

## Chapter 15

# Grand Canonical Distribution

The general convolution law, for  $n$  independent subsystems, is

$$\frac{\Omega(E, N)}{N!} = \sum_{\{N_j\}} \delta_{N, \sum_j N_j} \int \delta(E - \sum_j E_j) \prod_j \frac{\Omega_j(E_j, N_j)}{N_j!} dE_j. \quad (15.1)$$

Define a generating function for  $\Omega(E, N)/N!$ :

$$\mathcal{W}(E, z) = \sum_{N=0}^{\infty} z^N \frac{\Omega(E, N)}{N!}. \quad (15.2)$$

We call  $\mathcal{W}$  the “Grand structure function.” Using the convolution law, we find,

$$\begin{aligned} \mathcal{W}(E, z) &= \sum_N \sum_{\{N_j\}} \delta_{N, \sum_j N_j} z^{\sum_j N_j} \\ &\quad \times \int \delta(E - \sum_j E_j) \prod_j \frac{\Omega_j(E_j, N_j)}{N_j!} dE_j \\ &= \int \delta(E - \sum_j E_j) \sum_{\{N_j\}} \prod_j \frac{z^{N_j} \Omega_j(E_j, N_j)}{N_j!} dE_j \\ &= \int \delta(E - \sum_j E_j) \prod_j \sum_{N_j=0}^{\infty} \frac{z^{N_j} \Omega_j(E_j, N_j)}{N_j!} dE_j \\ &= \int \delta(E - \sum_j E_j) \prod_j \mathcal{W}_j(E_j, z) dE_j, \end{aligned} \quad (15.3)$$

which is the ordinary convolution law again.

In analogy with the partition function, define the *grand partition function*:

$$\mathcal{X}(\alpha, z) = \int_0^{\infty} dE e^{-\alpha E} \mathcal{W}(E, z)$$

$$\begin{aligned}
&= \sum_{N=0}^{\infty} \frac{z^N}{N!} \int_0^{\infty} dE e^{-\alpha E} \Omega(E, N) \\
&= \sum_{N=0}^{\infty} \frac{z^N}{N!} \chi(\alpha, N), \tag{15.4}
\end{aligned}$$

the same relation as between  $\Omega$  and  $\mathcal{W}$ , in Eq. (15.2). For a composite system,

$$\begin{aligned}
\mathcal{X}(\alpha, z) &= \int_0^{\infty} dE e^{-\alpha E} \delta(E - \sum_j E_j) \prod_j \mathcal{W}_j(E_j, z) dE_j \\
&= \prod_j \int dE_j e^{-\alpha E_j} \mathcal{W}_j(E_j, z) \\
&= \prod_j \mathcal{X}_j(\alpha, z), \tag{15.5}
\end{aligned}$$

the product of the grand partition functions for the subsystems.

We now ask what is the probability of finding one of the systems, say the first one, with  $N_1$  molecules and at the phase-space point  $x_1 = \{q_{1i}, p_{1i}\}$ , with corresponding phase-space element  $dx_1 = (dq dp)_1$ . That probability density we call  $\mathcal{P}_1(N_1, x_1)$ ; the probability of finding the subsystem with  $N_1$  molecules and in a phase-space region between  $x_1$  and  $x_1 + dx_1$  is  $\mathcal{P}_1(N_1, x_1) dx_1$ . We determine  $\mathcal{P}_1$  by starting with the generalization of the microcanonical distribution for the whole system

$$\rho(\{N_j\}, \{x_j\}) = \frac{N!}{\prod_j N_j!} \delta_{N, \sum_j N_j} \frac{\delta(E - \sum_j H_j(N_j, x_j))}{\Omega(E, N)}. \tag{15.6}$$

The combinatorial factor is the number of ways of distributing  $N$  particles among the subsystems so that there are  $N_j$  particles in the  $j$ th subsystem. We check this by verifying the normalization condition,

$$\sum_{\{N_j\}} \int \rho(\{N_j\}, \{x_j\}) \prod_j dx_j = 1. \tag{15.7}$$

If this is so, then

$$\begin{aligned}
\frac{\Omega(E, N)}{N!} &= \sum_{\{N_j\}} \delta_{N, \sum_j N_j} \int \delta(E - \sum_j H_j) \prod_j \frac{dx_j}{N_j!} \\
&= \sum_{\{N_j\}} \delta_{N, \sum_j N_j} \int \prod_j dE_j \delta(E - \sum_j E_j) \prod_j \frac{1}{N_j!} \int dx_j \delta(E_j - H_j) \\
&= \sum_{\{N_j\}} \delta_{N, \sum_j N_j} \int \delta(E - \sum_j E_j) \prod_j \frac{\Omega_j(E_j, N_j)}{N_j!} dE_j, \tag{15.8}
\end{aligned}$$

which is the correct convolution law (15.1).

Now the single-system probability density is

$$\begin{aligned}
\mathcal{P}_1(N_1, x_1) &= \sum_{N_2, N_3, \dots} \rho(\{N_j\}, \{x_j\}) \prod_{j=2}^n dx_j \\
&= \frac{N!}{N_1! \Omega(E, N)} \sum_{N_2, N_3, \dots} \delta_{N-N_1, \sum_{j=2}^n N_j} \\
&\quad \times \int \delta(E - H_1 - \sum_{j=2}^n H_j) \prod_{j=2}^n \frac{dx_j}{N_j!} \\
&= \frac{N!}{N_1!(N-N_1)!} \frac{\Omega^{(n-1)}(E - H_1, N - N_1)}{\Omega^{(n)}(E, N)}, \tag{15.9}
\end{aligned}$$

which generalizes Eq. (9.69), with the addition of the combinatorial factor  $\binom{N}{N_1}$ .

As before, we want to make an asymptotic evaluation, [see Eq. (9.14)]

$$\begin{aligned}
\frac{\Omega(E, N)}{N!} &= \sum_{\{N_j\}} \delta_{N, \sum_j N_j} \int \delta(E - \sum_j E_j) \prod_j \frac{\Omega_j(E_j, N_j)}{N_j!} dE_j \\
&= \frac{1}{2\pi i} \sum_{\{N_j\}} \delta_{N, \sum_j N_j} \int_C d\alpha e^{\alpha(E - \sum_j E_j)} \prod_j \frac{\Omega_j(E_j, N_j)}{N_j!} dE_j \\
&= \frac{1}{2\pi i} \sum_{\{N_j\}} \delta_{N, \sum_j N_j} \int_C d\alpha e^{\alpha E} \prod_j \frac{\chi_j(\alpha, N_j)}{N_j!}. \tag{15.10}
\end{aligned}$$

But we recall further [Eq. (12.11)]

$$\delta_{N, N'} = \frac{1}{2\pi i} \oint_{\gamma} \frac{dz}{z^{N-N'+1}}, \tag{15.11}$$

so from Eq. (15.4)

$$\begin{aligned}
\frac{\Omega(E, N)}{N!} &= \frac{1}{(2\pi i)^2} \oint_{\gamma} dz \int_C d\alpha \frac{e^{\alpha E}}{z^{N+1}} \sum_{\{N_j\}} \prod_j z^{N_j} \frac{\chi_j(\alpha, N_j)}{N_j!} \\
&= \frac{1}{(2\pi i)^2} \oint_{\gamma} dz \int_C d\alpha \frac{e^{\alpha E}}{z^{N+1}} \prod_j \mathcal{X}_j(\alpha, z) \\
&= \frac{1}{(2\pi i)^2} \oint_{\gamma} dz \int_C d\alpha \frac{e^{\alpha E}}{z^{N+1}} \mathcal{X}(\alpha, z). \tag{15.12}
\end{aligned}$$

This result can be seen directly from Eq. (15.4):

$$\begin{aligned}
\frac{1}{(2\pi i)^2} \oint_{\gamma} \frac{dz}{z^{M+1}} \int_C d\alpha e^{\alpha E} \mathcal{X}(\alpha, z) &= \sum_{N=0}^{\infty} \frac{1}{N!} \delta_{N, M} \int_0^{\infty} dE' \delta(E - E') \Omega(E', N) \\
&= \frac{1}{M!} \Omega(E, M). \tag{15.13}
\end{aligned}$$

Now we put this relation in the form suitable for asymptotic analysis:

$$\frac{\Omega(E, N)}{N!} = \frac{1}{(2\pi i)^2} \int \int dz d\alpha e^{\alpha E - (N+1) \ln z + \ln \mathcal{X}(\alpha, z)}. \quad (15.14)$$

Let  $z = e^\nu$ ,  $dx = e^\nu d\nu$ , where if  $\gamma$  is a circle of radius  $R$  about the origin,  $\nu$  ranges from  $A - i\pi$  to  $A + i\pi$ ,  $A = \ln R$ , a finite path parallel to the imaginary axis. Thus we write

$$\frac{\Omega(E, N)}{N!} = \frac{1}{(2\pi i)^2} \int d\nu d\alpha e^{\alpha E - \nu N + \ln \mathcal{X}(\alpha, \nu)}. \quad (15.15)$$

Consider the real  $\nu$ , real  $\alpha$  plane. There is only one minimum of the exponent in Eq. (15.15), which is determined by

$$E = -\frac{\partial}{\partial \alpha} \ln \mathcal{X}(\alpha, \nu), \quad N = \frac{\partial}{\partial \nu} \ln \mathcal{X}(\alpha, \nu), \quad (15.16)$$

which roots we will denote by  $\alpha = \beta$  and  $\nu = \beta\mu$ . To demonstrate this assertion, consider the quadratic form

$$Q = \left[ (\alpha - \beta)^2 \frac{\partial^2}{\partial \alpha^2} + 2(\alpha - \beta)(\nu - \beta\mu) \frac{\partial^2}{\partial \alpha \partial \nu} + (\nu - \beta\mu)^2 \frac{\partial^2}{\partial \nu^2} \right] \ln \mathcal{X}(\alpha, \nu). \quad (15.17)$$

Define a distribution function by

$$p(E, N) = \frac{e^{-\alpha E + \nu N} \Omega(E, N)}{\mathcal{X}(\alpha, \nu) N!}, \quad (15.18)$$

which is a generalization of Eq. (9.60). This is properly normalized:

$$\sum_{N=0}^{\infty} \int dE p(E, N) = \sum_{N=0}^{\infty} e^{\nu N} \int_0^{\infty} dE e^{-\alpha E} \frac{\Omega(E, N)}{N!} \frac{1}{\mathcal{X}(\alpha, \nu)} = 1. \quad (15.19)$$

Then, denoting by a prime the derivative with respect to  $\alpha$ ,

$$\frac{\partial^2}{\partial \alpha^2} \ln \mathcal{X} = \frac{\mathcal{X}''}{\mathcal{X}} - \left( \frac{\mathcal{X}'}{\mathcal{X}} \right)^2 \quad (15.20)$$

involves

$$\frac{\mathcal{X}'}{\mathcal{X}} = \sum_{N=0}^{\infty} \frac{e^{\nu N}}{N!} \int_0^{\infty} dE (-E) e^{-\alpha E} \frac{\Omega(E, N)}{\mathcal{X}(\alpha, \nu)} = -\langle E \rangle, \quad (15.21)$$

and

$$\frac{\mathcal{X}''}{\mathcal{X}} = \langle E^2 \rangle, \quad (15.22)$$

so

$$\frac{\partial^2}{\partial \alpha^2} \ln \mathcal{X} = \langle E^2 \rangle - \langle E \rangle^2 = \langle (E - \langle E \rangle)^2 \rangle. \quad (15.23)$$

Similarly,

$$\frac{\partial^2}{\partial \nu^2} \ln \mathcal{X} = \langle (N - \langle N \rangle)^2 \rangle, \quad (15.24)$$

and

$$\begin{aligned} \frac{\partial}{\partial \alpha} \frac{\partial}{\partial \nu} \ln \mathcal{X} &= \frac{\partial}{\partial \alpha} \left( \frac{1}{\mathcal{X}} \frac{\partial}{\partial \nu} \mathcal{X} \right) \\ &= \frac{1}{\mathcal{X}} \frac{\partial}{\partial \alpha} \frac{\partial}{\partial \nu} \mathcal{X} - \frac{1}{\mathcal{X}^2} \left( \frac{\partial}{\partial \alpha} \mathcal{X} \right) \left( \frac{\partial}{\partial \nu} \mathcal{X} \right) \\ &= -\langle EN \rangle + \langle E \rangle \langle N \rangle = -\langle (E - \langle E \rangle)(N - \langle N \rangle) \rangle. \end{aligned} \quad (15.25)$$

Thus

$$Q = \langle [(\alpha - \beta)(E - \langle E \rangle) - (\nu - \beta\mu)(N - \langle N \rangle)]^2 \rangle > 0. \quad (15.26)$$

This proves that there is only one minimum of  $\alpha E - \nu N + \ln \mathcal{X}(\alpha, \nu)$  for real  $\alpha, \nu$ .

Now that we have shown there is a unique saddle point in the  $\alpha$ - $\nu$  plane, we carry out the integral asymptotically through the saddle point (details are given in Sec. 15.1):

$$\frac{\Omega(E, N)}{N!} = e^{\beta E - \beta\mu N} \mathcal{X}(\beta, \mu) \frac{1}{2\pi\sqrt{\Delta}}, \quad (15.27)$$

where

$$\Delta = \left[ \frac{\partial^2}{\partial \alpha^2} \ln \mathcal{X} \frac{\partial^2}{\partial \nu^2} \ln \mathcal{X} - \left( \frac{\partial^2}{\partial \alpha \partial \nu} \ln \mathcal{X} \right)^2 \right]_{\alpha=\beta, \nu=\beta\mu}. \quad (15.28)$$

Then from the single-particle distribution formula (15.9), we deduce the “grand canonical distribution function,”

$$\mathcal{P}_1(N_1, x_1) = \frac{1}{N_1!} \frac{e^{-\beta(H_1 - \mu N_1)}}{\mathcal{X}_1(\beta, \mu)}. \quad (15.29)$$

We check that this is properly normalized:

$$\sum_{N_1=0}^{\infty} \int dx_1 \mathcal{P}_1(N_1, x_1) = \sum_{N_1=0}^{\infty} \frac{e^{\beta\mu N_1}}{N_1!} \chi(\beta, N_1) \frac{1}{\mathcal{X}_1(\beta, \mu)} = 1, \quad (15.30)$$

The energy distribution function is (because  $\mathcal{P}$  depends on  $x_1$  only through  $H_1(x_1)$ )

$$\begin{aligned} p(E, N) &= \int \mathcal{P}(N, x) \delta(E - H(x)) dx_1 = \mathcal{P}(N, E) \Omega(E, N) \\ &= \frac{e^{-\beta E + \beta\mu N} \Omega(E, N)}{N! \mathcal{X}(\beta, \mu)}, \end{aligned} \quad (15.31)$$

which is just the distribution introduced in Eq. (15.18) to prove the uniqueness of the saddle point.

## 15.1 Details of saddle point integration

Write the double saddle-point integration in Eq. (15.15) as (the subscripts denote partial derivatives)

$$\int d\nu d\alpha e^{\alpha^2 \frac{1}{2}(\ln \mathcal{X})_{\alpha\alpha} + \nu^2 \frac{1}{2}(\ln \mathcal{X})_{\nu\nu} + \alpha\nu(\ln \mathcal{X})_{\alpha\nu}} = - \int d^2 x e^{-\frac{1}{2}x \cdot A \cdot x}, \quad (15.32)$$

where  $x$  is a two-component vector,

$$ix = \begin{pmatrix} \nu \\ \alpha \end{pmatrix}, \quad (15.33)$$

and  $A$  is the matrix

$$A = \begin{pmatrix} (\ln \mathcal{X})_{\nu\nu} & (\ln \mathcal{X})_{\nu\alpha} \\ (\ln \mathcal{X})_{\alpha\nu} & (\ln \mathcal{X})_{\alpha\alpha} \end{pmatrix}. \quad (15.34)$$

Now the matrix may be diagonalized, in which form the diagonal elements are the eigenvalues  $\lambda_1$  and  $\lambda_2$ , with the corresponding eigenvectors  $x_1$  and  $x_2$ . Then the above integral may be written as the product of two Gaussian integrals

$$\begin{aligned} - \int dx_1 dx_2 e^{-\frac{\lambda_1}{2}x_1^2} e^{-\frac{\lambda_2}{2}x_2^2} &= - \frac{2\pi}{\sqrt{\lambda_1 \lambda_2}} = - \frac{2\pi}{\sqrt{\det A}} \\ &= -2\pi [(\ln \mathcal{X})_{\nu\nu}(\ln \mathcal{X})_{\alpha\alpha} - (\ln \mathcal{X})_{\nu\alpha}^2]^{-1/2}. \end{aligned} \quad (15.35)$$

This is the result given in Eqs. (15.27) and (15.28).