G25.2651: Statistical Mechanics

Notes for Lecture 8

I. INTRODUCTION TO SPIN

The path integral formulation of quantum statistical mechanics is particularly useful for situations in which particle spin statistics can be largely ignored. In the quantum ideal gases, we have a situation in which the spin statistics determine *all* of the interesting behavior! The fully quantum treatment of the ideal gas will be the subject of the next several lectures.

The spin degree of freedom of a particle is a purely quantum mechanical aspect (with no classical analog). In quantum mechanics, spin is analogous to an angular momentum. It is described by a Hermitian operator $\mathbf{S} = (S_x, S_y, S_z)$, where the components satisfy angular momentum type commutation relations:

$$[S_x, S_y] = i\hbar S_z \qquad [S_y, S_z] = i\hbar S_x \qquad [S_z, S_x] = i\hbar S_y$$

The spin operators for a spin-s particle are represented by $(2s+1) \times (2s+1)$ matrices (which define different representations of the group SU(2)). For example, for a spin-1/2 particle, such as an electron, the three spin operators are

$$S_x = \frac{\hbar}{2}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad S_y = \frac{\hbar}{2}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad S_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

which can be shown to satisfy the above commutation relations. Since the three components of spin to do not commute, we choose, by convention, to work in a basis in which S_z is diagonal. Thus, there will be $(2s+1)$ eigenvalues given by $-s\hbar, ..., s\hbar$. In the example of the spin-1/2 particle, we see that the allowed spin eigenvalues (denoted m) are $m = -hbar/2$ and $m = \hbar/2$. The corresponding eigenstates are just

$$|m = \hbar/2\rangle \equiv |\chi_{1/2}\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad |m = -\hbar/2\rangle \equiv |\chi_{-1/2}\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

which are denoted the "spin-up" and "spin-down" states, respectively. Note that the operator $S^2 = S_x^2 + S_y^2 + S_z^2$ is also diagonal so that the spin-up and spin-down eigenstates of S_z are also eigenstate of S^2, both having the eigenvalue $s(s+1)\hbar^2$. Thus, given a Hamiltonian H for a system, if H is independent of spin, then the eigenstates of H must also be eigenstates of S^2 and S_z since all three can be simultaneously diagonalized.

What happens in quantum mechanics when we have systems of identical particles of a given type of spin? Consider the simple example of a system of two identical spin-1/2 particles. Suppose we perform a measurement which is able to determine that one of the particles has an S_z eigenvalue of $m_a\hbar$ and the other $m_b\hbar$ such that $m_a \neq m_b$. Is the state vector of the total system just after this measurement

$$|m_a; m_b\rangle \qquad \text{or} \qquad |m_b; m_a\rangle$$

where, in the first state, particles 1 and 2 have S_z eigenvalues $m_a\hbar$ and $m_b\hbar$, respectively, and, in the second state, it is the reverse of this? The answer is that neither state is the correct state vector since the measurement is not able to assign the particular spin states of each particle. In fact, the two state $|m_a; m_b\rangle$ and $|m_b; m_a\rangle$ are not physically equivalent states. Two states $|\psi\rangle$ and $|\psi'\rangle$ can only be physicall equivalent if there is a complex number α such that

$$|\psi\rangle = \alpha|\psi'\rangle$$

and there is no such number connecting $|m_a; m_b\rangle$ and $|m_b; m_a\rangle$. However, it is possible to construct a new state vector $|\Psi(m_a, m_b)\rangle$ such that $|\Psi(m_b, m_a)\rangle$ is physically equivalent to $|\psi(m_a, m_b)\rangle$. Let

$$|\Psi(m_a, m_b)\rangle = C|m_a; m_b\rangle + C'|m_b; m_a\rangle$$

If we require that

$$|\Psi(m_a, m_b)\rangle = \alpha|\Psi(m_b, m_a)\rangle$$

then

$$C|m_a;m_b\rangle + C'|m_b;m_a\rangle = \alpha\left(C|m_b;m_a\rangle + C'|m_a;m_b\rangle\right)$$

from which we see that

$$C = \alpha C' \qquad C' = \alpha C$$

or

$$C' = \alpha^2 C'$$

from which $\alpha = \pm 1$ and $C = \pm C'$. This gives us two possible physical states of the system

$$|\Psi_S(m_a,m_b)\rangle \propto |m_a;m_b\rangle + |m_b;m_a\rangle$$

$$|\Psi_A(m_a,m_b)\rangle \propto |m_a;m_b\rangle - |m_b;m_a\rangle$$

which are symmetric and antisymmetric, respectively, with respect to an exchange of the particle spin eigenvalues. The analog in ordinary one-dimensional quantum mechanics would be the case of two identical particles moving along the x axis. If a measurement performed on the system determined that a particle was at position $x = a$ and the other was at $x = b$, then the state of the system after the measurement would be one of the two following possibilities:

$$|\Psi_S(a,b)\rangle \propto |a\ b\rangle + |b\ a\rangle$$

$$|\Psi_A(a,b)\rangle \propto |a\ b\rangle - |b\ a\rangle$$

The standard postulates of quantum mechanics now need to supplemented by an additional postulate that allows us to determine which of the two possible physical states a system will assume. The new postulate states the following: In nature, particles are of two possible types – those that are always found in symmetric (S) states and those that are always found in antisymmetric (A) states. The former of these are known as bosons and the latter are known as fermions. Moreover, fermions possess only half-integer spin, s=1/2,3/2,5/2,..., while bosons possess only integer spin, s=0,1,2,....

Suppose a system is composed of N identical fermions or bosons with coordinate labels $\mathbf{r}_1,...,\mathbf{r}_N$ and spin labels $s_1,...,s_N$. Let us define, for each particle, a combined lable $\mathbf{x}_i \equiv \mathbf{r}_i, s_i$. Then, for a given permutation $P(1),...,P(N)$ of the particle indices 1,..,N, the wave function will be totally symmetric if the particles are bosons:

$$\Psi_{\rm B}(\mathbf{x}_1,...,\mathbf{x}_N) = \Psi_{\rm B}(\mathbf{x}_{P(1)},....,\mathbf{x}_{P(N)})$$

For fermions, as a result of the Pauli exclusion principle, the wave function is antisymmetric with respect to an exchange of any two particles in the systems. Therefore, in creating the given permutation, the wave function will pick up a factor of -1 for *each* exchange of two particles that is performed:

$$\Psi_{\rm F}(\mathbf{x}_1,...,\mathbf{x}_N) = (-1)^{N_{\rm ex}}\Psi_{\rm F}(\mathbf{x}_{P(1)},....,\mathbf{x}_{P(N)})$$

where $N_{\rm ex}$ is the total number of exchanges of two particles required in order to achieve the permutation $P(1),...,P(N)$. An N-particle bosonic or fermionic state can be created from a state $\Phi(\mathbf{x}_1,...,\mathbf{x}_N)$ which is not properly symmetrized but which, nevertheless, is an eigenfunction of the Hamiltonian

$$H\Phi = E\Phi$$

Noting that there will be $N!$ possible permutations of the N particle labels in an N-particle state, the bosonic state $\Psi_{\rm B}(\mathbf{x}_1,...,\mathbf{x}_N)$ is created from $\Phi(\mathbf{x}_1,...,\mathbf{x}_N)$ according to

$$\Psi_{\rm B}(\mathbf{x}_1,...,\mathbf{x}_N) = \frac{1}{N!}\sum_{\alpha=1}^{N!} P_\alpha \Phi(\mathbf{x}_1,...,\mathbf{x}_N)$$

where $P_{\rm alpha}$ creates 1 of the $N!$ possible permutations of the indices. The fermionic state is created from

$$\Psi_{\rm F}(\mathbf{x}_1,...,\mathbf{x}_N) = \frac{1}{N!}\sum_{\alpha=1}^{N!} (-1)^{N_{\rm ex}(\alpha)}\, P_\alpha \Phi(\mathbf{x}_1,...,\mathbf{x}_N)$$

where $N_{\rm ex}(\alpha)$ is the number of exchanges needed to create permutation α.

This simple difference in the symmetry of the wavefunction leads to stark contrasts in the properties of fermonic and bosonic systems. With these quantum mechanical rules in mind, let us work out what these properties are.

II. SOLUTION OF THE N-PARTICLE EIGENVALUE PROBLEM

The Hamiltonian for an ideal gas of N particles is

$$H = \sum_{i=1}^{N} \frac{\mathbf{P}_i^2}{2m}$$

The eigenvalue problem for the Hamiltonian is in the form of the time-independent Schrödinger equation for the (unsymmetrized) eigenfunctions

$$-\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 \Phi(\mathbf{x}_1, ..., \mathbf{x}_N) = E\Phi(\mathbf{x}_1, ..., \mathbf{x}_N)$$

First, we notice that the equation is completely separable in the N particle coordinate/spin labels $\mathbf{x}_1, ..., \mathbf{x}_N$, meaning that the Hamiltonian is of the form

$$H = \sum_{i=1}^{N} h_i$$
$$h_i = \frac{\mathbf{P}_i^2}{2m}$$

Note, further, that H is independent of spin, hence, the eigenfunctions must also be eigenfunctions of S^2 and S_z. Therefore, the solution can be written as

$$\Phi_{\alpha_1 m_1, ..., \alpha_N m_N}(\mathbf{x}_1, ..., \mathbf{x}_N) = \prod_{i=1}^{N} \phi_{\alpha_i m_i}(\mathbf{x}_i)$$

where $\phi_{\alpha_i m_i}(\mathbf{x}_i)$ is a single particle wave function characterized by a set of spatial quantum numbers α_i and S_z eigenvalues m_i. The spatial quantum numbers α_i are chose to characterized the spatial part of the eigenfunctions in terms of appropriately chosen observables that commute with the Hamiltonian. Note that each single-particle function $\phi_{\alpha_i m_i}(\mathbf{x}_i)$ can be further decomposed into a product of a spatial function $\psi_{\alpha_i}(\mathbf{r}_i)$ and a spin eigenfunction $\chi_{m_i}(s_i)$, where

$$\chi_m(s) = \langle s|\chi_m\rangle = \delta_{ms}$$

Substituting this ansatz in to the wave equation yields a *single-particle wave equation* for each single particle function:

$$-\frac{\hbar^2}{2m}\nabla_i^2 \psi_{\alpha_i}(\mathbf{r}_i) = \varepsilon_{\alpha_i}\psi_{\alpha_i}(\mathbf{r}_i)$$

Here, ε_{α_i} is a single particle eigenvalue, and the N-particle eigenvalue is, therefore, given by

$$E_{\alpha_1, ..., \alpha_N} = \sum_{i=1}^{N} \varepsilon_{\alpha_i}$$

We will solve the single-particle wave equation in a cubic box of side L for single particle wave functions that satisfy periodic boundary conditions:

$$\psi_{\alpha_i}(x_i, y_i, z_i) = \psi_{\alpha_i}(x_i + L, y_i, z_i) = \psi_{\alpha_i}(x_i, y_i + L, z_i) = \psi_{\alpha_i}(x_i, y_i, z_i + L)$$

Note that the momentum operator $\mathbf{P}_i$ commutes with the corresponding single-particle Hamiltonian

$$[\mathbf{P}_i, h_i] = 0$$

This means that the the momentum eigenvalue $\mathbf{p}_i$ is a good number for characterizing the single particle states $\psi_{\alpha_i} = \psi_{\mathbf{p}_i}$. In fact, the solutions of the single-particle wave equation are of the form

$$\psi_{\mathbf{p}_i}(\mathbf{r}_i) = Ce^{i\mathbf{p}_i\cdot\mathbf{r}_i/\hbar}$$

provided that the single particle eigenvalues are given by

$$\varepsilon_{\mathbf{p}_i} = \frac{\mathbf{p}_i^2}{2m}$$

The constant C is an overall normalization constant on the single-particle states to ensure that $\int d^3\mathbf{r}_i|\psi_i(\mathbf{r}_i)|^2 = 1$.

Now, we apply the periodic boundary condition. Consider the boundary condition in the x-direction. The condition

$$\psi_{\mathbf{p}_i}(x_i, y_i, z_i) = \psi_{\mathbf{p}_i}(x_i + L, y_i, z_i)$$

leads to

$$e^{ip_{x_i}x_i/\hbar} = e^{ip_{x_i}(x_i+L)/\hbar}$$

or

$$1 = e^{ip_{x_i}L/\hbar} = \cos\left(\frac{p_{x_i}L}{\hbar}\right) + i\sin\left(\frac{p_{x_i}L}{\hbar}\right)$$

which will be satisfied if

$$\frac{p_{x_i}L}{\hbar} = 2\pi n_{x_i}$$

where n_{x_i} is an integer, $0, \pm1, \pm2$,.... Thus, the momentum p_{x_i} can take on only discrete values, i.e., it is quantized, and is given by

$$p_{x_i} = \frac{2\pi\hbar}{L}n_{x_i}$$

Applying the boundary conditions in y and z leads to the conditions

$$p_{y_i} = \frac{2\pi\hbar}{L}n_{y_i}$$
$$p_{z_i} = \frac{2\pi\hbar}{L}n_{z_i}$$

Thus, the momentum vector $\mathbf{p}_i$ can be written generally as

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

where $\mathbf{n}_i$ is a vector of integers $\mathbf{n}_i = (n_{x_i}, n_{y_i}, n_{z_i})$. This vector of integers can be used in place of $\mathbf{p}_i$ to characterize the single-particle eigenvalues and wave functions. The single-particle energy eigenvalues will be given by

$$\varepsilon_{\mathbf{n}_i} = \frac{\mathbf{p}_i^2}{2m} = \frac{2\pi^2\hbar^2}{mL^2}|\mathbf{n}_i|^2$$

and the single-particle eigenfunctions are given by

$$\psi_{\mathbf{n}_i}(\mathbf{r}_i) = Ce^{2\pi i\mathbf{n}_i\cdot\mathbf{r}_i/L}$$

Finally, the normalization constant C is determined by the condition

$$\int d^3r_i|\psi_{\mathbf{n}_i}(\mathbf{r}_i)|^2 = |C|^2\int_0^L dx_i\int_0^L dy_i\int_0^L dz_i e^{-2\pi i\mathbf{n}_i\cdot\mathbf{r}_i/L}e^{2\pi i\mathbf{n}_i\cdot\mathbf{r}_i/L} = 1$$

$$|C|^2\int_0^L dx_i\int_0^L dy_i\int_0^L dz_i = |C|^2L^3 = 1$$

$$C = \frac{1}{\sqrt{V}}$$

Therefore, the complete solution for the single-particle eigenvalues and eigenfunctions is

$$\langle \mathbf{x}_i | \mathbf{n}_i \; m_i \rangle = \phi_{\mathbf{n}_i m_i}(\mathbf{x}_i) = \frac{1}{\sqrt{V}} e^{2\pi i \mathbf{n}_i \cdot \mathbf{r}_i / L} \chi_{m_i}(s_i)$$

$$\varepsilon_{\mathbf{n}_i} = \frac{2\pi^2 \hbar^2}{mL^2} |\mathbf{n}_i|^2$$

and the total energy eigenvalues are given by

$$E_{\mathbf{n}_1, \ldots, \mathbf{n}_N} = \sum_{i=1}^{N} \frac{2\pi^2 \hbar^2}{mL^2} |\mathbf{n}_i|^2$$

Another way to formulate the solution of the eigenvalue problem is to consider the single particle eigenvalue and eigenfunction for a given vector of integers $\mathbf{n}$:

$$\psi_{\mathbf{n}}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{2\pi i \mathbf{n} \cdot \mathbf{r} / L}$$

$$\varepsilon_{\mathbf{n}} = \frac{2\pi^2 \hbar^2}{mL^2} |\mathbf{n}|^2$$

and ask how many particles in the N-particle system occupy this state. Let this number be $f_{\mathbf{n}m}$. $f_{\mathbf{n}m}$ is called an occupation number and it tells just how many particles occupy the state characterized by a vector of integers $\mathbf{n}$. Since there are an infinite number of possible choices for $\mathbf{n}$, there is an infinite number of occupation numbers. However, they must satisfy the obvious restriction

$$\sum_m \sum_{\mathbf{n}} f_{\mathbf{n}m} = N$$

where

$$\sum_{\mathbf{n}} \equiv \sum_{n_x=-\infty}^{\infty} \sum_{n_y=-\infty}^{\infty} \sum_{n_z=-\infty}^{\infty}$$

and

$$\sum_m \equiv \sum_{m=-s}^{s}$$

runs over the $(2s+1)$ possible values of m for a spin-s particle. These occupation numbers can be used to characterize the total energy eigenvalues of the system. The total energy eigenvalue will be given by

$$E_{\{f_{\mathbf{n}m}\}} = \sum_m \sum_{\mathbf{n}} \varepsilon_{\mathbf{n}} f_{\mathbf{n}m}$$

III. AN IDEAL GAS OF DISTINGUISHABLE QUANTUM PARTICLES

As an illustration of the use of occupation numbers in the evaluation of the quantum partition function, let us consider the simple case of Boltzmann statistics (ignoring spin statistics or treating the particles as distinguishable). The canonical partition function $Q(N,V,T)$ can be expressed as a sum over the quantum numbers $\mathbf{n}_1, ..., \mathbf{n}_N$ for each particle:

$$\begin{aligned} Q(N,V,T) &= \sum_{\mathbf{n}_1} \sum_{\mathbf{n}_2} \cdots \sum_{\mathbf{n}_N} e^{-\beta E_{\mathbf{n}_1, \ldots, \mathbf{n}_N}} \\ &= \sum_{\mathbf{n}_1} \sum_{\mathbf{n}_2} \cdots \sum_{\mathbf{n}_N} e^{-\beta \varepsilon_{\mathbf{n}_1}} e^{-\beta \varepsilon_{\mathbf{n}_2}} \cdots e^{-\beta \varepsilon_{\mathbf{n}_N}} \\ &= \left(\sum_{\mathbf{n}_1} e^{-\beta \varepsilon_{\mathbf{n}_1}} \right) \left(\sum_{\mathbf{n}_2} e^{-\beta \varepsilon_{\mathbf{n}_2}} \right) \cdots \left(\sum_{\mathbf{n}_N} e^{-\beta \varepsilon_{\mathbf{n}_N}} \right) \\ &= \left(\sum_{\mathbf{n}} e^{-\beta \varepsilon_{\mathbf{n}_N}} \right)^N \end{aligned}$$

In terms of occupation numbers, the partition is

$$Q(N,V,T) = \sum_{\{f\}} g(\{f\}) e^{-\beta \sum_{\mathbf{n}} \varepsilon_{\mathbf{n}} f_{\mathbf{n}}}$$

where $g(\{f\})$ is a factor that tells how many *different* physical states can be represented by a given set of occupation numbers $\{f\}$. For Boltzmann particles, exchanging the momentum labels of two particles leads to a different physical state but leaves the occupation numbers unchanged. In fact the counting problem is merely one of determining how many different ways can N particles be placed in the different physical states. This is just

$$g(\{f\}) = \frac{N!}{\prod_{\mathbf{n}} f_{\mathbf{n}}!}$$

For example, if there are just two states, then the occupation numbers must be N_1 and N_2 where $N_1 + N_2 = N$. The above formula gives

$$g(N_1, N_2) = \frac{N!}{N_1! N_2!} = \frac{N!}{N_1!(N-N_1)!}$$

which is the expected binomial coefficient.

The partition function therefore becomes

$$Q(N,V,T) = \sum_{\{f\}} \frac{N!}{\prod_{\mathbf{n}} f_{\mathbf{n}}!} \prod_{\mathbf{n}} e^{-\beta f_{\mathbf{n}} \varepsilon_{\mathbf{n}}}$$

which is just the multinomial expansion for

$$Q(N,V,T) = \left(\sum_{\mathbf{n}} e^{-\beta \varepsilon_{\mathbf{n}}} \right)^N$$

Again, if there were two states, then the partition function would be

$$(e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2})^N = \sum_{N_1, N_2, N_1+N_2=N} \frac{N!}{N_1! N_2!} e^{-N_1 \beta \varepsilon_1} e^{-N_2 \beta \varepsilon_2}$$

using the binomial theorem.

Therefore, we just need to be able to evaluate the sum

$$\sum_{\mathbf{n}} e^{-\beta \varepsilon_{\mathbf{n}}} = \sum_{\mathbf{n}} e^{-2\pi^2 \beta \hbar^2 |\mathbf{n}|^2 / m L^2}$$

But we are interested in the thermodynamic limit, where $L \to \infty$. In this limit, the spacing between the single-particle energy levels becomes quite small, and the discrete sum over $\mathbf{n}$ can, to a very good approximation, be replaced by an integral over a continuous variable:

$$\sum_{\mathbf{n}} e^{-2\pi^2 \beta \hbar^2 |\mathbf{n}|^2 / m L^2} = \int d^3 n e^{-2\pi^2 \beta \hbar^2 |\mathbf{n}|^2 / m L^2}$$

Since the single-particle eigenvalues only depend on the magnitude of $\mathbf{n}$, this becomes

$$4\pi \int_0^\infty dn n^2 e^{-2\pi^2 \beta \hbar^2 |\mathbf{n}|^2 / m L^2} = V \left(\frac{m}{2\pi\beta\hbar^2} \right)^{3/2} = \left(\frac{V}{\lambda^3} \right)$$

where λ is the thermal deBroglie wavelength.

Hence,

$$Q(N,V,T) = \left(\frac{V}{\lambda^3} \right)^N$$

which is just the classical result. Therefore, we see that an ideal gas of distinguishable particles, even when treated fully quantum mechanically, will have precisely the same properties as a classical ideal gas. Clearly, all of the quantum effects are contained in the particle spin statistics. In the next few lectures we will see just how profound an effect the spin statistics can have on the equilibrium properties.

IV. GENERAL FORMULATION FOR FERMIONS AND BOSONS

For systems of identical femions and identical bosons, an exchange of particles does not change the physical state. Therefore the factor $g(\{f_{\mathbf{n}m}\})$ is just 1 for both of kinds of systems. Moreover, the occupation number of a state characterized by $\mathbf{n}$ for a system of identical bosons can be any number between 0 and N:

$$f_{\mathbf{n}m} = 0, 1, 2, ..., N$$

For fermions, the Pauli exclusion principle forbids two identical particles from occupying the same quantum state. This restricts the occupation numbers to be either 0 or 1:

$$f_{\mathbf{n}m} = 0, 1$$

Given these possibilities for the occupation numbers, the canonical partition function can be formulated:

$$Q(N,V,T) = \sum_{\{f_{\mathbf{n}m}\}} e^{-\beta \sum_m \sum_{\mathbf{n}} f_{\mathbf{n}m}\varepsilon_{\mathbf{n}}} = \sum_{\{f_{\mathbf{n}m}\}} \prod_{\mathbf{n}} \prod_{m} e^{-\beta f_{\mathbf{n}}\varepsilon_{\mathbf{n}}}$$

Note that the sum over occupation numbers must be performed subject to the restriction

$$\sum_m \sum_{\mathbf{n}} f_{\mathbf{n}m} = N$$

a condition that makes the evaluation of $Q(N,V,T)$ extremely difficult. Therefore, it seems that the canonical ensemble is not the best choice for carrying out the calculation. No worry, there are other ensembles from which to choose, and of these, it turns out that the grand canonical ensemble is significantly easier to work with. Recall that in the grand canonical ensemble, μ, V and T are the control variables and the partition function is given by

$$\begin{aligned}\mathcal{Z}(\mu,V,T) &= \sum_{N=0}^{\infty} \zeta^N Q(N,V,T) \\ &= \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_{\{f_{\mathbf{n}m}\}} \prod_m \prod_{\mathbf{n}} e^{-\beta f_{\mathbf{n}m}\varepsilon_{\mathbf{n}}}\end{aligned}$$

Note that the inner sum over occupation numbers is still subject to the restriction $\sum_m \sum_{\mathbf{n}} f_{\mathbf{n}m} = N$. However, there is a final sum over all possible values that N, the number that restricts the sum over occupation numbers, can take on. Therefore, if we let the sum over occupation numbers be unrestricted, then they could sum to any value they liked. This would be equivalent to performing an unrestricted sum over occupation numbers without performing the final sum over N, since in the course of summing, unrestricted, over occupation numbers, we would obtain every possible value of N as required by the final sum over N. This is the main advantage of using this ensemble for bosonic and fermonic systems. Thus, the grand canonical partition function becomes

$$\mathcal{Z}(\mu,V,T) = \sum_{\{f_{\mathbf{n}m}\}} \prod_m \prod_{\mathbf{n}} e^{\beta(\mu-\varepsilon_{\mathbf{n}})f_{\mathbf{n}}}$$

Note also that the sum of products is just

$$\begin{aligned}\sum_{f_1}\sum_{f_2}\sum_{f_3} \cdots e^{\beta(\mu-\varepsilon_1)f_1} e^{\beta(\mu-\varepsilon_2)f_2} e^{\beta(\mu-\varepsilon_3)f_3} \cdots &= \left(\sum_{f_1} e^{\beta(\mu-\varepsilon_1)f_1}\right)\left(\sum_{f_2} e^{\beta(\mu-\varepsilon_1)f_2}\right)\left(\sum_{f_3} e^{\beta(\mu-\varepsilon_1)f_3}\right)\cdots \\ &= \prod_m \prod_{\mathbf{n}} \sum_{\{f_{\mathbf{n}m}\}} e^{\beta(\mu-\varepsilon_{\mathbf{n}})f_{\mathbf{n}m}}\end{aligned}$$

For bosons, each individual sum is just the sum of a geometric series. Hence,

$$\mathcal{Z}(\mu,V,T) = \prod_m \prod_{\mathbf{n}} \frac{1}{1 - e^{\beta(\mu-\varepsilon_{\mathbf{n}})}}$$

whereas, for fermions, each individual sum contains only two terms corresponding to $f_{\mathbf{n}} = 0$ and $f_{\mathbf{n}} = 1$. Thus, for fermions:

$$\mathcal{Z}(\mu, V, T) = \prod_m \prod_{\mathbf{n}} \left(1 + e^{\beta(\mu - \varepsilon_{\mathbf{n}})}\right)$$

Note that the summands are independent of the quantum number m so that we may perform the product over m values trivially with the result

$$\mathcal{Z}(\mu, V, T) = \left[\prod_{\mathbf{n}} \frac{1}{1 - e^{\beta(\mu - \varepsilon_{\mathbf{n}})}}\right]^g$$

for bosons and

$$\mathcal{Z}(\mu, V, T) = \left[\prod_{\mathbf{n}} \left(1 + e^{\beta(\mu - \varepsilon_{\mathbf{n}})}\right)\right]^g$$

for fermions, where $g = (2s + 1)$ is the number of eigenstates of S_z (also known as the *spin degeneracy*).

At this point, let us recall the procedure for calculating the equation of state in the grand canonical ensemble. The free energy in this ensemble is PV/kT given by

$$\frac{PV}{kT} = \ln \mathcal{Z}(\zeta, V, T)$$

and the average particle number is given by

$$\langle N \rangle = \zeta \frac{\partial}{\partial \zeta} \ln \mathcal{Z}(\zeta, V, T)$$

The fugacity ζ must be eliminated in favor of $\langle N \rangle$ using the second equation and substituted into the first equation to yield the equation of state. Recall that, for the classical ideal gas,

$$\begin{aligned} \mathcal{Z}(\zeta, V, T) &= e^{V\zeta/\lambda^3} \\ \frac{PV}{kT} &= \frac{V\zeta}{\lambda^3} \\ \langle N \rangle &= \zeta \frac{\partial}{\partial \zeta} \ln \mathcal{Z} = \frac{V\zeta}{\lambda^3} \end{aligned}$$

Eliminating ζ in favor $\langle N \rangle$ is trivial in this case, leading to the classical ideal gas equation

$$PV = \langle N \rangle kT$$

For the ideal gas of identical fermions, the equations one must solve are

$$\begin{aligned} \frac{PV}{kT} &= \ln \mathcal{Z}(\zeta, V, T) = \ln \left[\prod_{\mathbf{n}} \left(1 + \zeta e^{-\beta\varepsilon_{\mathbf{n}}}\right)\right]^g = g \sum_{\mathbf{n}} \ln \left(1 + \zeta e^{-\beta\varepsilon_{\mathbf{n}}}\right) \\ \langle N \rangle &= \zeta \frac{\partial}{\partial \zeta} \ln \mathcal{Z} = g \sum_{\mathbf{n}} \frac{\zeta e^{-\beta\varepsilon_{\mathbf{n}}}}{1 + \zeta e^{-\beta\varepsilon_{\mathbf{n}}}} \end{aligned}$$

and for bosons, they are

$$\begin{aligned} \frac{PV}{kT} &= \ln \mathcal{Z}(\zeta, V, T) = \ln \left[\prod_{\mathbf{n}} \frac{1}{1 - \zeta e^{-\beta\varepsilon_{\mathbf{n}}}}\right]^g = -g \sum_{\mathbf{n}} \ln \left(1 - \zeta e^{-\beta\varepsilon_{\mathbf{n}}}\right) \\ \langle N \rangle &= \zeta \frac{\partial}{\partial \zeta} \ln \mathcal{Z} = g \sum_{\mathbf{n}} \frac{\zeta e^{-\beta\varepsilon_{\mathbf{n}}}}{1 - \zeta e^{-\beta\varepsilon_{\mathbf{n}}}} \end{aligned}$$

It is not difficult to see that the problem of solving for ζ in terms of $\langle N \rangle$ is highly non-trivial for both systems. The next two lectures will be devoted to just this problem and exploring the rich behavior that the quantum ideal gases exhibit.