Chapter 16

Quantum Grand Canonical Ensemble

A straightforward analysis, parallelling that in Chapter 15, shows that the density operator describing a system which is part of a large ensemble of intercommunicating systems with definite energy and particle number, is

$$\rho = \frac{e^{-\beta(H-\mu\mathcal{N})}}{\mathcal{X}(\beta,\mu)}, \tag{16.1}$$

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. 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

$$\operatorname{Tr}\rho = 1, \tag{16.2}$$

the grand partition function is

$$\begin{aligned}\mathcal{X}(\beta,\mu) &= \operatorname{Tr} e^{-\beta(H-\mu\mathcal{N})} \\ &= \sum_{E,N,k} \langle E,N,k|e^{-\beta(H-\mu\mathcal{N})}|E,N,k\rangle \\ &= \sum_{E,N} e^{-\beta(E-\mu N)} g_{E,N},\end{aligned} \tag{16.3}$$

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

Now

$$-\frac{\partial}{\partial\beta}\ln\mathcal{X}(\beta,\mu) = \langle H-\mu\mathcal{N}\rangle \equiv U-\mu N, \tag{16.4}$$

$$\frac{1}{\beta}\frac{\partial}{\partial\mu}\ln\mathcal{X}(\beta,\mu) = \langle\mathcal{N}\rangle = N, \tag{16.5}$$

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

$$p = \langle \mathcal{F}_V \rangle = -\langle \frac{\partial H}{\partial V} \rangle = \frac{1}{\beta} \frac{\partial}{\partial V} \ln \mathcal{X}(\beta, \mu), \tag{16.6}$$

so therefore

$$d \ln \mathcal{X}(\beta, \mu, V) = -(U - \mu N) d\beta + \beta N \, d\mu + \beta p \, dV, \tag{16.7}$$

or from Eq. (14.26)

$$\begin{aligned} d[\beta(U - \mu N) + \ln \mathcal{X}] &= \beta(dU - d(\mu N)) + \beta N \, d\mu + \beta p \, dV \\ &= \beta[dU + p \, dV - \mu \, dN] = \beta \delta Q = \frac{dS}{k}, \end{aligned} \tag{16.8}$$

so, up to a constant,

$$\frac{S}{k} = \beta(U - \mu N) + \ln \mathcal{X}, \tag{16.9}$$

or

$$TS = U - \mu N + kT \ln \mathcal{X}. \tag{16.10}$$

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

$$J = F - \mu N = U - TS - \mu N = -kT \ln \mathcal{X}, \tag{16.11}$$

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

$$\begin{aligned} dJ &= T \, dS - p \, dV + \mu \, dN - d(TS) - d(\mu N) \\ &= -p \, dV - S \, dT - N \, d\mu, \end{aligned} \tag{16.12}$$

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

$$\left(\frac{\partial J}{\partial T}\right)_{\mu,V} = -S, \quad \left(\frac{\partial J}{\partial \mu}\right)_{T,V} = -N, \quad \left(\frac{\partial J}{\partial V}\right)_{T,\mu} = -p. \tag{16.13}$$

The last two equations are just those given in Eqs. (16.6) and (16.5), while the last is

$$\begin{aligned} \frac{\partial J}{\partial T} &= -k \ln \mathcal{X} - kT \frac{\partial}{\partial T} \ln \mathcal{X} \\ &= -k \ln \mathcal{X} + \frac{1}{T} \frac{\partial}{\partial \beta} \ln \mathcal{X} \\ &= \frac{1}{T}[-U + \mu N - kT \ln \mathcal{X}] = -S. \end{aligned} \tag{16.14}$$

16.1 Bose-Einstein and Fermi-Dirac Distributions

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

$$\mathcal{X} = \sum_N z^N \chi(\alpha, N), \tag{16.15}$$

where

$$\chi(\alpha, N) = \sum_{\{n_j\}} \delta_{N,\sum_j n_j} \prod_j e^{-\beta n_j \varepsilon_j}, \tag{16.16}$$

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

$$\begin{aligned} \mathcal{X} &= \sum_{\{n_j\}} \prod_j z^{n_j} e^{-\beta n_j \varepsilon_j} \\ &= \prod_j \sum_{n_j} e^{\beta[\mu n_j - n_j \varepsilon_j]}, \end{aligned} \tag{16.17}$$

which also immediately follows from

$$\mathcal{X} = \sum_{N,E} e^{-\beta(E-\mu N)} = \sum_{\{n_j\}} e^{-\beta \sum_j n_j \varepsilon_j + \beta\mu \sum_j n_j}. \tag{16.18}$$

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

$$\sum_{n_y=0}^{\infty} z^{n_j} e^{-\beta n_j \varepsilon_j} = \frac{1}{1 - z e^{-\beta \varepsilon_j}}, \tag{16.19}$$

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

$$\sum_{n_j=0}^{1} z^{n_j} e^{-\beta n_j \varepsilon_j} = 1 + z e^{-\beta \varepsilon_j}. \tag{16.20}$$

so in general

$$\sum_{n_j} z^{n_j} e^{-\beta n_j \varepsilon_j} = (1 \pm z e^{-\beta \varepsilon_j})^{\pm 1}, \tag{16.21}$$

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

$$\mathcal{X} = \prod_j (1 \pm z e^{-\beta \varepsilon_j})^{\pm 1}, \tag{16.22}$$

and

$$\ln \mathcal{X} = \pm \sum_j \ln(1 \pm z e^{-\beta \varepsilon_j}) = \pm \sum_j \ln(1 \pm e^{\beta\mu} e^{-\beta \varepsilon_j}). \tag{16.23}$$

Then, the total number of particles is

$$\begin{aligned} N &= \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln \mathcal{X} = \sum_j \frac{e^{\beta(\mu - \varepsilon_j)}}{1 \pm e^{\beta(\mu - \varepsilon_j)}} \\ &= \sum_j \frac{1}{e^{\beta(\varepsilon_j - \mu)} \pm 1}, \end{aligned} \tag{16.24}$$

and

$$U - \mu N = -\frac{\partial}{\partial\beta}\ln\mathcal{X} = \sum_j \frac{\varepsilon_j - \mu}{e^{\beta(\varepsilon_j-\mu)} \pm 1}, \tag{16.25}$$

which implies that the thermodynamic energy is

$$U = \sum_j \frac{\varepsilon_j}{e^{\beta(\varepsilon_j-\mu)} \pm 1}. \tag{16.26}$$

The mean number of particles in the l energy level is

$$\begin{aligned}\langle n_l\rangle &= -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_l}\ln\mathcal{X} = \frac{e^{\beta(\mu-\varepsilon_l)}}{1 \pm e^{\beta(\mu-\varepsilon_l)}} \\ &= \frac{1}{e^{\beta(\varepsilon_l-\mu)} \pm 1},\end{aligned} \tag{16.27}$$

so as expected

$$N = \sum_l \langle n_l\rangle, \quad U = \sum_l \langle n_l\rangle\varepsilon_l. \tag{16.28}$$

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 $\mu = 0$:

$$\mathcal{X} = \sum_{\{n_j\}}\prod_j e^{-\beta n_j\varepsilon_j} = \prod_j (1 - e^{-\beta\varepsilon_j})^{-1}, \tag{16.29}$$

$$U = -\frac{\partial}{\partial\beta}\ln X = \sum_j \frac{\varepsilon_j}{e^{\beta\varepsilon_j} - 1}, \tag{16.30}$$

$$\langle n_j\rangle = -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_j}\ln\mathcal{X} = \frac{1}{e^{\beta\varepsilon_j} - 1}. \tag{16.31}$$

The fluctuation in the individual level occupation numbers is

$$\begin{aligned}\langle(n_l - \langle n_l\rangle)^2\rangle &= \langle n_l^2\rangle - \langle n_l\rangle^2 \\ &= \frac{1}{\beta^2}\frac{1}{\mathcal{X}}\frac{\partial^2}{\partial\varepsilon_l^2}\mathcal{X} - \frac{1}{\beta^2}\left(\frac{1}{\mathcal{X}}\frac{\partial}{\partial\varepsilon_l}\mathcal{X}\right)^2 \\ &= \frac{1}{\beta^2}\frac{\partial^2}{\partial\varepsilon_l^2}\ln\mathcal{X} = -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_l}\langle n_l\rangle \\ &= \frac{e^{\beta\varepsilon_l}}{(e^{\beta\varepsilon_l} - 1)^2} = \langle n_l\rangle + \langle n_l^2\rangle \\ &= \langle n_l\rangle(1 + \langle n_l\rangle).\end{aligned} \tag{16.32}$$