Chapter 12

Bose and Fermi Gases

Now let's consider a noninteracting gas. At first let us suppose there is no constraint on the number of particles, that is, that particles can created and destroyed, as with an ultrarelativistic gas such as of photons. The partition function is

$$Z = \sum_E e^{-\beta E}, \tag{12.1}$$

so if the energy levels of the particles are ε_j, and the corresponding occupation numbers are n_j,

$$Z = \sum_{\{n_j\}} e^{-\beta \sum_j n_j \varepsilon_j}. \tag{12.2}$$

If the total number of particles is unconstrained, we can write this as, in terms of $z_i = e^{-\beta\varepsilon_j}$,

$$Z = \sum_{\{n_j\}} \prod_i z_i^{n_i} = \prod_i \sum_{n_i} z_i^{n_i}. \tag{12.3}$$

For a Bose gas, $n_i = 0, 1, 2, 3, \ldots$, while for a Fermi gas $n_i = 0, 1$, since only one Fermion can occupy a single state, the Pauli exclusion principle. Thus

$$\sum_{n_i} z_i^{n_i} = \begin{cases} \frac{1}{1-z_i}, & \text{Bose,} \\ 1 + z_i, & \text{Fermi,} \end{cases} = (1 \mp z_i)^{\mp 1}. \tag{12.4}$$

We saw these distributions before in Eqs. (6.40) and (6.44). So the partition function is

$$Z = \prod_j (1 \mp z_j)^{\mp 1} = \prod_j \left(1 \mp e^{-\beta\varepsilon_j}\right)^{\mp 1}. \tag{12.5}$$

The average occupation number for the jth level is

$$\langle n_j \rangle = \frac{\sum_{\{n_j\}} n_j e^{-\beta \sum_i n_i \varepsilon_i}}{\sum_{\{n_j\}} e^{-\beta \sum_i n_i \varepsilon_i}}$$

$$= -\frac{\partial}{\partial(\beta\varepsilon_j)} \ln Z = \pm\frac{\partial}{\partial\beta\varepsilon_j} \ln(1 \mp e^{-\beta\varepsilon_j})$$
$$= \frac{e^{-\beta\varepsilon_j}}{1 \mp e^{-\beta\varepsilon_j}} = \frac{1}{e^{\beta\varepsilon_j} \mp 1}. \quad (12.6)$$

Thus we see the Planck distribution for photons:

$$\langle n_j \rangle = \frac{1}{e^{h\nu_j/kT} - 1}, \quad (12.7)$$
$$U = \sum_j \frac{h\nu_j}{e^{h\nu_j/kT} - 1} = -\frac{\partial}{\partial\beta} \ln Z. \quad (12.8)$$

For fermions, note that $\langle n_j \rangle < 1$.

12.1 Fixed number of particles

For nonrelativistic particles, we cannot freely create and destroy them, so the number of particles are fixed:

$$N = \sum_j n_j. \quad (12.9)$$

How do we enforce this constraint? With a contour integral. Define

$$f(\zeta) = \sum_{\{n_j\}} \prod_j (\zeta z_j)^{n_j} = \prod_j (1 \mp \zeta z_j)^{\mp 1}. \quad (12.10)$$

Then because

$$\frac{1}{2\pi i} \oint_\gamma \frac{d\zeta}{\zeta} \frac{\zeta^M}{\zeta^N} = \delta_{MN}, \quad (12.11)$$

provided M and N are both integers [see Eq. (11.25)], and γ is a contour which encircles the origin once in a counterclockwise sense, we see that the partition function, with the constraint (12.9) imposed, is

$$Z = \frac{1}{2\pi i} \oint_\gamma \frac{d\zeta}{\zeta} \frac{f(\zeta)}{\zeta^N}, \quad (12.12)$$

because only the power of ζ for which the constraint (12.9) holds survives.

We proceed by asymptotic analysis. We approximately evaluate the integral by the saddle-point method:

$$Z = \frac{1}{2\pi i} \oint_\gamma d\zeta\, e^{g(\zeta)}, \quad g(\zeta) = \ln f(\zeta) - (N+1)\ln\zeta, \quad (12.13)$$

where the saddle point ζ_0 is defined by the point where the derivative of g,

$$g'(\zeta) = \frac{d}{d\zeta} \ln f(\zeta) - \frac{N+1}{\zeta}, \quad (12.14)$$

vanishes,

$$\frac{d}{d\zeta_0}\ln f(\zeta_0) = \mp\sum_j \frac{d}{d\zeta_0}\ln(1\mp\zeta_0 z_j) = \sum_j \frac{z_j}{1\mp\zeta_0 z_j} = \frac{N+1}{\zeta_0}, \tag{12.15}$$

or

$$\sum_j \frac{1}{\zeta_0^{-1} z_j^{-1} \mp 1} = N, \tag{12.16}$$

where for $N \gg 1$ we have dropped the distinction between $N+1$ and N. This gives an equation that determines ζ_0, the "fugacity," in terms of N.

The second derivative of the exponent in the contour integral is

$$g''(\zeta_0) = \frac{N}{\zeta_0^2} + \frac{d^2}{d\zeta^2}\ln f(\zeta_0) = \frac{N}{\zeta_0^2} \pm \sum_j \frac{z_j^2}{(1\mp\zeta_0 z_j)^2}. \tag{12.17}$$

Here, again, $g''(\zeta_0) > 0$. For the upper sign, this is obvious, while for the lower sign, from Eq. (12.16),

$$g''(\zeta_0) = \frac{1}{\zeta_0^2}\sum_j \left[\frac{\zeta_0 z_j}{1+\zeta_0 z_j} - \left(\frac{\zeta_0 z_j}{1+\zeta_0 z_j}\right)^2\right] > 0, \tag{12.18}$$

because

$$\frac{\zeta_0 z_j}{1+\zeta_0 z_j} < 1 \quad \text{for} \quad \zeta_0 > 0. \tag{12.19}$$

So, once again, we evaluate the integral defining Z by the method of steepest descents. The result is

$$Z = \frac{f(\zeta_0)}{\zeta_0^{N+1}} \frac{1}{\sqrt{2\pi g''(\zeta_0)}}, \tag{12.20}$$

and

$$\begin{aligned} \ln Z &= \ln f(\zeta_0) - (N+1)\ln\zeta_0 - \frac{1}{2}\ln(2\pi g''(\zeta_0)) \\ &= -N\ln\zeta_0 \mp \sum_j \ln\left(1\mp\zeta_0 e^{-\beta\varepsilon_j}\right). \end{aligned} \tag{12.21}$$

Here, we have recognized that the first two terms in the first line of this equation are of order N, while the third is only of order $\ln N$, so may be neglected. Now we calculate the mean occupation numbers

$$\langle n_j\rangle = -\frac{1}{\beta}\frac{\partial}{\partial\varepsilon_j}\ln Z = \frac{\zeta_0 e^{-\beta\varepsilon_j}}{1\mp\zeta_0 e^{-\beta\varepsilon_j}} = \frac{1}{\zeta_0^{-1}e^{\beta\varepsilon_j}\mp 1}, \tag{12.22}$$

where we have recognized that since $\ln Z$ is the same as $g(\zeta_0)$, the stationarity condition (12.14) implies that the implicit dependence of ζ_0 on ε_j cancels out.

[This is the same reason that the implicit dependence of β on E cancelled out in Eq. (10.26).] This is consistent with Eq. (12.16) in that

$$\sum_j \langle n_j \rangle = N. \tag{12.23}$$

We also may easily calculate the energy:

$$U = -\frac{d}{d\beta} \ln Z = \sum_j \langle n_j \rangle \varepsilon_j = \sum_j \frac{\varepsilon_j}{\zeta_0^{-1} e^{\beta \varepsilon_j} \mp 1}. \tag{12.24}$$