Statistical Mechanics Notes

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Contents

1 Preliminaries

1.1 Overview

The course will be mostly focused on learning by simple models. These are not always relevant to fully describing a system, but they are a good way to learn statistical mechanics which can then be applied to more complex models. So we are going to do this in a limit without interactions first, but still have the topics such as entropy, energy, etc. In the second part of the course we will talk about interacting systems, but we first need to get a firm handle on simple models which teach us how to count and what statistical mechanics is all about.

1.2 Introduction to Statistical Mechanics

Statistical mechanics relates microscopic to macroscopic phenomena. Usually for us this will mean relating atoms and molecules (length scales of $\approx .5 - 5\text{Å}$) to macroscopic scales. We also have the mesoscopic scale, which is on the order of 100Å to microns. This is often the scale of the problems in physics or chemistry. Often the macroscopic scale can be simple since it follows the laws of thermodynamics, however the mesoscopic scale can be more tricky since thermodynamics breaks down. Instead, we need to coarse grain in the correct way to get reasonable answers. Associated with these length scales are the corresponding time scales. Microscopic scales such as electronic scales are $10^{-14} - 10^{-9}$s, mesoscopic scales are nanoseconds to milliseconds and the macroscopic scales are anything larger than this.

When doing thermodynamics, we learned about extensive and intensive variables. Extensive variables scale with system size and intensive variables do not. We also know that in general finite volumes cannot be described completely without the boundary conditions including interactions with the walls. However, since volume scales as l^3 and area goes as l^2, usually, we can make a sufficiently large enough area that the boundary condition terms can be ignored. This is true only in the limit of short range interactions. With long range interactions such as the Coulomb interactions, we need to consider these boundary terms. Mathematically, we can think of this as the scaling of terms in the description. When doing computer simulations, we can also include periodic boundaries which can help.

We will often work with condensed matter systems in this course, in Table 1 we give common scales for this type of system. Often we think of statistical mechanics as "deriving" thermodynamics from systems such as this. Weather or not this makes statistical mechanics more fundamental than thermodynamics is debatable.

Sometimes, we are interested in going the other way and learning about statistical mechanics from thermodynamics given a macroscopic observation. One example of this is the heat capacity of some simple metal. Heat capacity is defined as

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V, \tag{1.1}$$

and has been measured for a long time. What they realized was that the heat capacity was constant at high temperatures and then started to drop to zero at about 300 K. Classical statistical mechanics did not get this right until Einstein figured out that lattice vibrations

Volume	1 cm^3
Atomic spacing	3Å
Number of atoms	10^{22}
Number of surface atoms	10^{15}
Number of atoms on edge	3×10^7
Typical gas density	$\frac{1}{1000}$ of liquid density

Table 1: Useful numbers for a block of copper, which is a typical solid we will be studying in this course. For a gas, we can divide these typical atom numbers and spacings by a factor of about 1000. These numbers are still large.

need to be quantized, and with the addition of quantum mechanics to the statistical mechanics pictures, the experiment was able to be predicted. A more modern example of this is high temperature superconductors which was completely unexpected and is still attempting to be understood.

It is clear that we must do some averaging. The idea in statistical mechanics is that we will associate the time average with some sort of equilibrium measurement. In classical mechanics simulations of interacting atoms, we have N atoms in some volume V. We can think of the positions of all the atoms and their momentum as functions of time

$$(r^N(t), p^N(t)) = f(r^N(t_0), p^N(t_0)), \tag{1.2}$$

where r^n, p^N are N- dimensional vectors, and f represents Newton's equations. By integrating Newton's equations we can solve for these at any time given initial conditions at t_0. We can think about this whole system as a point in a high dimensional space which moves around and relate this to average energy and other thermodynamic properties. So if we suppose we have some mechanical property m (something like pressure) and we want to compute the average value. So we can compute this as

$$\langle m \rangle = \frac{1}{\Delta t} \int_{t_e}^{t_e + \Delta t} m(t)\, dt, \tag{1.3}$$

where t_e is an equilibrium time. The result is that at some point corresponding to a properly chosen t_e, this becomes independent of Δt. This length of time is equilibrium and it is hard to quantify in general. However, for simple systems, it tends to be around 10^{-8} time scales which is short on our time scales but long on molecular time scales.

One important remark is that the systems are ergodic, thus if we wait long enough, they will visit all the points in the phase space we are studying (or at least enough points). In a classical system, this means that paths cannot cross (we are assuming we can label particles), in a quantum system, we cannot even label the particles and things are somewhat more complicated.

Often in statistical mechanics we will use the idea of an ensemble which is all the possible microstates consistent with all given macro constraints. The equilibrium conditions should be given by various averages over these microstates. So we will define ν as number of possible microstates. So we can define again an average as

$$\langle m \rangle = \sum_\nu P_\nu m_\nu. \tag{1.4}$$

Then we assume that the initial conditions don't matter, and so the probability of being in any microstate of ν is equal. This is the basis for our our further work.

1.3 Notes From Thermodynamics Review

- Memorize

$$dE = TdS - pdV + \mu dN. \tag{1.5}$$

- Use the dimensionless entropy, $S \rightarrow S/k_B$ and use β.

- Useful relation

$$\frac{\partial \beta A}{\partial \beta} = E \tag{1.6}$$

- Signs of second derivatives are important, but you want to think about what representation you are in and whether the derivative is extensive or intensive variable. So if we are in the entropy representation $S(E, V, N)$, which we know is maximized, we know that the second derivative of entropy with respect to the extensive variables E, V, N is negative since the entropy is concave with respect to its variabels. Obviously $E(S, V, N)$ would be convex with respect to entropy. In sum

$$\frac{\partial^2 E}{\partial S^2} > 0 \, ; \, \frac{\partial^2 S}{\partial E^2} < 0. \tag{1.7}$$

- When one does a Legendre transform, since there is a minus sign, it makes the new potential concave in the transformed variable. For example $A(T, V, N)$, where $A = E - TS$, is concave in T.

2 Microcanonical Ensemble

In the microcanonical ensemble, we have the simplest possible macro conditions, which is that P_ν is independent of ν. Physically this corresponds to no barriers in phase space. So we can define $\Omega(E, V, N; \delta E)$ as the number of microstates with energy between E and $E - \delta E$. E is a macroscopic energy and δE is a macroscopic small measurement error in the sense that $\delta E/E$ is small on the energy scale of the problem. So Boltzmann wrote down that

$$S(E, V, N) = k_B \ln \Omega(E, V, N; \delta E), \tag{2.1}$$

but he didn't really know how to count, which is something we will resolve (and is completely resolved in a quantum system).

We define the microcanonical ensemble as the system which has constraints on the variables E, V, N. As long as these constraints are satisfied, if we run some sort of simulation, the initial conditions will not change anything about the long time equilbrium. We again take our general formula for some physical variable m as

$$\langle m \rangle = \sum_\nu P_\nu m_\nu = P \sum_\nu m_\nu, \tag{2.2}$$

since in the microcanonical ensemble, P is independent of ν. When we count without quantum, we don't really know what the proper partition size of the system should be, however, we can still do something classically. Going back to Ω, we will further assume that Ω is a very rapidly increasing function of E. In the microcanonical ensemble we can define

$$P = \frac{1}{\Omega(E, V, N; \delta E)}, \tag{2.3}$$

which as we stated before is independent of ν.

Boltzmann made his guess of Eq. (2.1) for several reasons, namely that if we have two disjoint systems A, B, then $S_{AB} = S_A + S_B$. We can see this by considering ν_A, the possible microstates of A and ν_B, the possible microstates of B. So this corresponds to Ω_A and Ω_B respectively. So $\nu_{AB} = (\nu_A, \nu_B)$ which implies that

$$\Omega_{AB} = \Omega_A \cdot \Omega_B, \tag{2.4}$$

which is a combinatorial result. So by defining entropy as the $\ln \Omega$, we get

$$S_{AB} = k_B \ln \Omega_{AB} = k_B \ln(\Omega_A \Omega_B) = S_A + S_B. \tag{2.5}$$

The second reason has to do with probability. We can see that

$$P_{AB} = \frac{1}{\Omega_{AB}} = \frac{1}{\Omega_A} \cdot \frac{1}{\Omega_B} = P_A \cdot P_B, \tag{2.6}$$

which satisfies the probability laws for two disjoint systems.

We know from thermodynamics that we would like entropy to satisfy

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} > 0, \tag{2.7}$$

which is true in the current formulation. If we write $\beta = 1/k_B T$, then we have that

$$\beta = \left(\frac{\partial \ln(\Omega)}{\partial E}\right)_{V,N}. \tag{2.8}$$

It is sometimes useful to think about the magnitude of Ω. Ω is a number whose logarithm is 10^{23}, so it is on the order of $10^{10^{23}}$. This is a really big number. Because this number is so big, we have some tolerance in how we define it.

Perhaps, the most important thing about entropy that we know from thermodynamics is that the equilibrium entropy of a system with fixed E, V, N is greater than the same system with some internal constraint. This the second law of thermodynamics. In statistical mechanics we can interpret an internal constraint as removing possible states from the system. So lack of internal constraints will require Ω to be larger and therefore higher entropy.

Now we will look at the density of states and note that the number of states in a given interval $E - \delta E$ increases rapidly with E. So we can write

$$\Omega(E, V, N, \delta E) \leq \Omega(E, V, N, 2\delta E) < 2\Omega(E, V, N, \delta E). \tag{2.9}$$

If we take the log of the these things, we get that

$$S < \tilde{S} < S + k_B \ln 2. \tag{2.10}$$

the term $k_b \ln 2$ is very small which means that the choice of Ω is very insensitive to the final entropy. This means when we count states, we do not have to be perfect.

2.1 Gibb-Entropy Formula

If we note that $\sum_\nu P_\nu = 1$, then we can write that

$$S = -k_B \ln P_\nu$$
$$= -k_B \sum_\nu P_\nu \ln P_\nu, \tag{2.11}$$

which is the Gibb's entropy formula. Here we have used the fact that P_ν is independent of ν. This formula will be generally applicable and is often considered the fundamental formulation of entropy. This is because it works for all ensembles at once.

3 Canonical Ensemble

3.1 Formulation

Now we remove the constraint that the total energy is fixed. The idea is that we have a system in contact with a heat bath with specifies the temperature of the system. Another way to think about it is transforming to the Helmholtz free energy.

So we have a system and a bath where only energy can be exchanged where the bath is much larger than the system in the sense that

$$E^B \gg E^s. \tag{3.1}$$

We will consider both systems subsystems of an entire system which itself is described by the microcanonical ensemble. We would like to study the small subsystem which we assume is in a particular microstate E_ν at any point in time. We will assume that the total system has energy $E^T = E^B + E_\nu^S$. We want to derive $P_S(E_\nu)$.

3.2 Mathematical Description

We know that since E^T is conserved, then the probability of finding the subsystem in a single state E_ν is the same as finding the bath in the state $E^T - E_\nu$. Since the bath is described well by the microcanonical ensemble (better as size increased), we can write

$$P_S(E_\nu) = \frac{\Omega_B(E^T - E_\nu)}{\Omega_T(E_T)}, \tag{3.2}$$

where the denominator is a normalization factor independent of E_ν. Now we can Taylor expand as

$$\ln \Omega(E^T - E_\nu) = \ln \Omega_B(E^T) - E_\nu \underbrace{\left(\frac{\partial \ln \Omega_B}{\partial E} \right)_{E^T}}_{\beta} + \frac{1}{2} E_\nu^2 \left(\frac{\partial^2 \ln \Omega_B}{\partial E^2} \right)_{E^T}. \tag{3.3}$$

We will show that the last term can be ignored by order of magnitude arguments and therefore we can truncate the Taylor series at the second term which gives that

$$P_S(E_\nu) = c e^{-\beta E_\nu}, \tag{3.4}$$

where c is a normalization factor independent of ν. So we know that β is a property of the bath. Now we will sum over the probability to ensure that it is normalized and impose the condition

$$P_\nu = \frac{1}{Q} e^{-\beta E_v}, \tag{3.5}$$

where

$$Q(\beta, N, V) = \sum_\nu e^{-\beta E_\nu}, \tag{3.6}$$

and Q is called the canonical partition function. This is analogous the Ω function in the microcanonical ensemble. From Q we can derive all thermodynamic variables when our variables are β, N, V, so it must be related to the Helmholtz free energy.

3.3   Partition Function and Thermodynamics

We want to find the average energy, which is given as

$$
\begin{aligned}
\langle E \rangle &= \langle E_\nu \rangle \\
&= \sum_\nu P_\nu E_\nu \\
&= \sum_\nu \frac{E_\nu e^{-\beta E_\nu}}{Q} \\
&= \frac{-1}{Q} \frac{\partial}{\partial \beta} \left(\sum_\nu e^{-\beta e_\nu} \right) \\
&= \frac{-1}{Q} \frac{\partial Q}{\partial \beta} \\
&= -\left(\frac{\partial \ln Q}{\partial \beta} \right)_{N,V}.
\end{aligned}
\tag{3.7}
$$

So we can derive this purely based on th partition function. We can now use the Gibbs-Helmholtz equation

$$\frac{\partial \beta A}{\partial \beta} = E, \tag{3.8}$$

which implies

$$-\beta A = \ln Q + c, \tag{3.9}$$

where A is the Helmholtz free energy, and c is some constant independent of β which we will prove later is 0. This is the analogy between Q,A and Ω,S.

Notes from Snow Day on ELMS

4   Probability Distributions

We have often talked about Boltzmann distributions, but we want to think more generally about them.

4.1 Average and Most Probable

Suppose I have a variable E (could be energy) and we have some probability distribution $P(E)$. It has some sort of maximum and goes to zero as $E \to \infty$. The most probable energy is the one which corresponds to the maximal value of $P(E)$. To find the average energy, we need to to take

$$\langle E \rangle = \int dE \, E P(E), \tag{4.1}$$

or as similar summation in the discrete case, which is not in general equal to the most probable energy. The most probable energy is a local phenomena and the average energy takes account for the whole distribution. They are only equal for the case of a symmetric probability distribution.

4.2 Approximation by Gaussian Distribution

Often we can approximate a probability distribution (ex Boltzmann distribution) by a Gaussian distribution around the peak, which will still retain some of its properties. We can write the Boltzmann distribution as

$$P(E) = \frac{1}{Q} \Omega(E) e^{-\beta E}. \tag{4.2}$$

To find the most probable energy, we can take the first derivative with respect to energy, set this equal to zero, then solve for E. Since $P(E)$ is always positive, we can also use the derivative of the logarithm of the probability distribution function.

$$\frac{d}{dE} \ln P(E) = 0 = \frac{\partial \ln \Omega}{\partial E} - \beta. \tag{4.3}$$

It is useful to note that β comes from the bath. If we look at the system as a microcanonical ensemble, then it has a $\beta = \frac{\partial \ln \Omega}{\partial E}$, which means that the system in its most probable state has equal β to the bath. We can now perform a Taylor series expansion to second order which will yield a symmetric distribution. So we have that $E_{avg} = E_{mp}$ and we will expand about E_{mp} (most probable energy). If we introduce $\delta E = E - \langle E \rangle$,

$$\ln P(E) \approx \ln P(E_{mp}) + \left(\frac{\partial \ln P(E)}{\partial E} \right)_{E_{mp}} \delta E + \frac{1}{2} \left(\frac{\partial^2 P(E)}{\partial E^2} \right)_{E_{mp}} (\delta E)^2. \tag{4.4}$$

So if we exponentiate this, the linear term is zero, and we get the Gaussian approximation $P_G(E)$

$$P_G(E) = P(\langle E \rangle) \exp\left(-\frac{(\delta E)^2}{2 \langle (\delta E)^2 \rangle} \right) = \frac{1}{\sqrt{2\pi}\sigma_E} \exp\left(-\frac{(\delta E)^2}{2\sigma_E^2} \right), \tag{4.5}$$

where we have normalized in the last step. Note this is technically only a valid approximation for the region around $\langle E \rangle$, but it is really quite good everywhere. So we can see that

$$\frac{P(E)}{P(\langle E \rangle)} = \exp\left(-\frac{(\delta E)^2}{2\sigma_E^2} \right). \tag{4.6}$$

4.3 Applications

4.3.1 Maximum Term Method

We want to think of the partition function

$$Q = \sum_l \Omega(E_l) e^{-\beta E_l}, \tag{4.7}$$

if we pull out $\langle E \rangle$ from the summation, we have

$$Q = \Omega(\langle E \rangle) e^{-\beta \langle E \rangle} \sum_l \frac{\Omega(E_l)}{\Omega(\langle E \rangle)} e^{-\beta(E_l - \langle E \rangle)}. \tag{4.8}$$

If we take the logarithm, we get

$$\ln Q = \ln \Omega(\langle E \rangle) - \beta \langle E \rangle + \ln \left[\sum_l \frac{\Omega(E_l)}{\Omega(\langle E \rangle)} e^{-\beta(E_l - \langle E \rangle)} \right], \tag{4.9}$$

where we will argue that we can ignore the last term to a good approximation. If we assume that, then we have

$$\ln Q \approx \frac{S(\langle E \rangle)}{k_B} - \beta \langle E \rangle = -\beta A, \tag{4.10}$$

where A is the usual Helmholtz free energy. We must prove that the term is small. So if we look at the correction term

$$\ln \left[\sum_l \frac{\Omega(E_l)}{\Omega(\langle E \rangle)} e^{-\beta E_l - \langle E \rangle} \right] = \ln \left[\sum_l \frac{P(E)}{P(\langle E \rangle)} \right], \tag{4.11}$$

and now we will evaluate using the Gaussian approximation which says that

$$\frac{P(E)}{P(\langle E \rangle)} = e^{-(E - \langle E \rangle)^2 / 2\sigma_E}, \tag{4.12}$$

which is valid around $E \approx \langle E \rangle$. So we can write the correction term as

$$\ln \left[\int_{-\infty}^{\infty} dE \, e^{-\frac{(E - \langle E \rangle)^2}{2\sigma_E}} \right] = \ln \left[\sqrt{2\pi} \sigma_E \right] = \frac{1}{2} \ln \left[2\pi \sigma_E^2 \right] \tag{4.13}$$

where the limits are chosen such that we can do the integral ($-\infty$ won't contribute anything). So, we know that $\sigma_E^2 \propto C_v$ and C_v is extensive. So this means the correction term is proportional to $\ln[N]$. The leading order term is proportional to N. So this means that

$$\ln Q = -\beta A + O(\ln N). \tag{4.14}$$

So at a very large system size, we can ignore this correction term. This argument is known as the maximum term method.

Now we will do a similar argument backwards starting from the Gibb's entropy formula with some $\hat{S}$ (which we will late argue is entropy) equivalent to

$$\hat{S} = -k_B \sum_\nu P_\nu \ln P_\nu \tag{4.15}$$

where the partition function is $Q = e^{-\beta A}$ and so we can write

$$P_\nu = \frac{1}{Q} e^{-\beta E_\nu} = e^{\beta A - \beta E_\nu}. \tag{4.16}$$

So if we substitute (4.16) into (4.15), we get that

$$\hat{S} = -k_B \sum_\nu P_\nu \left[\beta A - \beta E_\nu \right]. \tag{4.17}$$

We can now notice that the first term is constant and since $\sum_\nu P_\nu = 1$, we get that

$$\hat{S} = -k_B \beta A + k_B \sum_\nu P_\nu \beta E_\nu, \tag{4.18}$$

Now if we notice that $\sum_\nu P_\nu E_\nu = \langle E \rangle$, we have that

$$\hat{S} = -k_B \beta A + k_B \beta \langle E \rangle = S_{thermo} \tag{4.19}$$

5 Two Level System

5.1 General Formulation

We now consider N distinguishable particles, where N is large. Each particle has only two energies, ground state and excited. We will call these 0 and ϵ. This is obviously wrong for any physical system, but it is an illustrative system. So to define a microstate for the system, we simply need to determine the atomic energy (ϵ or 0) for each particle. So we define an occupation number n_i which is either 0 or 1 for the ground and excited state respectively. This implies that the energy of the microstate is given as

$$E_\nu = \sum_{j=1}^{N} n_j \epsilon. \tag{5.1}$$

Alternatively, we can think of ν as a vector

$$\nu = (n_1, n_2, \ldots, n_N). \tag{5.2}$$

Note that the system energy levels are given by $E_m = m\epsilon$, where $0 \leq m \leq N$, and almost all are degenerate ($E_\nu = 0$ and $E_\nu = \epsilon N$) are not.

Two pertinent observations relating to the physical reality of this model is that there is a maximum energy $N\epsilon$ and this system only has a degeneracy of 1. We have supposed

prior that higher energy generally corresponded with higher degeneracy. This is a flaw in the model brought about by limiting to only two states. We will come back to this later as the degeneracy increasing is related to $\beta > 0$ which is a key feature of thermodynamics.

So now we will compute the degeneracy. There are $N + 1$ possible energies and we can provide a simple combinatorial argument to compute the degeneracies. So the mth energy level is obtained by choosing m particles and raising them to the exited state. Since we move up one at a time, for the first particle, there are N choices, $N - 1$ for the second one, etc. So

$$\Omega(E_m, N) = \frac{N(N-1)(N-2)\cdots(N-(m-1))}{m!} = \frac{N!}{(N-m)!m!} \tag{5.3}$$

where the denominator in the middle fraction comes from the ways in which we can choose the m particles. This is often referred to as N choose m with the symbol give as

$$\binom{N}{m}, \tag{5.4}$$

where it is important to remember that the order of choice does not matter.

5.2 Microcanonical Ensemble

Now we fix E_m of the system. Now we will compute $\beta(E_m)$. We know that

$$\beta = \frac{\partial \ln \Omega(E)m, N)}{\partial E_m} = \frac{1}{\epsilon} \frac{\partial \ln \Omega}{\partial m}, \tag{5.5}$$

where we can take the derivative, even though we are dealing with a discrete set of values instead of a function in the continuum limit. So we know that

$$\begin{aligned} \beta\epsilon &= \frac{\partial}{\partial m} \ln \left[\frac{N!}{(N-m)!m!} \right] \\ &= \ln \left[\frac{N}{m} - 1 \right], \end{aligned} \tag{5.6}$$

where we have used Stirling's approximation in the lowest order given as

$$\ln N! \approx N \ln N - N, \tag{5.7}$$

and a bunch of algebra. We can also write this as

$$\beta\epsilon = \ln \left[\frac{E_{max}}{E_m} - 1 \right]. \tag{5.8}$$

We can see here that if $E_m > E_{max}/2$, we can actually get a negative temperature, a huge energy. This is because this is the point where the degeneracy of the states starts to decrease with increasing m. Thermodynamics does not envision that this is possible. In fact, if we put the system in contact with a heat bath, this is not possible.

Now we can solve for E_m as a function of β which is what we should get in the canonical ensemble. So we may be able to guess this result as

$$E_m(\beta) = \frac{E_{max}}{1 + e^{\beta\epsilon}} = \frac{E_{max}e^{-\beta\epsilon}}{1 + e^{-\beta\epsilon}}. \tag{5.9}$$

We will see later that this is correct.

6 Ideal Non-Interacting Systems

6.1 Classical Review

We usually have an idea in gases that we can take a limit where the gases do not collide with the wall. Classically, if we have two systems A and B which do not interact with each other, but we consider the composite system C, then for $\nu(\nu_A, \nu_B)$, is given as

$$E_\nu^C = E_{\nu_A}^A + E_{\nu_B}^B, \tag{6.1}$$

and

$$P(E_\nu^C) = P(E_{\nu_A}^A)P(E_{\nu_B}^B), \tag{6.2}$$

and so the partition function (Canonical) is given as

$$Q^C = Q^A \cdot Q^B, \tag{6.3}$$

and this generalizes to many different systems. So in general suppose there are m non-interacting systems, the

$$Q = \prod_{j=1}^m Q_j. \tag{6.4}$$

However, quantum mechanics says that for identical particles, we need to modify this.

6.2 Quantum Ideal Systems

6.2.1 Basical Formalism

Suppose that we have N quantum particles where we have a wavefunction given as

$$\psi_\nu(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) \tag{6.5}$$

where $\vec{r}_1$ describes both spacial and spin coordinates. So we can write the Hamiltonian as

$$H^{(N)}(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \sum_{i=1}^n H^{(1)}(\vec{r}_i, \tag{6.6}$$

the sum of single particle Hamiltonians. So we can solve the single particle Schrodinger equation

$$H^{(1)}\phi_m(\vec{r} = \epsilon_m \phi_m(\vec{r}). \tag{6.7}$$

Now we can write the wavefunction as

$$\psi_\nu(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = S\left[\phi_{m_1}(\vec{r}_1)\phi_{m_1}(\vec{r}_2)\cdots\phi_{m_N}(\vec{r}_N)\right], \tag{6.8}$$

where S is the symmetrized product. The index ν is specified by set of occupation numbers of single particle states. The symmetry operator relates to defining the number of states which are possible. More specifically, we will write

$$\nu \to (n_a, n_b, \ldots n_p), \tag{6.9}$$

14

(a) Bose Statistics, there can be any combination of two particles in both states as long as the particles remain indistinguishable.

(b) Fermi Statistics, the particles can only be arranged as one in each state.

Figure 1: Bose and Fermi Statistics illustrated for the two state, two particle case.

where n_a is the number of particles in state a. After we symmetrize the wavefunction, we don't know which particles are in what state, but we do know the number of particles in each state. Different statistics will allow different values of these n_i. For Bosons, any values of n_i can be chosen which are permitted by the Hamiltonian. For Fermions, the occupation numbers can only be $n_j = 0, 1$ due to the Pauli exclusion principle.

6.2.2 Simple Example

Suppose that we have $P = 2$ and $N = 2$ which means we have two particles and two possible states. If we have a symmetric wavefunction (Bose), then we have

$$\psi_S = \frac{1}{\sqrt{2}} \left[\phi_a(\vec{r}_1)\phi_b(\vec{r}_2) + \phi_a(\vec{r}_2)\phi_b(\vec{r}_1) \right]. \tag{6.10}$$

The antisymmetric combination (Fermi) is given as

$$\psi_A = \frac{1}{\sqrt{2}} \left[\phi_a(\vec{r}_1)\phi_b(\vec{r}_2) - \phi_a(\vec{r}_2)\phi_b(\vec{r}_1) \right]. \tag{6.11}$$

So we can illustrate these two cases in Figure 1.

6.3 Lattice Vibrations

6.3.1 Formalism

Suppose we have a perfect crystal that forms a lattice, we assume that the atoms are in the lattice such that the they can only move in small perturbations around their lattice with a displacement from equilibrium given as

$$\vec{\xi}_i = (\xi_{ix}, \xi_{iy}, \xi_{iz}), \tag{6.12}$$

in three dimensions (can be generalized). So we can write the kinetic energy of the particles classically as

$$T = \frac{1}{2} \sum_{i=1}^{N} \sum_{\alpha=1}^{3} m_i \left(\frac{d\xi_{i\alpha}}{dt} \right)^2, \tag{6.13}$$

and we will condense the notatoin by letting $p \to 1, \dots 3N$ (all spacial coordinates) which gives us

$$T = \frac{1}{2} \sum_p m_p \dot{\xi}_p^2. \tag{6.14}$$

15

This is relatively simple, it is uncoupled and diagonal in the coordinate basis. However, the potential energy will couple the coordinates and therefore is not diagonal. We can write the potential $U(\{\xi_p\})$ as a Taylor expansion

$$U(\{\xi_p\}) = U(0,0,\dots,0) + \sum_{p=1}^{3N} \left(\frac{\partial U}{\partial \xi_p}\right)_{\xi=0} \xi_p + \frac{1}{2} \sum_{p=1}^{3N} \sum_{q=1}^{3n} \left(\frac{\partial^2 U}{\partial \xi_p \xi_q}\right)_{\xi=0} \xi_p \xi_q + \dots \quad (6.15)$$

Now if we let $K_{pq} = \left(\frac{\partial^2 U}{\partial \xi_p \xi_q}\right)_{\xi=0}$ and notice that the first derivative and the zero order terms will be zero since we are expanding about equilibrium, we recover the Hamiltonian

$$H = \frac{1}{2} \sum_p m_p \dot{\xi}_p^2 + \frac{1}{2} \sum_{p=1}^{3N} \sum_{q=1}^{3n} \xi_p K_{pq} \xi_q. \quad (6.16)$$

There is a linear algebra theorem which says that there is a linear combination of ξ which will diagonalize this Hamiltonian. These are called normal modes, η given as

$$\eta_p = \sum_{q=1}^{3n} a_{pq} \xi_q, \quad (6.17)$$

More concretely, we can choose a_{pq} such that $\{\eta_p\}$ diagonalizes the Hamiltonian which now appears as

$$H = \frac{1}{2} \sum_{p=1}^{3N} \tilde{m} \dot{\eta}_p^2 + \frac{1}{2} \sum_{p=1}^{3N} \tilde{K}_p \eta_p^2 = \sum_{p=1}^{3n} H_p \quad (6.18)$$

where $\tilde{m}$ is an effective mass, and $\tilde{K}_p$ is an effective spring constant, and H_p is a single particle Hamiltonian. Notice that this is a harmonic oscillator which we can solve exactly. The latter parts of these notes are given on ELMS since we missed class.

When we go to normal coordinates, we get a set of quantum harmonic oscillators with

$$\epsilon_{pn} = \hbar \omega_p \left(n + \frac{1}{2}\right). \quad (6.19)$$

So we can then get that

$$\beta A = \int_0^\infty d\omega \, g(\omega) \ln \left[2 \sinh \left(\frac{1}{2} \beta \hbar \omega_p\right)\right] + \beta U_0$$

$$= \beta U_0 + \underbrace{\frac{1}{2} \beta \hbar \int_0^\infty d\omega \, \omega g(\omega)}_{\text{zero point } E} + \int_0^\infty d\omega \, g(\omega) \ln \left[1 - e^{-\beta \hbar \omega}\right], \quad (6.20)$$

where we haved dropped the p in ω for notational symmetry. So we can write the enrgy as

$$E = \frac{\partial}{\partial \beta}(\beta A)$$

$$= U_0 + \frac{\hbar}{2} \int_0^\infty d\omega \, g(\omega) \omega + \int_0^\infty d\omega g(\omega) \frac{\hbar \omega e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}. \quad (6.21)$$

The first term is the classical energy from the atoms sitting on the lattice. The second term is the zero point energy of the quantum system. The third term is the temperature dependent energy of the normal mode motion. If we want to look at heat capacity, we can calculate

$$
\begin{aligned}
C_V &= \left(\frac{\partial E}{\partial T}\right)_{V,N} \\
&= k_B \int_0^\infty d\omega \, \frac{g(\omega)(\beta\hbar\omega)^2 e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2}.
\end{aligned} \tag{6.22}
$$

Note that $g(\omega)$ is a density of modes and we can often use simple models for good results in different regimes.

6.3.2 Einstein Model

If we have d dimensions, then we have

$$
\int_0^\infty d\omega \, g(\omega) = dN, \tag{6.23}
$$

and for $\omega > \omega_{max}$, $g(\omega) = 0$. So for d dimensions, we have that

$$
g_E(\omega) = dN\delta(\omega - \omega_E). \tag{6.24}
$$

We will now work in three dimensions. This is really a mean field picture and for high energy modes it works pretty well. We can choose an Einstein energy

$$
\theta_E = \frac{\hbar\omega_E}{k_B}, \tag{6.25}
$$

and the Einstein model will produce the heat capacity curves. This was the first model to replicate experimental curves at lower temperatures where the Dulong-Petit law does not hold since it does not go to zero. However, the Einstein model does not predict the correct approach to zero as experiments show it is not exponential.

6.3.3 Debye Model

This model corrects the most substantial error in the Einstein model which is its low temperature behavior. The physical error with the Einstein model is that it is treated as each particle vibrating in the fixed mean field of the other atoms. So this means that we should change some of the frequencies. What we get is that for long wavelength modes

$$
g(\omega) \propto \omega^{d-1}, \tag{6.26}
$$

which corresponds to fewer modes at lower energies. This fixes the low temperature issue. We know that Einstein's result works at higher temperatures, so the final result is some sort of interpolation formula,

$$
g_D(\omega) = \begin{cases} c_D\omega^{d-1} & \omega < \omega_d \\ 0 & \omega > \omega_D \end{cases} \tag{6.27}
$$

17

where c_D is evaluated from the requirement that the integral of g is dN, and ω_D determined from experiment. This yields

$$c_D = \frac{Nd^2}{\omega_D^d}, \tag{6.28}$$

which gives the full Debeye model

$$g_D(\omega) = \begin{cases} \frac{Nd^2}{\omega_D^d}\omega^{d-1} & \omega < \omega_d \\ 0 & \omega > \omega_D \end{cases} \tag{6.29}$$

Now we can compute the heat capacity as

$$\begin{aligned} C_v^D &= k_B \int_0^\infty d\omega\, \frac{g(\omega)(\beta\hbar\omega)^2 e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2} \\ &= \frac{k_B Nd^2}{\omega_D^d} \int_0^{\omega_D} d\omega\, \omega^{d-1} \frac{(\beta\hbar\omega)^2 e^{-\beta\hbar\omega}}{(1-e^{-\beta\hbar\omega})^2}. \end{aligned} \tag{6.30}$$

Now we switch variables to $x = \beta\hbar\omega$, which gives that

$$C_V^D = \frac{k_B Nd^2}{\omega_D^d} \frac{1}{(\beta\hbar)^d} \int_0^{\beta\hbar\omega_d} dx\, \frac{x^{d-1}x^2 e^{-x}}{(1-e^{-x})^2}, \tag{6.31}$$

which is not exactly solvable. However, we can solve it in the the two important limits $T \to \infty, T \to 0$.

As $T \to 0$, $\beta \to \infty$, we can evaluate the integral exactly, however, it is not simple to do. It is enough to know that it is a constant. So we get that

$$\lim_{T\to 0} C_v^D = \frac{k_B Nd^2}{\omega_D^d} \left(\frac{k_B T}{\hbar}\right)^d C, \tag{6.32}$$

where C is the value of the integral. So we get that $C_v^d \propto T^d$. This is the correct behavior for insulating solids.

As $T \to \infty$, $\beta \to 0$, and so we can expand the exponentials as a Taylor series, which leads to

$$\lim_{T\to\infty} C_v^D = \frac{k_B Nd^2}{\omega_D^d} \int_0^{\omega_D} d\omega\, \omega^{d-1} = dNk_B, \tag{6.33}$$

which also agrees with experiment.

The mid temperature region, can be fit to experimental data and gets the physics better than the Einstein model for simple materials.

6.4 Identical Ideal Quantum Particles

Start with a system of N quantum particles. Since they are non-interacting, we can still have single particles states, so let ϵ_j be the energy of the jth single particle state. So if we suppose that there are M single particle states, where M can be greater or less than N. The classical limit will turn out to be when $M \gg N$. So we can write down a $\nu_N = (n_1, n_2, \ldots, n_M)$ which

is the vector of occupation number in each states. Since we know how many particles we have

$$\sum_{j=1}^{M} n_j = N. \tag{6.34}$$

So this means that the energy of this configuration can be given as

$$E_{\nu_N} = \sum_{j=1}^{M} n_j \epsilon_j. \tag{6.35}$$

6.4.1 Canonical Ensemble Formalism

In the Canonical ensemble, we can look at the partition function Q, given as

$$Q = \sum_{\nu_N} \exp\left[-\beta E_{\nu_N}\right] = \sum_{\{n_j\}}' \exp\left[-\beta \sum_{j=1}^{M} n_j \epsilon_j\right], \tag{6.36}$$

where the prime indicates we must satisfy the total number condition. So we pick a correct choice of $\{n_j\}$ in the outer sum and do the inner sum, then choose the next choice. So it is in the outer sum where we must satisfy the number condition. However, this is quite hard to do in general, so we will instead use the grand ensemble.

6.4.2 Grand Ensemble Formalism

So we can write the grand partition function as

$$\Xi = \sum_{\nu} e^{-\beta(E_\nu - \mu N_\nu)}, \tag{6.37}$$

where ν is a state with N_ν particles and energy E_ν. We will want to get $\langle N \rangle_{\beta\mu} = N$, so that we can have a correspondence to the problem we want. We can write that

$$E_\nu \sum_{j=1}^{M} \epsilon_j n_j \; ; \; N_\nu \sum_{j=1}^{M} n_j, \tag{6.38}$$

and we have no restrictions on the set n_j we can take as of now (since we are not fixing N). So we have that

$$\Xi = \sum_{\{n_j\}} \exp\left[-\beta \sum_j (\epsilon_j - \mu) n_j\right] = \prod_{j=1}^{M} \left[\sum_{n_j} e^{-\beta(\epsilon_j - \mu) n_j}\right], \tag{6.39}$$

where we have used properties of exponentials. If we let

$$\xi_j(\beta\epsilon_j, \beta\mu) = \sum_{n_j} e^{-\beta(\epsilon_j - \mu) n_j}, \tag{6.40}$$

then we have that

$$\Xi = \prod_{j=1}^{M} \xi_j. \tag{6.41}$$

So if take the logarithm of Ξ, we thermodynamically get $\beta p V$ and from our previous formula, we see it is also

$$\ln \Xi = \beta p V = \sum_{j=1}^{M} \ln \xi_j. \tag{6.42}$$

So now to get average n_j, we get that

$$\langle n_j \rangle = \frac{\sum_{n_j} n_j e^{-\beta(\epsilon_j - \mu) n_j)}}{\sum_{n_j} e^{-\beta(\epsilon_j - \mu) n_j)}} = \frac{\partial \ln \zeta_j}{\partial(-\beta\epsilon_j)} = \frac{\partial \ln \zeta_j}{\partial \beta \mu} \tag{6.43}$$

Now we will see the difference between Bose and Fermi particles rests in the allowed n_j.

6.4.3 Fermi Particles

Here we can only have $n_j = 0, 1$. So anywhere we have summations, we only have two terms. So we get that

$$x_j^F = 1_e^{-\beta(\epsilon_j - \mu)}, \tag{6.44}$$

which implies that for $\beta p V$, we just need to take the natural log of this result and sum to get

$$\beta p v = \ln \Xi^B = \sum_{j=1}^{m} \ln \left[1 + e^{-\beta(\epsilon_j - \mu)} \right]. \tag{6.45}$$

We can now compute the average n_j as

$$\langle n_j \rangle^F = \frac{e^{-\beta(\epsilon_j - \mu)}}{1 + e^{-\beta(\epsilon_j - \mu)}} = \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1}, \tag{6.46}$$

which is the famous result for the Fermi distribution.

6.4.4 Bose Particles

Now we have Bose particles, where we do not have the easy summations of Fermi particles. Now we will do the same procedure, except we can sum to ∞. So

$$\xi_j^B = \sum_{n=0}^{\infty} e^{-\beta(\epsilon_j - \mu)n} = \frac{1}{1 - e^{-\beta(\epsilon_j - \mu)}} \tag{6.47}$$

where we have let $n_j \to n$ for ease of notation. Note that this sum assumes a geometric series, which only works if $e^{-\beta(\epsilon_j - \mu)} < 1$. This means that the chemical potential must be constrained such that for any state j, $\mu < \epsilon_j$. So this means we want

$$\mu \le \epsilon_0, \tag{6.48}$$

20

where ϵ_0 is the lowest energy single particle state. It will then be guaranteed to be less than the others. For now we will assume this is true and come back to it later. We can calculate the partition function as

$$\ln \Xi^B = -\sum_{j=1}^{M} \ln \left[1 - e^{-\beta(\epsilon_j - \mu)} \right],$$
(6.49)

and finally,

$$\langle n_j \rangle^B - \frac{e^{-\beta(\epsilon_j - \mu)}}{1 - e^{-\beta(\epsilon_j - \mu)}} = \frac{1}{e^{\beta(\epsilon_j - \mu)} - 1},$$
(6.50)

which is the famous Bose distribution. Note this allows $\langle n_j \rangle^B > 1$. Note that this requires $\mu < \epsilon_0$ and not equal to since we cannot have a zero denominator. However, very interesting number of physics if $\mu \to \epsilon_0$.

So to sum, we can write

$$\langle n_j \rangle = \frac{e^{-\beta(\epsilon_j - \mu)}}{1 \pm e^{-\beta(\epsilon_j - \mu)}},$$
(6.51)

and also

$$\ln \Xi = \pm \sum_{j} \ln \left[1 \pm e^{-\beta(\epsilon_j - \mu)} \right],$$
(6.52)

where $-$ is for Bose and $+$ is for Fermi.

6.4.5 Total Number Conservation

Next we will look at the average number of particles and attempt to make it equal to N

$$\langle N \rangle = \sum_{j} \langle n_j \rangle = \left. \frac{\partial \ln \Xi}{\partial \beta \mu} \right|_{\beta, V}.$$
(6.53)

6.5 Ideal Fermi System

6.5.1 Free electron model of metal

We will treat these as non-interacting, since this is the only easy thing we can do. However, this may be true since we need to put many electrons in many states, and as we put electrons in higher states, the kinetic energies get more important. The kinetic energies of the electrons in these higher states dominate the physics over the potential energy of the interactions. So we will treat this as a collection of particle in a box states.

So we we know that

$$\langle n_j \rangle = \frac{1}{e^{\beta(\epsilon_j - \mu)} + 1},$$
(6.54)

and we are interested in the limit $\beta \to \infty$ ($T \to 0$). We can write Eq. (6.54) as $F(\epsilon_J, \mu, T)$ which is referred to as the Fermi function and often just written as $F(\epsilon_j)$. We will use the grand canonical ensemble, but we must choose μ such that the $\langle N \rangle = N$. In the limit of large N, this will produce the correct answers since fluctuations are small.
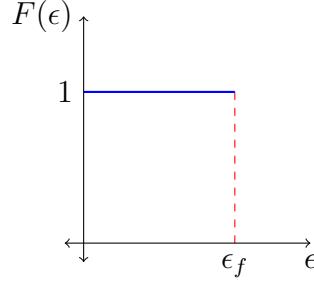
Figure 2: Plot of the Fermi function at $T = 0$ as a function of energy ϵ.

So we will write write $\mu_0 = \epsilon_F$ which is the Fermi energy and defined as the chemical potential as $T \to 0$. Note that

$$\lim_{T \to 0} F(\epsilon) = \begin{cases} 1 & \epsilon < \epsilon_F \\ 0 & \epsilon > \epsilon_F. \end{cases} \tag{6.55}$$

So this means that ϵ_F is the energy of the highest state if we fill all the levels as $T \to 0$. This can visualized by thinking about the Fermi function at $T = 0$, which is shown in Figure 2 Sow we have N atoms and we want to make sure that

$$N = 2 \sum_{j=0}^{\infty} \langle n_j \rangle, \tag{6.56}$$

where 2 comes from the spin degree of freedom. So now we wish to write this as a density of states. We can write this as

$$N = 2 \int_0^{\infty} d\epsilon \, g(\epsilon) F(\epsilon), \tag{6.57}$$

where $g(\epsilon)$ is the density of states and $g(\epsilon)d\epsilon$ is the number of states between ϵ and $\epsilon + d\epsilon$. We can find ϵ_F by looking at $T = 0$, where

$$N = 2 \int_0^{\epsilon_F} g(\epsilon) \, d\epsilon = 2\Phi(\epsilon_F). \tag{6.58}$$

and therefore by choosing ϵ_F (sometimes called μ_0) to satisfy the equality. Note that

$$g(\epsilon) = \frac{d\Phi}{d\epsilon}. \tag{6.59}$$

So $\Phi(\mu)$ is the number of single particles states which have energy less than or equal to μ. Now we model the particle as a particle in a box whose energy is given as

$$\epsilon_j = \frac{\hbar^2 \pi^2 j^2}{2mL^2}, \tag{6.60}$$

where $j^2 = j_x^2 + j_y^2 + j_z^2$. Now we want to determine $g(\epsilon)$ or $\Phi(\epsilon)$. We do this by solving for ϵ by noting that

$$j_\epsilon^2 = \frac{2mL^2\epsilon}{\hbar^2\pi^2} \tag{6.61}$$

22

So for a particular large energy ϵ, we can integrate to find

$$\Phi(\epsilon) = \int_0^{j_\epsilon} dj_x \int_0^{j_\epsilon} dj_y \int_0^{j_\epsilon} dj_z (1) = \frac{1}{8} \underbrace{\left(\frac{4}{3} \pi j_\epsilon^3 \right)}_{\text{Volume of Sphere}} \tag{6.62}$$

So we find that

$$\Phi(\epsilon) = \frac{V}{(2\pi)^3} \frac{4}{3} \pi \left(\frac{2m\epsilon}{\hbar^2} \right)^{3/2}, \tag{6.63}$$

where $V = L^3$. So now we can find $g(\epsilon)$ as

$$g(\epsilon) = \frac{d\phi}{d\epsilon} = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2}. \tag{6.64}$$

Note, this is only true for three dimensions. Now given this, we want to determine what ϵ_F or μ_0 must be. So using Eq. (6.58), we have

$$\epsilon_F = \mu_0 = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{N}{V} \right)^{2/3}, \tag{6.65}$$

which implies that the Fermi energy depends on the density of the sample. To see the size of this define $a = (V/N)^{1/3}$ and then we have that

$$\epsilon_F = c_1 \frac{\hbar^2}{ma^2}, \tag{6.66}$$

where $c_1 = (3\pi)^{2/3}/2 \approx 4.79$ of order unity. So we use Hartree E_h units where

$$1E_h = 27.2eV = \frac{\hbar^2}{ma_0^2}, \tag{6.67}$$

and a_0 is the Bohr radius. a_0 is about half an angstrom and in a normal metal the atomic spaces is a few angstroms. So this means that the Fermi energy is some fraction of a Hartree, order eV.

After some trivial algebra, we can write

$$g(\epsilon) = \frac{3N}{4\epsilon_F} \left(\frac{\epsilon}{\epsilon_F} \right)^{1/2}, \tag{6.68}$$

and also that

$$g(\epsilon_F) = \frac{3N}{4\epsilon_F}. \tag{6.69}$$

This means we can find

$$E(T=0) = 2 \int_0^{\epsilon_F} d\epsilon \, g(\epsilon)\epsilon = \frac{3}{5} N\epsilon_F. \tag{6.70}$$

If we go to finite temperatures, but $T \ll T_F$, where $T_F = \epsilon_F/k_B$, we have a different scenario. Here we want to evaluate the energy, which we can write as

$$E = 2 \int_0^\infty d\epsilon\, \epsilon g(\epsilon) F(\epsilon), \tag{6.71}$$

and we want

$$N = 2 \int_0^\infty d\epsilon\, g(\epsilon) F(\epsilon). \tag{6.72}$$

So we can solve these two equations, but note that we want to the number of particles to remain the same as at zero temperature. In principle, we need to write $\mu(T)$ in order to keep the number of particles constant, however, we can approximate a fixed chemical potential of μ_0, which is valid for this low temperature regime. In this regime

$$\frac{1}{e^{\beta(\epsilon-\mu)} - 1}, \tag{6.73}$$

is either 1 or 0, except for a very small region about the Fermi temperature, since β is very large compared to β_F. Here we have some electrons which are excited, although they go to low lying levels above ϵ_F. These small changes are called finite temperature effects. So we can compute (in a rather non-rigorous way) $E(T) - E(0)$ which is approximately the number of states excited multiplied by the energy of the excitation. The number of states can be approximated by $g(\epsilon_F)d\epsilon$, and so we have

$$E(T) - E(0) \propto g(\epsilon_F)k_B T \cdot k_B T, \tag{6.74}$$

since $d\epsilon = k_B T$ approximately. So we have that

$$E(T) - E(0) \propto g(\epsilon_F)(k_B T)^2. \tag{6.75}$$

One can also do this exactly which gives

$$E(T) - E(0) = \frac{\pi^2}{6} g(\epsilon_F)(k_B T)^2, \tag{6.76}$$

so the crude method was only off by a factor of 1.6, not bad. Now we can find the heat capacity as

$$C_V = \frac{\partial E}{\partial T} \propto g(\epsilon_F)k_B T, \tag{6.77}$$

which says that there exists contribution to the heat capacity from only electronic considerations.

6.6 Classical Limit of Quantum Ideal Gases

6.6.1 Derivation of Canonical Partition Function

We recall that we can write (with some different notation),

$$\ln \Xi = \beta p V = \pm \sum \ln \left[1 \pm z e^{-\beta \epsilon_j}\right], \tag{6.78}$$

24

where $+$ corresponds to Fermi particles, $-$ to Bose particles, and $z = e^{\beta\mu}$ is the activity. By convention we choose ϵ_0 as the lowest single particle energy as our zero. Now using the fact that for very small x, $\ln(1 + x) \approx x$, we have for $z \ll 1$, ($\beta\mu \ll 0$ with our zero energy convention),

$$\beta pV \approx z \sum_j e^{-\beta\epsilon_j} = zq, \tag{6.79}$$

where

$$q = \sum_j e^{-\beta\epsilon_j}. \tag{6.80}$$

This is sort of like a single particle partition function. Similarly, in the grand ensemble, we have an expression for the average number of particles

$$\langle N \rangle = \sum_j \langle n_j \rangle = \sum_j \frac{ze^{-\beta\epsilon_j}}{1 \pm ze^{-\beta\epsilon_j}}. \tag{6.81}$$

We can now expand this for small z which yields,

$$\langle N \rangle \approx zq \tag{6.82}$$

Now we can combine equations (6.79) and (6.82) to get that

$$\beta pV = \langle N \rangle, \tag{6.83}$$

independent of Bose or Fermi statistics. This is the classical ideal gas law. Now we notice that from eq. (6.82),

$$z = \frac{\langle N \rangle}{q}, \tag{6.84}$$

which we need to be much less than unity. This says that the number of accessible single particle states must be much less than the number of particles. So this is where we start to see classical behavior. Here there is no difference between Bose and Fermi statistics. Now if we note

$$\Xi = \sum_\nu e^{-\beta(E_\nu - N_\nu\mu)} = \sum_{N=0}^{\infty} e^{\beta N\mu} \sum_{\nu_N} e^{-\beta E\nu_N}, \tag{6.85}$$

and if we use the maximum term method, we can notice the second term is the canonical partition function, which gives that

$$\Xi \approx e^{\langle N \rangle \beta\mu} Q(\beta, V, \langle N \rangle). \tag{6.86}$$

Now we notice that

$$\ln \Xi = \beta pV = \langle N \rangle, \tag{6.87}$$

which we have shown is true in the classical limit. So we get that

$$\langle N \rangle = \langle N \rangle \beta\mu + \ln Q(\beta, V, \langle N \rangle), \tag{6.88}$$

and now using eq. (6.82) and the definition of activity, we have

$$\beta\mu = \ln \langle N \rangle - \ln q, \tag{6.89}$$

and upon substitution, we obtain

$$\ln Q = \langle N \rangle - \langle N \rangle \ln \langle N \rangle + \langle N \rangle \ln q \tag{6.90}$$

If we let $\langle N \rangle \to N$ and note that $\ln N! = N \ln N - N$ in the limit of large N, we get that

$$Q = \frac{1}{N!} q^n = \frac{1}{N!} \left(\sum_j e^{-\beta\epsilon_j} \right)^N, \tag{6.91}$$

which is equivalent to our classical canonical partition function. Now we can write q as an integral

$$q = \int_0^\infty d\epsilon \, g(\epsilon) e^{-\beta\epsilon}, \tag{6.92}$$

where $g(\epsilon)$ is as defined before. So we have that

$$q = \int_0^\infty d\epsilon \, \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2}. \tag{6.93}$$

Now we define $x = \beta\epsilon$, which implies that $dx = \beta d\epsilon$, and so we have that

$$\begin{aligned} q &= \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \beta^{-3/2} \int_0^\infty dx \, x^{1/2} e^{-x} \\ &= \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \beta^{-3/2} \frac{\sqrt{\pi}}{2} \\ &= V \left(\frac{mk_B T}{2\pi\hbar^2} \right)^{3/2}, \end{aligned} \tag{6.94}$$

and if we define the thermal de Broglie wavelength as

$$\Lambda = \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{1/2}, \tag{6.95}$$

then we can write

$$q = \frac{V}{\Lambda^3}, \tag{6.96}$$

and subsequently, we can write

$$Q = \frac{1}{N!} \left(\frac{V}{\Lambda^3} \right)^N. \tag{6.97}$$

6.6.2 Classical Results

We now can calculate the classical results from the derived partition function. For the energy,

$$E = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{V,N} = 3N\frac{\partial \ln \Lambda}{\partial \beta} = \frac{3}{2}Nk_BT. \tag{6.98}$$

Now we can write the pressure as

$$\beta p = \left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = N\frac{\partial \ln V}{\partial V} = \frac{N}{V} = \rho, \tag{6.99}$$

which is the ideal gas law. We can also calculate the chemical potential as

$$\beta\mu = \left(\frac{\partial \ln Q}{\partial N}\right)_{V,\beta} = \frac{\partial lnN!}{\partial N} - \ln q, \tag{6.100}$$

qhich after applying Stirling's approximation, gives that

$$\beta\mu = \ln \rho\Lambda^3, \tag{6.101}$$

which is somewhat odd since $\hbar$ is still there, however, if we exponentiate this, we see that

$$e^{\beta\mu} = z, \tag{6.102}$$

which must be very small. This is self consistent. In general, the size of the de Broglie wavelength gives us a measure of the "quantumness"" of the system.

7 Interacting Particles

7.1 Formulation

We will first consider on a fucntion like the Leohnard Jones potential which is of the form

$$w(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{7.1}$$

We will focus on the canonical partition function $Q(\beta, N, V)$, which for a system of particles in this potential are

$$Q(\beta, N, V) = \frac{1}{c}\int dr^N \int dp^N e^{-\beta H_N(p^N, R^N)}, \tag{7.2}$$

where c is a normalization factor of dimensions $r^N \cdot p^N$ which is the action to the $3N$ power and H_N is the Hamiltonian, which we define as

$$H_N = K(p^N) + U(r^N), \tag{7.3}$$

where K is the classical kinetic energy given as

$$K(p^N) = \sum_{i=1}^{N} \frac{p_i^2}{2m}, \tag{7.4}$$

and U is the potential energy from inter particle relations. The nice thing about classical mechanics is the separation between momentum and position. This is not true for quantum mechanics. This allows us to do these two separately.

7.1.1 Ideal Gas

For $U = 0$, the ideal gas, we can write

$$Q_{ideal}^{classical} = \frac{1}{c} \left[\int dp_x \int dp_y \int dp_z e^{-\frac{\beta}{2m}\left(p_x^2 + p_y^2 + p_z^2\right)} \right]^N V^N, \tag{7.5}$$

where the V^N is saying all the particles have to be in the box and then integrating over the radial coordinates. So evaluating the Gaussian integral, we get that

$$Q_{ideal}^{classical} = \frac{1}{c} \left(2\pi m k_B T\right)^{3N/2} \cdot V^N. \tag{7.6}$$

Yet from quantum theory we have already done, we know that the classical limit of the quantum partition function is given as

$$Q_{ideal}^{quantum} = \frac{1}{N!} \left(\frac{V}{\Lambda^3}\right)^N, \tag{7.7}$$

where $\Lambda = h^{1/2}(2\pi m k_B T)^{-1/2}$, and so we can compare these two results to find

$$c = N! h^{3N}. \tag{7.8}$$

This is exact for the ideal gas. We are going to assume that turning on interactions does not change this.

From now on, we can think about

$$Q = \frac{1}{N! h^{3N}} \int dr^N \int dp^N \, e^{-\beta H(r^n, p^N)}, \tag{7.9}$$

and we can look at

$$\frac{Q}{Q_{ideal}} = e^{-\beta(A - A_{ideal})} = \frac{\int dr^N \, e^{-\beta U(r^N)}}{V^N} = \frac{Z}{V^N}, \tag{7.10}$$

where Z is called the configuration integral.

7.1.2 General System

Now we write the correlation (or distribution) function which we can write as

$$P(r^N) = \frac{e^{-\beta U(r^N)}}{Z}, \tag{7.11}$$

and in general we look at the reduced distribution function in which we integrate over all but a few particles. One example is the pair correlation function in which we integrate over all but two particles which we can write as

$$P^{(2)}(r_1, r_2) = \int dr_3 \int dr_4 \cdots \int dr_N \, P(r^N). \tag{7.12}$$

Sometimes these will be written with tildes. If this was an ideal gas, then this function would just be

$$P^{(2)}_{ideal}(r_1, r_2) = P^{(1)}(r_1)P^{(1)}(r_2), \tag{7.13}$$

where

$$P^{(1)}(r_1) = \int dr_2 P^{(2)}(r_1, r_2). \tag{7.14}$$

For a correlated system, eq. (7.13) does not hold.

Often we are interested in asking questions about finding any particle at some position and having any position at some other position instead of asking about particular particles. To do this, we define a probability density

$$\rho^{(2)}(r_1, r_2) = N(N-1)P^{(2)}(r_1, r_2), \tag{7.15}$$

with the assumption that all the particles are the same.

7.1.3 Fluids

For a fluid well away from walls (could be a gas), $P^{(1)}(r_1)$ is a constant and since its integral must be 1, we get that

$$P^{(1)}_{fluid}(r_1) = \frac{1}{V}, \tag{7.16}$$

and we can see that

$$\rho^{(1)}_{fluid} = \frac{N}{V} = \rho. \tag{7.17}$$

Now we want to look at $p^{(2)}_{fluid}(r_1, r_2)$ and so for an ideal gas, we get that

$$\rho^{(2)}_{ideal} = \frac{N(N-1)}{V^2} = \rho^2 \left(1 - \frac{1}{N}\right). \tag{7.18}$$

Motivated by this, we can define

$$g^{(2)}(r_1, r_2) = g(r_1, r_2) = \frac{\rho^{(2)}(r_1, r_2)}{\rho^2}, \tag{7.19}$$

which essentially is dividing by $\rho^{(2)}$ of an ideal gas, and so for particles far apart $g(r_1, r_2) \to 1$.

Now if we think about a simple fluid with spherically symmetric particles which are rather close together. In principle, this depends on r_1, r_2 which are both vectors, however, at close distances, it only depends on the distance between the particles for particles that don't have shape (spheres). So

$$g^{(2)}(r_1, r_2) = g^{(2)}(|r_1 - r_2|) \tag{7.20}$$

This function wiggles around 1, goes to 1 at large distances, and is zero for less than the particle size. A gas won't have the wiggles. See Chandler 7.1 and 7.2.

Now we want to know about condition probabilities $P(r_1|r_2)$ which is the probability of r_1, given r_2. In a disordered system this probability decays as r grows radially. So particles close

to a fixed particle "see" it, and particles fair away do not. These conditional probabilities are just ratios of pair probabilities given as

$$P(r_1|r_2) = \frac{P^{(2)}(r_1, r_2)}{P^{(1)}(r_2)}. \tag{7.21}$$

Its clear to see this is normalized. Now we can also define this for an arbitrary particle

$$\rho^{(1)}(r_1|r_2) = \frac{\rho^{(2)}(r_1, r_2)}{\rho^{(1)}(r_2)}. \tag{7.22}$$

Missed one class about pairwise potential. Often we write

$$U(r^N) = \frac{1}{2} \sum_{i=1}^{N} \left[\sum_{j=1}^{N} \right]' u(r_{ij}) = \sum_{i<j}^{N} u(r_{ij}), \tag{7.23}$$

where the primed sum means we ignore terms where $j = i$.

7.2 Examples

7.2.1 Leonard-Jones Potential

We are concerned with the LJ potential which is given by

$$U = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right]. \tag{7.24}$$

We will assume a radially symmetric fluid. We will use the canonical ensemble, which means we can write

$$e^{-\beta(A - A_{ideal})} = \frac{Z}{V^N}, \tag{7.25}$$

where

$$Z = \int dr^N \, e^{-\beta \sum_{i<j} u(r_{ij})}, \tag{7.26}$$

the configuration integral. We have already done the ideal case, so we are concerned here only with the difference. We know that

$$\beta E = \beta \frac{\partial}{\partial \beta}(\beta A), \tag{7.27}$$

which we can use to find that

$$\begin{aligned}
\beta E - \beta E_{ideal} &= \frac{1}{Z} \beta \int dr^N \sum_{i<j} u(r_{ij}) e^{-\beta \sum_{i<j} u(r_{ij})} \\
&= Z^{-1} \beta \frac{N(N-1)}{2} \int d\vec{r_1} \int d\vec{r_2} \, u(r_{12}) \int d\vec{r_3} \int d\vec{r_4} \ldots e^{-\beta \sum_{i<j} U(r_{ij})} \\
&= \frac{\beta}{2} \int d\vec{r_1} \int d\vec{r_2} \, u(r_{12}) \rho^{(2)}(\vec{r_1}, \vec{r_2}),
\end{aligned} \tag{7.28}$$

where we have used the logarithmic derivative of both sides. Since this is a pair potential, we can integrate over everything except the pairs. When we integrate, we will get the same thing for each one, so we can do only one pair and multiply by the $N(N-1)/2$ independent pairs. So we get an exact expression reliant on only the pair potential and pair distribution for the expression.

Now for a fluid, we can simplify this expression by noting that $\rho^{(2)}(\vec{r}_1, \vec{r}_2) = \rho^2 g(r_{12})$, where $\rho = N/V$. So we can write

$$\int d\vec{r}_1 \int d\vec{r}_2 = \int d\vec{r}_1 \int d\vec{r}_{12}, \tag{7.29}$$

where $\vec{r}_{12}$ is the vector between the particles. So we can write

$$\beta E = \beta E_{ideal} \rho^2 V \int d\vec{r} u(r) g(r), \tag{7.30}$$

where we have used the fact that integrating over $\vec{r}_1$ gives the volume. We could simplify this by integrating over the angular coordinates and noting that $\rho = N/V$ to get that

$$\frac{\beta E}{N} = \frac{\beta E_{ideal}}{N} + \frac{\beta \rho}{2}(4\pi) \int_0^\infty dr \, r^2 u(r) g(r), \tag{7.31}$$

which is exact for a radially symmetric fluid. For a simple monotonic gas, $\beta E_{ideal}/N = 3/2$.

Just as one can get a formula for the energy, one can get a formula for the pressure. This will be a homework problem, but we will go over some of the details first. First we write that

$$\frac{\beta p}{\rho} = 1 - \frac{\beta p}{6} \int d\vec{r} \, r u'(r) g(r), \tag{7.32}$$

where we have noticed that $F = -u'(r)$. We also know if we take a derivative with respect to volume,

$$-\left(\frac{\partial \beta(A - A_{ideal})}{\partial V}\right)_{N,\beta} = \frac{\partial \ln Q/Q_{ideal}}{\partial V} = \frac{\partial \ln Z}{\partial V} = \beta(p - p_{ideal}) \tag{7.33}$$

So we need to differentiate a function of Z with respect to V, which can be aided by taking a cubic box with the origin at the lower left corner with side length L. In this case $L = V^{1/3}$. So we can write

$$Z = \int_0^{V^{1/3}} dx_1 \int_0^{V^{1/3}} dy_1 \int_0^{V^{1/3}} dz_1 \ldots \int_0^{V^{1/3}} dx_N \int_0^{V^{1/3}} dy_N \int_0^{V^{1/3}} dz_N \, e^{-U(r^N)}, \tag{7.34}$$

which we can do by using a trick. If we transform coordinates, by changing to dimensionless variables $x'_i = \frac{x_i}{V^{1/3}}$. So now we know that $V^{1/3}\vec{r}' = \vec{r}$. So we have that

$$U(r^N) = \sum_{i<j}^N u(r_{ij}) = \sum_{i<j}^N u(V^{1/3} r'_{ij}). \tag{7.35}$$

Now if we substitute this into the equation and do the proper chain rule, we can do the integral and then substitute back to the real coordinate for the answer.

31

We have the exact pressure equations for a pair potential $u(r)$, we have

$$\beta p = \rho - \frac{\beta \rho^2}{6} \int d\vec{r}\, g(r) r \frac{du}{dr} = \rho - \frac{\beta \rho^2}{6} 4\pi \int_0^\infty dr\, r^3 g(r) \frac{du}{dr}. \tag{7.36}$$

In the past, people were able to come up with empirical corrections to the ideal gas law $\beta p = \rho$ known as the Viral expansion,

$$\beta p = \rho + \rho^2 B_2(T) \tag{7.37}$$

If we want to take $g(r)$ to a low density limit, note that $g(r) = e^{-\beta w(r,\beta,\rho)}$ and we can approximate only two particles, so we know that $w \approx u$. So as $\rho \to 0$, $g(r) = e^{-\beta u(r)}$.

We start with the equation for pressure given by

$$\beta p = \rho - \frac{\beta \rho^2}{6} \int d\vec{r}\, g(r) r \frac{du}{dr} = \rho - \frac{\beta \rho^2}{6} 4\pi \int_0^\infty dr\, r^3 g(r) \frac{du}{dr}, \tag{7.38}$$

where we have performed the angular integration. Now we note that in the low density limit $g(r) = e^{-\beta u(r)}$. Now noting that

$$e^{-\beta u(r)} \frac{du}{dr} = \frac{d}{dr} \left[e^{-\beta u(r)} - 1 \right], \tag{7.39}$$

we can integrate by parts and wrhite

$$\int_0^\infty dr\, r^3 \frac{d}{dr} \left[e^{-\beta u(r)} - 1 \right] = \left[r^3 \left(e^{-\beta u(r)} - 1 \right) \right]_0^\infty - \int_0^\infty dr\, 3r^2 \left[e^{-\beta u(r)} - 1 \right]$$

$$= -\frac{3}{4\pi} \int d\vec{r} \left[e^{-\beta u(r)} - 1 \right], \tag{7.40}$$

where in the last step we have noticed that at long distances $e^{-\beta u(r)}$ goes as $e^{-\beta/r^6}$ since pairwise potentials go to zero as $1/r^6$ at long distances. Expanding in a power series to second order, we see that

$$r^3 \left(e^{-\beta u(r)} - 1 \right) \approx 1 - \frac{\beta}{r^3} - 1 = -\frac{\beta}{r^3} \tag{7.41}$$

which vanishes at ∞. It is clear that r^3 vanishes at zero, so the first term in the integration by parts is in fact zero. Plugging this back into our previous expression, we get

$$\beta p = \rho 0 \frac{\rho^2}{2} \int d\vec{r} \left[e^{-\beta u(r)} - 1 \right] \tag{7.42}$$

and comparing to the Virial expansion given as

$$\beta p = \rho + \rho^2 B_2(T), \tag{7.43}$$

we can solve for $B_2(T)$ as

$$\boxed{B_2(T) = -\frac{1}{2} \int d\vec{r} \left[e^{-\beta u(r)} - 1 \right]} \tag{7.44}$$

Higher order Virial coefficients involve integrals over more particles and get more complicated very quickly.

8 Ising Model

8.1 Formalism

We start with the idea of Ising spins which are either up or down, they are not really quantum mechanical, but can be treated as such. We have a lattice of points and a variable of $S_i = \pm 1$ which indicates the spin up or down for lattice site i. We have an Ising spin Hamiltonian given as

$$\mathcal{H}_I = -J \sum_{i<j}^{N} S_i S_j - H \sum_{i=1}^{N} S_i, \tag{8.1}$$

where $J > 0$ and the first sum is only over nearest neighbor pairs (not including diagonal neighbors), and H is the magnetic field. The sign of J is such that favorable energetic interactions lower the energy.

Now we write the canonical partition function Q as

$$Q(\beta, N, H) = \sum_{\{S_i\}=-1}^{+1} e^{-\beta \mathcal{H}_I(\{S_I\})} \tag{8.2}$$

So we can find the magnetization as

$$\langle m \rangle = \frac{1}{N} \sum_{i=1}^{N} \langle S_i \rangle, \tag{8.3}$$

where $\langle S_i \rangle$ is ± 1 and the case of $H = 0$, is interesting because there is no preferential spin and some interesting physics emerges.

8.2 Monte Carlo

Monte Carlo simulations are generally useful and we will give a brief overview of it here, mostly in context of the Ising model. We we look at

$$\langle A \rangle = \sum_{\nu} P_\nu^{eq} A_\nu, \tag{8.4}$$

where

$$P_\nu^{eq} = \frac{e^{-\beta E_\nu}}{\sum_{\nu} e^{-\beta e_\nu}}. \tag{8.5}$$

In a molecular dynamics simulation, we follow a path through phase space and we can take a time average through space of something like pressure or energy. This would yield the equilibrium value of anything we want to do. The price is that it is very computationally intensive and we may not know the correct way to integrate the equations. So often we cannot simulate on time scales that we care about, especially for long time processes.

To do this without solving the equations, we can take a subset of states to estimate $\langle A \rangle$, picking them with some randomness.

The first way we could think about doing this is the uniform way

$$\langle A \rangle_{uniform} = \sum_{t=1}^{t_N} A_t \frac{e^{-\beta E_t}}{\sum_{t=1}^{t_N} e^{-\beta E_t}} \tag{8.6}$$

In the limit as $t \to \infty$ this would work, however, it fails massively in any other general sense. The reason is we are not constraining our system (for example cores not overlapping). So most random states we pick will have zero weight in the sum. We need to pick better.

Monte Carlo starts with a configuration which is chosen properly, then it only changes the system by a tiny amount (in the Ising Model, flip only one spin). We can then check if the system satisfies reasonable constraints. In the Ising Model, we flip a spin and if it goes down, we accept it, and if it goes up, we accept it only part of the time based on the change to the Boltzmann factor. For the Ising model this is the Metropolis algorithm.

8.3 Solutions

Onsager's exact solution was for two dimensions and $H = 0$. It is historically important because it is the first place where phase transitions occur in statistical mechanics. Exact solutions cannot be found for three dimensions.

8.3.1 Exact $2d$ $H = 0$ Solution

Now we define $m = \langle S \rangle$ and we find that as $T \to T_c$, and $T \leq T_c$,

$$m \sim (T_c - T)^\beta, \tag{8.7}$$

where β is NOT $k_B T$, but is instead called a critical exponent. Onsager was able to prove that in $2d$, $\beta = 1/8$. The solution gives the critical temperature as

$$k_B T_c \approx 2.27 J, \tag{8.8}$$

and there is an exact expression for 2.27. We can also evaluate the heat capacity

$$C = \frac{\partial \langle E \rangle}{\partial T}\Big|_{H=0} \sim \ln \left[\frac{1}{|T - T_c|} \right], \tag{8.9}$$

which is unexpected. While this diverges, it diverges very slowly.

8.3.2 Numerical Solution for $3d$

For $3d$, we know $\beta = 0.313\ldots$, and we can evaluate more digits. It is important to note that this is not equal to 1/3, which was a prior thought. The heat capacity diverges, but it goes as

$$C = |T - T_c|^{-\alpha}, \tag{8.10}$$

where α is another critical exponent where

$$\alpha \approx 0.125\ldots, \tag{8.11}$$

and is not exactly $1/8$. One can show that near the critical point these numbers are independent of the lattice shaped used. So while they have a dependence on dimensionality, some of the microscopic details don't actually matter. Away from the critical points, these do matter.

8.4   Correlation Functions near T_c

We can define
$$C_{ij} = \langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle, \tag{8.12}$$
which will vanish at large distances. We can also talk about particles, where we have
$$n_i = \frac{S_i + 1}{2}, \tag{8.13}$$
and substitute this into eq. (8.12) to get
$$\frac{C_{ij}}{4} = \langle n_i n_j \rangle - \langle n_i \rangle \langle n_j \rangle. \tag{8.14}$$
This is similar to $\rho^{(2)}(\vec{r}_i, \vec{r}_j) - \rho^{(1)}(\vec{r}_i)\rho^{(1)}(\vec{r}_j)$. For fluids this gets simpler. So if we write
$$\langle M \rangle = \sum_{i=1}^{N} \langle S_i \rangle = \frac{\partial \ln Q_I}{\partial \beta H}, \tag{8.15}$$
where
$$Q_I = \sum_{\{S_i\}} e^{\beta H \sum_{i=1}^{N} S_i + \beta J \sum_{i<j} S_i S_j} \tag{8.16}$$
The more interesting function is the pair correlation function called the susceptibility χ given a
$$\chi = \frac{1}{N} \left(\frac{\partial \langle M \rangle}{\partial \beta H} \right)_\beta, \tag{8.17}$$
which is actually the second derivative of the Ising partition function. We can calculate this as
$$\chi = \frac{1}{N} \left\langle (\delta M)^2 \right\rangle, \tag{8.18}$$
where
$$\delta M = M - \langle M \rangle = \sum_{i=1}^{N} \left(S_i - \langle S \rangle \right). \tag{8.19}$$
Another way to think about this is if we start with some magnetization and we change the field by a small perturbation, what is the response and stability. How *susceptible* is the magnetization to perturbation. So after a bit of algebra, we get that
$$\chi = \frac{1}{N} \sum_{i,j} \left(\langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle \right) = \sum_{j=1}^{N} C_{1j} \tag{8.20}$$
Onsager also calculated this, so in the $2d$ model, it diverges strongly as
$$\chi \sim |T_c - T|^{-\gamma}, \tag{8.21}$$
where $\gamma = 7/4$. In three dimensions $\gamma \approx 1.26$.

8.5 Mean Field Theory

8.5.1 Overview

Mean field theory is a very simple approximation where we replace the spins with their average value. So the spin we are considering interacts with the magnetic field and an effective field from the rest of the spins. To compute the average value, we can compute the solution to a self consistency equation. This will allow us to perform the calculations.

8.5.2 Formalism

So we consider one spin S_0 among the other spins. We have that $S_0 = \pm 1$ and we have z neighbors. So we can write the mean field energy as

$$E_{MF}(S_0) = -S_0 H - JzS_0 \langle S \rangle = -S_0 H_{eff}, \tag{8.22}$$

where $H_{eff} = H + Jz \langle S \rangle$. We can write the probability as

$$P(S_0) = \frac{e^{\beta S_0 H_{eff}}}{q}, \tag{8.23}$$

where q is the normalization factor given as

$$q = e^{\beta H_{eff}} + e^{-\beta H_{eff}} = 2\cosh(BH_{eff}) \tag{8.24}$$

Now we can write the self consistency condition

$$\begin{aligned}
\langle S_0 \rangle &= \langle S \rangle \\
&= \sum_{S_0 = 1, -1} S_0 P(S_0) \\
&= \frac{e^{\beta H_{eff}} - e^{-\beta H_{eff}}}{2\cosh(\beta H_{eff})} \\
&= \tanh(\beta H_{eff}).
\end{aligned} \tag{8.25}$$

so we can write that

$$\langle S \rangle = \tanh[\beta(H + Jz \langle S \rangle)]. \tag{8.26}$$

8.5.3 Results for $H = 0$

Now we note that $\tanh(x) \approx x$ for small x. So if we want to get $\langle S \rangle = 0$, then we need $H = 0$. If $\beta Jz < 1$, then the only self consistent solution is that $\langle S \rangle = 0$, which says that at high temperatures, the magnetization vanishes. This is the proper equation. However, when $\beta Jz > 1$, there are two other (symmetric) solutions besides the $\langle S \rangle = 0$. So there are two broken symmetry states. These solutions are better at low temperatures. So we can define

$$k_B T_c^{MF} = Jz, \tag{8.27}$$

which is the coupling constant times the number of nearest neighbors. This is great because it predicts a critical temperature. The approximation should be very good at extreme temperatures, but the middle is sort of an interpolation, so it is good that it predicts a critical point. However, it misses dimensionality. Basically, when the system is stable against fluctuations, this method is quite good. When the system is not stable, this method is not as good. So mean field theory really ignored correlations. Obviously, this will not allows us to capture the entire picture and it is up to interpretation whether we can capture enough.

Now we want to find the critical exponent β, which is the β which gives as $m \to 0$ $((T_c - T)^\beta)$, note that this is not β in the sense of temperature. We will again take $H = 0$ and solve

$$\langle S \rangle = \tanh[\beta J z \langle S \rangle], \tag{8.28}$$

for small $\langle S \rangle$ as $T \to T_c$ from below. So we will take the first two terms in the Taylor series which gives

$$\langle S \rangle = \beta J z \langle S \rangle - \frac{1}{3}[\beta J z \langle S \rangle]^3 \tag{8.29}$$

Now since $\langle S \rangle$ is non-zero, although close, we can divide, which gives after some algebra

$$\langle S \rangle^2 = \frac{3(\beta J z - 1)}{(\beta J z)^3}. \tag{8.30}$$

We now express this in terms of critical temperature $k_B T_c = J z$ and define

$$t = \frac{T - T_c}{T_c}, \tag{8.31}$$

which gives how close we are to T_c, which allows us to write

$$m = \langle S \rangle = \pm\sqrt{3}\left(\frac{T}{T_c}\right)|t|^{1/2} \tag{8.32}$$

So this says that $\beta = 1/2$. This is not the same exponent as the exact solution (1/8 in two dimensions, .313 in three dimensions), however, it has the right qualitative behavior.

The energy of any given configuration in the mean field picture is given as

$$\langle E \rangle_{MF} = -J \sum -i < j \langle S_i \rangle \langle S_j \rangle. \tag{8.33}$$

So in this approximation for $T > T_c$, $\langle E \rangle_{MF} = 0$. This is not a very good result. This would also imply the heat capacity vanishes above T_c. For $T < T_c$

$$\langle E(T < T_F) \rangle_{MF} = \frac{-NJz}{2} \langle S \rangle^2, \tag{8.34}$$

and so we can calculate the heat capacity

$$\frac{\partial E}{\partial T} = \frac{-NJz}{2} \frac{\partial \langle S \rangle^2}{\partial t}, \tag{8.35}$$

where we have used t instead of T and ignored the constants since we only want to see the behavior. Since $\langle S \rangle^2 \propto t$, the heat capacity is constant below T_c.

8.6 One Dimensional Ising Model with $H = 0$

8.6.1 Formulation

In the one dimension we have spins enumerated as s_i. In order to learn what happens, we want to calculate the partition function. We will need to develop a new technique to do this, one can do it with renormalization groups or the transfer matrix method.

We will impose periodic boundary solutions by placing the spins on a ring which locally does not change anything, however, the N spin interacts with spin 1. We want to calculate

$$Q = \sum_{s_i = \pm 1} \exp \left[k \sum_{i < j} S_i S_j \right], \tag{8.36}$$

where $k = \beta J$, where the first sum is understood to be N sums.

8.6.2 Solution

So we are going to let $e^{k S_i S_j} = P_{S_i S_j}$, which can be understood as

$$e^{kSS'} = P_{SS'} = \begin{pmatrix} e^k & e^{-k} \\ e^{-k} & e^k \end{pmatrix}. \tag{8.37}$$

Now in the language of P, we can write

$$Q = \sum_{S_1} \cdots \sum_{S_N} P_{S_1 S_2} P_{S_2 S_3} \cdots P_{S_{N-1} S_N} P_{S_N S_1}. \tag{8.38}$$

Now we note that each index variables corresponds to same matrix P, so we can see that

$$Q = Tr[P^N], \tag{8.39}$$

by the definition of the trace. With Dirac notation, we can see this a bit more clearly as $P_{SS'} = \left\langle S | \hat{P} | S' \right\rangle$, and we can write

$$Q = \sum_{S_1} \cdots \sum_{S_N} \left\langle S_1 | \hat{P} | S_2 \right\rangle \left\langle S_2 | \hat{P} | S_3 \right\rangle \ldots \left\langle S_{N-1} | \hat{P} | S_N \right\rangle \left\langle S_N | \hat{P} | S_1 \right\rangle, \tag{8.40}$$

and using the definition of the completeness operator $I = \sum_x |x\rangle \langle X|$, we get that

$$Q = \sum_{S_1} \left\langle S_1 | \hat{P}^n | S_1 \right\rangle = Tr[\hat{P}^N], \tag{8.41}$$

which is the same as the previous result identifying the operator $\hat{P}$ with the matrix P. It can be shown that

$$Tr[P^N] = \lambda_+^N + \lambda_-^N = \lambda_+^N \left(1 + \left(\frac{\lambda_-}{\lambda_+} \right)^N \right), \tag{8.42}$$

where λ_+, λ_- are the eigenvalues of P. In the limit of $N \to \infty$, if $\lambda_+ > \lambda_-$, then

$$Q = \lambda_+^N. \tag{8.43}$$

So we can compute the characteristic equation as

$$\left(e^k - \lambda\right) - e^{-2k} = 0, \tag{8.44}$$

which is solved by

$$\lambda_\pm = e^k \pm e^{-k} \tag{8.45}$$

which implies that

$$\lambda_+ = e^k + e^{-k} = 2\cosh k, \tag{8.46}$$

and so

$$g = -\beta \frac{A}{N} - \frac{1}{N} \ln Q = \ln[2\cosh k], \tag{8.47}$$

where we have used that fact that $Q = [2\cosh k]^N$.

8.6.3   Phase Transitions in 1D (or not)

We already know there is no phase transition in this system. We can argue this on physics grounds as follows. If we have an Ising chain in its ground state (all up), then this has energy $E_0 = -NJ$. If we introduce a defect, then $E = E_0 + 4J$. If we flip another spin, then $E = E_0 + 4J$. Note that this is not higher in energy. So if we flip N spins in a domain (spins next to each other), $E = E_) + 4J$. The reason is that the defects only exist on the boundary since $1 \cdot 1 = -1 \cdot -1$. So no matter how large the domain, only the edge terms matter.

Due to this, it is clear that the it will be entropically favorable to not undergo a phase transition since configuration space will increase if we create domains, but energy will not. So it will not all be found in up or down.

8.7   Phase Transitions

We have already considered the magnetic susceptibility

$$\chi = \frac{1}{N} \frac{\partial \langle m \rangle}{\partial \beta H} = \sum_{i<j} [\langle S_i S_j \rangle - \langle S_i \rangle \langle S_j \rangle] = \sum_{i<j} C_{ij} \tag{8.48}$$

which diverges near the critical point T_c. Many other important quantities also do this. These divergences are what characterize phase transitions. In 1D, g is continuous and analytic and so none of these divergences can occur.

We know that in general $C_{ij} \propto C(r)$ and $\lim_{r \to \infty} C(r) = 0$. So we can speak of a correlation length ξ_B with characterizes the correlations length. At T_c this correlation length goes to ∞. So a diverging susceptibility is the same as a diverging correlation length scale. This allows us to write

$$C(r) \sim r^{-p} e^{-r/\xi_B}, \tag{8.49}$$

So there is a power law component with undetermined coefficient p and a exponential part. So close by, we are scale free, and at far distance, the correlation is strongly suppressed. In

the mean field approximation $p = d - 2 + \eta$, where d is the dimension of the system and η is a correction. For $d = 2$, $\eta = 1/4$ and for $d = 3$, $\eta = 0.07$. So the mean field gets better as the dimension grows higher. In fact, it is correct in four dimensions and higher.

In this problem, we are going to have three different length scales $a \ll r \ll \zeta_B$, where a is the lattice spacing. Now we want to look at the divergence of

$$\xi_B \propto |T - T_c|^{-\nu}, \tag{8.50}$$

and it can be found that in 2D, $\nu = 1$ and in 3D, $\nu = 0.63$. We can connect these together by noting that

$$\chi \sim \int d\vec{r} c(\vec{r}) \sim \int r^{d-1} \frac{e^{-r/\xi_B}}{r^{d-2+\eta}} \, dr \sim \xi_B^{2-\eta} \int_0^\infty x^{1-\eta} e^{-x} \, dx, \tag{8.51}$$

and so the divergence, must come from the first term and not the integral, since the integral does not diverge. Ths implies that

$$\chi \sim \xi_B^{2-\eta} \sim |t|^{-\nu(2-\eta)}, \tag{8.52}$$

and on the other hand $\chi \sim |T - T_c|^{-\gamma}$, which says that

$$\gamma = \nu(2 - \eta). \tag{8.53}$$

This is an example of a scaling relation.

8.7.1 Kadanoff Block Spin Picture

The general idea here is to take chunks of the system and scale it, while keeping the functional interactions the same. So in the simplest approximation, we create new coarse grain sites with spin variables $S_i^{(l)}$ which comes from course graining at a length scale l in terms of a. In the simplest terms, we can say these coarse $S_i^{(l)}$ will be ± 1, which is not a great approximation, but we can do better with $\pm m$ where m is less than one and then rescale to make it one.

By doing this, we are essentially thinning the degrees of freedom (this is somewhat related to what happens in the renormalization group). By doing this, we have created a new block spin system which is further away from criticality since the critical length has become smaller.

In this new system, we have the same Hamiltonian, but the constants are scaled as

$$\tilde{H} = Hl^x \, ; \, \tilde{T} = Tl^y, \tag{8.54}$$

and so we can derive equations connecting the new system parameters to the old ones, which are given as

$$\xi_B(T, H) = l\xi_B(l^y T, l^x H), \tag{8.55}$$

and for the free energy

$$A(T, H) = l^{-d} A(l^y T, l^x H), \tag{8.56}$$

and we can substitute something like $l = |t|^{-1/y}$ and get some of the scaling relations. This is a normal thing to use although in principle l is arbitrary.