Chapter 9

Derivation of Canonical Distribution from Microcanonical

9.1 Structure and Partition Functions

Consider first the structure function of a composite system. For two noninteracting systems,

$$H = H_1 + H_2, \quad dp\, dp = (dp\, dp)_1 (dp\, dq)_2, \tag{9.1}$$

the structure function is decomposed as follows:

$$\begin{aligned}
\Omega(E) &= \int \delta(E - H_1 - H_2)(dp\, dq)_1 (dp\, dq)_2 \\
&= \int \Omega_2(E - H_1)(dp\, dq)_1 = \int \Omega_1(E - H_2)(dp\, dq)_2 \qquad (9.2) \\
&= \int dE_1 \delta(E_1 - H_1)\Omega_2(E - E_1)(dp\, dq)_1 \\
&= \int \Omega_1(E_1)\Omega_2(E - E_1) dE_1; \qquad (9.3)
\end{aligned}$$

the composition law is that of a *convolution.* For n noninteracting subsystems,

$$\begin{aligned}
\Omega(E) &= \int \delta\left(E - \sum_{j=1}^{n} H_j\right) \prod_{k=1}^{n} (dp\, dq)_k \\
&= \int \delta\left(E - \sum_{j=1}^{n} E_j\right) \prod_{k=1}^{n} \delta(E_k - H_k) dE_k (dp\, dq)_k
\end{aligned}$$

$$= \int \delta\left(E - \sum_{j=1}^{n} E_j\right) \prod_{k=1}^{n} \Omega_k(E_k) dE_k, \tag{9.4}$$

a generalized convolution law.

Next, consider a phase-space volume A. The corresponding characteristic function is

$$\psi_A = \begin{cases} 1 & \text{for phase-space point in } A, \\ 0 & \text{for phase-space point outside } A. \end{cases} \tag{9.5}$$

The probability of finding the system in A is

$$P_A = \langle \psi_A \rangle = \frac{1}{\Omega_E} \int \delta(E - H) \psi_A dp\, dq. \tag{9.6}$$

Suppose A depends on variables of system 1 only; then,

$$\begin{aligned} P_A &= \frac{1}{\Omega(E)} \int \delta(E - H_1 - H_2) \psi_A (dp\, dq)_1 (dp\, dq)_2 \\ &= \frac{1}{\Omega(E)} \int \Omega_2(E - H_1) \psi_A (dp\, dq)_1. \end{aligned} \tag{9.7}$$

Suppose A is a very small volume $(\Delta p\, \Delta q)_1$:

$$P_{(\Delta p\, \Delta q)_1} = \frac{1}{\Omega(E)} \Omega_2(E - H_1)(\Delta p\, \Delta q)_1 = \rho_1(\{p, q\}_1)(\Delta p\, \Delta q)_1, \tag{9.8}$$

where ρ_1 is the distribution function for system 1:

$$\rho_1(\{p, q\}_1) = \frac{\Omega_2(E - H_1)}{\Omega(E)}. \tag{9.9}$$

Indeed, this is properly normalized,

$$\int \rho_1(\{p, q\}_1)(dp\, dq)_1 = 1, \tag{9.10}$$

according to Eq. (9.2).

The energy distribution function for system 1 is

$$\begin{aligned} P(E_1) &= \int \delta(E_1 - H_1) \rho_1(\{p, q\}_1)(dp\, dq)_1 \\ &= \int \delta(E_1 - H_1)(dp\, dq)_1 \frac{\Omega_2(E - E_1)}{\Omega(E)} \\ &= \frac{\Omega_1(E_1) \Omega_2(E - E_1)}{\Omega(E)}, \end{aligned} \tag{9.11}$$

which is properly normalized,

$$\int P(E_1) dE_1 = 1, \tag{9.12}$$

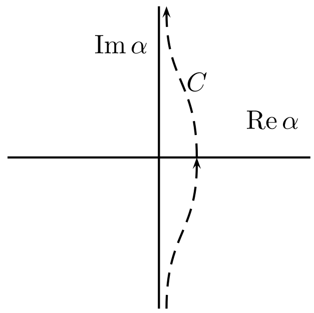

Figure 9.1: Contour C defining the partition function, the Laplace transform of the structure function.

which is consistent with the convolution law (9.3).

Let us rewrite the generalized convolution law (9.4) by using the Fourier representation of the delta function,

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{i\lambda x}d\lambda = \frac{1}{2\pi i}\int_{-i\infty}^{i\infty} e^{\alpha x}d\alpha, \tag{9.13}$$

where we have changed variables, $\alpha = i\lambda$, where in the second integral the integral extends along the imaginary axis. Thus, Eq. (9.4) reads

$$\begin{aligned}\Omega(E) &= \int \delta\left(E - \sum_{n=1}^{n} E_j\right)\prod_{k=1}^{n}\Omega_k(E_k)\,dE_k \\ &= \frac{1}{2\pi i}\int_C d\alpha\, e^{a\left(E-\sum_j E_j\right)}\prod_{k=1}^{n}\Omega_k(E_k)\,dE_k \\ &= \frac{1}{2\pi i}\int_C d\alpha\, e^{\alpha E}\prod_{j=1}^{n}\int e^{-\alpha E_j}\Omega_j(E_j)\,dE_j\,d\alpha. \end{aligned}\tag{9.14}$$

Here the contour of integration C is initially taken to be the imaginary α axis, but will be deformed below. This is really a Laplace transform.

Ordinarily, the structure function $\Omega(E)$ increases with E as a power; for example, for an ideal gas, $\Omega(E) \propto E^{(3N-2)/2}$, see Eq. (8.25). Let us suppose that we choose the zero of energy so that $\Omega(E) = 0$ if $E < 0$. (Physical systems must have energies bounded from below.) Then the Laplace transform of the structure function, defined by

$$\chi(\alpha) = \int_0^{\infty} e^{-\alpha E}\Omega(E)dE, \tag{9.15}$$

is well-defined in the right-half complex α plane, $\operatorname{Re}\alpha > 0$, and the contour C is as illustrated in Fig. 9.1. χ is called the partition function. Indeed,

$$\chi(\alpha) = \int e^{-\alpha E}\delta(E-H)dp\,dq\,dE = \int e^{-\alpha H}dp\,dq, \tag{9.16}$$

which has the form of the partition function

$$Z(\beta) = \int e^{-\beta H} dp\, dq \tag{9.17}$$

in the canonical distribution function [see Eq. (1.34)].

Now from Eq. (9.14) we have

$$\Omega(E) = \frac{1}{2\pi i} \int_C d\alpha\, e^{\alpha E} \prod_j \chi_j(\alpha). \tag{9.18}$$

On the other hand, for a composite system,

$$\begin{aligned} \chi(\alpha) &= \int_0^\infty dE\, e^{-\alpha E} \Omega(E) \\ &= \int_0^\infty dE\, e^{-\alpha E} \int \delta\left(E - \sum_j E_j\right) \prod_k \Omega_k(E_k) dE_k \\ &= \prod_k \int_0^\infty dE_k e^{-\alpha E_k} \Omega_k(E_k) = \prod_{k=1}^n \chi_k(\alpha), \end{aligned} \tag{9.19}$$

as we have already seen for the partition functions [Eq. (1.35)], so indeed

$$\Omega(E) = \frac{1}{2\pi i} \int_C d\alpha\, e^{\alpha E} \chi(\alpha). \tag{9.20}$$

We see here the *Mellin Inversion Theorem*: If

$$\chi(\alpha) = \int_0^\infty dE\, e^{-\alpha E} \Omega(E) \tag{9.21}$$

is such that

$$\int_0^\infty dE\, |\Omega(E)| e^{-\alpha E} \tag{9.22}$$

exists for $\mathrm{Re}\,\alpha_1 > 0$, then for $\alpha_2 > \mathrm{Re}\,\alpha_1$

$$\Omega(E) = \frac{1}{2\pi i} \int_{\alpha_2 - i\infty}^{\alpha_2 + i\infty} d\alpha\, e^{\alpha E} \chi(\alpha). \tag{9.23}$$

9.2 Example

Suppose we have N identical subsystems, so

$$\Omega(E) = \frac{1}{2\pi i} \int_C d\alpha\, e^{\alpha E} [\chi(\alpha)]^N, \tag{9.24}$$

where

$$\chi(\alpha) = \int_0^\infty dE\, e^{-\alpha E} \omega(E), \tag{9.25}$$

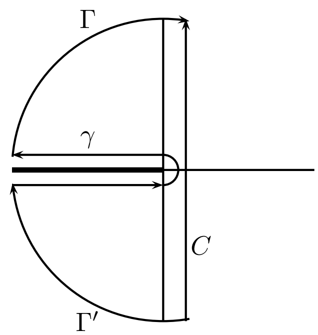

Figure 9.2: Contour C, parallel to the imaginary axis, can be distorted into a contour γ which encircles the branch line on the negative real axis.

where $\omega(E) = \Omega_j(E)$, $j = 1, 2, \ldots, N$. If, for example, $\omega(E) = BE^\nu$, the partition function for one subsystem is

$$\chi(\alpha) = B\int_0^\infty dE\, E^\nu e^{-\alpha E} = \frac{B}{\alpha^{1+\nu}}\int_0^\infty \frac{dx}{x} x^{1+\nu} e^{-x} = \frac{B\Gamma(\nu+1)}{\alpha^{1+\nu}}, \tag{9.26}$$

and then the structure function for the whole system is

$$\Omega(E) = [B\Gamma(1+\nu)]^N E^{N(1+\nu)-1}\frac{1}{2\pi i}\int_C dz \frac{e^z}{z^{N(1+\nu)}}. \tag{9.27}$$

In general, $N\nu$ is not an integer, so $z^{N\nu}$ has a branch point at $z = 0$, and a branch line starting from that point and extending off to infinity. Let us choose the branch line to lie along the negative real z axis. Then we can distort the contour of integration C as shown in Fig. 9.2. Thus the desired integral can be written as a closed contour integral plus two integrals on quarter circular arcs, Γ and Γ' of large radius R, plus an integral around a contour γ which encircles the branch line on the negative real axis:

$$\int_C dz\frac{e^z}{z^s} = \oint dz\frac{e^z}{z^s} + \int_\gamma dz\frac{e^z}{z^s} + \int_{\Gamma+\Gamma'} dz\frac{e^z}{z^s}. \tag{9.28}$$

The closed contour integral is zero, by Cauchy's theorem, since it encircles no singularities of the integrand. The last integral is also zero, since there $z = Re^{i\theta}$, and so it equals

$$-\int_{\pi/2}^{3\pi/2} Re^{i\theta} i d\theta \frac{e^{R\cos\theta + iR\sin\theta}}{R^s e^{is\theta}}. \tag{9.29}$$

Since $\cos\theta < 0$ except at the endpoints, we conclude that this integral vanishes as $R \to \infty$ provided $s > 1$. (Jordan's lemma shows that the endpoints do not alter this conclusion.) Finally, the integral around γ is Hankel's representation of the gamma function, as shown in Sec. 9.4:

$$\frac{1}{2\pi i}\int_\gamma dz \frac{e^z}{z^s} = \frac{1}{\Gamma(s)}, \tag{9.30}$$

and therefore

$$\Omega(E) = \frac{[B\Gamma(1+\nu)]^N}{\Gamma(N(1+\nu))} E^{N(1+\nu)-1}. \tag{9.31}$$

For an ideal gas, recall from Eq. (8.25) that we have for a single molecule

$$\omega(E) = 4\pi m V\sqrt{2mE}, \tag{9.32}$$

so $B = 4\pi m V\sqrt{2m}$ and $\nu = 1/2$. Then the partition function for one molecule is from Eq. (9.26)

$$\chi(\alpha) = \frac{2\pi(2m)^{3/2}V\Gamma(3/2)}{\alpha^{3/2}} = V\left(\frac{2m\pi}{\alpha}\right)^{3/2}, \tag{9.33}$$

and the partition function for the systems of N molecules is

$$\chi^N = V^N\left(\frac{2\pi m}{\alpha}\right)^{3N/2}, \tag{9.34}$$

which is the partition function $Z(\alpha)$ we found before in Eq. (5.44), and the structure function is

$$\Omega(E) = \frac{V^N(2\pi m)^{3N/2}E^{3N/2-1}}{\Gamma(3N/2)}, \tag{9.35}$$

which is the result found before in Eq. (8.25).

9.3 Asymptotic approximation

Such an expression must be approximated to be useful. It would be desirable to obtain such an approximation directly. What we are talking about is an *asymptotic approximation*. Let us illustrate this by deriving the Stirling approximation from Hankel's representation for the gamma function (9.30). Let us write the latter as

$$\frac{1}{\Gamma(n)} = \frac{1}{2\pi i}\int_\gamma dz\, e^{f(z)}, \quad f(z) = z - n\ln z, \quad n > 0. \tag{9.36}$$

Let us expand f in a Taylor series about some point x_0:

$$f(z) = f(x_0) + (z-x_0)f'(x_0) + \frac{1}{2}(z-x_0)^2 f''(x_0) + \dots, \tag{9.37}$$

where

$$f(x_0) = x_0 - n\ln x_0, \tag{9.38}$$
$$f'(x_0) = 1 - \frac{n}{x_0}, \tag{9.39}$$
$$f''(x_0) = \frac{n}{x_0^2}, \tag{9.40}$$

etc. We will choose the contour γ so that it passes through a saddle point, where $f'(x_0) = 0$, which here implies $x_0 = n$. In this case, $f''(x_0) = 1/n > 0$, so if $z - x_0$ is real (so $(z - x_0)^2 > 0$), f has a minimum at x_0, while if $z - x_0$ is imaginary (so $(z - x_0)^2 < 0$), f has a maximum at x_0. To be precise, we choose γ to be the path of steepest descents, which climbs up to the maximum at x_0 along the steepest ascending path, and the descends along the steepest descending path. But we need, in the first (leading) approximation, keep only the first two (nonzero) terms in the Taylor series,

$$f(z) \approx f(x_0) + \frac{1}{2}(z - x_0)^2 f''(x_0), \tag{9.41}$$

and in the immediate neighborhood of the saddle point the steepest descents path lies parallel to the imaginary axis:

$$f(x_0 + iy) \approx (n - n\ln n) - \frac{y^2}{2n}, \tag{9.42}$$

and then the Hankel representation becomes ($n \to \infty$)

$$\frac{1}{\Gamma(n)} \sim \frac{1}{2\pi i} e^{n - n\ln n} \int_{-i\infty}^{i\infty} i\,dy\, e^{-y^2/2n} = \frac{1}{\sqrt{2\pi}} \frac{e^n}{n^{n-1/2}}, \tag{9.43}$$

or

$$\ln\Gamma(n) \sim \left(n - \frac{1}{2}\right)\ln n - n + \frac{1}{2}\ln 2\pi + O\left(\frac{1}{n}\right). \tag{9.44}$$

This is the Stirling approximation, accurate for large n. In fact, the error is less than 4% even for $n = 3$.

If one were to keep the next term in the expansion for f,

$$\frac{1}{3!}(z - x_0)^3 f'''(x_0) = \frac{i}{3}\frac{y^3}{n^2}, \tag{9.45}$$

since the Gaussian term forces y to be no larger than order $\sqrt{n}$, the next term is of order $1/\sqrt{n}$. In fact, as the homework shows, this term cancels out, and the correction is of order $1/n$.

9.4 Derivation of the Hankel Representation of the Gamma Function

Start from the Euler representation of the gamma function for $\mathrm{Re}\, z > 0$,

$$\Gamma(z) = \int_0^\infty dt\, e^{-t} t^{z-1}. \tag{9.46}$$

Consider the integral for z not an integer, but $\mathrm{Re}\, z > 0$:

$$I(z) = \int_C dt\, e^{-t}(-t)^{z-1}, \tag{9.47}$$

where

$$(-t)^{z-1} = e^{(z-1)\ln(-t)}, \tag{9.48}$$

and where C is a contour that encircles (in a clockwise sense) the branch line of $\ln(-t)$ along the positive t axis. So if $t > 0$, just above or just below the positive real t axis

$$-t = te^{\mp i\pi}. \tag{9.49}$$

Therefore,

$$I(z) = \left(e^{-i\pi(z-1)} - e^{i\pi(z-1)}\right)\Gamma(z) = 2i\sin\pi z\Gamma(z). \tag{9.50}$$

But now we recall the reflection formula

$$\Gamma(z)\Gamma(1-z) = \frac{\pi}{\sin\pi z}, \tag{9.51}$$

so

$$\begin{aligned}\frac{1}{\Gamma(z)} &= \frac{1}{2\pi i}I(1-z) = \frac{1}{2\pi i}\int_C dte^{-t}(-t)^{-z}\\ &= -\frac{1}{2\pi i}\int_{-C} dt\,\frac{e^t}{t^z} = \frac{1}{2\pi i}\int_\gamma dt\frac{e^t}{t^z},\end{aligned} \tag{9.52}$$

where is the Hankel representation (9.30). Here in the last line we substituted $t \to -t$ and consequently $C \to -C$, where $-C$ is the same as γ as defined for the Hankel representation (see Fig. 9.2), except traversed in the opposite sense.

9.5 Asymptotic Analysis

We now return to the discussion in Sec. 9.1. We want to evaluate

$$\Omega(E) = \frac{1}{2\pi i}\int_C d\alpha\, e^{\alpha E}\chi(\alpha) \tag{9.53}$$

by the saddle-point method. Thus we rewrite it as

$$\Omega(E) = \frac{1}{2\pi i}\int_C d\alpha\, e^{f(\alpha)}, \quad f(\alpha) = \alpha E + \ln\chi(\alpha). \tag{9.54}$$

When the system consists of N identical subsystems, $N \gg 1$, both E and $\ln\chi$ are of order N. Now

$$\chi(0) = \int dp\, dq = \infty, \tag{9.55}$$

while to determine what happens as $\alpha \to \infty$, we use the following inequality: for arbitrary $\epsilon > 0$

$$\begin{aligned}\chi(\alpha) &\geq \int_0^\epsilon dE\, e^{-\alpha E}\Omega(E) \geq e^{-\alpha\epsilon}\int_0^\epsilon dE\,\Omega(E) \\ &= e^{-\alpha\epsilon}\int_0^\epsilon dE\,\frac{dV}{dE} = e^{-\alpha\epsilon}V(\epsilon),\end{aligned} \tag{9.56}$$

where the first inequality follows because $\Omega \geq 0$, and the last because the volume of phase space having energy less than or equal to zero, $V(0)$, is zero. Therefore,

$$\ln\chi(\alpha) \geq -\alpha\epsilon + \ln V(\epsilon), \tag{9.57}$$

and so for $\epsilon < E$,

$$f(\alpha) \geq \alpha(E-\epsilon) + \ln V(\epsilon) \to \infty, \quad \text{as } \alpha \to \infty. \tag{9.58}$$

Therefore, there is at least one minimum of $f(\alpha)$ for real α between $\alpha = 0$ and $\alpha = \infty$. It occurs where

$$0 = f'(\alpha) = E + \frac{d}{d\alpha}\ln\chi(\alpha) = E + \frac{\chi'(\alpha)}{\chi(\alpha)}. \tag{9.59}$$

Can this have more than one root? No, because $\frac{d}{d\alpha}\ln\chi(\alpha)$ increases monotonically with α for positive α. We have already essentially seen the proof of this in Sec. 6.2. Let us define an energy probability function

$$p(E) = \frac{1}{\chi(\alpha)}e^{-\alpha E}\Omega(E). \tag{9.60}$$

This is positive, and properly normalized,

$$\int_0^\infty dE\, p(E) = 1, \tag{9.61}$$

according to the definition (9.15) of the partition function. Now, with the mean defined in terms of this probability function,

$$\begin{aligned}\frac{\chi'(\alpha)}{\chi(\alpha)} &= -\frac{1}{\chi(\alpha)}\int_0^\infty dE\, E\, e^{-\alpha E}\Omega(E) = -\int_0^\infty dE\, E\, p(E) = -\langle E\rangle, \\ \frac{\chi''(\alpha)}{\chi(\alpha)} &= \frac{1}{\chi(\alpha)}\int_0^\infty dE\, E^2\, e^{-\alpha E}\Omega(E) = \int_0^\infty dE\, E^2\, p(E) = \langle E^2\rangle,\end{aligned} \tag{9.62}$$

so

$$\begin{aligned}\frac{d^2}{d\alpha^2}\ln\chi(\alpha) &= \frac{d}{d\alpha}\frac{\chi'(\alpha)}{\chi(\alpha)} = \frac{\chi''(\alpha)}{\chi(\alpha)} - \left(\frac{\chi'(\alpha)}{\chi(\alpha)}\right)^2 \\ &= \langle E^2\rangle - \langle E\rangle^2 = \langle (E-\langle E\rangle)^2\rangle \geq 0,\end{aligned} \tag{9.63}$$

which was already stated in Eq. (6.51).

Therefore $f(\alpha)$ has a single minimum for positive α, say at the point β, defined by

$$\frac{d}{d\beta}\ln\chi(\beta) = \frac{\chi'(\beta)}{\chi(\beta)} = -E, \tag{9.64}$$

which has the same form as Eq. (6.20):

$$U = -\frac{d}{d\beta}\ln Z(\beta). \tag{9.65}$$

We now expand $f(\alpha)$ about the saddle point,

$$f(\alpha) \approx f(\beta) + (\alpha-\beta)^2\frac{1}{2}f''(\beta) = f(\beta) + \frac{1}{2}(\alpha-\beta)^2(\ln\chi(\beta))'', \tag{9.66}$$

and so asymptotically, for large N, Eq. (9.53) becomes

$$\Omega(E) \sim \frac{1}{2\pi i}e^{\beta E}\chi(\beta)\int_C d\alpha\, e^{(\alpha-\beta)^2\frac{1}{2}(\ln\chi)''(\beta)}. \tag{9.67}$$

Because, as we have just proved, $(\ln\chi)''(\beta) > 0$, the path of steepest descents passes through the saddle point β in the imaginary directions, $\alpha = \beta + iy$, $d\alpha = i\,dy$. Thus, as with the gamma function in Sec. 9.3, we encounter a Gaussian integral

$$\begin{aligned}\Omega(E) &\sim e^{\beta E}\chi(\beta)\frac{1}{2\pi}\int_{-\infty}^{\infty} dy\, e^{-y^2\frac{1}{2}(\ln\chi)''(\beta)} \\ &= e^{\beta E}\chi(\beta)\left[2\pi(\ln\chi)''(\beta)\right]^{-1/2}.\end{aligned} \tag{9.68}$$

Now suppose the system is composed of N, $N \gg 1$, subsystems. Recall, from Eq. (9.9), that the distribution function for one subsystem is

$$\rho_1 = \frac{\Omega^{(N-1)}(E-H_1)}{\Omega^{(N)}(E)}. \tag{9.69}$$

If we use the above asymptotic analysis, the saddle points for numerator and denominator are different. But in fact, for $N \gg 1$, the two saddle points are nearly the same, as we shall now see.

9.5.1 Example of an ideal gas

A perfect gas of N free particles has a partition function, according to Eq. (9.34),

$$\chi(\alpha) \propto \alpha^{-3N/2}, \tag{9.70}$$

so

$$\frac{d}{d\alpha}\ln\chi(\alpha) = -\frac{3N}{2}\frac{1}{\alpha}, \tag{9.71}$$

so the saddle point condition (9.64) is

$$\frac{d}{d\beta}\ln\chi(\beta) = -\frac{3N}{2\beta} = -E, \tag{9.72}$$

which gives β as

$$\beta = \frac{3N}{2E} = \frac{1}{kT}, \tag{9.73}$$

according to the equipartition theorem (3.11). Thus, from Eq. (9.68),

$$\Omega(E) = \frac{e^{3N/2}[\chi_{\rm mol}(\beta)]^N}{\sqrt{2\pi(2E^2/3N)}}, \tag{9.74}$$

where

$$\chi_{\rm mol} = V\left(\frac{2\pi m}{\beta}\right)^{3/2} = V\left(\frac{4\pi mE}{3N}\right)^{3/2}, \tag{9.75}$$

because

$$\frac{d^2}{d\beta^2}\ln\chi(\beta) = \frac{3N}{2\beta^2} = \frac{2E^2}{3N}. \tag{9.76}$$

It is easy to check that Eq. (9.74) agrees with Eq. (9.35), if the gamma function there is replaced by the asymptotic expansion (9.43).

9.5.2 Difference in saddle points

In general if the system is composed of N identical subsystems,

$$\chi(\alpha) = [\xi(\alpha)]^N, \tag{9.77}$$

the equation that defines β is

$$\frac{d}{d\beta}\ln\chi(\beta) = N\frac{\xi'(\beta)}{\xi(\beta)} = -E, \tag{9.78}$$

while for $\Omega^{(N-1)}(E-H_1)$, the saddle point β' is defined by

$$(N-1)\frac{\xi'(\beta')}{\xi(\beta')} = -(E-H_1). \tag{9.79}$$

Therefore,

$$\begin{aligned}\frac{\xi'(\beta')}{\xi(\beta')} &= -\frac{E-H_1}{N-1} = -\frac{E(1-H_1/E)}{N(1-1/N)}\\ &\approx -\frac{E}{N}\left(1+\frac{1}{N}-\frac{H_1}{E}\right)\\ &\approx \frac{\xi'(\beta)}{\xi(\beta)} + (\beta'-\beta)\frac{d^2}{d\beta^2}\ln\xi(\beta)\\ &= -\frac{E}{N} + (\beta'-\beta)\frac{d^2}{d\beta^2}\ln\xi(\beta),\end{aligned} \tag{9.80}$$

so the change in the saddle point is

$$\beta' - \beta = -\frac{\frac{E}{N}\left(\frac{1}{N} - \frac{H_1}{E}\right)}{(\ln\xi)''(\beta)} = \frac{(\ln\xi)'(\beta)}{(\ln\xi)''(\beta)}\left(\frac{1}{N} - \frac{H_1}{E}\right). \tag{9.81}$$

The prefactor is of order β. (For example, for an ideal gas, $(\ln\xi)'(\beta) = -3/2\beta$, while $(\ln\xi)''(\beta) = 3/2\beta^2$, so the ratio is $-\beta$, and $\beta'/\beta - 1 = -1/N + H_1/E$.)

9.5.3 Canonical distribution

Since H_1/E is of order $1/N$, the two saddle points approach each other as $N \to \infty$. So we may take the two saddle points to be the same. Thus, from Eqs. (9.69) and (9.68), the distribution function for one subsystem is (this becomes exact as $N \to \infty$)

$$\begin{aligned}\rho_1 &\sim \frac{e^{\beta(E-H_1)}\prod_{j=2}^N \chi_j(\beta)}{\sqrt{2\pi\sum_{j=2}^N(\ln\chi_j)''(\beta)}} \frac{\sqrt{2\pi\sum_{j=1}^N(\ln\chi_j)''(\beta)}}{e^{\beta E}\prod_{j=1}^N \chi_j(\beta)} \\ &\sim \frac{e^{-\beta H_1}}{\chi_1(\beta)},\end{aligned} \tag{9.82}$$

because the square root factor is of order

$$\sqrt{\frac{N}{N-1}} \approx 1 + \frac{1}{2N} \to 1, \quad N \to \infty. \tag{9.83}$$

Thus we have "rederived" the canonical distribution.

9.5.4 Non PSD

If we had chosen a path C passing not through the stationary point β, but crossing the real α axis at a different point $\bar\beta$ along a path perpendicular to the real axis,

$$\Omega(E) \sim \frac{1}{2\pi i} e^{\bar\beta E}\chi(\bar\beta)\int_{-\infty}^{\infty} i\,dy\, e^{iy[(\ln\chi)'(\bar\beta)+E]-y^2\frac{1}{2}(\ln\chi)''(\bar\beta)]}. \tag{9.84}$$

We complete the square in the exponent,

$$\begin{aligned}&\left[(E + (\ln\chi)'(\bar\beta))/\sqrt{2(\ln\chi)''(\bar\beta)} + \frac{iy}{\sqrt{2}}\sqrt{(\ln\chi)''(\bar\beta)}\right]^2 \\ &\quad - \left[E + (\ln\chi)'(\bar\beta)\right]^2/2(\ln\chi)''(\bar\beta),\end{aligned} \tag{9.85}$$

and then carry out the Gaussian integral (it is permissible to shift the integration variable by an imaginary constant, because that amounts to a distortion of the path of integration in the complex plane, which crosses no singularities), with the result

$$\Omega(E) \sim \frac{1}{2\pi} e^{\bar\beta E} \chi(\bar\beta) \sqrt{\frac{2\pi}{(\ln\chi)''(\bar\beta)}} e^{-[E+(\ln\chi)'(\bar\beta)]^2/2(\ln\chi)''(\bar\beta)}. \tag{9.86}$$

In homework, you will show that this approximation is valid providing

$$\bar\beta - \beta = \delta\beta, \quad \left|\frac{\delta\beta}{\beta}\right| \ll N^{-1/3}, \tag{9.87}$$

for a system with $N \gg 1$ noninteracting components. Then, if in Eq. (9.9) we choose $\bar\beta$ to be the saddle point β for the denominator $\Omega^{(N)}(E)$,

$$\rho_1 \sim \frac{e^{-\beta H_1}}{\chi_1(\beta)} \exp\left[-\left(E - H_1 + \sum_{j=2}^N (\ln\chi_j)'(\beta)\right)^2 \Bigg/ 2\sum_{j=2}^N (\ln\chi_j)''(\beta)\right]. \tag{9.88}$$

But the saddle point condition for the denominator is

$$\sum_{j=1}^N (\ln\chi_j)'(\beta) + E = 0, \tag{9.89}$$

so the last exponent here is

$$-[H_1 + (\ln\chi_1)'(\beta)]^2/2\sum_{j=2}^N (\ln\chi_j)''(\beta). \tag{9.90}$$

For example, for an ideal gas,

$$(\ln\chi_1)'(\beta) = (\ln\xi)'(\beta) = -\frac{E}{N}, \quad \sum_{j=2}^N (\ln\chi_j)''(\beta) \approx N(\ln\xi)''(\beta) = \frac{2E^2}{3N}, \tag{9.91}$$

so the correction factor in Eq. (9.88) is

$$e^{-\frac{3}{4}N(H_1 - E/N)^2/E^2}. \tag{9.92}$$

This means that the correction factor is negligible provided

$$\left|H_1 - \frac{E}{N}\right| \ll \frac{2E}{\sqrt{3N}} = \frac{2}{\sqrt{3}}\sqrt{N}\frac{E}{N}, \tag{9.93}$$

which is, not surprisingly, exactly the condition we found earlier for the validity of the Maxwell distribution, Eq. (5.21). We can use this bound to refine our estimate (9.81) of the difference of saddle points for the numerator and denominator of Eq. (9.9):

$$\left|\frac{\beta' - \beta}{\beta}\right| \sim \left|\frac{1}{N} - \frac{H_1}{E}\right| = \frac{1}{E}\left|\frac{E}{N} - H_1\right| \ll \frac{2}{\sqrt{3}}\frac{1}{\sqrt{N}}, \tag{9.94}$$

which is a stronger condition than the estimate (9.87).