Chapter 16

Quantum Grand Canonical Ensemble

How do we proceed quantum mechanically? For *fermions* the wavefunction is antisymmetric. An N particle basis function can be constructed in terms of single-particle wavefunctions as follows:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\cdots\phi_N(\mathbf{r}_N), \tag{16.1}$$

where P is the permutation operator, and $(-1)^P = \pm 1$ depending on whether P is an even or odd permutation. This result can be written as a (Slater) determinant

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \det \phi_i(\mathbf{r}_j). \tag{16.2}$$

For *bosons*, the wavefunction must be symmetric:

$$\psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N_1! \cdots N_l!}} \frac{1}{\sqrt{N!}} \sum_P P \phi_1(\mathbf{r}_1)\cdots\phi_N(\mathbf{r}_N), \tag{16.3}$$

where N_j is the number of occurrences of ϕ_j. The extra combinatorial factor comes from the fact that you get a distinct wavefunction $N_1!N_2!\cdots N_l!$ times.

A *subsystem* consists of N_j particles, with total energy E_j. It is described by a state vector $|E_j, N_j, k_j\rangle$, where k_j are the other quantum numbers necessary to specify the state. The *system* consists of subsystems which do not interact with each other. For fermions, the system is described by a state vector

$$|E, N, k\rangle = \sum_P (-1)^P P \frac{1}{\sqrt{N!}} \prod_{j=1}^{n} |E_j, N_j, k_j\rangle \sqrt{N_j!}, \tag{16.4}$$

where the outer product is over vectors in different Hilbert spaces, and P permutes particle between the different spaces. For bosons, the $(-1)^P$ factor would not be present.

The microcanonical distribution for the entire system is described by the density operator

$$\rho_\epsilon(E) = \frac{1}{\Omega_\epsilon(E,N)} \int_{E-\epsilon/2}^{E+\epsilon/2} dE' \delta(E'-H)$$
$$= \frac{1}{\Omega_\epsilon(E,N)} \sum_k |E,N,k\rangle\langle E,N,k|, \qquad (16.5)$$

where the sum is over all states having energies beween $E-\epsilon/2$ and $E+\epsilon/2$. Here, as before, energies are measured in units of ϵ, so all these energies are considered the same. The averaged structure function is

$$\Omega_\epsilon(E,N) = \sum_k \langle E,N,k|E,N,k\rangle, \qquad (16.6)$$

which is the number of states in the energy interval $[E-\epsilon/2, E+\epsilon/2]$ and with occupation number N. The total degeneracy of the entire system is again given by the convolution law

$$\Omega_\epsilon(E,N) = \sum_{\{N_j\}\{E_j\}} \delta_{E,\sum_j E_j} \delta_{N,\sum_j N_j} \prod_j \Omega_{\epsilon j}(E_j, N_j). \qquad (16.7)$$

Note that there are *no* $N!s$ because they are included in the definitions of the physical states.

The single-subsystem distribution function is

$$\mathcal{P}^{(1)}_{E_1,N_1} = \frac{\Omega_\epsilon^{(n-1)}(E-E_1, N-N_1)}{\Omega_\epsilon^{(n)}(E,N)}, \qquad (16.8)$$

which is the ratio of the number of states for which subsystem 1 has energy E_1 and occupation number N_1 to the total number of states. Again, there are no $N!$s. The grand structure function is here defined by

$$\mathcal{W}_\epsilon(E,z) = \sum_{N=0}^{\infty} z^N \Omega_\epsilon(E,N). \qquad (16.9)$$

For the composite system

$$\mathcal{W}_\epsilon(E,z) = \sum_N \sum_{\{E_j\}} \delta_{E,\sum_j E_j} \delta_{N,\sum_j N_j} \prod_j \sum_{N_j} z^{N_j} \Omega_\epsilon(E_j, N_j)$$
$$= \sum_{\{E_j\}} \delta_{E,\sum_j E_j} \prod_j \mathcal{W}_{\epsilon j}(E_j, z). \qquad (16.10)$$

The grand partition function is

$$\mathcal{X}_\epsilon(\alpha,z) = \sum_E e^{-\alpha E} \mathcal{W}_\epsilon(E,z) = \sum_N z^N \chi(\alpha,N)$$
$$= \prod_j \mathcal{X}_{\epsilon j}(\alpha,z). \qquad (16.11)$$

Once again, we do an asymptotic evaluation using

$$\delta_{E,E'} = \frac{\epsilon}{2\pi i}\int_C d\alpha\, e^{\alpha(E-e')}, \tag{16.12}$$

from which we deduce

$$\mathcal{P}^{(1)}_{E_1,N_1} = \frac{e^{-\beta(E_1-\mu N_1)}}{\mathcal{X}_1(\beta,\mu)}, \tag{16.13}$$

and in turn, by recognizing E_1, N_1 as the eigenvalues of the Hamiltonian and number operator for the single subsystem, we deduce the density operator

$$\rho = \frac{e^{-\beta(H-\mu\mathcal{N})}}{\mathcal{X}(\beta,\mu)}, \tag{16.14}$$

where H is the Hamiltonian operator, whose eigenvalues are the possible energy states of the system, and $\mathcal{N}$ is the number operator, whose eigenvalues are the number of particles in the system. Again note, in contradistinction with the classical probability distribution, there is no $N!$ because the combinatorical factors are taken care of in the definition of the quantum state vectors. This holds whether the particles are bosons or fermions. Because

$$\mathrm{Tr}\,\rho = 1, \tag{16.15}$$

the grand partition function is

$$\begin{aligned}\mathcal{X}(\beta,\mu) &= \mathrm{Tr}\, e^{-\beta(H-\mu\mathcal{N})}\\ &= \sum_{E,N,k}\langle E,N,k|e^{-\beta(H-\mu\mathcal{N})}|E,N,k\rangle\\ &= \sum_{E,N} e^{-\beta(E-\mu N)} g_{E,N},\end{aligned} \tag{16.16}$$

where $g_{E,N}$ is the degeneracy of the state with energy E and number of particles N.

Now

$$-\frac{\partial}{\partial\beta}\ln\mathcal{X}(\beta,\mu) = \langle H-\mu\mathcal{N}\rangle \equiv U-\mu N, \tag{16.17}$$

$$\frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\mathcal{X}(\beta,\mu) = \langle\mathcal{N}\rangle = N, \tag{16.18}$$

where U and N are the thermodynamic quantities. The pressure is

$$p = \langle\mathcal{F}_V\rangle = -\langle\frac{\partial H}{\partial V}\rangle = \frac{1}{\beta}\frac{\partial}{\partial V}\ln\mathcal{X}(\beta,\mu), \tag{16.19}$$

so therefore

$$d\ln\mathcal{X}(\beta,\mu,V) = -(U-\mu N)d\beta + \beta N\, d\mu + \beta p\, dV, \tag{16.20}$$

or from Eq. (14.26)

$$d[\beta(U-\mu N)+\ln\mathcal{X}] = \beta(dU - d(\mu N)) + \beta N\,d\mu + \beta p\,dV$$
$$= \beta[dU + p\,dV - \mu\,dN] = \beta\delta Q = \frac{dS}{k}, \quad (16.21)$$

so, up to a constant,

$$\frac{S}{k} = \beta(U-\mu N) + \ln\mathcal{X}, \quad (16.22)$$

or

$$TS = U - \mu N + kT\ln\mathcal{X}. \quad (16.23)$$

This suggests defining still another kind of free energy, the grand potential,

$$J = F - \mu N = U - TS - \mu N = -kT\ln\mathcal{X}, \quad (16.24)$$

which is analogous to $F = -kT\ln\chi$. Note that

$$dJ = T\,dS - p\,dV + \mu\,dN - d(TS) - d(\mu N)$$
$$= -p\,dV - S\,dT - N\,d\mu, \quad (16.25)$$

which says that $J(T,\mu,V)$ is a function of the indicated variables, that is,

$$\left(\frac{\partial J}{\partial T}\right)_{\mu,V} = -S, \quad \left(\frac{\partial J}{\partial \mu}\right)_{T,V} = -N, \quad \left(\frac{\partial J}{\partial V}\right)_{T,\mu} = -p. \quad (16.26)$$

The last two equations are just those given in Eqs. (16.19) and (16.18), while the last is

$$\frac{\partial J}{\partial T} = -k\ln\mathcal{X} - kT\frac{\partial}{\partial T}\ln\mathcal{X}$$
$$= -k\ln\mathcal{X} + \frac{1}{T}\frac{\partial}{\partial\beta}\ln\mathcal{X}$$
$$= \frac{1}{T}[-U + \mu N - kT\ln\mathcal{X}] = -S. \quad (16.27)$$

16.1 Bose-Einstein and Fermi-Dirac Distributions

The grand structure function for a gas of noninteracting particles is (no $N!$)

$$\mathcal{X} = \sum_N z^N \chi(\alpha, N), \quad (16.28)$$

where

$$\chi(\alpha, N) = \sum_{\{n_j\}} \delta_{N,\sum_j n_j} \prod_j e^{-\beta n_j \varepsilon_j}, \quad (16.29)$$

where n_j is the number of particles in the single-particle energy state ε_j. Thus

$$\begin{aligned}\mathcal{X} &= \sum_{\{n_j\}} \prod_j z^{n_j} e^{-\beta n_j \varepsilon_j} \\ &= \prod_j \sum_{n_j} e^{\beta[\mu n_j - n_j \varepsilon_j]},\end{aligned} \tag{16.30}$$

which also immediately follows from

$$\mathcal{X} = \sum_{N,E} e^{-\beta(E-\mu N)} = \sum_{\{n_j\}} e^{-\beta \sum_j n_j \varepsilon_j + \beta\mu \sum_j n_j}. \tag{16.31}$$

For particles obeying Bose-Einstein statistics, bosons, the sum on n_j ranges from 0 to ∞, so

$$\sum_{n_y=0}^{\infty} z^{n_j} e^{-\beta n_j \varepsilon_j} = \frac{1}{1 - z e^{-\beta \varepsilon_j}}, \tag{16.32}$$

while for particles obeying Fermi-Dirac statistics, fermions, the sum on n_j ranges only from 0 to 1:

$$\sum_{n_j=0}^{1} z^{n_j} e^{-\beta n_j \varepsilon_j} = 1 + z e^{-\beta \varepsilon_j}. \tag{16.33}$$

so in general

$$\sum_{n_j} z^{n_j} e^{-\beta n_j \varepsilon_j} = (1 \pm z e^{-\beta \varepsilon_j})^{\pm 1}, \tag{16.34}$$

where the upper sign refers to fermions, and the lower to bosons. Thus the grand partition function is

$$\mathcal{X} = \prod_j (1 \pm z e^{-\beta \varepsilon_j})^{\pm 1}, \tag{16.35}$$

and

$$\ln \mathcal{X} = \pm \sum_j \ln(1 \pm z e^{-\beta \varepsilon_j}) = \pm \sum_j \ln(1 \pm e^{\beta\mu} e^{-\beta \varepsilon_j}). \tag{16.36}$$

Then, the total number of particles is

$$\begin{aligned}N &= \frac{1}{\beta}\frac{\partial}{\partial \mu} \ln \mathcal{X} = \sum_j \frac{e^{\beta(\mu - \varepsilon_j)}}{1 \pm e^{\beta(\mu - \varepsilon_j)}} \\ &= \sum_j \frac{1}{e^{\beta(\varepsilon_j - \mu)} \pm 1},\end{aligned} \tag{16.37}$$

and

$$U - \mu N = -\frac{\partial}{\partial \beta} \ln \mathcal{X} = \sum_j \frac{\varepsilon_j - \mu}{e^{\beta(\varepsilon_j - \mu)} \pm 1}, \tag{16.38}$$

which implies that the thermodynamic energy is

$$U = \sum_j \frac{\varepsilon_j}{e^{\beta(\varepsilon_j-\mu)} \pm 1}. \tag{16.39}$$

The mean number of particles in the l energy level is

$$\begin{aligned}\langle n_l\rangle &= -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_l}\ln\mathcal{X} = \frac{e^{\beta(\mu-\varepsilon_l)}}{1\pm e^{\beta(\mu-\varepsilon_l)}}\\ &= \frac{1}{e^{\beta(\varepsilon_l-\mu)}\pm 1},\end{aligned} \tag{16.40}$$

so as expected

$$N = \sum_l \langle n_l\rangle, \quad U = \sum_l \langle n_l\rangle\varepsilon_l. \tag{16.41}$$

These results coincide with those found in Sec. 12.1, with $\zeta_0 = e^{\beta\mu}$.

16.2 Photons

For photons, there is no restriction on the number of particles, so we can set $z = 1$ or $\mu = 0$:

$$\mathcal{X} = \sum_{\{n_j\}}\prod_j e^{-\beta n_j\varepsilon_j} = \prod_j (1-e^{-\beta\varepsilon_j})^{-1}, \tag{16.42}$$

$$U = -\frac{\partial}{\partial\beta}\ln\mathcal{X} = \sum_j \frac{\varepsilon_j}{e^{\beta\varepsilon_j}-1}, \tag{16.43}$$

$$\langle n_j\rangle = -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_j}\ln\mathcal{X} = \frac{1}{e^{\beta\varepsilon_j}-1}. \tag{16.44}$$

The fluctuation in the individual level occupation numbers is

$$\begin{aligned}\langle(n_l-\langle n_l\rangle)^2\rangle &= \langle n_l^2\rangle - \langle n_l\rangle^2\\ &= \frac{1}{\beta^2}\frac{1}{\mathcal{X}}\frac{\partial^2}{\partial\varepsilon_l^2}\mathcal{X} - \frac{1}{\beta^2}\left(\frac{1}{\mathcal{X}}\frac{\partial}{\partial\varepsilon_l}\mathcal{X}\right)^2\\ &= \frac{1}{\beta^2}\frac{\partial^2}{\partial\varepsilon_l^2}\ln\mathcal{X} = -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_l}\langle n_l\rangle\\ &= \frac{e^{\beta\varepsilon_l}}{(e^{\beta\varepsilon_l}-1)^2} = \langle n_l\rangle + \langle n_l^2\rangle\\ &= \langle n_l\rangle(1+\langle n_l\rangle).\end{aligned} \tag{16.45}$$

16.3 Planck Distribution

For a photon gas in a volume V, the number of states in a wavenumber interval $(d\mathbf{k})$ is

$$\frac{2\,V\,(d\mathbf{k})}{(2\pi)^3}, \quad \hbar\mathbf{k} = \mathbf{p}, \quad E = pc, \tag{16.46}$$

where the factor of 2 emerges because photons are helicity 2 particles; that is, there are two polarization states for each momentum state. Then the logarithm of the grand partition function is

$$\begin{aligned}
\ln \mathcal{X} &= -\sum_j \ln\left(1 - e^{-\beta\varepsilon_j}\right) \\
&= -\frac{8\pi V}{(2\pi)^3}\int_0^\infty dk\, k^2 \ln\left(1 - e^{-\beta\hbar ck}\right) \\
&= -\frac{V}{\pi^2}\left[\frac{1}{3}k^3 \ln\left(1 - e^{-\beta\hbar ck}\right)\Big|_0^\infty - \frac{1}{3}\int_0^\infty dk\, k^3 \frac{e^{-\beta\hbar ck}}{1 - e^{-\beta\hbar kc}}\beta\hbar c\right] \\
&= \frac{V\beta\hbar c}{3\pi^2}\int_0^\infty dk\, k^3 \frac{1}{e^{\beta\hbar ck} - 1} = -\frac{F}{kT},
\end{aligned} \tag{16.47}$$

where F is either the Helmholtz free energy or the grand potential (the distinction disappears when $\mu = 0$).

The internal energy is

$$U = -\frac{\partial}{\partial\beta}\ln \mathcal{X} = \sum_l \frac{\varepsilon_l}{e^{\beta\varepsilon_l} - 1} = \frac{V}{\pi^2}\hbar c \int_0^\infty \frac{dk\, k^3}{e^{\beta\hbar ck} - 1}. \tag{16.48}$$

We see here the characteristic Planck distribution. In the classical limit, $\hbar \to 0$,

$$V \to \frac{V}{\pi^2}kT \int_0^\infty dk\, k^2. \tag{16.49}$$

which exhibits the Rayleigh-Jeans law, and exhibits the famous *ultraviolet catastrophe*. This breakdown of classical physics led Planck to the introduction of the quantum of light, the photon.

Note that here

$$F = -\frac{1}{3}U, \tag{16.50}$$

and so the pressure is

$$p = -\frac{\partial F}{\partial V} = \frac{1}{3}\frac{U}{V}, \tag{16.51}$$

the characteristic law for a radiation gas.

To determine the total energy, recall that from Eq. (7.16)

$$\int_0^\infty dx \frac{x^{n-1}}{e^x - 1} = \Gamma(n)\zeta(n), \tag{16.52}$$

where $\zeta(n)$ is the Riemann zeta function. For integer argument the zeta function may be expressed as a Bernoulli number,

$$\zeta(2n) = \frac{(2\pi)^{2n}}{2(2n)!}B_n. \tag{16.53}$$

In this way we find

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \frac{\pi^4}{15}, \tag{16.54}$$

and then we recover Stefan's law:

$$U = -3F = \frac{\pi^2}{15} \frac{k^4}{(\hbar c)^3} T^4 V, \tag{16.55}$$

and the specific heat for the photon gas,

$$c_v = \frac{\partial U}{\partial T} = \frac{4\pi^2}{15} \frac{k^4}{(\hbar c)^3} T^3 V. \tag{16.56}$$