

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

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

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

$$H|E_l, k\rangle = E_l|E_l, k\rangle, \quad (11.2)$$

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

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

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

$$\text{Tr } \rho = 1, \quad (11.4)$$

which implies that the structure function satisfies

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

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

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

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

$$\begin{aligned}
\Omega(E) &= \text{Tr} \delta(E - H_1 - H_2) = \sum_{l,m} g_{1,l} g_{2,m} \delta(E - E_l^{(1)} - E_m^{(2)}) \\
&= \text{Tr} \sum_{lm, k_1 k_2} |E_l^{(1)}, k_1\rangle |E_m^{(2)}, k_2\rangle \delta(E - E_l^{(1)} - E_m^{(2)}) \langle E_l^{(1)}, k_1 | \langle E_m^{(2)}, k_2 | \\
&= \text{Tr} \int dE'_1 \sum_{lk_1} |E_l^{(1)}, k_1\rangle \delta(E'_1 - E_l^{(1)}) \langle E_l^{(1)}, k_1 | \\
&\quad \times \sum_{m, k_2} |E_m^{(2)}, k_2\rangle \delta(E - E'_1 - E_m^{(2)}) \langle E_m^{(2)}, k_2 | \\
&= \int dE'_1 \Omega_1(E'_1) \Omega_2(E - E'_1), \tag{11.7}
\end{aligned}$$

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,

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

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

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

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

$$\psi(0) = \psi(a) = 0. \tag{11.10}$$

Thus

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

and the energy levels are

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

so the typical energy spacing is

$$\Delta E = \frac{\hbar^2 \pi^2}{2ma^2}. \tag{11.13}$$

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

$$\hbar c \approx 2 \times 10^{-5} \text{ eV cm}, \quad (11.14)$$

so

$$\Delta E \approx 10^{-18} \text{ eV}, \quad (11.15)$$

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

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

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

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

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:

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

The spectral resolution of this

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

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

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

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 $(n - \frac{1}{2})\epsilon$ and $(n + \frac{1}{2})\epsilon$. Then because $\Omega_\epsilon(E)$ is the number of states in the E bin, we have

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

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 $H = \sum_j H_j$,

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

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,

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

so again for a compound system

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

the expected product law.

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

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

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

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

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

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

where because

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

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

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

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

the exact analog of the classical formula (9.23).

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

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

where β is the unique positive real root of

$$(\ln \chi)'(\beta) = -E. \quad (11.31)$$

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

$$\frac{\Delta\beta}{\beta} \sim \frac{1}{\sqrt{N}}, \quad (11.32)$$

so as long as

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

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)

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

so the density operator for system 1 is

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

which is the canonical distribution, with

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

which is consistent with

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

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