Statistical Physics

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Contents

Chapter 1

Thermodynamics

1.1 Clausius-Clapeyron Equation Derivation

Consider 2 phases A and B that can coexist on some line. At this point, the Gibbs energy of the 2 phases are equal or,

$$dG_A = dG_B$$

Recalling that $dG = -SdT + VdP + \mu dN$,

$$-S_A dT + V_A dP + \mu_A dN = -S_B dT + V_B dP + \mu_B dN$$

We have $dN = 0$ due to particle number conservation.

$$\Rightarrow \Delta S dT = \Delta V dP$$

$$\frac{dP}{dT} = \frac{\Delta s}{\Delta v}$$

where we have multiplied by $\frac{M}{M}$ to get the specific values. Since latent heat is defined by $l = T_C \Delta s$,

$$\frac{dP}{dT} = \frac{l}{T_C \Delta v}$$

This gives the slope of the line that separates the phases on a PT diagram. One immediate consequence is that for a first order phase transition, the volume must change.

Chapter 2

Framework for Statistical Physics

The way we formulate statistical physics will be established in this section. The idea of a state of a system will be established followed by a development of the distribution function.

2.1 Γ-Space

How do we classify the state of a system of N particles? In classical mechanics, a state of a particle is specified by momentum and position; $\mathbf{p}$, $\mathbf{r}$. The vectors belong in a 6-dimensional space called the phase space. For N particles, the phase space is $6N$-dimensional. Denote $(\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N, \mathbf{r}_1, \ldots, \mathbf{r}_N) = (p, r)$. The Hamiltonian is,

$$H(p,r) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \frac{1}{2} \sum_{i \neq j} V(\mathbf{r}_i - \mathbf{r}_j)$$

The half in front of the potential is to prevent double counting. Hamilton's equations of motion govern how the particles move.

Definition: The $6N$-dimensional space spanned by (p, r) is called the Γ-*space*. A point, (p, r), in this space is called a *representative point*.

As time evolves, a point traces out a trajectory in Γ-space. If the Hamiltonian has no explicit dependence on time, then energy is conserved. The points, (p, r), are constrained to a hypersurface $H(p, r) = E$ in Γ-space.

2.2 μ-space

Another way to consider the motion of particles is to consider a 6-dimensional phase space called the *μ-space*. Each particle is described by a point, (p_1, p_2, p_3, x, y, z). For N particles, there are N points. These points evolve in time and can collide with each other.

To summarise, in Γ-space, N particles are described by a single point in $6N$-dimensional space. In μ-space, N particles are described by N points in 6-dimensional space.

2.3 Microstates and Macrostates

A *microstate* is a state that specifies all the parameters of the system. In a system of N particles, we know the position and momentum of each particle. The state can be described by one of the spaces mentioned above.

A *macrostate* is a state that describes the system as whole. For example, a system with a fixed pressure, volume and temperature is a particular macrostate. There are many different possible microstates that can give rise to a particular macrostate.

2.4 Ergodic Hypothesis

The *ergodic hypothesis* assumes,

> "Given a sufficiently long time, the representative point of an isolated system will come arbitrarily close to any given point on the energy surface."

Essentially, what we need from this is that all microstates that correspond to a given macrostate at thermal equilibrium are equally likely to occur. There is no preferred microstate.

2.5 Distribution Function

Having established the spaces that describe the particles, we seek a distribution function that tells us statistical properties of the entire system. Consider dividing μ-space into i number of cells. The cells have volume element,

$$\Delta\tau_i = \Delta p_x \Delta p_y \Delta p_z \Delta x \Delta y \Delta z$$

We assume that a cell contains a large number of atoms but is infinitesimal on a macroscopic scale. From a macroscopic view, particles in the ith cell have the same energy ϵ_i.

Definition: The number of particles in cell i at time t; n_i, is called the *occupation number*.

Definition: The *distribution function*, $f(p,r,t)$, is defined as the occupation number per unit volume:

$$f(p,r,t) = \frac{n_i}{\Delta\tau}$$

$$\Rightarrow f(p,r,t)\Delta\tau = n_i \tag{2.5.1}$$

There is a total of N particles with total energy E. This gives constraints,

$$\sum_i n_i = N$$

$$\sum_i n_i \epsilon_i = E$$

Rewriting these in terms of f,

$$\sum_i f(p,r,t)\tau_i = N \tag{2.5.2}$$

$$\sum_i f(p,r,t)\tau_i \epsilon_i = E \tag{2.5.3}$$

In the thermodyamic limit, assume f is continuous and treat $\Delta\tau$ as an infinitesimal. That is,

$$\Delta\tau = \Delta p_x \Delta p_y \Delta p_z \Delta x \Delta y \Delta z \to d^3p \; d^3r$$

In this limit, equations (2.5.2), (2.5.3), become Riemann sums. They can be rewritten as,

$$\int d^3p \; d^3r \; f(p,r,t) = N \tag{2.5.4}$$

$$\int d^3p \; d^3r \; f(p,r,t)\frac{\mathbf{p}^2}{2m} = E \tag{2.5.5}$$

If the density is uniform, f is independent of $\mathbf{r}$. This gives,

$$\int d^3p \; f(p,t) = \frac{N}{V} \tag{2.5.6}$$

$$\int d^3p \; f(p,t)\frac{\mathbf{p}^2}{2m} = \frac{E}{V} \tag{2.5.7}$$

Thus, it is possible to find the state of a system once we know the distribution function.

Chapter 3

Ensembles

3.1 Entropy

Definition: The *entropy* of a system is defined to be $S = k \ln \Omega$ where Ω is the number of possible microstates corresponding to a given macrostate. The reason why we use logarithms is because for two systems with entropy S_1, S_2; the total entropy is $S_1 + S_2$. However, looking in terms of the microstates of the systems, Ω_1, Ω_2; the total number of microstates is $\Omega_1\Omega_2$. This is reconciled with logarithms.

Entropy can be thought of as a measure of information. For a macrostate with only one microstate(highly ordered), eg all particles are stationary, the entropy is a minimum. The macrostate with the most microstates available(disordered) has maximum entropy and is the most likely state.

If we talk about the probability of states, then the entropy can be defined by

$$S = -\sum_i k p_i \ln p_i$$

3.2 Statistical Ensembles

In the statistical treatment, we consider a suitable state of a system corresponding to our constraints. We group all these possible systems and then we average over the collection of systems called a *statistical ensemble* to get the value we want. This collection of systems is characterised by a density function $\rho(p,r,t)$ in Γ-space. From (2.5.1), this is defined as

$$\rho(p,r,t)dpdr = \text{Number of systems in } dpdr \text{ at time } t$$

where $(p,r) = (\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N; \mathbf{r}_1, \ldots, \mathbf{r}_N)$ and $dp\ dr = d^{3N}p\ d^{3N}r$ since this is $6N$-dimensional Γ-space.

The probability of finding the system in $dpdr$ at time t is

$$\tilde{P} = \frac{\rho(p,r,t)dpdr}{N} = \frac{\rho(p,r,t)dpdr}{\int \rho(p,r,t)dpdr}$$

This can also be expressed as a probability density (ie probability per unit phase-space volume),

$$P = \frac{\rho(p,r,t)}{\int \rho(p,r,t)dpdr}$$

The *ensemble average* of a physical quantity $O(p,r)$ is

$$< O >= \frac{\int \rho(p,r,t)O(p,r)dpdr}{\int \rho(p,r,t)dpdr}$$

Why? Consider the discrete case and apply the normal definition of the average. You should get a sum. Take the infinitesimal limit to turn it into an integral. At thermal equilibrium, these averages give us meaningful thermodynamic quantities. The density function should be time independent at equilibrium. Also, assume that $\rho(p,r) = \rho(H(p,r))$ ie the density function depends only on the Hamiltonian. This automatically makes it time independent.

We now consider different ensembles that characterise the system.

3.3 Microcanonical Ensemble

In the microcanonical ensemble, we assume the energy and particle number is constant. This corresponds to an isolated system. This can be characterised by a density function $\rho = \delta(H(p,q) - E)$. The total volume occupied by the ensemble is $\Omega = \int dpdq\delta(H(p,q) - E)$.

If you haven't understood most of the stuff I've talked about so far, here is a brief idea of what's happening next that doesn't rely too much on the things before.

To give a brief description of what's happening in this section, the system has total energy E. There are many ways to distribute this energy amongst N particles. Take all the particles with the same energy ϵ_i, say, and group them into a set i. Call the number of these particles n_i. Do this for every $\epsilon_1, \dots, \epsilon_k$ so that we have a distribution $\{n_1, \dots, n_k\}$. We find out the number of permutations that we can distribute N particles into different energies. The most probable distribution is the set of occupation numbers that maximises the entropy and corresponds to thermal equilibrium. We maximise the permutation with respect to the constraints E and N.

Given that there are N particles, there are Ω ways to distribute these particles into $\{n_i\}$. We choose degeneracy(?) of each level to be g_i. There are n_i particles so there is a factor of $(g_i)^{n_i}$. The number of permutations is

$$\Omega = N! \prod_i \frac{g_i^{n_i}}{n_i!}$$

The most probable distribution $\{\bar{n}_i\}$ is the set of occupation numbers that maximises the entropy and corresponds to thermal equilibrium. At maximum,

$$\delta\Omega = 0$$

But we can also consider maximising $\ln\Omega$ because

$$\delta(\ln\Omega) = \frac{1}{\Omega}\delta\Omega = 0$$

It is more convenient to maximise $\ln\Omega$. Plugging in Ω,

$$\ln\Omega = \ln N! \prod_i \frac{g_i^{n_i}}{n_i!} \approx N\ln N + \sum_i (n_i \ln\frac{g_i}{n_i})$$

$$\Rightarrow \delta(\ln\Omega) = \sum_i \ln\frac{g_i}{n_i}\delta n_i = 0$$

using Stirling's formula assuming N, n_i large. The constraints are

$$\sum_i n_i = N \tag{3.3.1}$$

$$\sum_i n_i\epsilon_i = E \tag{3.3.2}$$

This gives $\sum_i \delta n_i = 0$ and $\sum_i \epsilon_i\delta n_i = 0$.

At this point, take $g_i = 1$. Using Lagrangian Multipliers(read back on Simms' notes we took down in class or somewhere else or I might appendix this someday),

$$\delta(\ln\Omega + \alpha\sum_i n_i - \beta\sum_i \epsilon_i n_i) = 0$$

$$\left(\sum_i (\ln\frac{1}{n_i} + \alpha - \beta\epsilon_i)\right)\delta n_i = 0$$

δn_i is arbitrary so

$$\ln n_i = \alpha - \beta\epsilon_i$$

$$\Rightarrow n_i = Ce^{-\beta\epsilon_i}$$

where $C = e^{\alpha}$ which can be determined by plugging n_i back in to the constraints (3.3.1)(3.3.2). $C \sum e^{-\beta\epsilon_i} = N$ so $C = \frac{N}{\sum e^{-\beta\epsilon_i}}$. We call $\sum_i e^{-\beta\epsilon_i}$ the partition function Z. Hence,

$$n_i(\epsilon_i, \beta) = \frac{N}{Z} e^{-\beta\epsilon_i} \tag{3.3.3}$$

This is the Maxwell-Boltzmann distribution function. This function corresponds to the most probable macrostate. Later, it will be shown that $\beta = \frac{1}{kT}$. At fixed temperature and total particle number, this function tells us the number of particles that have energy ϵ_i ie. how the energy is distributed amongst the particles.

Chapter 4

Canonical Ensemble

In the canonical ensemble, the number of particles is constant but the energy can change. Consider a system of N particles. Let p_m be the probability that the system has energy E_m. We require the constriant that the system has an average energy,

$$\sum_m p_m E_m = \langle E \rangle \equiv E$$

Also require normalisation.

$$\sum_m p_m = 1$$

The entropy is $S = -\sum_m k p_m \ln p_m$. If we maximise the entropy subject to these constraints, we want to maximise the function

$$-\sum_m k p_m \ln p_m + \lambda \sum_m (p_m - 1) - \beta \sum_m (p_m E_m - E)$$

Taking the derivative $\frac{\partial}{\partial p_i}$ and setting to zero,

$$-k \ln p_i - k + \lambda - \beta E_i = 0$$

$$\begin{aligned} p_i &= e^{\lambda - k} e^{-\beta E_i} \\ &= C e^{-\beta E_i} \end{aligned}$$

To find C, we use the constraints.

$$\sum_i p_i = \sum_i C e^{-\beta E_i} = 1$$

$$\Rightarrow C = \frac{1}{\sum_i e^{-\beta E_i}}$$

Call

$$Z = \sum_i e^{-\beta E_i}$$

the partition function of the canonical ensemble.

Hence, the distribution of the canonical ensemble is

$$p_i = \frac{1}{Z} e^{-\beta E_i}$$

Although this has the same form as the microcanonical ensemble, this functino has a different meaning. It is the probability for the system to be in energy E_i whereas in the microcanonical ensemble, it's the number of particles with energy E_i.

4.1 Connection with Thermodynamics

Lets see how we get thermodynamics from this. If p_n is the probability of finding the system in some energy E_n, then we can find the average energy to be

$$\langle E \rangle = \sum_n p_n E_n = \frac{\sum_n E_n e^{-\beta E_n}}{Z}$$

Upon inspection, this can be written nicely as

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z \equiv U$$

Physically, the expectation value of the energy is the internal energy.

Consider now the variance in the energy.

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

If you expand these out, it turns out that you can write this nicely as

$$(\Delta E)^2 = \frac{\partial^2}{\partial \beta^2} \ln Z$$

But we know that the heat capacity is defined as $\frac{\partial U}{\partial T}$. Using $\beta = \frac{1}{kT}$,

$$(\Delta E)^2 = kT^2 C_v$$

This equation tells us the system's ability to absorb/dissipate energy is related to its energy fluctuations. Note that $E \sim N$ and $C_v \sim N$. Therefore, $\frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}}$. As $N \to \infty$ in the thermodynamic limit, the energy fluctuation goes to zero and the canonical and microcanonical ensembles coincide. Since the system we are normally looking at have large N, we can consider ourselves in the thermodynamic limit.

4.2 $\beta = \frac{1}{kT}$

This will finally be shown. Lets substitute the distribution into the entropy. We get

$$S = -k \sum_i \frac{1}{Z} e^{-\beta E_i} \ln\left(\frac{1}{Z} e^{-\beta E_i}\right)$$

$$= -k \sum_i \frac{1}{Z} e^{-\beta E_i} (-\beta E_i - \ln Z)$$

$$= k\beta U + k \ln Z$$

$$\Rightarrow U = \frac{1}{k\beta} S - \frac{1}{\beta} \ln Z$$

We connect this with the expression from thermodynamics,

$$U = TS + A$$

where A is the Helmohltz free energy. Therefore,

$$\beta = \frac{1}{kT}$$

And as a bonus,

$$A = -kT \ln Z$$

It is now possible to derive thermodynamic quantities from the Maxwell relations involving the free energy.

4.3 The Ideal Gas

For the ideal gas, the Hamiltonian is $H = \sum_i \frac{\mathbf{p}_i^2}{2m}$. Therefore, the partition function becomes

$$Z = \int \frac{d^{3N} p d^{3N} q}{N! h^{3N}} e^{-\beta(\sum_i \mathbf{p}_i^2/2m)}$$

where the $N!$ comes from correct Boltzmann counting(all particles are indistinguishable) and the h is some arbritrary constant to nondimensionalise Z. The integral is straightforward. It is just a Gaussian integral and gives,

$$Z = \frac{V^N}{N! h^{3N}} (2\pi m k T)^{3N/2}$$

Let $\lambda = \sqrt{\frac{h^2}{2\pi m k T}}$ be the thermal wavelength. Then,

$$Z = \frac{1}{N!} \left(\frac{V}{\lambda^3}\right)^N$$

Computing the Helmholtz Free Energy, $-kT\ln Z = A$,

$$A = -kT\ln\frac{1}{N!}\left(\frac{V}{\lambda^3}\right)^N$$

$$A = -kT(\ln(n\lambda^3) - 1)$$

where $n = \frac{N}{V}$ and Stirling's approximation has been used. The entropy can also be found using thermodynamic relation $S = -(\frac{\partial A}{\partial T})_V$,

$$S = -Nk(\ln(n\lambda^3) + \frac{T}{n\lambda^3}n(\frac{-3}{2})(\frac{h^2}{2\pi mkT})^{\frac{3}{2}}T^{-\frac{3}{2}} - 1$$

which simplifies nicely to

$$S = Nk[\frac{5}{2} - \ln(n\lambda^3)]$$

If we didn't have the original $\frac{1}{N!}$ Boltzmann factor in the partition function, we would get Gibb's Paradox. We need to use a semiclassical interpretation that all particles are indistinguishable.

Lets also use the thermodynamic relation, $P = -\frac{\partial A}{\partial V}$.

$$\Rightarrow PV = NkT$$

which is the familiar equation of state.

4.4 Equipartition of Energy

The average energy is

$$E = -\frac{\partial}{\partial\beta}\ln Z = \frac{3}{2}NkT$$

The 3 comes from the lambda $Z = \frac{1}{N!}\left(\frac{V}{\lambda^3}\right)$ which is directly related to the degrees of freedom that the particle has. Every degree of freedom contributes $\frac{1}{2}kT$ to the system. It is also easy to see that

$$C_V = \frac{\partial E}{\partial T}_V = \frac{3}{2}Nk$$

This shows that the heat capacity does not depend on temperature.

Chapter 5

Grand Canonical Ensemble

In the grand canonical ensemble, the system can exchange heat and particles. So our constraints are given by the average value of energy and particle number which are

$$\sum_j p_j E_j = E$$

$$\sum_j p_j N_j = N$$

where I am using E, N to denote the average. p_j is the probability to find the system in the jth state ie with energy E_j and particle number N_j. The probabilities are normalised.

$$\sum_j p_j = 1$$

The entropy is given as

$$S = -k \sum_j p_j \ln p_j$$

We want to maximise S. This is done with Lagrange multipliers and it works out to be

$$p_j = \frac{e^{-\beta E_j + \beta\mu N_j}}{\sum_j e^{-\beta E_j + \beta\mu N_j}}$$

where the Lagrange multipliers can be found from $TdS = dU + pdV - \mu dN$.

We define the partition function of the grand canonical ensemble to be

$$\mathcal{Z} = \sum_j e^{-\beta E_j + \beta\mu N_j} = \sum_N e^{\beta\mu N} Z(V, T, N_j) = \sum_N z^N Z(V, T, N_j)$$

$\mathcal{Z}$ may also be denoted $\mathcal{Q}$. I like the fancy Z so I'm sticking with this for now. We refer to z as the fugacity. The canonical partition function depends on N_j which is a particular number of particles for a given state. So the grand canonical partition function is a weighted sum of the canonical ensemble partition function.

5.1 Thermodynamics

Let us now connect this with thermodynamics. Firstly, the internal energy is the average energy.

$$\sum_j p_j E_j = E = U$$

$$U = \frac{\sum E_j z^j Z(V,T,N_j)}{\sum z^j Z(V,T,N_j)}$$

But $Z = \sum e^{-\beta E_j}$ so,

$$= -\frac{\frac{\partial}{\partial \beta}(\sum Z)}{\sum z^j Z} = -\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial \beta}$$

$$\Rightarrow U = -\frac{\partial}{\partial \beta}\ln \mathcal{Z}$$

The average number of particles is(which I will denote N, I should technically use $\bar{N}$ but more on that later)

$$N \equiv \langle N \rangle = \frac{\sum_N N e^{\beta\mu N} Z}{\sum e^{\beta\mu N} Z} = \frac{1}{\beta \mathcal{Z}}\frac{\partial}{\partial \mu}(\sum e^{\beta\mu N} Z)$$

$$= \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln \mathcal{Z}$$

Noting that $\frac{\partial}{\partial \mu} = \frac{\partial z}{\partial \mu}\frac{\partial}{\partial z} = \beta z \frac{\partial}{\partial z}$,

$$N = z\frac{\partial}{\partial z}\ln \mathcal{Z}$$

We can also find what the variance in the particle number is.

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

This works out nicely to be

$$(\Delta N)^2 = z\frac{\partial}{\partial z} z\frac{\partial}{\partial z}\ln \mathcal{Z}$$

$$= (kT)^2 \frac{\partial^2}{\partial \mu^2}\ln \mathcal{Z}$$

Dividing by V^2 gives the number density fluctuation,

$$(\Delta n)^2 = \frac{(kT)^2}{V^2}\frac{\partial^2}{\partial \mu^2}\ln \mathcal{Z}$$

We see that $\frac{\Delta N}{\langle N \rangle} \sim \frac{1}{\sqrt{\langle N \rangle}}$. Therefore, for $N \to \infty$, the number fluctuations go to zero. The three ensembles coincide in the thermodynamic of infinite volume and infinite particle number. This is why I don't bother with writing $\bar{N}$ and denote it N.

5.2 Grand Canonical Potential

In the canonical ensemble, we were able to connect the Helmholtz Potential with the partition function. It is also possible to do it with the grand canonical partition function. Define the grand canonical potential to be,

$$\Phi = E - TS - \mu N$$

Recalling the Helmoltz Free Energy,

$$\Phi = A - \mu N$$

The grand canonical partition function in terms of the Helmholtz free energy is,

$$\mathcal{Z} = \sum_N e^{\beta\mu N} e^{-\beta A}$$

This suggests that

$$\Phi = -kT \ln \mathcal{Z}$$

This connects the potential with the grand canonical partition function. From the thermodynamic definition,

$$d\Phi = -SdT - PdV - Nd\mu$$

We can then derive thermodynamic relations from this. One of them is

$$(\frac{\partial \Phi}{\partial V})_{T,\mu} = -P$$

5.3 The Ideal Gas

Consider an ideal gas with Hamiltonian $H = \sum_i \frac{\mathbf{p}_i^2}{2m}$. The partition function looks like

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{1}{N!} \int \frac{d^{3N}pd^{3N}p}{h^{3N}} e^{-\beta \frac{\sum \mathbf{p}_i^2}{2m}}$$

$$= \sum_{N=0}^{\infty} \frac{1}{N!} e^{\beta\mu N} \left(\frac{V^N}{\lambda^{3N}} \right)$$

where $\lambda = \sqrt{\frac{h^2}{2\pi mkT}}$.

$$= \sum_{N=0}^{\infty} \frac{1}{N!} \left(e^{\beta\mu} \frac{V}{\lambda^3} \right)^N$$

This is just the definition of the exponential function so we get,

$$\mathcal{Z} = \exp(e^{\beta\mu} \frac{V}{\lambda^3})$$

The average particle number is

$$N = \frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\mathcal{Z} = \frac{e^{\beta\mu}V}{\lambda^3}$$

This gives an expression for the chemical potential.

$$\mu = kT\ln(\frac{\lambda^3 N}{V})$$

Now take the grand canonical potential,

$$\Phi = -kT\ln\mathcal{Z} = -kTe^{\beta\mu}\frac{V}{\lambda^3}$$

The pressure is

$$P = -(\frac{\partial\Phi}{\partial V})_{T,\mu}$$

$$P = kT\frac{e^{\beta\mu}}{\lambda^3}$$

$$P = kTN\frac{\lambda^3}{V\lambda^3}$$

from the expression for the chemical potential.

$$\Rightarrow PV = NkT$$

which is the familiar equation of state.

Chapter 6

An Interacting Gas

So far, we have only considered an ideal gas in which the particles do not interact. The ideal gas is a good starting point as an approximation to the interacting gas. We expect that when the interactions become negligible, the ideal gas equation holds. Therefore, we consider the ideal gas equation and look at how we can correct it for an interacting gas. The most general equation of state is the *virial expansion*

$$\frac{P}{kT} = \frac{N}{V} + B_2(T)(\frac{N}{V})^2 + B_3(T)(\frac{N}{V})^3 + \dots$$

$B_i(T)$ are known as the virial coefficients.

We want to find a suitable potential that models the forces between the particles. The potential should consist of an attractive term that arises from the induced dipoles of the particles and a repulsive term that arises from Fermi repulsion. One possible potential is the Lennard-Jones potential which looks like

$$U(r) \sim (\frac{r_0}{r})^{12} - (\frac{r_0}{r})^6$$

For small r, the repulsive potential dominates and for large r, the attractive potential dominates and the potential goes to zero for $r \to \infty$.

However, although this is a nice model, it is not easy to compute. We replace it with a simplified potential that looks like

$$U(r) = \begin{cases} \infty & \text{if } r < r_0 \\ -U_0(\frac{r_0}{r})^6 & \text{if } r > r_0 \end{cases}$$

6.1 Computing the Partition Function

Then the Hamiltonian of the system is

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i>j} U(r_{ij})$$

Inserting into the partition function,

$$Z(N,V,T) = \frac{1}{N!h^{3N}} \int d^{3N}p \; d^{3N}r \; e^{-\beta H}$$

$$= \frac{1}{N!h^{3N}} \int d^{3N}p \; e^{-\beta p_i^2/2m} \int d^{3N}r \; e^{-\beta \sum_{i>j} U(r_{ij})}$$

The momentum integral has been done before and is just a Gaussian.

$$= \frac{1}{N!\lambda^{3N}} \int d^{3N}r \; e^{-\beta \sum_{i>j} U(r_{ij})}$$

The second integral is not as easy. We could try Taylor expanding but this doesn't work since as $r_{ij} \to 0$, $U(r_{ij}) \to \infty$ so this would not converge. Instead, define

$$f(r) = e^{-\beta U(r)} - 1$$

which is known as the *Mayer f function.* We denote $f_{ij} = f(r_{ij})$.

Then taking the arithmetic sum out of the exponential to give a geometric sum and replacing with f,

$$Z = \frac{1}{N!\lambda^{3N}} \int d^{3N}r \prod_{j>k} (1 + f_{jk})$$

$$= \frac{1}{N!\lambda^{3N}} \int d^{3N}r (1 + \sum_{j>k} f_{jk} + \sum_{j>k} \sum_{l>m} f_{jk} f_{lm} + \dots)$$

The first integral gives V^N. Ignoring quadratic terms, the second term works out such that the partition function looks like,

$$Z = \frac{V^N}{N!\lambda^{3N}} (1 + \frac{N}{2V} \int d^3r \; f(r) + \dots)^N$$

The Helmholtz free energy is,

$$A = -kT \ln Z = -kT \ln \frac{V^N}{N!\lambda^{3N}} - NkT \ln(1 + \frac{N}{2V} \int d^3r f)$$

Now we want to find out how to integrate the f function. Using the potential mentioned above,

$$\int d^3r \; f(r) = \int_0^{r_0} d^3r(-1) + \int_{r_0}^{\infty} d^3r (e^{\beta U_0 (r_0/r)^6} - 1)$$

We assume $\beta \ll 1$ for high temperature. Then we can Taylor expand and this gives,

$$\int d^3r \ f(r) = \frac{4\pi r_0^3}{3}(\frac{U_0}{kT} - 1)$$

Using the thermodynamic relations,

$$\frac{PV}{NkT} = 1 - \frac{N}{V}(\frac{a}{kT} - b)$$

where $a = \frac{2\pi r_0^3 U_0}{3}$ and $b = \frac{2\pi r_0^3}{3}$.

This can be rewritten in the form,

$$(P + \frac{N^2}{V^2}a)(\frac{V}{N} - b) = kT$$

which is the Van Der Waals equation of state!

6.2 Cluster Expansion

In deriving the Van Der Waals eos, higher order terms were neglected. It is possible to compute the higher order terms to get the correction terms. This will not be done.

Chapter 7

Magnetism

Consider N fixed magnetic dipoles with magnetic moment μ. Let B be an external magnetic field. Then the interaction Hamiltonian is,

$$H = -\sum_{l=1}^{N} \mu_l \cdot \mathbf{B}$$

$$= -\mu B \sum_{l=1}^{N} \cos\theta_l$$

We choose our coordinate system so the z-axis aligns with the magnetic field.

The partition function looks like

$$Z = \prod_{i=1}^{N} \int_0^{\pi} d\theta_i \int_0^{2\pi} d\phi_i \; e^{-\beta\mu B\cos\theta_i}$$

(Not too sure about this yet. Think it has something to do with integrating over all possible dipole directions.)

This integrates to,

$$Z = \left(4\pi \frac{\sinh(\beta\mu B)}{\beta\mu B}\right)^N$$

The magnetisation is the expectation value of the z component.

$$\langle \mu_z \rangle = \frac{1}{Z}\mu\cos\theta_i \int_0^{\pi} d\theta_i \int_0^{2\pi} d\phi_i \; e^{-\beta\mu B\cos\theta_i}$$

It might be possible to compute this but this is tedious so recognise that we can rewrite this as,

$$\langle \mu_z \rangle = \frac{1}{ZB}\frac{\partial}{\partial\beta}Z$$

Recall the Z computed earlier. The magnetisation is the total magnetisation of N particles,

$$M_z = N\langle \mu_z \rangle = N\mu\mathcal{L}(\beta\mu B)$$

where $\mathcal{L}$ is the Langevin function. For the high temperature limit, Taylor expanding and ignoring higher order terms gives

$$M_z = \frac{N\mu^2}{3kT}B$$

This is the Curie Law.

I'll probably go into more detail when I do quantum stat mech.

Chapter 8

Quantum Statistical Mechanics

We now move into a quantum framework. In classical mechanics, the microstates are described by momentum and position and in quantum mechanics, the microstates are described by wavefunctions. Consider a system with N particles. Each particle is described by a wavefunction ψ_a, $a = 1, \ldots, N$. Observables correspond to a Hermitian operator O. The expectation value of O in state $|\psi_a\rangle$ is,

$$\langle O\rangle_a = \langle\psi_a|O|\psi_a\rangle$$

Define the average expectation value to be,

$$\begin{aligned}\langle O\rangle &= \frac{1}{N}\sum_{a=1}^{N}\langle\psi_a|O|\psi_a\rangle \\ &\equiv \langle\psi|O|\psi\rangle\end{aligned}$$

Now consider an orthonormal basis of the Hilbert space $\{|\phi_n\rangle\}_{n=1,2,\ldots}$. We can express the states as a linear combination.

$$|\psi_a\rangle = \sum_{n=1}^{\infty} c_n^a|\phi_a\rangle$$

This gives,

$$\langle\psi|O|\psi\rangle = \frac{1}{N}\sum_{a=1}^{N}\sum_{n,m} c_n^{a*}c_m^a\langle\phi_n|O|\phi_m\rangle$$

Define $\rho_{mn} = \frac{1}{N}\sum_a c_n^{a*}c_m^a$ and $O_{nm} = \langle\phi_n|O|\phi_m\rangle$. Then,

$$\langle O\rangle = \sum_{n,m}\rho_{mn}O_{nm}$$

ρ_{mn} can be interpreted as matrix elements of an operator ρ such that $\rho_{mn} = \langle\phi_m|\rho|\phi_n\rangle$. ρ is called the density operator/matrix.

ρ is equivalent to $\rho = \sum |\psi_a\rangle\langle\psi_a|$ where p_a can be thought of as the probability for the system to be in th. This can be seen by getting the matrix elements of ρ,

$$\langle\phi_m|\rho|\phi_n\rangle = \sum\langle\phi_m|\psi_a\rangle\langle\psi_a|\phi_n\rangle = \sum c_m^a c_n^{a*}$$

Expressing in terms of a basis, it will look like

$$\rho = \sum_a \sum_{n,m} c_n^{a*} c_m^a |\phi_m\rangle\langle\phi_n| = \sum_a \sum_n |c_n^a|^2 |\phi_n\rangle\langle\phi_n| = \sum p_n |\phi_n\rangle\langle\phi_n|$$

(that may be slightly wrong, if it is just take the last bit as a definition) Interpret p_n as the probability to be in the state ϕ_n.

Finally,

$$\begin{aligned}\langle O\rangle &= \sum_{n,m}\langle\phi_m|\rho|\phi_n\rangle\langle\phi_n|O|\phi_m\rangle \\ &= \sum_m \langle\phi_m|\rho O|\phi_m\rangle \\ &= \mathrm{Tr}(\rho O)\end{aligned}$$

Properties of ρ

1. $\mathrm{Tr}\rho = 1$
2. $\rho = \rho^\dagger$
3. $\rho \geq 0$

The proof will be left as an exercise for the reader. (I've always wanted to do that) They're pretty trivial anyway.

8.1 Time Evolution of the Density Operator

Choose an orthonormal basis $\{\phi_n\}$ that are eigenfunctions of the Hamiltonian of our system. Then we have,

$$H\phi_n = E_n\phi_n$$

Our wavefunction can be expressed in terms of the basis as

$$\psi_a(t) = \sum_n c_n^a(t)\phi_n$$

Then the time dependent Schrodinger equation is,

$$i\hbar\frac{\partial}{\partial t}\psi_a(t) = H\psi_a(t)$$

Putting in $\psi_a(t)$ in terms of the basis,

$$\sum_n i\hbar\dot{c}_n^a(t)\phi_n = \sum_n i\hbar c_n^a(t)H\phi_n$$

$$\sum_n i\hbar\dot{c}_n^a(t)\phi_n = \sum_n i\hbar c_n^a(t)E_n\phi_n$$

We project out the kth component by taking $(\phi_k, \cdot)$.

$$i\hbar\dot{c}_k^a(t) = E_k c_k^a(t)$$

and the complex conjugate is

$$-i\hbar\dot{c}_k^{a*}(t) = E_k c_k^{a*}(t)$$

Now lets consider the derivative of the density matrix.

$$\rho_{mn} = \frac{1}{N}\sum_a c_n^{a*}c_m^a$$

$$\Rightarrow i\hbar\dot{\rho}_{mn} = i\hbar\frac{1}{N}\sum_a [\dot{c}_n^{a*}c_m^a + c_n^{a*}\dot{c}_m^a]$$

We computed the values for $\dot{c}$ above. This gives,

$$i\hbar\dot{\rho}_{mn} = \frac{1}{N}\sum_a [-E_n c_n^{a*}c_m^a + E_m c_n^{a*}c_m^a]$$

$$= (E_m - E_n)\frac{1}{N}\sum_a c_n^{a*}c_m^a$$

$$= (E_m - E_n)\rho_{mn}$$

Denoting $\rho_{mn} = (\phi_m, \rho\phi_n)$ to be the matrix element,

$$\Rightarrow i\hbar(\phi_m, \dot{\rho}\phi_n) = (E_m - E_n)(\phi_m, \rho\phi_n)$$

$$= (E_m\phi_m, \rho\phi_n) - (\phi_m, \rho E_n\phi_n)$$

$$= (H\phi_m, \rho\phi_n) - (\phi_m, \rho H\phi_n)$$

$$= (\phi_m, H\rho\phi_n) - (\phi_m, \rho H\phi_n)$$

$$= (\phi_m, [H, \rho]\phi_n)$$

Since this holds for arbitrary basis and m, n,

$$ih\dot{\rho} = [H, \rho]$$

This is a very important result. What this says that if we want $\langle O\rangle$ to be time independent at equilibrium, then ρ must also be time independent since $\langle O\rangle = \mathrm{Tr}(\rho O)$. Therefore, $[H, \rho] = 0$.

8.2 Partition Functions

We want to find expressions for ρ in our ensembles. Recall the derivations for the canonical ensemble. When we were deriving the probability for the system to be in the E_nth state, we did not use classical mechanics so the derivation should also work for quantum mechanics. Therefore, the probability to be in the E_nth state is,

$$p_n = \frac{1}{Z} e^{-\beta E_n}$$

But we have from earlier,

$$\rho = \sum p_n |\phi_n\rangle\langle\phi_n|$$

$$\Rightarrow \rho = \frac{1}{Z} \sum e^{-\beta E_n} |\phi_n\rangle\langle\phi_n|$$

$$\rho = \frac{1}{Z} \sum e^{-\beta H} |\phi_n\rangle\langle\phi_n|$$

Since ϕ_n is complete,

$$\rho = \frac{e^{-\beta H}}{\text{Tr } e^{-\beta H}}$$

Similarly, the density operator looks like

$$\rho = \frac{e^{-(\beta H - \mu \hat{N})}}{\text{Tr } (e^{-(\beta H - \mu \hat{N})})}$$

where $\hat{N}$ is the particle number operator and denote $\mathcal{Q} = \text{Tr } (e^{-(\beta H - \mu \hat{N})})$. Also the fugacity is given by $z = e^{\beta \mu}$.

Since we have the expectation of an operator to be $\langle O \rangle = \text{Tr}(\rho O)$, in the canonical ensemble,

$$\langle O \rangle = \frac{1}{Z} \text{Tr}(O e^{-\beta H})$$

For the internal energy, this is,

$$U = \langle H \rangle = \frac{1}{Z} \text{Tr}(H e^{-\beta H})$$

$$= \frac{1}{Z} (-\frac{\partial}{\partial \beta}) \text{Tr}(H e^{-\beta H})$$

$$= \frac{1}{Z} (-\frac{\partial}{\partial \beta}) Z = -\frac{\partial}{\partial \beta} \ln Z$$

The free energy is identified by

$$F = -kT \ln Z$$

And thermodynamics falls from the usual thermodynamic relations like $P = -\frac{\partial F}{\partial V}$.

In the grand canonical ensemble, we have

$$\langle \hat{N} \rangle = \bar{N} = z \frac{\partial}{\partial z} \ln Q$$

$$F = \bar{N}\mu - kT \ln Q$$

$$PV = kT \ln Q$$

The grand canonical potential is

$$\Omega = -kT \ln Q$$

So nothing too special and pretty similar to the classical case. Most of the things derived above in the classical case can be applied here like how the energy and number fluctuations are negligible in the thermodynamic limit.

Chapter 9

Identical Particles

There are two types of particles, bosons and fermions which are either symmetric or antisymmetric under particle exchange. This gives rise to the Pauli exclusion principle for fermions. Let us define the occupation number n_i to be the number of particles in the system to be in the ith state where this state contains all of the particles properties like momentum, position and spin. While I use i to denote a state that has complete information, at times I may switch to denote a state by $\mathbf{p}, \lambda$ where λ is the polarisation state eg spin. We have

$$n_i = \begin{cases} 0, 1 & \text{for fermions} \\ 0, 1, 2, \dots & \text{for bosons} \end{cases}$$

We then have a set of occupation numbers of a system $\{n_i\}$. Also, there is a constraint that the sum is the total number of particles in the system.

$$\sum_i n_i = N$$

And if ϵ_i is the energy of the ith state, then the total energy must be the total sum,

$$\sum_i n_i \epsilon_i = E$$

Now consider the grand canonical partition function,

$$\mathcal{Q} = \sum_N z^N Z_N = \sum_N \sum_{n_i} z^N e^{-\beta \sum \epsilon_i n_i}$$

$$\sum_{n_i} \prod_i (ze^{-\beta\epsilon_i})^{n_i} = \prod_i \sum_{n_i} (ze^{-\beta\epsilon_i})^{n_i}$$

9.1 Bose-Einstein Distribution

For bosons, $n_i = 0, 1, 2, \ldots$. Using $\sum_{n=1}^{\infty} x^n = \frac{1}{1-x}$,

$$\mathcal{Q} = \prod_i \frac{1}{1 - ze^{-\beta\epsilon_i}}$$

This only converges of course if $|ze^{-\beta\epsilon_i}| < 1$ which is valid but lets not get into the physics of that.

Having computed the partition function, we can get,

$$\frac{PV}{kT} = \ln Q$$

$$= -\sum_i \ln(1 - ze^{-\beta\epsilon_i})$$

The average particle number is

$$\bar{N} = z\frac{\partial}{\partial z}\ln Q$$

$$= \sum_i \frac{ze^{-\beta\epsilon_i}}{1 - ze^{-\beta\epsilon_i}}$$

$$= \sum_i \frac{1}{z^{-1}e^{\beta\epsilon_i} - 1}$$

9.2 Fermi-Dirac Distribution

For fermions, $n_i = 0, 1$.

$$\Rightarrow \mathcal{Q} = \prod_i (1 + ze^{-\beta\epsilon_i})$$

Then we find that,

$$\frac{PV}{kT} = \ln Q = \sum_i \ln(1 + ze^{-\beta\epsilon_i})$$

The average particle number is

$$\bar{N} = z\frac{\partial}{\partial z}\ln Q = \sum_i \frac{1}{z^{-1}e^{\beta\epsilon_i} + 1}$$

9.3 Expected Occupation Numbers

Consider the expectation value of the occupation number.

$$\langle \hat{n}_i \rangle = \mathrm{Tr}(\rho \hat{n}_i) = \sum \frac{z^N}{Q} \mathrm{Tr}_N(\hat{n}_i e^{-\beta H_N})$$

Using $H_N = \sum_i \hat{n}_i \epsilon_i$,

$$\frac{\partial H_N}{\partial \epsilon_i} = \hat{n}_i$$

Therefore,

$$\begin{aligned}
\langle \hat{n}_i \rangle &= \frac{1}{Q} \sum_N z^N (-\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \mathrm{Tr}_N(e^{-\beta H_N})) \\
&= \frac{-1}{\beta Q} \frac{\partial}{\partial \epsilon_i} Q \\
&= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_i} \ln Q \\
&= \frac{1}{z^{-1} e^{\beta \epsilon_i} \mp 1}
\end{aligned}$$

Therefore,

$$\bar{N} = \sum_i \langle \hat{n}_i \rangle$$

The average total number of particles is just the sum of the average occupation numbers which of course makes sense.

To summarise, we call

$$\langle \hat{n}_i \rangle = \frac{1}{z^{-1} e^{\beta \epsilon_i} \mp +1}$$

the Bose-Einstein/Fermi-Dirac distribution function. It tells us the average number of particles that occupy the state i.

Chapter 10

Ideal Quantum Gas

10.1 Density of States

Consider an ideal gas in a cubic box with volume $V = L^3$. Due to the boundary conditions, the momenta must satisfy,

$$\mathbf{p} = \hbar\frac{2\pi\mathbf{n}}{L}$$

$$\Rightarrow \Delta p_i = \hbar\frac{2\pi}{L}$$

Suppose now we have a distribution function $f(\mathbf{p})$. Taking the large volume limit $V \to \infty$,

$$\Delta p_x \Delta p_y \Delta p_z \sum_{\mathbf{p}} f(\mathbf{p}) \to \int d^3\mathbf{p} f(\mathbf{p})$$

since the LHS becomes a Riemann sum in the limit.

$$\sum_{\mathbf{p}} f(\mathbf{p}) \to (\Delta p_x \Delta p_y \Delta p_z)^{-1} \int d^3\mathbf{p} f(\mathbf{p})$$

$$\sum_{\mathbf{p}} f(\mathbf{p}) \to \frac{V}{h^3} \int d^3\mathbf{p} f(\mathbf{p})$$

To change this to an integral over the magnitude of p, use spherical coordinates and integrate over all angles to get a factor of 4π,

$$\frac{4\pi V}{h^3} \int_0^\infty dp\ p^2 f(p)$$

It is often more useful to integrate over the energies. Use the fact that $\sqrt{2m\epsilon} = p$. Then we get,

$$\frac{2\pi V}{h^3}(2m)^{\frac{3}{2}} \int_0^\infty d^3\epsilon\ \epsilon^{\frac{1}{2}} f$$

The quantity $g(\epsilon) \equiv \frac{2\pi V}{h^3}(2m)^{\frac{3}{2}}\epsilon^{\frac{1}{2}}$ is refered to as the *density of states.* The quantity $g(\epsilon)d\epsilon$ measures the number of states within energy $\epsilon, \epsilon + d\epsilon$.

Lets find the equation of state. This is given by, (upper for bosons, lower for fermions)

$$\frac{PV}{kT} = \ln \mathcal{Q}(z, \mathbf{p}, V) = \frac{V}{h^3}\int d^3\mathbf{p} \sum_{\mathbf{p}} [\mp \ln(1 \mp ze^{-\beta\epsilon_{\mathbf{p}}})]$$

$$= \frac{V}{h^3} n_{pol} 4\pi \int_0^\infty p^2 dp (\mp \ln(1 \mp ze^{-\beta\epsilon_{\mathbf{p}}}))$$

where n_{pol} is the number of polarisation states(such as spin). This is due to degeneracy that may arise. It's very important for fermions since only one fermion can occupy one state. I began denoting this n_{pol} since that is how Sint denotes it. However, I should've used a g as it is the degeneracy factor that appeared in classical physics.

Sticking in our density of states stuff,

$$= \mp\frac{2\pi}{h^3}(2m)^{3/2} n_{pol} \int_0^\infty d\epsilon \ \epsilon^{1/2} \ln(1 \mp ze^{-\beta\epsilon})$$

Integrating by parts gives

$$P = \frac{2}{3} n_{pol} \frac{2\pi}{h^3}(2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}}{z^{-1} \mp 1} \tag{10.1.1}$$

Similarly, since the expression for the average particle number from above is,

$$N = \sum \frac{1}{z^{-1}e^{\beta\epsilon \mp 1}}$$

Changing this to an integral and working it out gives,

$$\frac{N}{V} = n_{pol} \frac{2\pi}{h^3}(2m)^{3/2} \int_0^\infty d\epsilon \ \frac{\epsilon^{1/2}}{z^{-1}e^{\beta\epsilon} \mp 1} \tag{10.1.2}$$

Finally, lets compute the internal energy.

$$U = -\frac{\partial}{\partial\beta} \ln \mathcal{Q}$$

We have

$$\ln \mathcal{Q} = \mp n_{pol} V \frac{2\pi}{h^3}(2m)^{3/2} \int_0^\infty d\epsilon \ \epsilon^{1/2} \ln(1 \mp ze^{-\beta\epsilon})$$

So

$$U = n_{pol} V \frac{2\pi}{h^3}(2m)^{3/2} \int_0^\infty d\epsilon \frac{\epsilon^{3/2}}{z^{-1}e^{\beta\epsilon \mp 1}}$$

$$U = \frac{3}{2} PV \tag{10.1.3}$$

This is a result that can also be computed classically.

Chapter 11

Fermi Gas

So far we have some general expressions for both distributions. Lets now examine the Fermi-Dirac distribution. Examples of Fermi gases are electrons in a metal. Recall the thermal wavelength,

$$\lambda^3 = (\frac{h^2}{2\pi mkT})^{3/2}$$

In the classical framework, this was a mysterious quantity that didn't really have any meaning. In quantum mechanics, we can interpret this as the spatial extent of the particles' wavefunction. For large interatomic spacing, quantum effects are negligible but when the wavefunctions start overlapping, we can no longer neglect them. Approximate the volume one particle occupies by $\frac{V}{N}$. Then the average interatomic spacing is $(\frac{V}{N})^{1/3}$. If the average interatomic spacing is greater than the thermal wavelength, ie,

$$\frac{V}{N\lambda^3} \gg 1$$

we can neglect quantum effects. On the other hand, this means quantum effects are apparent when,

$$\frac{V}{N\lambda^3} < 1$$

which happens for low temperature or high density.

For a Fermi-Dirac system, we have from equation (10.1.2)

$$\frac{N}{V} = n_{pol}\frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty d\epsilon\ \frac{\epsilon^{1/2}}{z^{-1}e^{\beta\epsilon}+1}$$

$$= n_{pol}\frac{2\pi}{\lambda^3(2\pi mkT)^{3/2}}(2m)^{3/2}\int_0^\infty d\epsilon\ \frac{\epsilon^{1/2}}{z^{-1}e^{\beta\epsilon}+1}$$

To solve this integral, change variable $x = \beta\epsilon$ so $dx = \beta d\epsilon$.

$$\frac{N}{V} = n_{pol}\frac{2\pi}{\lambda^3(\pi)^{3/2}}\beta^{3/2}\int_0^\infty \frac{dx}{\beta^{3/2}}\frac{x^{1/2}}{z^{-1}e^x+1}$$
$$= n_{pol}\frac{2}{\sqrt{pi}}\lambda^{-3}\int_0^\infty dx x^{1/2} z e^{-x}\frac{1}{1+ze^{-x}}$$

Expand in powers of z assuming that $|ze^{-x}| < 1$,

$$\frac{N}{V} = n_{pol}\frac{2}{\sqrt{pi}}\lambda^{-3}\int_0^\infty dx\ x^{1/2} z e^{-x}\sum_{k=0}^{\infty}(-z)^k e^{-kx}$$

Recall the definition of the gamma function, $\Gamma(n) = \int_0^\infty dt\ t^{n-1}e^{-t}$. We define,

$$f_n(z) = \frac{1}{\Gamma(n)}\int_0^\infty \frac{x^{n-1}dx}{z^{-1}e^x+1}$$

It can be shown that,

$$\frac{1}{\Gamma(n)}\int_0^\infty \frac{x^{n-1}dx}{z^{-1}e^x+1} = \sum_{k=1}^{\infty}(-1)^{k-1}\frac{z^k}{k^n}$$

Therefore, using the fact that $\Gamma(\frac{3}{2}) = \frac{\pi}{2}$,

$$\frac{N}{V} = n_{pol}\lambda^{-3}f_{3/2}(z)$$

Now equation (10.1.1) can be analysed in the same way to give

$$\frac{PV}{kT} = n_{pol}\frac{V}{\lambda^{-3}}f_{5/2}(z)$$

We can obtain an equation of state then from the two expressions.

$$\frac{PV}{NkT} = \frac{f_{5/2}(z)}{f_{3/2}(z)} = \frac{\sum_{k=1}^{\infty}(-1)^{k-1}\frac{z^k}{k^{5/2}}}{\sum_{k=1}^{\infty}(-1)^{k-1}\frac{z^k}{k^{3/2}}}$$
$$= \frac{-(-z+\frac{z^2}{2^{5/2}}-\frac{z^3}{3^{5/2}}+\mathcal{O}(z^3))}{-(-z+\frac{z^2}{2^{3/2}}-\frac{z^3}{3^{3/2}}+\mathcal{O}(z^3))}$$
$$= 1-(\frac{1}{2^{5/2}}-\frac{1}{2^{3/2}})z+\mathcal{O}(z^2)$$

Denote

$$t \equiv \frac{N\lambda^3}{Vn_{pol}} = f_{3/2}(z)$$

Writing out f explicitly gives,

$$t = f_{3/2}(z) = \sum_{k=1}^{\infty}(-1)^{k-1}\frac{z^k}{k^{3/2}} = z - \frac{z^3}{2^{3/2}} + \mathcal{O}(z^3)$$

We want z in terms of powers of t. Use an ansatz $z = z_1 t + z_2 t^2 + \mathcal{O}(t^3)$,

$$t = [z_1 t + z_2 t^2 + \mathcal{O}(t^3)] - [\frac{1}{2^3/2}(z_1 t + z_2 t^2 + \mathcal{O}(t^3))^2] + \mathcal{O}(z^3)$$

We equate the coefficients on the LHS and RHS to find $z_1, z_2, \ldots$. This gives,

$$z = t + \frac{1}{2^{3/2}}t^2 + \mathcal{O}(t^3)$$

Plugging in $\frac{PV}{NkT}$ gives,

$$\frac{PV}{NkT} = 1 + (\frac{1}{2^{3/2}} - \frac{1}{2^{5/2}})t + \mathcal{O}(t^2)$$

Recalling that $t \equiv \frac{N\lambda^3}{Vn_{pol}}$,

$$\frac{PV}{NkT} = 1 + \frac{1}{4\sqrt{2}n_{pol}}\frac{N\lambda^3}{V} + \mathcal{O}(t^2)$$

Also, note that since $t \equiv \frac{N\lambda^3}{Vn_{pol}}$ which is related to the conditions for noticeable quantum effects, we see that for small t, we get the classical limit. Also, the correction to the classical ideal gas is positive. This means the pressure due to the fermionic nature of particles is larger.

11.1 Fermi Gas at Zero Temperature

It has been shown that a Fermi Gas at high temperature is just a classical ideal gas and quantum effects are negligible. Lets examine the properties when $T \to 0$.

Consider the Fermi-Dirac distribution,

$$\langle n_i \rangle = \frac{1}{e^{\beta(\epsilon-\mu)} + 1}$$

When $T \to 0$, $\beta \to \infty$. Hence,

$$\lim_{\beta\to\infty}\frac{1}{e^{\beta(\epsilon-\mu)} + 1} = \begin{cases} 0 & \text{if } \epsilon > \mu \\ 1 & \text{if } \epsilon < \mu \end{cases}$$

$$= \theta(\mu - \epsilon)$$

where θ is the Heaviside step function. Then,

$$\frac{N}{V} = n_{pol}\frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty d\epsilon\ \epsilon^{1/2}\theta(\mu - \epsilon)$$

$$= n_{pol}\frac{2\pi}{h^3}(2m)^{3/2}\int_0^\mu d\epsilon\ \epsilon^{1/2}$$

$$= n_{pol}\frac{2\pi}{h^3}(2m)^{3/2}\frac{2}{3}\mu^{3/2}$$

We also have for the pressure,

$$P = \frac{2}{3}n_{pol}\frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty d\epsilon\ \epsilon^{3/2}\theta(\mu - \epsilon)$$

$$P = \frac{2}{3}n_{pol}\frac{2\pi}{h^3}(2m)^{3/2}\frac{2}{5}\mu^{5/2}$$

Dividing two expressions gives,

$$PV = \frac{2}{5}N\mu$$

Eliminate μ to get,

$$PV = \frac{2}{5}N\left[\frac{2}{3}n_{pol}\frac{2\pi}{h^3}(2m)^{3/2}\frac{V}{N}\right]^{-2/3}$$

$$\Rightarrow PV^{5/3} = \frac{2h^2N^{-5/3}}{10m}\left(\frac{4\pi}{3}n_{pol}\right)^{-2/3}$$

This is the equation of state for $T = 0$. What it shows it that pressure does not vanish at $T = 0$.

We also see that

$$\mu \sim N^{2/3}$$

This means that the chemical potential can be quite large at $T = 0$. Since the particles we are dealing with are fermions, only one particle can fill one state. Define $\mu(T = 0) \equiv \epsilon_F$ to be the Fermi energy which is the energy of the highest occupied state at $T = 0$. It also means that it is the minimal energy of any new particle that is added to the system.

11.2 Fermi Gas near Zero Temperature

We have examined the properties of a Fermi gas at zero temperature. We now want to find how it behaves near zero. This can be done by Taylor expanding our integrals. Lets obtain a general form. Consider the integral of some function along with the Fermi-Dirac distribution,

$$I(\mu) = \int_0^\infty \frac{f(\epsilon)}{e^{\beta(\epsilon-\mu)}+1} d\epsilon$$

Splitting integrals, Taylor expanding and doing some generally tricky manipulation gives,

$$I(\mu) = \int_0^\mu d\epsilon f(\epsilon) + \frac{2}{\beta^2}\frac{\pi^2}{12} f'(\mu) + \mathcal{O}(\beta^{-4})$$

Lets get

$$\frac{N}{V} = n_{pol}\frac{2\pi}{h^3}(2m)^{3/2}\int_0^\infty d\epsilon \ \frac{\epsilon^{1/2}}{z^{-1}e^{\beta\epsilon}+1}$$

Call $A = n_{pol}V\frac{2\pi}{h^3}(2m)^{3/2}$ for convenience. Then using the result above gives,

$$\begin{aligned} N &= A\left[\int_0^\mu d\epsilon \ \epsilon^{1/2} + \frac{2}{\beta^2}\frac{\pi^2}{12}\frac{d}{d\epsilon}\epsilon^{1/2} + \mathcal{O}(\beta^{-4})\right] \\ &= A\left[\frac{2}{3}\mu^{3/2} + \frac{1}{\beta^2}\frac{\pi^2}{12}\mu^{-1/2} + \mathcal{O}(\beta^{-1/4})\right] \end{aligned}$$

I'm going to skip a lot of things here since it's all maths and no physics. We can use an ansatz method again to get μ in powers of β^{-2}. Then we also compute the integral for the grand canonical potential $\Omega = -kT\ln\mathcal{Q} = -PV$. An ansatz method is used again to get μ. Putting everything together gives the equation of state

$$PV = \frac{4}{15}A\left(\frac{3N}{2A}\right)^{5/3} + \frac{\pi^2}{9}\beta^{-2}A\left(\frac{3N}{2A}\right)^{1/3} + \mathcal{O}(\beta^{-4})$$

I haven't done it yet but I'm pretty sure for $\beta \to \infty$, you can manipulate this into the equation of state at zero temperature.

11.3 Entropy

Recall from the definition of the grand canonical potential, the entropy is

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}$$

This works out to be

$$S = \frac{\pi^2}{3}A\mu_0^{1/2}k^2T + \mathcal{O}(T^3)$$

or

$$S = \frac{\pi^2}{3}Nk\frac{kT}{\epsilon_F} + \mathcal{O}(T^3)$$

Note that this is in agreement with the third law of thermodynamics.

11.4 Heat Capacity

The heat capacity is

$$C_v = \frac{dQ}{dT}_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = T\left(\frac{\partial S}{\partial T}\right)_{V,N}$$
$$= Nk\frac{\pi^2}{3}\frac{kT}{\epsilon_F} + \mathcal{O}(T^3)$$

This is a divergence from classical mechanics and predicts that the heat capacity goes to zero when the temperature does.

Chapter 12

Bose Gas

We now look at the Bose gas. The treatment is quite similar as the Fermi gas. Start with the grand canonical potential and the average particle number.

$$-PV = \Omega = -kT \ln \mathcal{Q} = -\frac{2}{3}A \int_0^\infty d\epsilon \ \frac{\epsilon^{3/2}}{z^{-1}e^{\beta\epsilon} - 1}$$

$$N = A \int_0^\infty d\epsilon \ \frac{\epsilon^{1/2}}{z^{-1}e^{\beta\epsilon} - 1}$$

with

$$A = n_{pol} V \frac{2}{\sqrt{\pi}} \lambda^{-3} \beta^{3/2}$$

Lets define a function,

$$g_l(z) = \frac{1}{\Gamma(l)} \int_0^\infty dx \ \frac{x^{l-1}}{z^{-1}e^x - 1}$$

which can be rewritten as a geometric series as

$$g_l(z) = \frac{1}{\Gamma(l)} \int_0^\infty dx \ x^{l-1}(ze^{-x} \sum_{n=0}^{\infty} (ze^{-x})^n$$

$$= \frac{1}{\Gamma(l)} \sum_{n=1}^{\infty} z^n \int_0^\infty dx \ x^{l-1} e^{-nx}$$

The integral is just the gamma function.

$$\Rightarrow g_l(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^l}$$

Note that this expansion converges only if $0 \le z \le 1$ so it is not defined for $z > 1$. This is important later since it defines a critical temperature.

Note the relationship between the Riemann Zeta function when $z = 1 (\mu = 0)$,

$$g_l(1) = \sum_{n=1}^{\infty} \frac{1}{n^l} = \zeta(l)$$

One thing we should know is that

$$g_{3/2}(1) = \zeta(\frac{3}{2}) \approx 2.612$$

and also that it is an increasing function.

So we can now rewrite the density in terms of this new function. The next section examines what happens when we change the temperature of the system and how we must change g to compensate.

12.1 Bose Einstein Condensation

We can write the density now as

$$\frac{N}{V} = n_{pol} \lambda^{-3} g_{3/2}(z)$$

Suppose we want to keep the density $\frac{N}{V}$ fixed whilst decreasing the temperature(ie λ). Then $g_{3/2}(z)$ must increase so z must increase. However, z can't take values greater than 1. Denote this temperature at $z = 1$ to be the critical temperature $T = T_c$. This can be solved pretty easily by recalling that $\lambda = \frac{h}{\sqrt{2\pi mkT}}$. Setting $z = 1$ gives,

$$T_c = \frac{h^2}{2\pi mk} \left(\frac{N}{V n_{pol} \zeta(\frac{3}{2})} \right)^{2/3}$$

Now there's another problem that we run into. Suppose we go below the critical temperature. z can only go at most to 1 so g can no longer change. This means that $\frac{N}{V}$ decreases when the temperature goes down which doesn't physically make sense. The problem is to do with the change from a sum to an integral. The contribution of the ground state $\epsilon = 0$ does not contribute to the integral so we must explicitly sum it. Therefore, the correct expression is,

$$\frac{N}{V} = \frac{n_{pol}}{V} \frac{z}{1-z} + n_{pol} \lambda^{-3} g_{3/2}(z) \tag{12.1.1}$$

and denote

$$N_0 = n_{pol} \frac{z}{1-z}$$

For small z, there is a negligible amount of particles in the ground state. However, as the temperature begins to decrease, the number diverges and a macroscopic amount of particles are in the ground state. This is the phenomenon of *Bose-Einstein condensation.*

What's incredible is that once there are a huge number of particles in the ground state, it's as if the particles merge into a collective single state such that quantum effects are noticeable on the macroscopic level.

We can also find the ratio of the particles in the ground state to the total number of particles. Some simple manipulation of (12.1.1) leads to,

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_c}\right)^{3/2}$$

Past the point T_c corresponds to a phase transition.

12.2 Equation of State for $T < T_c$

Up until now, the pressure has been completely ignored. Well, it can be written as

$$\frac{PV}{kT} = n_{pol} V \lambda^{-3} g_{5/2}(z)$$

For $T < T_c$,

$$\frac{PV}{kT} = n_{pol} V \lambda^{-3} \zeta(\frac{5}{2})$$

and this includes careful integrating and summing of the ground state. It's also handy to know that $\zeta(\frac{5}{2}) \approx 1.342$.

Rewrite the numer density to get

$$n_{pol} V \lambda^{-3} = \frac{N - N_0}{\zeta(\frac{3}{2})}$$

Then combining the two equations gives,

$$\frac{PV}{kT} = \frac{N - N_0}{\zeta(\frac{3}{2})} \zeta(\frac{5}{2}) = \left(\frac{T}{T_c}\right)^{3/2} N \frac{\zeta(5/2)}{\zeta(3/2)}$$

$$\Rightarrow \frac{PV}{NkT} = \frac{\zeta(5/2)}{\zeta(3/2)} \left(\frac{T}{T_c}\right)^{3/2} \approx 0.513 \left(\frac{T}{T_c}\right)^{3/2}$$

This can also be written as

$$\frac{PV}{kT} \approx 0.513 N \left(\frac{T}{T_c}\right)^{3/2}$$

The second last two quantities can be interpreted as the number of particles with $\epsilon \neq 0$. The pressure comes from particles with nonzero momentum/energy.

12.3 Equation of State for $T > T_c$

For $T > T_c$, we have

$$\frac{PV}{kT} = n_{pol} V \lambda^{-3} g_{5/2}(z)$$

$$\frac{N}{V} = \frac{N_0}{V} + n_{pol} \lambda^{-3} g_{3/2}(z)$$

For $T > T_c$, $\frac{N_0}{V} \to 0$. Combining the two equations gives,

$$\frac{PV}{NkT} = \frac{g_{5/2}(z)}{g_{3/2}(z)}$$

Recall that

$$g_l(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^l}$$

For $T \to \infty$, $z \to 0$. We can then expand and get,

$$\frac{PV}{NkT} = 1 + \mathcal{O}(z)$$

So we get the classical ideal gas for high temperature. The terms of $\mathcal{O}(z)$ can be computed using an ansatz method by expanding in a power series of $t = g_{3/2}(z) = \frac{N\lambda^3}{V n_{pol}}$ which I may or may not do at some point.

12.4 Heat Capacity

We look at states where there is no degeneracy, ie $n_{pol} = 1$. Recall that

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

Recall equation (10.1.3). For a Bose gas, we have

$$U = \frac{3}{2} PV = \begin{cases} \frac{3}{2} V kT \lambda^{-3} g_{5/2}(z) & (T > T_c) \\ \frac{3}{2} V kT \lambda^{-3} \zeta(\frac{5}{2}) & (T < T_c) \end{cases}$$

There are 3 straightforward computations then for each case of T.

Heat Capacity when $T < T_c$

$$C_V = \frac{\partial}{\partial T}\bigg(\frac{3}{2}VkT\lambda^{-3}\zeta(\frac{5}{2})\bigg)$$

$$C_V = \frac{15}{4}Vk\lambda^{-3} \propto T^{3/2}$$

Heat Capacity when $T = T_c$

At $T = T_c$, use $\frac{N}{V} = \lambda^{-3}g_{5/2}(1)$.

$$C_V = \frac{15}{4}Vk\frac{N}{V}\frac{\zeta(5/2)}{\zeta(3/2)} \approx 1.925Nk$$

Heat Capacity when $T > T_c$

$$C_V = \frac{\partial}{\partial T}\bigg(\frac{3}{2}VkT\lambda^{-3}g_{5/2}(z)\bigg)$$

$$= \frac{3}{2}Vk\lambda^{-3}g_{5/2}(z) + \frac{3}{2}VkT(-3)\lambda^{-4}\frac{\partial\lambda}{\partial T}g_{5/2}(z) + \frac{3}{2}VkT\lambda^{-3}\frac{\partial g_{5/2}(z)}{\partial z}\frac{\partial z}{\partial T}$$

Most of the derivatives are easy enough. $\frac{\partial g_{5/2}(z)}{\partial z} = \frac{1}{z}g_{3/2}(z)$ can be obtained from the series definition. To find $\frac{\partial z}{\partial T}$, take

$$\frac{N}{V} = \lambda^{-3}g_{3/2}(z)$$

Differentiate w.r.t T.

$$0 = \frac{\partial}{\partial T}\bigg(\lambda^{-3}g_{3/2}(z)\bigg)$$

Using the product rule,

$$\Rightarrow \frac{\partial z}{\partial T} = -z\frac{3}{2T}\frac{g_{3/2}(z)}{g_{1/2}(z)}$$

Therefore,

$$C_V = \frac{3}{2}Nk\bigg[\frac{5}{2}\frac{g_{5/2}(z)}{g_{3/2}(z)} - \frac{3}{2}\frac{g_{3/2}(z)}{g_{1/2}(z)}\bigg]$$

$$= \frac{3}{2}Nk\bigg[\frac{5}{2}\frac{z+\mathcal{O}(z^2)}{z+\mathcal{O}(z^2)} - \frac{3}{2}\frac{z+\mathcal{O}(z^2)}{z+\mathcal{O}(z^2)}\bigg]$$

For $T \to \infty$, $z \to 0$

$$C_V = \frac{3}{2}Nk + \mathcal{O}(z)$$

which is the same as a classical ideal gas.

More importantly, plotting a graph of this shows a discontinuity of the slope of the heat capacity. This is an example of a phase transition.

Chapter 13

Heat Capacity of a Solid

13.1 Classical Heat Capacity of a Solid

Consider a solid which consists of atoms held in place that are allowed to undergo small vibrations So essentially this is a system of N harmonic oscillators. The Hamiltonian is

$$H = \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m} + \frac{1}{2} k q_i^2 \right)$$

The canonical partition function is

$$Z = \int d^{3N}p \; d^{3N}q \; e^{-\beta H}$$

$$= \left[\int_{\infty}^{\infty} dp \int_{\infty}^{\infty} dq \; e^{-\beta \frac{p^2}{2m}} e^{-\frac{1}{2}\beta k q^2} \right]^{3N}$$

These are Gaussian integrals.

$$= \left[\left(\frac{2m\pi}{\beta} \right)^{1/2} \left(\frac{2\pi}{\beta k} \right)^{1/2} \right]^{3N}$$

The internal energy is

$$U = -\frac{\partial}{\partial \beta} \ln Z$$

$$= -\frac{\partial}{\partial T} \bigg(-\frac{3N}{2} \ln \beta - \frac{3N}{2} \ln \beta \bigg) + 0$$

$$= \frac{3N}{\beta} = 3NkT$$

Therefore, the heat capacity is,

$$C_V = 3Nk$$

This is the heat capacity predicted for a classical solid. While this is true for high temperature, experiments show that the heat capacity goes to zero as temperature goes to zero so clearly, we need a quantum explanation.

13.2 Einstein Model

In quantum mechanics, a harmonic oscillator's energy is quantised. Therefore, the solid's energy should have the form,

$$E = \sum_{i=1}^{3N} (n_i + \frac{1}{2})\hbar\omega_i$$

where n_i is a quantum number, $i = 1, \ldots, N$. Interpret n_i to be the number of 'particles' with energy $\hbar\omega_i$. These particles are known as phonons. Note that the number of particles is not conserved. This means that $\mu = 0$ so $z = 1$

Lets compute the grand canonical partition function.

$$\mathcal{Q} = \sum_{N_q=0}^{\infty} z^{N_q} \sum_{\{n_i\}_{i=1,\ldots,3N}} e^{-\beta \sum_{i=1}^{3N}(n_i+\frac{1}{2})\hbar\omega_i}$$

Use N_q to label the number of quanta or 'particles', $\sum_{i=1}^{3N} = N_q$. Since $z = 1$,

$$= \sum_{\{n_i\}_{i=1,\ldots,3N}} e^{-\beta \sum_{i=1}^{3N}(n_i+\frac{1}{2})\hbar\omega_i}$$

$$= \sum_{\{n_i\}} \prod_{i=1}^{3N} e^{-\beta(n_i+\frac{1}{2})\hbar\omega_i}$$

$$= \prod_{i=1}^{3N} \sum_{\{n_i\}} e^{-\beta(n_i+\frac{1}{2})\hbar\omega_i}$$

$$= \prod_{i=1}^{3N} e^{-\frac{1}{2}\beta\hbar\omega_i} \sum_{n_i=0}^{\infty} \left(e^{-\beta\hbar\omega_i}\right)^{n_i}$$

since the quantum number n_i has no limit.

$$\mathcal{Q} = \prod_{i=1}^{3N} e^{-\frac{1}{2}\beta\hbar\omega_i} \frac{1}{1 - e^{-\beta\hbar\omega_i}}$$

The internal energy is

$$\begin{aligned}U &= -\frac{\partial}{\partial \beta}\ln \mathcal{Q} \\ &= -\frac{\partial}{\partial \beta}\left(\sum_{i=1}^{3N}(-\frac{1}{2}\beta\hbar\omega_i - \ln(1-e^{-\beta\hbar\omega_i}))\right) \\ &= \sum_{i=1}^{3N}\hbar\omega_i\left(\frac{1}{2}+\frac{1}{e^{\beta\hbar\omega_i}-1}\right)\end{aligned}$$

Then the heat capacity is,

$$C_V = \frac{\partial U}{\partial T} = \sum_{i=1}^{3N} k(\beta\hbar\omega_i)^2\frac{e^{\beta\hbar\omega_i}}{(e^{\beta\hbar\omega_i}-1)^2}$$

We now make an assumption that all the particles vibrate at the same angular frequency which is a feature of the Einstein model. Set $\omega_i = \omega$.

$$\Rightarrow C_V = 3Nk(\beta\hbar\omega)^2\frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}$$

This is the Einstein heat capacity.

Lets look at the two limits for T

For $T \to \infty$, $\beta \to 0$.

$$\begin{aligned}C_V &= 3Nk(\beta\hbar\omega)^2\frac{1+\beta\hbar\omega+\mathcal{O}(\beta^2)}{(\beta\hbar\omega+\frac{(\beta\hbar\omega)^2}{2}+\mathcal{O}(\beta^3))^2} \\ &= 3Nk\frac{1+\beta\hbar\omega+\mathcal{O}(\beta^2)}{1+\frac{\beta\hbar\omega}{2}+\mathcal{O}(\beta^2)} \\ &= 3Nk(1+\beta\hbar\omega)(1-\beta\hbar\omega+\mathcal{O}(\beta^2))+\mathcal{O}(\beta^2) \\ &= 3Nk+\mathcal{O}(\beta^2)\end{aligned}$$

agreeing with the classical limit.

For $T \to 0$, $\beta \to \infty$

$$\begin{aligned}C_V &= 3Nk(\beta\hbar\omega)^2 e^{-2\beta\hbar\omega}\frac{e^{\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2} \\ &= 3Nk(\beta\hbar\omega)^2 e^{-\beta\hbar\omega}(1+\mathcal{O}(e^{-\beta}))\end{aligned}$$

Since the exponential goes to zero much faster than β goes to infinity,

$$C_V \to 0$$

Chapter 14

Blackbody Radiation

The next section examines the properties of a gas consisting of photons which gives rise to blackbody radiation.

14.1 Relativistic Bose Gas

Consider a system of N bosons with mass m. The relativistic energy is,

$$\epsilon = \sqrt{p^2c^2 + m^2c^4}$$

We need to reconsider how we change a momentum integral to an energy integral.

$$\frac{P}{kT} = \frac{n_{pol}}{h^3}\int d^3\mathbf{p}(-\ln(1 - ze^{-\beta\epsilon}))$$

$$= \frac{4\pi n_{pol}}{h^3}\int_0^\infty p^2dp(-\ln(1 - ze^{-\beta\epsilon}))$$

Use the fact that

$$d\epsilon = \frac{1}{2\sqrt{p^2c^2 + m^2c^4}}2pc^2dp$$

$$\Rightarrow p^2dp = \frac{\sqrt{\epsilon^2 - m^2c^4}}{c^3}\epsilon d\epsilon$$

Therefore, our relativistic expressions for the pressure and density are,

$$\frac{P}{kT} = n_{pol}\frac{4\pi}{(hc)^3}\int_{mc^2}^\infty d\epsilon\ \epsilon\sqrt{\epsilon^2 - m^2c^4}\Big[-\ln(1 - ze^{-\beta\epsilon})\Big]$$

$$\frac{N}{V} = n_{pol}\frac{4\pi}{(hc)^3}\int_{mc^2}^\infty d\epsilon\ \epsilon\sqrt{\epsilon^2 - m^2c^4}\frac{1}{z^{-1}e^{\beta\epsilon} - 1}$$

14.2 Photon Gas

For photons, set $m = 0$. Then we get,

$$\frac{P}{kT} = n_{pol}\frac{4\pi}{(hc)^3}\int_0^\infty d\epsilon\ \epsilon^2\Big[-\ln(1 - ze^{-\beta\epsilon})\Big]$$

$$\frac{N}{V} = n_{pol}\frac{4\pi}{(hc)^3}\int_0^\infty d\epsilon\ \frac{\epsilon^2}{z^{-1}e^{\beta\epsilon} - 1}$$

The first expression can be integrated by parts to give,

$$\frac{P}{kT} = n_{pol}\frac{4\pi\beta}{3(hc)^3}\int_0^\infty d\epsilon\ \frac{\epsilon^3}{z^{-1}e^{\beta\epsilon} - 1}$$

One of the first things we need to note is that photons can be created and destroyed without changing the free energy. $(\frac{\partial F}{\partial N})_{V,T} = \mu = 0 \Rightarrow z = 1$.

The energy of a photon is $\epsilon = \hbar\omega$. We change variables to integrate over ω. $d\epsilon = \hbar d\omega$. So our expressions now look like

$$PV = n_{pol}\frac{4\pi}{3}V\frac{\hbar^4}{(hc)^3}\int_0^\infty d\omega\ \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$

$$\frac{N}{V} = n_{pol}\frac{4\pi}{(hc)^3}\hbar^3\int_0^\infty d\omega\ \frac{\omega^2}{e^{\beta\hbar\omega} - 1}$$

Ok, so lets now look at the internal energy of the system which in discrete form is,

$$U = \sum_k \langle n_k\rangle\epsilon_k = \sum_k \frac{\epsilon_k}{z^{-1}e^{\beta\epsilon_k} - 1}$$

When $V \to \infty$, it is possible to change this to an energy integral and then to a frequency integral. We find that

$$U = V\frac{n_{pol}\hbar}{2\pi^2c^3}\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$

Denote

$$u(\omega, T) = \frac{n_{pol}\hbar}{2\pi^2c^3}\frac{\omega^3}{e^{\beta\hbar\omega} - 1}$$

This is known as *Planck's Law for Radiation.* It gives the distribution of energy per frequency per unit volume.

By inspection, we get an equation of state

$$U = 3PV$$

Carrying out the integral,

$$\begin{aligned}\frac{U}{V} &= \int_0^\infty d\omega\ u(\omega, T) \\ &= \frac{\hbar}{\pi^2 c^3}\int_0^\infty d\omega\ \frac{\omega^3}{e^{\beta\hbar\omega} - 1}\end{aligned}$$

Using the fact that $\int_0^\infty dx\ \frac{x^{2n-1}}{e^x - 1} = \frac{(2\pi)^{2n} B_n}{4n}$ where B_n are the Bernoulli numbers and $n_{pol} = 2$ for photons,

$$\frac{U}{V} = \frac{\pi^2}{15}\frac{(kT)^4}{(\hbar c)^3}$$

This is related to the Stefan-Boltzmann Law which scales $\sim T^4$. It gives the energy density of the photons and we can derive the Stefan-Boltzmann Law from it.

Consider the limit $\omega \to 0$. Then Planck's formula looks like

$$u(\omega, T) \sim \frac{kT}{\pi^2 c^3}\omega^2 + \dots$$

This is the Rayleigh-Jean Law.

Consider the limit $\omega \to \infty$. Then Planck's formula looks like

$$u(\omega, T) \sim \frac{\hbar}{\pi^2 c^3}\omega^3 e^{-\beta\hbar\omega}$$

This is Wien's approximation.

Finally, we can find the maximum ω_{max} of $u(\omega, T)$ by diferentiating. This gives,

$$\hbar\omega_{max} = 2.822kT$$

This is Wien's Law.

Chapter 15

Magnetic Systems

In a magnetic system, the state variables that we are concerned with are the temperature T, magnetic field B and the magnetisation M. Like the earlier systems we considered, the magnetic system can then be described by an equation of state,

$$f(M, B, T) = 0$$

The work performed by the system is $dW = -BdM$. Hence, the first law of thermodynamics for a magnetic system looks like

$$dU = dQ + BdM$$

15.1 Magnetic Susceptibility

Define the magnetic susceptibility to be

$$\chi_T = \left(\frac{\partial M}{\partial B}\right)_T$$

$$\chi_S = \left(\frac{\partial M}{\partial B}\right)_S$$

They can be interpreted as how magnetised something gets when there is a magnetic field present.

(I'm not too sure about this definition since normally it's $\chi = \frac{M}{B}$)

15.2 An Example of Paramagnetism

Consider N fixed magnetic dipoles with magnetic moments $\boldsymbol{\mu}_i$. Each particle's magnetic moment points in a certain direction. The magnetic moment's direction can be described by the angles (θ_i, ϕ_i). With no magnetic field, they point in random directions and the overal magnetisation is 0. Let there be a $\mathbf{B}$ field applied to the system. The magnetic moments will try to align with the field to minimise the potential. The Hamiltonian for the system is,

$$H = -\sum_{i=1}^{N} \boldsymbol{\mu}_i \cdot \mathbf{B}$$

Let the magnitude of each particle's magnetic moment be the same. If we choose our coordinate system such that $\mathbf{B} = (0, 0, B)$,

$$H = -\sum_{i=1}^{N} \mu B \cos\theta_i$$

The distribution over the angles follows Maxwell-Boltzmann statistics. The canonical partition function is,

$$Z_N = \prod_{i=1}^{N} \sum e^{-\beta E}$$

Summing over all configurations gives,

$$= \prod_{i=1}^{N} \int_0^{2\pi} d\phi \int_0^{\pi} d\theta_i \ \sin\theta_i \ e^{\beta\mu B\cos\theta_i}$$

Integrating this gives,

$$Z_N = \left(\frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)\right)^N$$

Let us now compute the expectation value of the overall magnetic moment.

$$\langle \boldsymbol{\mu} \rangle = \frac{1}{Z}\int d\theta_i \ d\phi \ \boldsymbol{\mu} e^{\beta\mu B\cos\theta_i}$$

If we express $\boldsymbol{\mu}$ in Cartesian coordinates, it is found that the x, y components are 0. This makes sense since the B field is in the z direction so the alignment of the magnetic moments are random in the x, y direction which will average to 0. Therefore,

$$\langle \mu_z \rangle \equiv \langle \mu \rangle = \frac{1}{Z}\int d\theta_i \ d\phi \ \mu\cos\theta_i \ e^{-\beta\mu B\cos\theta_i}$$

Observe that this can be rewritten as,

$$\langle \mu \rangle = \frac{1}{\beta}\frac{\partial}{\partial B}\ln Z_1$$

This is equivalent to the magnetisation of one particle. The total magnetisation then is the sum of the magnetic moments,

$$M = \frac{N}{\beta}\frac{\partial}{\partial B}\left[\ln\left(\frac{4\pi}{\beta\mu B}\sinh(\beta\mu B)\right)\right]$$

This works out to be,

$$M = N\mu(\coth(\beta\mu B) - \frac{1}{\beta\mu H}) = N\mu L(\beta\mu B)$$

where $L(x) = \coth(x) - \frac{1}{x}$ is the Langevin function. This is an equation of state.

Observe what happens in the high temperature limit $\beta \to 0$.

$$\begin{aligned} M &= N\mu\frac{\beta\mu B}{3} + \mathcal{O}(T^{-3}) \\ &= \frac{N\mu^2 B}{3kT} + \mathcal{O}(T^{-3}) \end{aligned}$$

The susceptibility is

$$\chi_T = \left(\frac{\partial M}{\partial B}\right)_T = \frac{N\mu^2}{3kT} + \mathcal{O}(T^{-3})$$

Notice that magnetisation goes to 0 for high temperature. Also, the susceptibility is positive and non-zero even when the magnetic field is turned off.

15.3 Paramagnetism and Diamagnetism

We can classify a system into two classes. We call a system *paramagnetic* if $\chi_T > 0$ This means that the magnetisation is in the direction of the applied magnetic field.

We call a system *diamagnetic* if $\chi_T < 0$. This means that the magnetisation opposes the magnetic field. The next sections will develop a simple model that exhibits diamagnetism.

15.4 Electron Moving in a Magnetic Field with no Spin

It can be shown that a charged particle moving in a magnetic field with no spin does not exhibit magnetisation classically so we look at a quantum picture.

The Hamiltonian for the particle is,

$$H = \frac{1}{2m}(\mathbf{p} + \frac{e}{c}\mathbf{A}(\mathbf{q}))^2$$

with

$$\mathbf{B} = \nabla \times \mathbf{A}$$

Due to gauge invariance, we choose $\mathbf{A}(\mathbf{q}) = (-By, 0, 0)$ and this gives the magnetic field pointing in the z direction. Then the Hamiltonian becomes,

$$H = \frac{1}{2m}((p_x - \frac{eB}{c}y)^2 + p_y^2 + p_z^2)$$

Solving the S-eqn gives,

$$\epsilon(p_z, j) = \frac{p_z^2}{2m} + \hbar\omega_0(j + \frac{1}{2})$$

where $\omega_0 = \frac{eB}{mc}$. We refer to a state with quantum number j as a Landau Level. The Landau Levels are degenerate due to the allowed values of k_x. (see Michael Fry) For example, for a particle in a box of volume L^3, the allowed values of k_x are,

$$k_x = \frac{2\pi n_x}{L_x}$$

It is found the largest n_x is $\frac{eBL^2}{hc}$. Since, n_x is positive and is integers, this is the number of degeneracies.

15.5 Landau Diamagnetism

Consider now N spinless electrons in a magnetic field and neglect the interaction between them. The Hamiltonian is

$$H = \frac{1}{2m}\sum_{i=1}^{N}(\mathbf{p}_i + \frac{e}{c}\mathbf{A})^2$$

We wish to compute the magnetisation and susceptibility. Define the magnetisation per unit volume $\mathcal{M} = \frac{M}{V}$. Then,

$$\mathcal{M} = \frac{kT}{V}\frac{\partial}{\partial B}\ln\mathcal{Q}$$

Since electrons are fermions, we use the Fermi-Dirac distribution.

$$\mathcal{Q} = \prod_{\lambda}(1 + ze^{-\beta\epsilon_\lambda})$$

λ here is an index that is identified with p_z, j, α where $\alpha = 1, \ldots, g$ is a degeneracy factor.

Lets compute $\ln\mathcal{Q}$.

$$\ln\mathcal{Q} = \prod \ln(1 + ze^{-\beta\epsilon_\lambda})$$

$$\ln \mathcal{Q} = g\frac{L}{h}\sum_{j=0}^{\infty}\sum_{p_z}\ln(1+ze^{-\beta\epsilon_{p_z,j}})$$

$$= g\frac{L}{h}\sum_{j=0}^{\infty}\int_{-\infty}^{\infty}dp_z\ \ln(1+ze^{-\beta\epsilon})$$

The $\frac{L}{h}$ factor comes from the density of states stuff. The average number of electrons is,

$$N = z\frac{\partial}{\partial z}\ln Q = \frac{2gL}{h}\sum_{j=0}^{\infty}\int_{0}^{\infty}dp_z\ \frac{1}{z^{-1}e^{\beta\epsilon}+1}$$

where we recognise the integral is an even integral.

Consider the high temperature limit $\beta \to 0$. For the particle number to remain finite, $z \to 0$. (not sure about this). Then the integral can be expanded in powers of z.

$$\ln \mathcal{Q} \approx \frac{2gL}{h}\sum_{j=0}^{\infty}\int_{0}^{\infty}dp\ ze^{-\beta\epsilon}$$

$$= \frac{2gLz}{h}\sum_{j=0}^{\infty}\int_{0}^{\infty}dp\ e^{\frac{-\beta p^2}{2m}}e^{-\beta\hbar\omega_0(j+1/2)}$$

$$= \frac{gLz}{h}e^{-\frac{\beta\hbar\omega_0}{2}}\sum_{j=0}^{\infty}(e^{-\beta\hbar\omega_0})^j\sqrt{\frac{2m\pi}{\beta}}$$

$$= \frac{gLz}{\lambda_{th}}e^{-\frac{\beta\hbar\omega_0}{2}}\frac{1}{1-e^{-\beta\hbar\omega_0}}$$

$$= \frac{gLz}{2\lambda_{th}}\frac{1}{\sinh(\frac{\beta\hbar\omega_0}{2})}$$

Now expand the sinh since $\beta \to 0$,

$$\ln \mathcal{Q} \approx \frac{gLz}{\lambda_{th}}(1-\frac{1}{24}(\beta\hbar\omega_0)^2+\mathcal{O}(\beta^4))$$

Plugging in values for g and ω_0 gives,

$$\ln \mathcal{Q} = \frac{Vz}{\lambda_{th}^3}(1-\frac{1}{24}(\beta\hbar\omega_0)^2$$

Therefore, the magnetisation density is,

$$\mathcal{M} = \frac{kT}{V}\frac{\partial}{\partial B}\ln \mathcal{Q}$$

$$= 2\frac{kT}{\lambda_{th}^3}(-\frac{\hbar^2}{24(kT)^2}\frac{\partial}{\partial B}(\frac{eB}{mc})^2)$$

$$= -\frac{2z}{24\lambda_{th}^3 kT}(\frac{e\hbar}{mc})^2 B$$

So the susceptibility density is,

$$\frac{\chi_T}{V} = \frac{\partial \mathcal{M}}{\partial B} = \frac{-z}{3kT\lambda^3}(\frac{e\hbar}{2mc})^2$$

This is an example of a diamagnetic system which has a negative susceptibility. What's essentially happening is that the magnetic field causes circular orbits and according to Lenz's Law, an opposing magnetic field must be created.

15.6 De Haas-Van Alphen Effect

Consider the low temperature limit of Landau diamagnetism where the system approaches its ground state. We also assume that motion only occurs in the xy plane. The energy can be rewritten to be

$$\epsilon_j = 2\mu_B B(j + \frac{1}{2})$$

where $\mu_B = \frac{e\hbar}{2mc}$ is the Bohr magneton.

Rewrite the degeneracy as

$$g = N\frac{B}{B_0}$$

where $B_0 = \frac{Nhc}{L^2 e}$.

If $B \geq B_0$, then $g \geq N$ so all the particles can fit into the ground state. The energy of the ground state is $E_0 = N\mu_B B$.

However, if $B < B_0$, then some particles are forced into the next state by the Pauli exclusion principle. Suppose $B < B_0$ and the levels j and below are filled and the level $j+1$ is partly filled and all higher levels are empty. Then (not sure about this)

$$(j+1)g < N < (j+2)g$$

$$\Rightarrow \frac{1}{j+2} < \frac{B}{B_0} < \frac{1}{j+1}$$

The energy of the system is,

$$E = g\sum_{i=1}^{j}\epsilon_i + (N - (j+1)g)\epsilon_{j+1}$$

where $N - (j+1)g$ is the number of remaining particles. This gives,

$$E = N\mu_B Bx(2j + 3 - (j+1)(j+2)x)$$

where $x = \frac{B}{B_0}$.

To summarise, the energy per particle of the system is,

$$\frac{E}{N} = \begin{cases} \mu_B B x & \text{if } x > 1 \\ \mu_B B x(2j + 3 - (j+1)(j+2)x) & \text{if } \frac{1}{j+2} < x < \frac{1}{j+1} \end{cases}$$

The magnetisation per unit area $\mathcal{M} = \frac{-1}{L^2}\frac{\partial}{\partial B}E$ is

$$\mathcal{M} = \begin{cases} \frac{-N\mu_B}{L^2} & \text{if } x > 1 \\ \mu_B B x(2j + 3 - (j+1)(j+2)x) & \text{if } \frac{1}{j+2} < x < \frac{1}{j+1} \end{cases}$$

Something is really wrong so stop here.

Chapter 16

Ferromagnetism

We now look at a different class of magnets called ferromagnets. These are magnets that have magnetisation even when not in the presence of a magnetic field. It is due to the electron's spin. It is energetically favoured to have parallel spin. In this model, we assume that the spins can either point in the positive or negative direction in the z direction(ie we measure S_z, for convenience the z is dropped). Consider a system of N particles. The Heisenberg model has the Hamiltonian

$$H = -\frac{1}{2}\sum_{i,j} J_{ij} S_i S_j - g\mu_B \sum_{i=1}^{N} \mathbf{S}_i \cdot \mathbf{B}$$

where $\mathbf{B}$ is the magnetic feld, S is the spin of the particle, g is the g-factor. $J_{ij} = J_{ij} > 0$ is a term that measures the interaction between the spins of neighbouring particles. There is $-J$ energy for parallel spins and J energy for antiparallel spins.

Firstly, lets develop a bit of the framework we will be using later. The spins follow the usual commutator relations for spin and the spin for the i and j particle commute. This means we can find a simultaenous diagonalised eigenstate for all the particles. The partition function looks like

$$Z = Tr(e^{-\beta H}) = \sum_{m_1=\pm\frac{1}{2}} \cdots \sum_{m_N=\pm\frac{1}{2}} \langle \psi_{m_1 \ldots m_N} | e^{-\beta H} | \psi_{m_1 \ldots m_N} \rangle$$

We also have the Gibbs potential energy to be

$$G(T, B) = -kT \ln Z$$

The expectation value of the energy is,

$$\langle H \rangle = \frac{1}{Z} Tr(He^{-\beta H})$$

$$= -\frac{\partial}{\partial\beta}\beta G(T,B)$$

The magnetiation is

$$M^\alpha = g\mu_B\langle\sum_{j=1}^{N} S_j^\alpha\rangle$$

$$= \frac{1}{Z}Tr(g\mu_B\sum_{j=1}^{N} S_i^\alpha e^{-\beta H})$$

$$= \frac{1}{\beta Z}Tr(\frac{\partial}{\partial B^\alpha}e^{-\beta H}) = \frac{1}{\beta}\frac{\partial}{\partial B^\alpha}\ln Z$$

α labels the coordinate x, y, z.

16.1 Non-Interacting Case

Lets now consider the case where $J = 0$ so the spins do not interact with each other. However, the spins interact with the magnetic field. Choose the coordinate system so that B points in the z-direction. Then the Hamiltonian is

$$H = -g\mu_B B\sum_{i=1}^{N} S_i^z$$

Therefore, the partition function is,

$$Z = \sum_{m_1=\pm\frac{1}{2}}\cdots\sum_{m_N=\pm\frac{1}{2}}\langle\psi_{m_1\ldots m_N}|e^{\beta g\mu_B B\sum S_i^z}|\psi_{m_1\ldots m_N}\rangle$$

$$= \sum_{m_1=\pm\frac{1}{2}}\cdots\sum_{m_N=\pm\frac{1}{2}} e^{\beta g\mu_B B\sum m_i}\langle\psi_{m_1\ldots m_N}|\psi_{m_1\ldots m_N}\rangle$$

$$= \sum_{m_1=\pm\frac{1}{2}}\cdots\sum_{m_N=\pm\frac{1}{2}} e^{\beta g\mu_B B\sum m_i}$$

$$= \left(\sum_{m=\pm\frac{1}{2}} e^{\beta g\mu_B B m}\right)^N$$

$$= (e^{\frac{1}{2}\beta g\mu_B B} + e^{-\frac{1}{2}\beta g\mu_B B})^N$$

$$= 2^N\cosh^N(\frac{\beta g\mu_B B}{2})$$

Therefore the magnetisation is,

$$M = kT\frac{\partial}{\partial B}\ln Z = M_0\tanh\frac{\beta g\mu_B B}{2}$$

where $M_0 = \frac{N g\mu_B}{2}$.

16.2 Mean Field Approximation

In the mean field approximation, we assume that the spin has the form,

$$\mathbf{S}_i = \langle \mathbf{S}_i \rangle + \Delta \mathbf{S}_i$$

We treat $\Delta \mathbf{S}_i$ as a small approximation. So,

$$\mathbf{S}_i \cdot \mathbf{S}_j = \langle \mathbf{S}_i \rangle \langle \mathbf{S}_j \rangle + \Delta \mathbf{S}_i \langle \mathbf{S}_j \rangle + \Delta \mathbf{S}_j \langle \mathbf{S}_i \rangle + \mathcal{O}(\Delta \mathbf{S}^2)$$

The Hamiltonian becomes,

$$H = -\frac{1}{2} \sum_{i \neq j} J_{ij} \Big[\langle \mathbf{S}_i \rangle \langle \mathbf{S} \rangle + 2 \Delta \mathbf{S} \langle \mathbf{S}_j \rangle \Big] - g\mu_B \sum \mathbf{S}_i \cdot \mathbf{B}$$

$$= -\sum J_{ij} \Big[\langle \mathbf{S}_i \rangle (\mathbf{S}_j - \langle \mathbf{S}_j \rangle) + \frac{1}{2} \langle \mathbf{S}_i \rangle \langle \mathbf{S}_j \rangle \Big] - g\mu_B \sum \mathbf{S}_i \cdot \mathbf{B}$$