4.1: Microcanonical Ensemble (μCE)

The microcanonical distribution function

We have seen how in an *ergodic* dynamical system, time averages can be replaced by phase space averages:

$$ergodicity \quad \Longleftrightarrow \quad \big\langle f(\varphi)\big\rangle_t = \big\langle f(\varphi)\big\rangle_S \ , \tag{4.1.1}$$

where

$$\big\langle f(\varphi)\big\rangle_t = \lim_{T\to\infty} \frac{1}{T}\int\limits_0^T\! dt\, f\big(\varphi(t)\big) \ . \tag{4.1.2}$$

and

$$\big\langle f(\varphi)\big\rangle_S = \int\! d\mu\, f(\varphi)\, \delta\big(E-\hat{H}(\varphi)\big) \Big/ \int\! d\mu\, \delta\big(E-\hat{H}(\varphi)\big) \ . \tag{4.1.3}$$

Here $\hat{H}(\varphi)=\hat{H}(\mathbf{q},\mathbf{p})$ is the Hamiltonian, and where $\delta(x)$ is the Dirac δ-function[1]. Thus, averages are taken over a constant energy hypersurface which is a subset of the entire phase space.

We've also seen how any phase space distribution $\varrho(\Lambda_1,\ldots,\Lambda_k)$ which is a function of conserved quantitied $\Lambda_a(\varphi)$ is automatically a stationary (time-independent) solution to Liouville's equation. Note that the microcanonical distribution,

$$\varrho_E(\varphi) = \delta\big(E-\hat{H}(\varphi)\big) \Big/ \int\! d\mu\, \delta\big(E-\hat{H}(\varphi)\big) \ , \tag{4.1.4}$$

is of this form, since $\hat{H}(\varphi)$ is conserved by the dynamics. Linear and angular momentum conservation generally are broken by elastic scattering off the walls of the sample.

So averages in the microcanonical ensemble are computed by evaluating the ratio

$$\big\langle A\big\rangle = \frac{\mathsf{Tr}\ A\,\delta(E-\hat{H})}{\mathsf{Tr}\ \delta(E-\hat{H})} \ , \tag{4.1.5}$$

where Tr means 'trace', which entails an integration over all phase space:

$$\mathsf{Tr}\ A(q,p) \equiv \frac{1}{N!}\prod_{i=1}^N \int\! \frac{d^dp_i\, d^dq_i}{(2\pi\hbar)^d}\, A(q,p) \ . \tag{4.1.6}$$

Here N is the total number of particles and d is the dimension of physical space in which each particle moves. The factor of $1/N!$, which cancels in the ratio between numerator and denominator, is present for *indistinguishable particles*[2]. The normalization factor $(2\pi\hbar)^{-Nd}$ renders the trace dimensionless. Again, this cancels between numerator and denominator. These factors may then seem arbitrary in the definition of the trace, but we'll see how they in fact are required from quantum mechanical considerations. So we now adopt the following metric for classical phase space integration:

$$d\mu = \frac{1}{N!}\prod_{i=1}^N \frac{d^dp_i\, d^dq_i}{(2\pi\hbar)^d} \ . \tag{4.1.7}$$

Density of States

The denominator,

$$D(E) = \mathsf{Tr}\ \delta(E-\hat{H}) \ , \tag{4.1.8}$$

is called the *density of states*. It has dimensions of inverse energy, such that

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$$D(E)\,\Delta E \;=\int\limits_{E}^{E+\Delta E}\!\!dE'\!\int\!d\mu\,\delta(E'-\hat{H})=\!\!\int\limits_{E<\hat{H}<E+\Delta E}\!\!\!d\mu \qquad (4.1.9)$$
$$= \backslash\#\text{ of states with energies between } E \text{ and } E+\Delta E\,.$$

Let us now compute $D(E)$ for the nonrelativistic ideal gas. The Hamiltonian is

$$\hat{H}(q,p)=\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m}\,. \qquad (4.1.10)$$

We assume that the gas is enclosed in a region of volume V, and we'll do a purely classical calculation, neglecting discreteness of its quantum spectrum. We must compute

$$D(E)=\frac{1}{N!}\int\prod_{i=1}^{N}\frac{d^dp_i\,d^dq_i}{(2\pi\hbar)^d}\;\delta\bigg(E-\sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m}\bigg)\,. \qquad (4.1.11)$$

We shall calculate $D(E)$ in two ways. The first method utilizes the *Laplace transform*, $Z(\beta)$:

$$Z(\beta)=\mathcal{L}\big[D(E)\big]\equiv\int\limits_{0}^{\infty}\!dE\,e^{-\beta E}\,D(E)=\mathsf{Tr}\;e^{-\beta\hat{H}}\,. \qquad (4.1.12)$$

The inverse Laplace transform is then

$$D(E)=\mathcal{L}^{-1}\big[Z(\beta)\big]\equiv\int\limits_{c-i\infty}^{c+i\infty}\!\frac{d\beta}{2\pi i}\,e^{\beta E}\,Z(\beta)\,, \qquad (4.1.13)$$

where c is such that the integration contour is to the right of any singularities of $Z(\beta)$ in the complex β-plane. We then have

$$\begin{aligned}
Z(\beta)&=\frac{1}{N!}\prod_{i=1}^{N}\int\frac{d^dx_i\,d^dp_i}{(2\pi\hbar)^d}\;e^{-\beta\mathbf{p}_i^2/2m}\\
&=\frac{V^N}{N!}\Bigg(\int\limits_{-\infty}^{\infty}\!\frac{dp}{2\pi\hbar}\;e^{-\beta p^2/2m}\Bigg)^{Nd}\\
&=\frac{V^N}{N!}\bigg(\frac{m}{2\pi\hbar^2}\bigg)^{Nd/2}\,\beta^{-Nd/2}\,.
\end{aligned}$$

The inverse Laplace transform is then

$$\begin{aligned}
D(E)&=\frac{V^N}{N!}\bigg(\frac{m}{2\pi\hbar^2}\bigg)^{Nd/2}\oint\limits_{\mathcal{C}}\frac{d\beta}{2\pi i}\;e^{\beta E}\;\beta^{-Nd/2}\\
&=\frac{V^N}{N!}\bigg(\frac{m}{2\pi\hbar^2}\bigg)^{Nd/2}\,\frac{E^{\frac{1}{2}Nd-1}}{\Gamma(Nd/2)}\,,
\end{aligned}$$

exactly as before. The integration contour for the inverse Laplace transform is extended in an infinite semicircle in the left half β-plane. When Nd is even, the function $\beta^{-Nd/2}$ has a simple pole of order $Nd/2$ at the origin. When Nd is odd, there is a branch cut extending along the negative $Re\,\beta$ axis, and the integration contour must avoid the cut, as shown in Figure 4.1.1. One can check that this results in the same expression above, we may analytically continue from even values of Nd to all positive values of Nd.

For a general system, the Laplace transform, $Z(\beta)=\mathcal{L}\big[D(E)\big]$ also is called the *partition function*. We shall again meet up with $Z(\beta)$ when we discuss the ordinary canonical ensemble.

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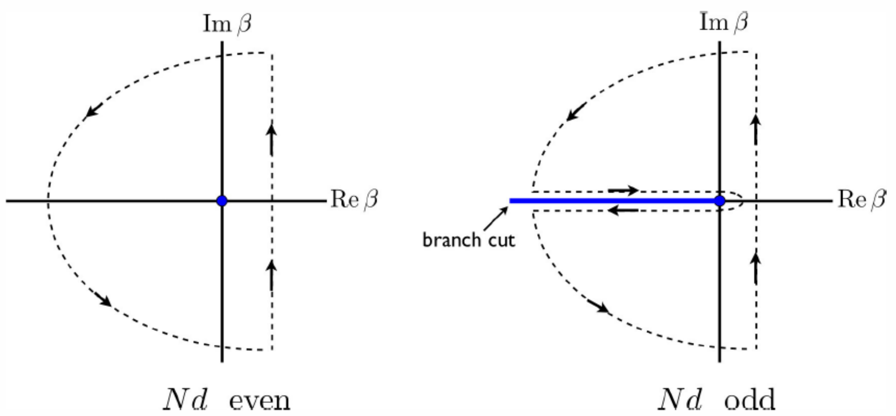

Figure 4.1.1: Complex integration contours $\mathcal{C}$ for inverse Laplace transform $\mathcal{L}^{-1}\big[Z(\beta)\big]=D(E)$. When the product dN is odd, there is a branch cut along the negative $Re\,\beta$ axis.

Our final result, then, is

$$D(E,V,N)=\frac{V^N}{N!}\left(\frac{m}{2\pi\hbar^2}\right)^{Nd/2}\frac{E^{\frac{1}{2}Nd-1}}{\Gamma(Nd/2)}\,. \tag{4.1.14}$$

Here we have emphasized that the density of states is a function of E, V, and N. Using Stirling's approximation,

$$\ln N!=N\ln N-N+\frac{1}{2}\ln N+\frac{1}{2}\ln(2\pi)+\mathcal{O}\big(N^{-1}\big)\,, \tag{4.1.15}$$

we may define the *statistical entropy*,

$$S(E,V,N)\equiv k_B\ln D(E,V,N)=Nk_B\,\phi\left(\frac{E}{N},\frac{V}{N}\right)+\mathcal{O}(\ln N)\,, \tag{4.1.16}$$

where

$$\phi\left(\frac{E}{N},\frac{V}{N}\right)=\frac{d}{2}\,\ln\left(\frac{E}{N}\right)+\ln\left(\frac{V}{N}\right)+\frac{d}{2}\,\ln\left(\frac{m}{d\pi\hbar^2}\right)+\big(1+\frac{1}{2}d\big)\,. \tag{4.1.17}$$

Recall $k_B=1.3806503\times10^{-16}\,erg/K$ is Boltzmann's constant.

Second method

The second method invokes a mathematical trick. First, let's rescale $p_i^\alpha\equiv\sqrt{2mE}\,u_i^\alpha$. We then have

$$D(E)=\frac{V^N}{N!}\left(\frac{\sqrt{2mE}}{h}\right)^{Nd}\frac{1}{E}\int\!d^Mu\;\delta\big(u_1^2+u_2^2+\ldots+u_M^2-1\big)\,. \tag{4.1.18}$$

Here we have written $\mathbf{u}=(u_1,u_2,\ldots,u_M)$ with $M=Nd$ as a M-dimensional vector. We've also used the rule $\delta(Ex)=E^{-1}\delta(x)$ for δ-functions. We can now write

$$d^Mu=u^{M-1}\,du\,d\Omega_M\,, \tag{4.1.19}$$

where $d\Omega_M$ is the M-dimensional differential solid angle. We now have our answer:[3]

$$D(E)=\frac{V^N}{N!}\left(\frac{\sqrt{2m}}{h}\right)^{Nd}E^{\frac{1}{2}Nd-1}\cdot\frac{1}{2}\,\Omega_{Nd}\,. \tag{4.1.20}$$

What remains is for us to compute Ω_M, the total solid angle in M dimensions. We do this by a nifty mathematical trick. Consider the integral

$$\begin{aligned}\mathcal{I}_M &= \int d^M u\, e^{-u^2} = \Omega_M \int\limits_0^\infty du\, u^{M-1}\, e^{-\mathbf{u}^2} \\ &= \frac{1}{2}\Omega_M \int\limits_0^\infty ds\, s^{\frac{1}{2}M-1}\, e^{-s} = \frac{1}{2}\Omega_M\, \Gamma\big(\frac{1}{2}M\big)\ ,\end{aligned}$$

where $s = u^2$, and where

$$\Gamma(z) = \int\limits_0^\infty dt\, t^{z-1}\, e^{-t} \tag{4.1.21}$$

is the Gamma function, which satisfies $z\,\Gamma(z) = \Gamma(z+1)$. [4] On the other hand, we can compute $\mathcal{I}_M$ in Cartesian coordinates, writing

$$\mathcal{I}_M = \left(\int\limits_{-\infty}^\infty du_1\, e^{-u_1^2}\right)^M = \big(\sqrt{\pi}\big)^M\ . \tag{4.1.22}$$

Therefore

$$\Omega_M = \frac{2\pi^{M/2}}{\Gamma(M/2)}\ . \tag{4.1.23}$$

We thereby obtain $\Omega_2 = 2\pi$, $\Omega_3 = 4\pi$, $\Omega_4 = 2\pi^2$, , the first two of which are familiar.

Arbitrariness in the definition of $S(E)$

Note that $D(E)$ has dimensions of inverse energy, so one might ask how we are to take the logarithm of a dimensionful quantity in Equation 4.1.16. We must introduce an energy scale, such as ΔE in Equation 4.1.9, and define $\tilde{D}(E;\Delta E) = D(E)\,\Delta E$ and $S(E;\Delta E) \equiv k_B \ln \tilde{D}(E;\Delta E)$. The definition of statistical entropy then involves the arbitrary parameter ΔE, however this only affects $S(E)$ in an additive way. That is,

$$S(E,V,N;\Delta E_1) = S(E,V,N;\Delta E_2) + k_B \ln\left(\frac{\Delta E_1}{\Delta E_2}\right)\ . \tag{4.1.24}$$

Note that the difference between the two definitions of S depends only on the ratio $\Delta E_1/\Delta E_2$, and is independent of E, V, and N.

Ultra-relativistic ideal gas

Consider an ultrarelativistic ideal gas, with single particle dispersion $\varepsilon(p) = cp$. We then have

$$\begin{aligned}Z(\beta) &= \frac{V^N}{N!}\,\frac{\Omega_d^N}{h^N d}\left(\int\limits_0^\infty dp\, p^{d-1}\, e^{-\beta cp}\right)^N \\ &= \frac{V^N}{N!}\left(\frac{\Gamma(d)\,\Omega_d}{c^d\, h^d\, \beta^d}\right)^N\ .\end{aligned}$$

The statistical entropy is $S(E,V,N) = k_B \ln D(E,V,N) = N k_B\, \phi\big(\frac{E}{N}, \frac{V}{N}\big)$, with

$$\phi\left(\frac{E}{N}, \frac{V}{N}\right) = d\, \ln\left(\frac{E}{N}\right) + \ln\left(\frac{V}{N}\right) + \ln\left(\frac{\Omega_d\,\Gamma(d)}{(dhc)^d}\right) + (d+1) \tag{4.1.25}$$

Discrete systems

For classical systems where the energy levels are discrete, the states of the system $|\,\sigma\,\rangle$ are labeled by a set of discrete quantities $\{\sigma_1, \sigma_2, \ldots\}$, where each variable σ_i takes discrete values. The number of ways of configuring the system at fixed energy E is then

$$\Omega(E,N)=\sum_{\sigma}\delta_{\hat{H}(\sigma),E}\ , \tag{4.1.26}$$

where the sum is over all possible configurations. Here N labels the total number of particles. For example, if we have N spin-$\frac{1}{2}$ particles on a lattice which are placed in a magnetic field H, so the individual particle energy is $\varepsilon_i=-\mu_0 H\sigma$, where $\sigma=\pm 1$, then in a configuration in which $N_\uparrow$ particles have $\sigma_i=+1$ and $N_\downarrow=N-N_\uparrow$ particles have $\sigma_i=-1$, the energy is $E=(N_\downarrow-N_\uparrow)\mu_0 H$. The number of configurations at fixed energy E is

$$\Omega(E,N)=\binom{N}{N_\uparrow}=\frac{N!}{\big(\frac{N}{2}-\frac{E}{2\mu_0 H}\big)!\,\big(\frac{N}{2}+\frac{E}{2\mu_0 H}\big)!}\ , \tag{4.1.27}$$

since $N_{\uparrow/\downarrow}=\frac{N}{2}\mp\frac{E}{2\mu_0 H}$. The statistical entropy is $S(E,N)=k_B\ln\Omega(E,N)$.

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