3.1 Microcanonical, Canonical, Grand Canonical Ensembles

In statistical mechanics, we deal with a situation in which even the quantum state of the system is unknown. The expectation value of an observable must be averaged over:

$$\langle O \rangle = \sum_i w_i |i \rangle \langle i| O |i \rangle$$

(3.1)

where the states $|i \rangle$ form an orthonormal basis of $\mathcal{H}$ and $w_i$ is the probability of being in state $|i \rangle$. The $w_i$'s must satisfy $\sum w_i = 1$. The expectation value can be written in a basis-independent form:

$$\langle O \rangle = Tr \{ \rho O \}$$

(3.2)

where $\rho$ is the density matrix. In the above example, $\rho = \sum_i w_i |i \rangle \langle i|$. The condition, $\sum w_i = 1$, i.e. that the probabilities add to 1, is:

$$Tr \{ \rho \} = 1$$

(3.3)

We usually deal with one of three ensembles: the microcanonical ensemble, the canonical ensemble, or the grand canonical ensemble. In the microcanonical ensemble,
we assume that our system is isolated, so the energy is fixed to be $E$, but all states with energy $E$ are taken with equal probability:

$$\rho = C \delta(H - E) \tag{3.4}$$

$C$ is a normalization constant which is determined by (3.3). The entropy is given by,

$$S = -\ln C \tag{3.5}$$

In other words,

$$S(E) = \ln \left( \# \text{ of states with energy } E \right) \tag{3.6}$$

Inverse temperature, $\beta = 1/(k_B T)$:

$$\beta \equiv \left( \frac{\partial S}{\partial E} \right)_V \tag{3.7}$$

Pressure, $P$:

$$\frac{P}{k_B T} \equiv \left( \frac{\partial S}{\partial V} \right)_E \tag{3.8}$$

where $V$ is the volume.

First law of thermodynamics:

$$dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV \tag{3.9}$$

$$dE = k_B T \, dS - P \, dV \tag{3.10}$$

Free energy:

$$F = E - k_B T S \tag{3.11}$$

Differential relation:

$$dF = -k_B S \, dT - P \, dV \tag{3.12}$$

or,

$$S = -\frac{1}{k_B} \left( \frac{\partial F}{\partial T} \right)_V \tag{3.13}$$
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\[ P = - \left( \frac{\partial F}{\partial V} \right)_T \]  

while

\[
E = F + k_B T S \\
= F - T \left( \frac{\partial F}{\partial T} \right)_V \\
= -T^2 \frac{\partial^2 F}{\partial T^2} \frac{1}{T} 
\]  

(3.15)

In the canonical ensemble, we assume that our system is in contact with a heat reservoir so that the temperature is constant. Then,

\[ \rho = C e^{-\beta H} \]  

(3.16)

It is useful to drop the normalization constant, \( C \), and work with an unnormalized density matrix so that we can define the partition function:

\[ Z = \text{Tr} \{ \rho \} \]  

(3.17)

or,

\[ Z = \sum_a e^{-\beta E_a} \]  

(3.18)

The average energy is:

\[
E = \frac{1}{Z} \sum_a E_a e^{-\beta E_a} \\
= -\frac{\partial}{\partial \beta} \ln Z \\
= -k_B T^2 \frac{\partial^2}{\partial T^2} \ln Z 
\]  

(3.19)

Hence,

\[ F = -k_B T \ln Z \]  

(3.20)

The chemical potential, \( \mu \), is defined by

\[ \mu = \frac{\partial F}{\partial N} \]  

(3.21)
where \( N \) is the particle number.

In the grand canonical ensemble, the system is in contact with a reservoir of heat \textit{and} particles. Thus, the temperature and chemical potential are held fixed and

\[
\rho = C e^{-\beta(H-\mu N)} \tag{3.22}
\]

We can again work with an unnormalized density matrix and construct the grand canonical partition function:

\[
Z = \sum_{N,a} e^{-\beta(E_a-\mu N)} \tag{3.23}
\]

The average number is:

\[
N = -k_B T \frac{\partial}{\partial \mu} \ln Z \tag{3.24}
\]

while the average energy is:

\[
E = - \frac{\partial}{\partial \beta} \ln Z + \mu k_B T \frac{\partial}{\partial \mu} \ln Z \tag{3.25}
\]

### 3.2 Bose-Einstein and Planck Distributions

#### 3.2.1 Bose-Einstein Statistics

For a system of free bosons, the partition function

\[
Z = \sum_{E_a,N} e^{-\beta(E_a-\mu N)} \tag{3.26}
\]

can be rewritten in terms of the \textit{single-particle eigenstates} and the single-particle energies \( \epsilon_i \):

\[
E_a = n_0 \epsilon_0 + n_1 \epsilon_1 + \ldots \tag{3.27}
\]

\[
Z = \sum_{\{n_i\}} e^{-\beta(\sum_i n_i \epsilon_i - \mu \sum_i n_i)}
= \prod_i \left( \sum_{n_i} e^{-\beta(n_i \epsilon_i - \mu n_i)} \right)
\]
\[ \prod_i \frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}} \]  
(3.28)

\[ \langle n_i \rangle = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \]  
(3.29)

The chemical potential is chosen so that

\[ N = \sum_i \langle n_i \rangle \]

\[ = \sum_i \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \]  
(3.30)

The energy is given by

\[ E = \sum_i \langle n_i \rangle \epsilon_i \]

\[ = \sum_i \frac{\epsilon_i}{e^{\beta(\epsilon_i - \mu)} - 1} \]  
(3.31)

\( N \) is increased by increasing \( \mu \) (\( \mu \leq 0 \) always). Bose-Einstein condensation occurs when

\[ N > \sum_{i \neq 0} \langle n_i \rangle \]  
(3.32)

In such a case, \( \langle n_0 \rangle \) must become large. This occurs when \( \mu = 0 \).

### 3.2.2 The Planck Distribution

Suppose \( N \) is not fixed, but is arbitrary, e.g. the numbers of photons and neutrinos are not fixed. Then there is no Lagrange multiplier \( \mu \) and

\[ \langle n_i \rangle = \frac{1}{e^{\beta \epsilon_i} - 1} \]  
(3.33)

Consider photons (two polarizations) in a cavity of side \( L \) with \( \epsilon_k = \hbar \omega_k = \hbar ck \) and

\[ k = \frac{2\pi}{L} (m_x, m_y, m_z) \]  
(3.34)

\[ E = 2 \sum_{m_x, m_y, m_z} \omega_{m_x, m_y, m_z} \langle n_{m_x, m_y, m_z} \rangle \]  
(3.35)
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We can take the thermodynamic limit, \( L \rightarrow \infty \), and convert the sum into an integral. Since the allowed \( \vec{k} \)'s are \( \frac{2\pi}{L} (m_x, m_y, m_z) \), the \( \vec{k} \)-space volume per allowed \( \vec{k} \) is \((2\pi)^3/L^3\). Hence, we can take the infinite-volume limit by making the replacement:

\[
\sum_k f(\vec{k}) = \frac{1}{(\Delta \vec{k})^3} \sum_k f(\vec{k}) (\Delta \vec{k})^3 = \frac{1}{L^3} \int d^3 \vec{k} f(\vec{k})
\]

Hence,

\[
E = 2V \int_{\epsilon_{\text{max}}}^{\hbar \omega_{\epsilon_{\text{max}}}} d^3k \frac{\hbar \omega_k}{e^{\beta \hbar \omega_k} - 1} = 2V \int_{0}^{\hbar \omega_{\epsilon_{\text{max}}}} d^3k \frac{\hbar \omega_k}{e^{\beta \hbar \omega_k} - 1} = \frac{V k_B^4}{\pi^2 (\hbar c)^3} T^4 \int_{0}^{\epsilon_{\text{max}}} x^3 dx e^x - 1 \quad (3.37)
\]

For \( \beta \hbar c \epsilon_{\text{max}} \gg 1 \),

\[
E = \frac{V k_B^4}{\pi^2 (\hbar c)^3} T^4 \int_{0}^{\infty} x^3 dx e^x - 1 \quad (3.38)
\]

and

\[
C_V = 4V k_B^3 \frac{3k_B T}{\pi^2 (\hbar c)^3} \int_{0}^{\epsilon_{\text{max}}} x^3 dx e^x - 1 \quad (3.39)
\]

For \( \beta \hbar c \epsilon_{\text{max}} \ll 1 \),

\[
E = \frac{V k_{\text{max}}^3}{3\pi^2} k_B T \quad (3.40)
\]

and

\[
C_V = \frac{V k_{\text{max}}^3 k_B}{3\pi^2} \quad (3.41)
\]

3.3 Fermi-Dirac Distribution

For a system of free fermions, the partition function

\[
Z = \sum_{E_n} e^{-\beta (E_n - \mu_N)} \quad (3.42)
\]
can again be rewritten in terms of the single-particle eigenstates and the single-particle energies $\epsilon_i$:

$$E_a = n_0 \epsilon_0 + n_1 \epsilon_1 + \ldots$$  \hspace{1cm} (3.43)

but now

$$n_i = 0, 1$$  \hspace{1cm} (3.44)

so that

$$Z = \sum_{\{n_i\}} e^{-\beta (\sum n_i \epsilon_i - \mu \sum n_i)}$$

$$= \prod_i \left( \sum_{n_i=0}^{1} e^{-\beta (n_i \epsilon_i - \mu n_i)} \right)$$

$$= \prod_i \left( 1 + e^{-\beta (\epsilon_i - \mu)} \right)$$  \hspace{1cm} (3.45)

$$\langle n_i \rangle = \frac{1}{e^{\beta (\epsilon_i + \mu)} + 1}$$  \hspace{1cm} (3.46)

The chemical potential is chosen so that

$$N = \sum_i \frac{1}{e^{\beta (\epsilon_i + \mu)} + 1}$$  \hspace{1cm} (3.47)

The energy is given by

$$E = \sum_i \frac{\epsilon_i}{e^{\beta (\epsilon_i + \mu)} + 1}$$  \hspace{1cm} (3.48)

### 3.4 Thermodynamics of the Free Fermion Gas

Free electron gas in a box of side $L$:

$$\epsilon_k = \frac{\hbar^2 k^2}{2m}$$  \hspace{1cm} (3.49)

with

$$k = \frac{2\pi}{L} (m_x, m_y, m_z)$$  \hspace{1cm} (3.50)
Then, taking into account the 2 spin states,

\[
E = 2 \sum_{m_x, m_y, m_z} \epsilon_{m_x, m_y, m_z} \langle n_{m_x, m_y, m_z} \rangle
\]

\[
= 2V \int_{k_{\text{max}}}^{k_{\text{max}}} d^3k \frac{\hbar^2 k^2}{(2\pi)^3} \frac{1}{e^{\beta (\frac{\hbar^2 k^2}{2m} - \mu)} + 1}
\]

(3.51)

\[
N = 2V \int_{k_{\text{max}}}^{k_{\text{max}}} d^3k \frac{1}{(2\pi)^3} \frac{1}{e^{\beta (\frac{\hbar^2 k^2}{2m} - \mu)} + 1}
\]

(3.52)

At \(T = 0\),

\[
\frac{1}{e^{\beta (\frac{\hbar^2 k^2}{2m} - \mu)} + 1} = \theta \left( \mu - \frac{\hbar^2 k^2}{2m} \right)
\]

(3.53)

All states with energies less than \(\mu\) are filled; all states with higher energies are empty.

We write

\[
k_F = \frac{\sqrt{2m\mu_{T=0}}}{\hbar}, \quad \epsilon_F = \mu_{T=0}
\]

(3.54)

\[
\frac{N}{V} = 2 \int_0^{k_F} \frac{d^3k}{(2\pi)^3} = \frac{k_F^2}{3\pi^2}
\]

(3.55)

\[
\frac{E}{V} = 2 \int_0^{k_F} \frac{d^3k}{(2\pi)^3} \frac{\hbar^2 k^2}{2m}
\]

\[
= \frac{1}{\pi^2} \frac{10m}{3} N
\]

\[
= \frac{5}{3} V \epsilon_F
\]

(3.56)

\[
2 \int \frac{d^3k}{(2\pi)^3} = \frac{m^2 \hbar^2}{\pi^2 h^3} \int d\epsilon \epsilon^2
\]

(3.57)

For \(k_B T \ll \epsilon_F\),

\[
\frac{N}{V} = \frac{m^2 \hbar^2}{\pi^2 h^3} \int_0^{\infty} d\epsilon \epsilon^2 \frac{1}{e^{\beta (\epsilon - \mu)} + 1}
\]

\[
= \frac{m^2 \hbar^2}{\pi^2 h^3} \int_0^\mu d\epsilon \epsilon^2 + \frac{m^2 \hbar^2}{\pi^2 h^3} \int_\mu^\infty d\epsilon \epsilon^2 \left( \frac{1}{e^{\beta (\epsilon - \mu)} + 1} - 1 \right) + \frac{m^2 \hbar^2}{\pi^2 h^3} \int_\mu^{\infty} d\epsilon \epsilon^2 \frac{1}{e^{\beta (\epsilon - \mu)} + 1}
\]
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To lowest order in $H$, hence, we will only need

\[ \frac{(2m)^3}{3\pi^2 \hbar^3} \mu^2 + \frac{m^3 2^4}{\pi^2 \hbar^3} \int_0^\mu \frac{dt}{e^{\beta(t)}} \frac{1}{e^{\beta(t)} + 1} + \frac{m^3 2^4}{\pi^2 \hbar^3} \int_\mu^\infty \frac{dt}{e^{\beta(t)}} \frac{1}{e^{\beta(t)} + 1} \]

\[ \frac{(2m)^3}{3\pi^2 \hbar^3} \mu^2 + \frac{m^3 2^4}{\pi^2 \hbar^3} \int_0^\infty k_B T \frac{dx}{e^x + 1} \left( (\mu + k_B T x)^{\frac32} - (\mu - k_B T x)^{\frac32} \right) + O \left( e^{-\beta \mu} \right) \]

\[ \frac{(2m)^3}{3\pi^2 \hbar^3} \mu^2 + \frac{(2m)^3}{2^4} \sum \frac{\Gamma \left( \frac32 \right)}{(2n - 1)! \Gamma \left( \frac52 - 2n \right)} \int_0^\infty \frac{dx}{x^{2n - 1}} \]

\[ = \frac{(2m)^3}{3\pi^2 \hbar^3} \mu^2 \left[ 1 + \frac{3}{2} \left( \frac{k_B T}{\mu} \right)^2 I_1 + O \left( T^4 \right) \right] \tag{3.58} \]

with

\[ I_k = \int_0^\infty \frac{dx}{x^{k} e^x + 1} \tag{3.59} \]

We will only need

\[ I_1 = \frac{\pi^2}{12} \tag{3.60} \]

Hence,

\[ (\epsilon_F)^{\frac32} = \mu^4 \left[ 1 + \frac{3}{2} \left( \frac{k_B T}{\mu} \right)^2 I_1 + O \left( T^4 \right) \right] \tag{3.61} \]

To lowest order in $T$, this gives:

\[ \mu = \epsilon_F \left( 1 - \frac{\left( \frac{k_B T}{\epsilon_F} \right)^2 I_1 + O(\epsilon_F^4) }{\epsilon_F^2 \left( \frac{k_B T}{\epsilon_F} \right)^2 + O(\epsilon_F^4)} \right) \tag{3.62} \]
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\[
= \frac{(2m)^{\frac{3}{2}}}{5\pi^2\hbar^3}\mu^2 \left[ 1 + \frac{15}{2} \left( \frac{k_B T}{\mu} \right)^2 I_1 + O(T^4) \right] \\
= \frac{3}{5} \frac{N}{V} \epsilon_F \left( 1 + \frac{5\pi^2}{12} \left( \frac{k_B T}{\epsilon_F} \right)^2 + O(T^4) \right) \tag{3.63}
\]

Hence, the specific heat of a gas of free fermions is:

\[
C_V = \frac{\pi^2}{2} N k_B \frac{k_B T}{\epsilon_F} \tag{3.64}
\]

Note that this can be written in the more general form:

\[
C_V = (\text{const.}) \cdot k_B \cdot g(\epsilon_F) k_B T \tag{3.65}
\]

The number of electrons which are thermally excited above the ground state is \( \sim g(\epsilon_F) k_B T \); each such electron contributes energy \( \sim k_B T \) and, hence, gives a specific heat contribution of \( k_B \). Electrons give such a contribution to the specific heat of a metal.

### 3.5 Ising Model, Mean Field Theory, Phases

Consider a model of spins on a lattice in a magnetic field:

\[
H = -g\mu_B B \sum_i S_i^z \equiv 2h \sum_i S_i^z \tag{3.66}
\]

with \( S_i^z = \pm 1/2 \). The partition function for such a system is:

\[
Z = \left( 2 \cosh \frac{h}{k_B T} \right)^N \tag{3.67}
\]

The average magnetization is:

\[
S_i^z = \frac{1}{2} \tanh \frac{h}{k_B T} \tag{3.68}
\]

The susceptibility, \( \chi \), is defined by

\[
\chi = \left( \frac{\partial}{\partial h} \sum_i S_i^z \right)_{h=0} \tag{3.69}
\]
For free spins on a lattice,
\[ \chi = \frac{1}{2} N \frac{1}{k_B T} \]  
(3.70)

A susceptibility which is inversely proportional to temperature is called a Curie susceptibility. In problem set 3, you will show that the susceptibility is much smaller for a system of electrons.

Now consider a model of spins on a lattice such that each spin interacts with its neighbors according to:
\[ H = -\frac{1}{2} \sum_{(i,j)} J S_i^z S_j^z \]  
(3.71)

This Hamiltonian has a symmetry
\[ S_i^z \rightarrow -S_i^z \]  
(3.72)

For \( k_B T \gg J \), the interaction between the spins will not be important and the susceptibility will be of the Curie form. For \( k_B T < J \), however, the behavior will be much different. We can understand this qualitatively using mean field theory.

Let us approximate the interaction of each spin with its neighbors by an interaction with a mean-field, \( h \):
\[ H = -\sum_i h S_i^z \]  
(3.73)

with \( h \) given by
\[ h = \sum_i J \langle S_i^z \rangle = J z \langle S_i^z \rangle \]  
(3.74)

where \( z \) is the coordination number. In this field, the partition function is just \( 2 \cosh \frac{h}{k_B T} \) and
\[ \langle S^z \rangle = \tanh \frac{h}{k_B T} \]  
(3.75)

Using the self-consistency condition, this is:
\[ \langle S^z \rangle = \tanh \frac{J z \langle S^z \rangle}{k_B T} \]  
(3.76)
For $k_B T < J_z$, this has non-zero solutions, $S^z \neq 0$ which break the symmetry $S_i^z \rightarrow -S_i^z$. In this phase, there is a spontaneous magnetization. For $k_B T > J_z$, there is only the solution $S^z = 0$. In this phase the symmetry is unbroken and there is no spontaneous magnetization. At $k_B T = J_z$, there is a critical point at which a phase transition occurs.