Chapter 11

The Quantum Microcanonical Distribution

At first blush, it seems we can define the microcanonical distribution for a quantum system just as classically. Define the density operator by

$$\rho(H) = \frac{1}{\Omega(E)}\delta(E-H), \tag{11.1}$$

where H is the Hamiltonian operator, so in terms of the eigenvectors and eigenvalues of the Hamiltonian,

$$H|E_l, k\rangle = E_l|E_l, k\rangle, \tag{11.2}$$

k corresponding to eigenvalues of other observables compatible with the Hamiltonian, we write the δ function as [cf. Eq. (4.42)]

$$\delta(E-H) = \sum_{l,k} |E_l, k\rangle\delta(E-E_l)\langle E_l, k|. \tag{11.3}$$

Now the density operator has unit trace, which is the statement of the conservation of probability,

$$\operatorname{Tr}\rho = 1, \tag{11.4}$$

which implies that the structure function satisfies

$$\begin{aligned}\Omega(E) &= \operatorname{Tr}\delta(E-H) = \sum_l \delta(E-E_l)\sum_k \langle E_l, k|E_l, k\rangle \\ &= \sum_l g_l\delta(E-E_l).\end{aligned} \tag{11.5}$$

Here we have used the fact that the states are represented by orthonormal vectors,

$$\langle E_l, k|E_{l'}, k'\rangle = \delta_{ll'}\delta_{kk'}, \tag{11.6}$$

and g_l, the degeneracy, is the number of states with energy E_l.

Now consider two independent systems, so $H = H_1 + H_2$, and so

$$\begin{aligned}
\Omega(E) &= \operatorname{Tr}\delta(E - H_1 - H_2) = \sum_{l,m} g_{1,l} g_{2,m} \delta(E - E_l^{(1)} - E_m^{(2)}) \\
&= \operatorname{Tr} \sum_{lm,k_1k_2} |E_l^{(1)}, k_1\rangle |E_m^{(2)}, k_2\rangle \delta(E - E_l^{(1)} - E_m^{(2)}) \langle E_l^{(1)}, k| \langle E_m^{(2)}, k_2| \\
&= \operatorname{Tr} \int dE_1' \sum_{lk_1} |E_l^{(1)}, k_1\rangle \delta(E_1' - E_l^{(1)}) \langle E_l^{(1)}, k_1| \\
&\qquad \times \sum_{m,k_2} |E_m^{(2)}, k_2\rangle \delta(E - E_1' - E_m^{(2)}) \langle E_m^{(2)}, k_2| \\
&= \int dE_1' \, \Omega_1(E_1') \Omega_2(E - E_1'), \qquad (11.7)
\end{aligned}$$

which is the same convolution law as seen classically.

However these definitions of ρ and $\Omega(E)$ are not satisfactory, because the spectrum of the Hamiltonian is in general discrete, so for example,

$$\Omega(E) = \begin{cases} 0 & \text{if } E \neq E_l, \text{ for all } l, \\ \infty & \text{if } E = E_l. \end{cases} \qquad (11.8)$$

Therefore, we need to average over a small energy range.

11.1 Smallness of energy spacings

We need to appreciate how closely the energy levels are spaced. Consider a system in a large box. The Schrödinger equation for a particle of mass m in a one-dimensional box of length a is

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) = E\psi(x), \qquad (11.9)$$

which for boundaries at $x = 0$ and $x = a$, is subject to the boundary conditions

$$\psi(0) = \psi(a) = 0. \qquad (11.10)$$

Thus

$$\psi(x) = A \sin \frac{n\pi}{a} x, \quad n = 1, 2, \ldots, \qquad (11.11)$$

and the energy levels are

$$E_n = \frac{\hbar^2 n^2}{2m} \frac{\pi^2}{a^2}, \qquad (11.12)$$

so the typical energy spacing is

$$\Delta E = \frac{\hbar^2 \pi^2}{2ma^2}. \qquad (11.13)$$

Suppose we consider a proton, of mass approximately $mc^2 = 1\,\mathrm{GeV} = 10^9\,\mathrm{eV}$, in a box of size $a = 1$ cm. The unit conversion factor is

$$\hbar c \approx 2 \times 10^{-5}\,\mathrm{eV\,cm}, \tag{11.14}$$

so

$$\Delta E \approx 10^{-18}\,\mathrm{eV}, \tag{11.15}$$

which is a very small energy, indeed. Such discreteness in the energy is practically imperceptible.

11.2 Smoothed MC distribution

So we can introduce a very small energy scale ϵ which is very large compared to the level spacing, but tiny on a macroscopic scale. Then, we define the density operator by

$$\rho_\epsilon = \frac{1}{\Omega_\epsilon} \int_{E-\epsilon/2}^{E+\epsilon/2} dE'\,\delta(E' - H). \tag{11.16}$$

Then $\operatorname{Tr} \rho_E = 1$ gives the smoothed structure function

$$\Omega_\epsilon(E) = \int_{E-\epsilon/2}^{E+\epsilon/2} dE' \operatorname{Tr} \delta(E' - H) = \int_{E-\epsilon/2}^{E+\epsilon/2} dE'\,\Omega(E'), \tag{11.17}$$

which is the number of states with energy between $E - \epsilon/2$ and $E + \epsilon/2$.

Now consider a compound system, $H = H_1 + H_2$, and consider the density operator for subsystem 1:

$$\begin{aligned}\rho_1 &= \operatorname{Tr} \rho_\epsilon = \frac{1}{\Omega_\epsilon(E)} \int_{E-\epsilon/2}^{E+\epsilon/2} dE' \operatorname{Tr}_2 \delta(E' - H_1 - H_2) \\ &= \frac{1}{\Omega_\epsilon(E)} \int_{E-\epsilon/2}^{E+\epsilon/2} dE'\,\Omega_2(E' - H_1) \\ &= \frac{\Omega_{2\epsilon}(E - H_1)}{\Omega_\epsilon(E)}.\end{aligned} \tag{11.18}$$

The spectral resolution of this

$$\rho_1 = \sum_{jk} |E_j^{(1)}, k\rangle \frac{\Omega_{2\epsilon}(E - E_j^{(1)})}{\Omega_\epsilon(E)} \langle E_j^{(1)}, k|, \tag{11.19}$$

means that $\Omega_{2\epsilon}(E - E_j^{(1)})/\Omega_\epsilon(E)$ is the probability of finding system 1 is the state $(E_j^{(1)}, k)$, and the probability of finding system 1 in any $E_j^{(1)}$ state

$$g_j \frac{\Omega_{2\epsilon}(E - E_j^{(1)})}{\Omega_\epsilon(E)}. \tag{11.20}$$

However, the averaging process has spoiled the convolution property given in Eq. (11.7). To fix this problem, let us divide the energy into discrete bins, $E = n\epsilon$, where by energy E we refer to all energies between $\left(n-\frac{1}{2}\right)\epsilon$ and $\left(n+\frac{1}{2}\right)\epsilon$. Then because $\Omega_\epsilon(E)$ is the number of states in the E bin, we have

$$\Omega_\epsilon(E) = \sum_{E'} \Omega_{1\epsilon}(E')\Omega_{2\epsilon}(E-E'), \tag{11.21}$$

where the summand is the number of states corresponding to a particular partitioning of the energy between the two subsystems. The general convolution law is, if $H = \sum_j H_j$,

$$\Omega_\epsilon(E) = \sum_{\{E_l\}} \delta_{E,\sum_l E_l} \prod_l \Omega_{l\epsilon}(E_l). \tag{11.22}$$

As previously, we assume that all energies are nonnegative. (This is just a choice of the zero of energy, assuming energies are bounded below.) Then we define the partition function by a discrete Laplace transform,

$$\chi(\alpha) = \sum_E e^{-\alpha E}\Omega_\epsilon(E), \tag{11.23}$$

so again for a compound system

$$\begin{aligned}\chi(\alpha) &= \sum_{E,\{E_l\}} e^{-\alpha E}\delta_{E,\sum_l E_l}\prod_l \Omega_{l\epsilon}(E_l)\\ &= \sum_{\{E_l\}}\prod_l e^{-\alpha E_l}\Omega_{l\epsilon}(E_l) = \prod_l \sum_{E_l} e^{-\alpha E_l}\Omega_{l\epsilon}(E_l)\\ &= \prod_l \chi_l(\alpha),\end{aligned} \tag{11.24}$$

the expected product law.

Again, we seek an asymptotic expansion for Ω. For this we first recall

$$\frac{1}{2\pi i}\oint_\gamma \frac{dz}{z} z^n = \delta_{n0}, \tag{11.25}$$

where γ is any closed contour which encircles the origin once in the positive (CCW) sense. That is, the integral is zero for any integer n, positive or negative, except for $n = 0$. Then, because we are now measuring E in integer multiples of ϵ, this is the same as

$$\frac{1}{2\pi i}\oint_\gamma \frac{dz}{z} z^{(E-E')/\epsilon} = \delta_{EE'}. \tag{11.26}$$

Next, let $z = e^{\alpha\epsilon}$, so $dz/z = \epsilon\, d\alpha$, and

$$\delta_{EE'} = \frac{\epsilon}{2\pi i}\int_{A-i\pi/\epsilon}^{A+i\pi/\epsilon} d\alpha\, e^{\alpha(E-E')}, \tag{11.27}$$

where because

$$\alpha = \frac{1}{\epsilon}\ln z = \frac{1}{\epsilon}[\ln R + i\theta], \tag{11.28}$$

if we choose γ to be a circle of radius R, $A = \frac{\ln R}{\epsilon}$. As $\epsilon \to 0$, the endpoints of the finite path recede to $\pm i\infty$.

So now we have, from the convolution formula (11.22)

$$\begin{aligned}
\Omega_\epsilon(E) &= \sum_{\{E_l\}} \delta_{E,\sum_l E_l} \prod_l \Omega_{l\epsilon}(E_l) \\
&= \frac{\epsilon}{2\pi i}\int d\alpha \sum_{\{E_l\}} e^{\alpha(E-\sum_l E_l)} \prod_l \Omega_{l\epsilon}(E_l) \\
&= \frac{\epsilon}{2\pi i}\int d\alpha\, e^{\alpha E} \prod_l \chi_l(\alpha) \\
&= \frac{\epsilon}{2\pi i}\int_{A-i\pi\epsilon}^{A+i\pi/\epsilon} d\alpha\, e^{\alpha E}\chi(\alpha),
\end{aligned} \tag{11.29}$$

the exact analog of the classical formula (9.23).

The asymptotic saddle-point analysis goes through just as before, with the result

$$\Omega_\epsilon(E) \sim \frac{\epsilon e^{\beta E}\chi(\beta)}{\sqrt{2\pi(\ln\chi)''(\beta)}}, \tag{11.30}$$

where β is the unique positive real root of

$$(\ln\chi)'(\beta) = -E. \tag{11.31}$$

[The fact that the path of integration is finite is immaterial, since the significant contributing region is very near the saddle point,

$$\frac{\Delta\beta}{\beta} \sim \frac{1}{\sqrt{N}}, \tag{11.32}$$

so as long as

$$\frac{\pi}{\epsilon} \gg \frac{\beta}{\sqrt{N}}, \quad \text{or} \quad \epsilon \ll \pi\sqrt{N}kT, \tag{11.33}$$

the endpoints are irrelevant.]

The probability that the system 1 is in a particular state with energy $E_j^{(1)}$ is from Eq. (11.19)

$$\frac{\Omega_\epsilon^{(N-1)}(E - E_j^{(1)})}{\Omega^{(N)}(E)} \sim \frac{e^{-\beta E_j^{(1)}}}{\chi_1(\beta)}, \tag{11.34}$$

so the density operator for system 1 is

$$\begin{aligned}
\rho_1 &= \sum_{jk} |E_j^{(1)}, k\rangle \frac{e^{-\beta E_j^{(1)}}}{\chi_1(\beta)} \langle E_j^{(1)}, k| \\
&= \frac{e^{-\beta H_1}}{\chi_1(\beta)},
\end{aligned} \tag{11.35}$$

which is the canonical distribution, with

$$\chi_1(\beta) = \mathrm{Tr}\, e^{-\beta H_1} = \sum_j g_j e^{-\beta E_j^{(1)}}, \tag{11.36}$$

which is consistent with

$$\chi(\alpha) = \sum_E e^{-\alpha E} \Omega_\epsilon(E), \tag{11.37}$$

where $\Omega_\epsilon(E)$ is the number of states with energy E.