Statistical Physics
Section 4: Assemblies of Weakly Interacting Constituents

Remember that an assembly comprises N microscopic constituents (atoms, spins etc) which we generally refer to as 'particles'.

By weakly interacting particles we mean that although there should be some mechanism for particles to exchange energy, *no energy is stored in any interaction potential.* Therefore we can write the total energy of the assembly as the sum of the individual energies.

4. 1. Localised Particles

Consider N identical particles situated on a regular lattice in three dimensions. For example, we could be concerned with an array of spins making up a macroscopic piece of magnetic material. Each particle has a permanent address within its assembly and is therefore *distinguishable.*

Under these circumstances each particle will have access to its own spectrum of states which we label by j_m say for particle m. If the particles are identical, which we generally assume, each has the same spectrum of states. We can specify the microstate i of the assembly by specifying the state j_m of each particle as follows:

- Particle 1 is in state j_1 with energy ϵ_{j_1}
- Particle 2 is in state j_2 with energy ϵ_{j_2}

  $\vdots$
- Particle N is in state j_N with energy ϵ_{j_N}

That is, the microstate of the assembly is specified by the set of labels $\{j_1, j_2, \ldots j_N\}$.

Now, assuming that the particles are weakly interacting, the energy for the assembly is

$$E_i = \epsilon_{j_1} + \epsilon_{j_2} + \cdots + \epsilon_{j_N}. \tag{1}$$

In the Canonical Ensemble we obtain the partition function of N distinguishable particles as

$$Z_c = \sum_{j_1, j_2 \cdots j_N} \exp -\beta[\epsilon_{j_1} + \epsilon_{j_2} + \cdots + \epsilon_{j_N}]$$

Using the properties of the exponential, we can *factorise* this result as

$$\boxed{Z_c = [Z(1)]^N} \tag{2}$$

where

$$Z(1) = \sum_j \exp(-\beta\epsilon_j) \tag{3}$$

is the *single-particle partition function* and the index j runs over the single-particle states.

Warning: $Z(1)$, as defined above, is sometimes referred to in texts as the microcanonical partition function. This is not to be confused with the microcanonical ensemble.

The thermodynamic properties of the assembly now follow quite straightforwardly from the use of the bridge equation:

$$F = -kT \ln Z_c = -NkT \ln Z(1) \ . \tag{4}$$

Moreover, due to the factorised nature of the partition function, the single-particle probability

> $p_j \equiv$ the probability of finding a particular particle (which belongs to the assembly) in a specific state j;

is given by,

$$p_j = \frac{\exp\left[-\beta\epsilon_j\right]}{Z(1)}, \tag{5}$$

which is, of course, just the Canonical or Boltzmann distribution for a single-particle.

Equation (2) is an example of a factorisation property whereby weakly interacting (or 'uncoupled') degrees of freedom lead to factorised pieces of the partition function. In turn, the bridge equation, then gives the free energy as the sum of these contributions. For example, in (4) the free energy of the assembly is just the sum of N contributions, one from each particle.

4. 2. Non-localised Particles

If identical particles are non-localised (e.g. in a gas) there is no way we can label the particles then keep track of them. This is due to quantum mechanics since if the particles collide we are unable to retain information about which is which. Therefore

Nonlocalised, identical particles are *indistinguishable*

In this case the microstate i of the assembly is specified by stating how many particles are in each quantum (or single-particle) state j. Thus

the set of occupation numbers $\{n_j\}$ specifies the microstate

That is

- state 1 whose energy is ϵ_1 contains n_1 particles
- state 2 whose energy is ϵ_2 contains n_2 particles

  ⋮

The sum over all microstates becomes a sum over the allowed occupation numbers. We write the energy of microstate i as

$$E_{i,N} = \sum_j n_j \epsilon_j \tag{6}$$

and the total number of particles in a microstate is

$$N = \sum_j n_j \; . \tag{7}$$

Working in the Canonical Ensemble would constrain the assembly to microstates with exactly N particles. This would make the sum over occupation numbers awkward due to the fact that all n_j should add to give precisely N i.e. there is a 'hard' constraint. However, in the Grand Canonical Ensemble we can sum over all possible values of N, i.e all possible values of each n_j, and just satisfy that on *average* we have $\overline{N}$ particles. This 'soft' constraint gives rise to the chemical potential μ as we saw in section 2. Thus we proceed in the GCE.

The grand canonical partition function takes the form using (6,7)

$$\mathcal{Z}_{gc} = \sum_{n_1, n_2 \ldots} \exp\{-\beta[n_1\epsilon_1 + n_2\epsilon_2 + \ldots] + \beta\mu[n_1 + n_2 + \ldots]\},$$

where the sum over n_j is over the allowed occupation of state j. Thus, the partition function may be written as

$$\boxed{\mathcal{Z}_{gc} = \prod_j \mathcal{Z}_j} \tag{8}$$

where

$$\mathcal{Z}_j = \sum_{n_j} \exp[\beta n_j(\mu - \epsilon_j)]. \tag{9}$$

is the *single-state partition function* for state j.

This result may be compared to equation (2) for the partition function of the canonical ensemble of nonconserved particles in the previous subsection. Here the factorisation is over states rather than particles.

The probability of finding the assembly in the microstate characterised by the set $\{n_j\}$, is just the Grand Canonical (or 'Gibbs') distribution,

$$p_{\{n_j\}} = \frac{\exp[\beta\mu \sum_j n_j - \beta \sum_j n_j\epsilon_j]}{\mathcal{Z}_{gc}} \; .$$

Due to the factorisation over states the probability of finding exactly n_j particles of the assembly in state j is given by

$$p_{n_j} = \frac{\exp \beta n_j[\mu - \epsilon_j]}{\mathcal{Z}_j}. \tag{10}$$

It follows that the mean number of particles in a specific state j, with energy ϵ_j, is just

$$\overline{n_j} = \sum_{n_j} n_j p_{n_j} = kT \frac{\partial \ln \mathcal{Z}_j}{\partial \mu} \tag{11}$$

where we have used the usual trick of section 3.

In order to perform the sums over allowed occupation numbers we need to consider whether the particles are Bosons or Fermions.

Fermions: Fermions have half integer spin (e.g. spin 1/2) and the exclusion principle limits the possible occupation numbers to $n_j = 0$ or 1. Hence the single-state partition function becomes

$$\mathcal{Z}_j = \exp 0 + \exp \beta(\mu - \epsilon_j) = 1 + \exp \beta[\mu - \epsilon_j].$$

Bosons: Bosons are those particles with integral spin, and the occupation number can take any nonnegative integer value. Thus the single-state partition function now becomes

$$\mathcal{Z}_j = \sum_{n_j=0}^{\infty} \exp \beta n_j[\mu - \epsilon_j]. \tag{12}$$

The sum is, of course, given by the geometric series

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \qquad \text{for} \quad |x| < 1 \tag{13}$$

and (12) takes the form

$$\mathcal{Z}_j = \{1 - \exp \beta[\mu - \epsilon_j]\}^{-1}.$$

Thus we can write the single-particle partition function for both cases as

$$\mathcal{Z}_j = \{1 \pm \exp \beta[\mu - \epsilon_j]\}^{\pm 1} \qquad \begin{array}{ll} + & \text{Fermion} \\ - & \text{Bosons} \end{array} \tag{14}$$

We now compute the mean number of particles in state j using (11)

$$\begin{aligned} \overline{n_j} &= \frac{1}{\beta}\frac{\partial \ln \mathcal{Z}_j}{\partial \mu} \\ &= \pm\frac{1}{\beta}\frac{\partial \ln\left[1 \pm \exp \beta[\mu - \epsilon_j]\right]}{\partial \mu} \\ &= \frac{\exp \beta[\mu - \epsilon_j]}{1 \pm \exp \beta[\mu - \epsilon_j]} . \end{aligned}$$

Finally, we can rearrange slightly to yield

$$\boxed{\overline{n_j} = \frac{1}{\exp \beta[\epsilon_j - \mu] \pm 1} \qquad \begin{array}{ll} + & \text{Fermi-Dirac} \\ - & \text{Bose-Einstein} \end{array}} \tag{15}$$

and these are the Fermi-Dirac and Bose-Einstein distributions for the *mean number of particles in a given state* j *which are to be memorised.*

Also we obtain for the grand potential

$$\Phi = -kT \ln \mathcal{Z}_{gc} = \mp kT \sum_j \ln\{1 \pm \exp \beta[\mu - \epsilon_j]\}, \tag{16}$$

and observable macroscopic properties then follow from the various thermodynamic relations.

4. 3. The Dilute Limit

We define the dilute limit as

$$\boxed{\exp\left[\beta\mu\right] \ll 1} \tag{17}$$

It can be shown (see P3) that this is achieved at either high temperatures or low particle densities, when the *de Broglie* wavelength of a particle is much smaller than the mean interparticle separation. Another criterion for the dilute (or classical) limit is that the probability of a given state being occupied is small. If there are many unoccupied states, then the exclusion principle for fermions becomes irrelevant as the chances of two particles trying to occupy the same state become vanishing small. In the previous subsection we derived an expression for this probability (10).

Now in the following we take, without loss of generality, the lowest energy state to be $\epsilon = 0$ so that $\epsilon_j \geq 0$. Therefore (17) ensures that

$$\exp\beta[\mu - \epsilon_j] \ll 1 \qquad \forall j \tag{18}$$

At this stage, it is convenient to work with the grand potential. Using the expansion for small x

$$\ln[1 + x] \simeq x$$

we find

$$\Phi \simeq \mp kT \sum_j (\pm) \exp\beta[\mu - \epsilon_j] = -kT \sum_j \exp\beta[\mu - \epsilon_j].$$

This is obviously consistent with our expectation that in the classical limit there is no distinction between the different kinds of particles and the equation is valid for both FD and BE statistics.

We can fix the chemical potential μ as follows. The mean particle number is given by

$$\begin{aligned} \overline{N} &= -\left(\frac{\partial\Phi}{\partial\mu}\right)_{T,V} \\ &= \sum_j \exp\beta[\mu - \epsilon_j] \\ &= \exp\beta\mu Z(1) \end{aligned}$$

where we have spotted $Z(1)$, the single-particle partition function (3). Rearranging this expression then yields

$$\mu = kT \ln\left[\frac{\overline{N}}{Z(1)}\right]$$

and also

$$\Phi = -kT\overline{N}\ .$$

Hence the Helmholtz free energy is

$$\begin{aligned} F &= \Phi + \mu \overline{N} \\ &= -kT\overline{N} + kT\overline{N} \ln \left[\frac{\overline{N}}{Z(1)} \right] \\ &\simeq -kT \ln \left[\frac{Z(1)^{\overline{N}}}{\overline{N}!} \right] \end{aligned}$$

where in the last step we have used Stirling's approximation for large N

$$\boxed{\ln N! = N \ln N - N} \tag{19}$$

This is an approximation that should be memorised. But we know that F is related to $\ln Z_c$ through the canonical bridge equation to $F = -kT \ln Z_c$. Therefore we deduce that in the dilute limit

$$Z_c = \frac{Z(1)^{\overline{N}}}{\overline{N}!} \tag{20}$$

for indistinguishable particles.

This recovers the semi-classical 'quick fix' i.e. the factor $N!$ corrects the overcounting of actually identical microstates for indistinguishable particle, in the partition function for distinguishable particles $Z(1)^{\overline{N}}$.

4. 4. The Density of states

For the purposes of calculating thermodynamic properties we will need to perform the sum over states apparent, for example, in (16) or in the calculation of the mean particle number

$$\overline{N} = \sum_j \overline{n_j} \ .$$

What we wish to do is approximate the sum by an integral using a function known as the density of states so that we can write

$$\overline{N} = \int_0^\infty \overline{n}(\epsilon, \mu) g(\epsilon) \mathrm{d}\epsilon \tag{21}$$

where we have acknowledged the fact that FD and BE distributions (15) are functions of ϵ and μ. Then the meaning of the density of states $g(\epsilon)$ is that

$$\boxed{g(\epsilon) d\epsilon = \text{ the number of states with energy between } \epsilon \text{ and } \epsilon + d\epsilon.}$$

The approximation of the sum by an integral facilitates the computation (integrals are usually easier than sums) and is generally expected to be a good approximation when there are many states with similar energies. This generally occurs at higher energies so we should be at sufficiently high temperature that higher energy states are dominant - see for example tutorial 2.3

4. 5. Density of states for a particle in a box

We now review a calculation done in some detail in Physics 3. We consider for the moment a spinless particle in a 3d box of side L. The time independent Schrödinger equation for the free particle (potential energy $U = 0$) reduces to the equation for standing waves:

$$\left(-\frac{\hbar^2}{2M}\nabla^2 - \epsilon\right)\psi = 0$$

where ϵ is the energy eigenvalue.

Consider first the one-dimensional case which becomes

$$\psi'' = -k^2\psi \quad \text{where} \quad k^2 = \frac{2M\epsilon}{\hbar^2}$$

We have to fit the boundary conditions that ψ vanishes at the boundaries $x = 0, L$. Thus

$$\psi = A\sin kx \quad \text{with} \quad k = \frac{n\pi}{L} \quad \text{and} \quad n = 1, 2, 3\ldots$$

and A is just a constant chosen to normalise the wavefunction.

The generalisation to three dimensions with the boundary conditions that ψ vanishes at $x, y, z = 0, L$ is straightforward:

$$\psi = A\sin k_x x\ \sin k_y y\ \sin k_z z \quad \text{with} \quad k_x = \frac{n_x\pi}{L} \quad k_y = \frac{n_y\pi}{L} \quad k_z = \frac{n_z\pi}{L} \tag{22}$$

$$\epsilon = \frac{\hbar^2}{2M}\left(k_x^2 + k_y^2 + k_z^2\right) \tag{23}$$

Warning: The ns here are not occupation numbers!

Figure 1: A 2-d representation of '$\underline{k}$-space'. The unit of area is $(\pi/L)^2$. A shell of radius k and thickness dk is indicated

For illustrative purposes Figure 1 shows the two dimensional case. Referring to Figure 1 we see that $\underline{k}$-space contains points, which represent the allowed quantum states of the particle, distributed with density $(L/\pi)^2$ per unit area of k-space, since each state occupies area $(\pi/L)^2$.

We wish to consider three dimensions. In three dimensions the points will be distributed with density $(L/\pi)^3$ per unit volume of $\underline{k}$-space.

Now the energy depends only on the *magnitude* k of the vector in $\underline{k}$-space

$$\epsilon = \frac{\hbar^2}{2M} k^2$$

where

$$k = (k_x^2 + k_y^2 + k_z^2)^{1/2} \ .$$

Let us consider the number of points in a spherical shell of radius k and width $\mathrm{d}k$. Actually we consider only the positive octant of the sphere because all n's in (22) are restricted to be positive. This gives us the density of states $\Gamma(k)$ in k space

$$\boxed{\Gamma(k)\mathrm{d}k = \text{ the number of states with wave vector } k \text{ between } k \text{ and } k + \mathrm{d}k.}$$

We find

$$\Gamma(k)\mathrm{d}k = \left(\frac{L}{\pi}\right)^3 \times \frac{4\pi k^2 \mathrm{d}k}{8}$$

The first factor on the right hand side is the number states per unit volume and the second factor is the volume of the octant shell.

Now to obtain the density of states in energy space, equate

$$g(\epsilon) = \Gamma(k)\left(\frac{\mathrm{d}k}{\mathrm{d}\epsilon}\right)$$

It is easiest to use () to calculate

$$\frac{\mathrm{d}\epsilon}{\mathrm{d}k} = \left(\frac{2\hbar^2}{M}\epsilon\right)^{1/2}$$

and after a little algebra we obtain

$$\boxed{g(\epsilon)\mathrm{d}\epsilon = \left(\frac{2M}{\hbar^2}\right)^{3/2} \frac{V}{4\pi^2}\epsilon^{1/2}\mathrm{d}\epsilon} \qquad (24)$$

The important features to note here are that the density of states increases with energy as $\epsilon^{1/2}$ and increases linearly with the volume V.

4. 6. Ideal Fermi and Bose Gases

We are now in a position to use the density of states (24) to calculate from (21) and (15) the chemical potential and so study the thermodynamics of the Ideal Fermi and Ideal Bose gases. In Physics 3 we studied the Ideal Fermi Gas in some detail particularly as a model for conduction electrons. Moreover, it also serves as a model for stars such as White Dwarfs and Neutron Stars. Sadly, we do not have time to explore further the Ideal Fermi Gas and you are referred to text books for inspiration. Instead will be focussing our attention on the Ideal Bose Gas which also has a wide range of applications and most importantly gives us our first example of a phase transition.