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# Review of Statistical Mechanics

## 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:

$$\langle \mathcal{O} \rangle = \sum_i w_i \langle i | \mathcal{O} | i \rangle \quad (3.1)$$

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:

$$\langle \mathcal{O} \rangle = Tr \{ \rho \mathcal{O} \} \quad (3.2)$$

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:

$$Tr \{ \rho \} = 1 \quad (3.3)$$

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:

$$\rho = C \delta(H - E) \quad (3.4)$$

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

$$S = -\ln C \quad (3.5)$$

In other words,

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

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

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

Pressure,  $P$ :

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

where  $V$  is the volume.

First law of thermodynamics:

$$dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV \quad (3.9)$$

$$dE = k_B T dS - P dV \quad (3.10)$$

Free energy:

$$F = E - k_B T S \quad (3.11)$$

Differential relation:

$$dF = -k_B S dT - P dV \quad (3.12)$$

or,

$$S = -\frac{1}{k_B} \left( \frac{\partial F}{\partial T} \right)_V \quad (3.13)$$

$$P = - \left( \frac{\partial F}{\partial V} \right)_T \quad (3.14)$$

while

$$\begin{aligned} E &= F + k_B T S \\ &= F - T \left( \frac{\partial F}{\partial T} \right)_V \\ &= -T^2 \frac{\partial}{\partial T} \left( \frac{F}{T} \right) \end{aligned} \quad (3.15)$$

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

$$\rho = C e^{-\beta H} \quad (3.16)$$

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

$$Z = \text{Tr} \{ \rho \} \quad (3.17)$$

or,

$$Z = \sum_a e^{-\beta E_a} \quad (3.18)$$

The average energy is:

$$\begin{aligned} E &= \frac{1}{Z} \sum_a E_a e^{-\beta E_a} \\ &= - \frac{\partial}{\partial \beta} \ln Z \\ &= -k_B T^2 \frac{\partial}{\partial T} \ln Z \end{aligned} \quad (3.19)$$

Hence,

$$F = -k_B T \ln Z \quad (3.20)$$

The chemical potential,  $\mu$ , is defined by

$$\mu = \frac{\partial F}{\partial N} \quad (3.21)$$

where  $N$  is the particle number.

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

$$\rho = C e^{-\beta(H-\mu N)} \quad (3.22)$$

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

$$\mathcal{Z} = \sum_{N,a} e^{-\beta(E_a - \mu N)} \quad (3.23)$$

The average number is:

$$N = -k_B T \frac{\partial}{\partial \mu} \ln \mathcal{Z} \quad (3.24)$$

while the average energy is:

$$E = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} + \mu k_B T \frac{\partial}{\partial \mu} \ln \mathcal{Z} \quad (3.25)$$

## 3.2 Bose-Einstein and Planck Distributions

### 3.2.1 Bose-Einstein Statistics

For a system of free bosons, the partition function

$$Z = \sum_{E_a, N} e^{-\beta(E_a - \mu N)} \quad (3.26)$$

can be rewritten in terms of the *single-particle eigenstates* and the single-particle energies  $\epsilon_i$ :

$$E_a = n_0 \epsilon_0 + n_1 \epsilon_1 + \dots \quad (3.27)$$

$$\begin{aligned} Z &= \sum_{\{n_i\}} e^{-\beta(\sum_i n_i \epsilon_i - \mu \sum_i n_i)} \\ &= \prod_i \left( \sum_{n_i} e^{-\beta(n_i \epsilon_i - \mu n_i)} \right) \end{aligned}$$

$$= \prod_i \frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}} \quad (3.28)$$

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

The chemical potential is chosen so that

$$\begin{aligned} N &= \sum_i \langle n_i \rangle \\ &= \sum_i \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \end{aligned} \quad (3.30)$$

The energy is given by

$$\begin{aligned} E &= \sum_i \langle n_i \rangle \epsilon_i \\ &= \sum_i \frac{\epsilon_i}{e^{\beta(\epsilon_i - \mu)} - 1} \end{aligned} \quad (3.31)$$

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

$$N > \sum_{i \neq 0} \langle n_i \rangle \quad (3.32)$$

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

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

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

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

$$E = 2 \sum_{m_x, m_y, m_z} \omega_{m_x, m_y, m_z} \langle n_{m_x, m_y, m_z} \rangle \quad (3.35)$$

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:

$$\begin{aligned}\sum_{\vec{k}} f(\vec{k}) &= \frac{1}{(\Delta\vec{k})^3} \sum_{\vec{k}} f(\vec{k}) (\Delta\vec{k})^3 \\ &= \frac{L^3}{(2\pi)^3} \int d^3\vec{k} f(\vec{k})\end{aligned}\quad (3.36)$$

Hence,

$$\begin{aligned}E &= 2V \int_0^{k_{\max}} \frac{d^3k}{(2\pi)^3} \frac{\hbar\omega_k}{e^{\beta\hbar\omega_k} - 1} \\ &= 2V \int_0^{k_{\max}} \frac{d^3k}{(2\pi)^3} \frac{\hbar ck}{e^{\beta\hbar ck} - 1} \\ &= \frac{Vk_B^4}{\pi^2(\hbar c)^3} T^4 \int_0^{\beta\hbar ck_{\max}} \frac{x^3 dx}{e^x - 1}\end{aligned}\quad (3.37)$$

For  $\beta\hbar ck_{\max} \gg 1$ ,

$$E = \frac{Vk_B^4}{\pi^2(\hbar c)^3} T^4 \int_0^\infty \frac{x^3 dx}{e^x - 1}\quad (3.38)$$

and

$$C_V = \frac{4Vk_B^4}{\pi^2(\hbar c)^3} T^3 \int_0^\infty \frac{x^3 dx}{e^x - 1}\quad (3.39)$$

For  $\beta\hbar ck_{\max} \ll 1$ ,

$$E = \frac{Vk_{\max}^3}{3\pi^2} k_B T\quad (3.40)$$

and

$$C_V = \frac{Vk_{\max}^3 k_B}{3\pi^2}\quad (3.41)$$

### 3.3 Fermi-Dirac Distribution

For a system of free fermions, the partition function

$$Z = \sum_{E_a, N} e^{-\beta(E_a - \mu N)}\quad (3.42)$$

can again be rewritten in terms of the *single-particle eigenstates* and the single-particle energies  $\epsilon_i$ :

$$E_a = n_0 \epsilon_0 + n_1 \epsilon_1 + \dots \quad (3.43)$$

but now

$$n_i = 0, 1 \quad (3.44)$$

so that

$$\begin{aligned} Z &= \sum_{\{n_i\}} e^{-\beta(\sum_i n_i \epsilon_i - \mu \sum_i n_i)} \\ &= \prod_i \left( \sum_{n_i=0}^1 e^{-\beta(n_i \epsilon_i - \mu n_i)} \right) \\ &= \prod_i \left( 1 + e^{-\beta(\epsilon_i - \mu)} \right) \end{aligned} \quad (3.45)$$

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

The chemical potential is chosen so that

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

The energy is given by

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

### 3.4 Thermodynamics of the Free Fermion Gas

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

$$\epsilon_k = \frac{\hbar^2 k^2}{2m} \quad (3.49)$$

with

$$k = \frac{2\pi}{L} (m_x, m_y, m_z) \quad (3.50)$$

Then, taking into account the 2 spin states,

$$\begin{aligned}
 E &= 2 \sum_{m_x, m_y, m_z} \epsilon_{m_x, m_y, m_z} \langle n_{m_x, m_y, m_z} \rangle \\
 &= 2V \int_0^{k_{\max}} \frac{d^3 k}{(2\pi)^3} \frac{\frac{\hbar^2 k^2}{2m}}{e^{\beta\left(\frac{\hbar^2 k^2}{2m} - \mu\right)} + 1} \\
 (3.51)
 \end{aligned}$$

$$N = 2V \int_0^{k_{\max}} \frac{d^3 k}{(2\pi)^3} \frac{1}{e^{\beta\left(\frac{\hbar^2 k^2}{2m} - \mu\right)} + 1} \quad (3.52)$$

At  $T = 0$ ,

$$\frac{1}{e^{\beta\left(\frac{\hbar^2 k^2}{2m} - \mu\right)} + 1} = \theta\left(\mu - \frac{\hbar^2 k^2}{2m}\right) \quad (3.53)$$

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

We write

$$k_F = \frac{\sqrt{2m\mu_{T=0}}}{\hbar}, \quad \epsilon_F = \mu_{T=0} \quad (3.54)$$

$$\frac{N}{V} = 2 \int_0^{k_F} \frac{d^3 k}{(2\pi)^3} = \frac{k_F^3}{3\pi^2} \quad (3.55)$$

$$\begin{aligned}
 \frac{E}{V} &= 2 \int_0^{k_F} \frac{d^3 k}{(2\pi)^3} \frac{\hbar^2 k^2}{2m} \\
 &= \frac{1}{\pi^2} \frac{\hbar^2 k_F^5}{10m} \\
 &= \frac{3}{5} \frac{N}{V} \epsilon_F \quad (3.56)
 \end{aligned}$$

$$2 \int \frac{d^3 k}{(2\pi)^3} = \frac{m^{\frac{3}{2}} 2^{\frac{1}{2}}}{\pi^2 \hbar^3} \int d\epsilon \epsilon^{\frac{1}{2}} \quad (3.57)$$

For  $k_B T \ll \epsilon_F$ ,

$$\begin{aligned}
 \frac{N}{V} &= \frac{m^{\frac{3}{2}} 2^{\frac{1}{2}}}{\pi^2 \hbar^3} \int_0^\infty d\epsilon \epsilon^{\frac{1}{2}} \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \\
 &= \frac{m^{\frac{3}{2}} 2^{\frac{1}{2}}}{\pi^2 \hbar^3} \int_0^\mu d\epsilon \epsilon^{\frac{1}{2}} + \frac{m^{\frac{3}{2}} 2^{\frac{1}{2}}}{\pi^2 \hbar^3} \int_0^\mu d\epsilon \epsilon^{\frac{1}{2}} \left( \frac{1}{e^{\beta(\epsilon - \mu)} + 1} - 1 \right) + \frac{m^{\frac{3}{2}} 2^{\frac{1}{2}}}{\pi^2 \hbar^3} \int_\mu^\infty d\epsilon \epsilon^{\frac{1}{2}} \frac{1}{e^{\beta(\epsilon - \mu)} + 1}
 \end{aligned}$$



$$\begin{aligned}
&= \frac{(2m)^{\frac{3}{2}}}{3\pi^2\hbar^3} \mu^{\frac{3}{2}} - \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_0^\mu d\epsilon \epsilon^{\frac{1}{2}} \frac{1}{e^{-\beta(\epsilon-\mu)} + 1} + \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_\mu^\infty d\epsilon \epsilon^{\frac{1}{2}} \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \\
&= \frac{(2m)^{\frac{3}{2}}}{3\pi^2\hbar^3} \mu^{\frac{3}{2}} + \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_0^\infty \frac{k_B T dx}{e^x + 1} \left( (\mu + k_B T x)^{\frac{1}{2}} - (\mu - k_B T x)^{\frac{1}{2}} \right) + O(e^{-\beta\mu}) \\
&= \frac{(2m)^{\frac{3}{2}}}{3\pi^2\hbar^3} \mu^{\frac{3}{2}} + \frac{(2m)^{\frac{3}{2}}}{\pi^2\hbar^3} \sum_{n=1}^{\infty} (k_B T)^{2n} \left[ \mu^{\frac{3}{2}-2n} \frac{1}{(2n-1)!} \frac{\Gamma\left(\frac{3}{2}\right)}{\Gamma\left(\frac{5}{2}-2n\right)} \int_0^\infty dx \frac{x^{2n-1}}{e^x + 1} \right] \\
&= \frac{(2m)^{\frac{3}{2}}}{3\pi^2\hbar^3} \mu^{\frac{3}{2}} \left[ 1 + \frac{3}{2} \left( \frac{k_B T}{\mu} \right)^2 I_1 + O(T^4) \right] \tag{3.58}
\end{aligned}$$

with

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

We will only need

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

Hence,

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

To lowest order in  $T$ , this gives:

$$\begin{aligned}
\mu &= \epsilon_F \left( 1 - \left( \frac{k_B T}{\epsilon_F} \right)^2 I_1 + O(T^4) \right) \\
&= \epsilon_F \left( 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{\epsilon_F} \right)^2 + O(T^4) \right) \tag{3.62}
\end{aligned}$$

$$\begin{aligned}
\frac{E}{V} &= \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_0^\infty d\epsilon \epsilon^{\frac{3}{2}} \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \\
&= \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_0^\mu d\epsilon \epsilon^{\frac{3}{2}} + \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_0^\mu d\epsilon \epsilon^{\frac{3}{2}} \left( \frac{1}{e^{\beta(\epsilon-\mu)} + 1} - 1 \right) + \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_\mu^\infty d\epsilon \epsilon^{\frac{3}{2}} \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \\
&= \frac{(2m)^{\frac{3}{2}}}{5\pi^2\hbar^3} \mu^{\frac{5}{2}} - \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_0^\mu d\epsilon \epsilon^{\frac{3}{2}} \frac{1}{e^{-\beta(\epsilon-\mu)} + 1} + \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_\mu^\infty d\epsilon \epsilon^{\frac{3}{2}} \frac{1}{e^{\beta(\epsilon-\mu)} + 1} \\
&= \frac{(2m)^{\frac{3}{2}}}{5\pi^2\hbar^3} \mu^{\frac{5}{2}} + \frac{m^{\frac{3}{2}}2^{\frac{1}{2}}}{\pi^2\hbar^3} \int_0^\infty \frac{k_B T dx}{e^x + 1} \left( (\mu + k_B T x)^{\frac{3}{2}} - (\mu - k_B T x)^{\frac{3}{2}} \right) + O(e^{-\beta\mu}) \\
&= \frac{(2m)^{\frac{3}{2}}}{5\pi^2\hbar^3} \mu^{\frac{5}{2}} + \frac{(2m)^{\frac{3}{2}}}{\pi^2\hbar^3} \sum_{n=1}^{\infty} (k_B T)^{2n} \left[ \mu^{\frac{5}{2}-2n} \frac{1}{(2n-1)!} \frac{\Gamma\left(\frac{5}{2}\right)}{\Gamma\left(\frac{7}{2}-2n\right)} \int_0^\infty dx \frac{x^{2n-1}}{e^x + 1} \right]
\end{aligned}$$

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

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,

$$\chi = \frac{1}{2} N \frac{1}{k_B T} \quad (3.70)$$

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:

$$H = -\frac{1}{2} \sum_{\langle i,j \rangle} J S_i^z S_j^z \quad (3.71)$$

This Hamiltonian has a symmetry

$$S_i^z \rightarrow -S_i^z \quad (3.72)$$

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,  $h$ :

$$H = -\sum_i h S_i^z \quad (3.73)$$

with  $h$  given by

$$h = \sum_i J \langle S_i^z \rangle = Jz \langle S_i^z \rangle \quad (3.74)$$

where  $z$  is the coordination number. In this field, the partition function is just  $2 \cosh \frac{h}{k_B T}$  and

$$\langle S^z \rangle = \tanh \frac{h}{k_B T} \quad (3.75)$$

Using the self-consistency condition, this is:

$$\langle S^z \rangle = \tanh \frac{Jz \langle S^z \rangle}{k_B T} \quad (3.76)$$

For  $k_B T < Jz$ , 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  $k_B T > Jz$ , there is only the solution  $S^z = 0$ . In this phase the symmetry is unbroken and there is no spontaneous magnetization. At  $k_B T = Jz$ , there is a critical point at which a phase transition occurs.