.$$

The derivative of $\mathcal{F}$ is discontinuous! We have

$$\langle M\rangle = -\frac{1}{N}\frac{\partial\mathcal{F}}{\partial H} = \begin{cases} 1, \ H > 0 \\ -1, H < 0 \end{cases}.$$

As $T \to 0$ or $J \to \infty$, there is very strong interaction between spins and all are aligned in the same direction.

4.2 Spatial Correlations

We can characterise the statistical causal relationship between two particles in the chain by a 2 point correlation function

$$G(i,j) = \langle \sigma_i \sigma_j \rangle - \langle \sigma_i \rangle \langle \sigma_j \rangle = \langle \sigma_i \sigma_j \rangle \,,$$

since $\sigma_i = \pm 1$, so $\langle \sigma_i \rangle = 0$. It can also be expressed as

$$G(i,j) = \langle (\sigma_i - \langle \sigma_i \rangle)(\sigma_j - \langle \sigma_j \rangle \rangle \,.$$

This function measures the correlation in the fluctuations of the different spins at different sites in the lattice/chain. $G(i,j)$ is related to the probability

$$P(\sigma_i = \sigma_j) = \frac{1}{Z} \sum_{i,j} \delta_{\sigma_i, \sigma_j} e^{-\beta \mathcal{H}(\sigma_i, \sigma_j)} = \langle \delta_{\sigma_i, \sigma_j} \rangle = \frac{1}{2} + \frac{1}{2} G(i,j).$$

We now note that

$$G(i, i+1) = \frac{1}{Z} \sum_{\sigma_1} \cdots \sum_{\sigma_N} \sigma_i \sigma_{i+1} e^{\beta J \sigma_1 \sigma_2 + \ldots + \beta J \sigma_{N-1} \sigma_N}$$

Re-generalising $J = J_{ij}$, we can write this as

$$G(i, i+1) = \frac{1}{\mathcal{Z}(J_i)} \frac{\partial}{\partial(\beta J_i)} \underbrace{\left[\sum_{\{\sigma_1, \ldots, \sigma_N\}} e^{\beta J_1 \sigma_1 \sigma_2 + \ldots \beta J_{N-1} \sigma_{N-1} \sigma_N} \right]}_{\mathcal{Z}(J_i)} = \frac{\partial}{\partial(\beta J_i)} \left[\ln \mathcal{Z}(J_i) \right].$$

Given our expression $\mathcal{Z}(J_i) = 2^N \prod_{i=1}^{N-1} \cosh(\beta J_i)$, we have

$$G(i, i+1) = \langle \sigma_i \sigma_{i+1} \rangle = \tanh(\beta J_i) \underset{J_i = J}{=} \tanh(\beta J).$$

We can show by induction that

$$G(i, i+j) = \tanh^j(\beta J_i).$$

If we consider $T \to 0$, $\beta J \to \infty$, then $\tanh(\beta J) \to 1$. Thus, we have $G(i, i+j) = 1$ for all j. This implies that the system at $T = 0$ is entirely in the same state. Each two particles has a "correlation" of 1, i.e. they have the same value. We showed that the probability $P(\sigma_i = \sigma_j) = \frac{1}{2} + \frac{1}{2} G(i, i+j)$, so if $G(i, i_j) = 1$, then $P(\sigma_i = \sigma_j) = 1$, so indeed the particles are all in the same state.

We can also see that as T gets bigger, the correlations decrease exponentially until for $T >> 1$, $\beta J << 1$, there is no correlation. We can define a correlation length,

$$l = \frac{1}{\ln(\coth(\beta J))},$$

measured in units of atomic/lattice spacing, gives the length over which spins are correlated with a probability of 1.

In the case of $H \neq 0$, we can show that we can write the transfer matrix as

$$\langle \sigma_i \rangle = \frac{1}{Z} \sum_{\sigma_1} \cdots \sum_{\sigma_N} e^{-\beta H} \sigma_i = \frac{1}{Z} \sum_{\sigma_1} \cdots \sum_{\sigma_i} \cdots \sum_{\sigma_N} \mathcal{T}_{\sigma_1 \sigma_2} \cdots \mathcal{T}_{\sigma_{i-1} \sigma_i} \sigma_i \mathcal{T}_{\sigma_i \sigma_{i+1}} \cdots \mathcal{T}_{\sigma_{N-1} \sigma_N},$$

but since $\sum_{\sigma_i} \mathcal{T}_{\sigma_{i-1} \sigma_i} \sigma_i \mathcal{T}_{\sigma_i \sigma_{i+1}} = \mathcal{T} \sigma_z \mathcal{T}$, where $\sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ is the third Pauli matrix, we have, for $\mathcal{T}_{\text{diag}} = \mathcal{O}^T \mathcal{T} \mathcal{O}$,

$$\langle \sigma_i \rangle = \frac{1}{Z} \text{Tr}(\sigma_z T^N) = \frac{\text{Tr}(\mathcal{O}^T \sigma_z \mathcal{O} \mathcal{T}_{\text{diag}}^N)}{\text{Tr}(\mathcal{T}_{\text{diag}}^N)}.$$