Lecture 25: The Canonical State
Monday, March 23, 2020

0.1 The Canonical State

Is the canonical distribution stable under the time-evolution of Hamiltonian dynamics? We can answer yes because of Liouville's Theorem.

$$\begin{aligned}
\frac{\partial}{\partial t}P(p,q,t) &= -\sum_{j=1}^{3N}\left(\frac{\partial P}{\partial q_j}\underbrace{\dot{q}_j}_{\frac{\partial H}{\partial p_j}} + \frac{\partial P}{\partial p_j}\underbrace{\dot{p}_j}_{-\frac{\partial H}{\partial q_j}}\right) \\
&= -\sum_{j=1}^{3N}\left(\frac{\partial P}{\partial q_j}\frac{\partial H}{\partial p_j} - \frac{\partial P}{\partial p_j}\frac{\partial H}{\partial q_j}\right) \\
&= -\{P, H\}
\end{aligned}$$

This is a nontrivial statement which follows from Liouville's theorem. We will not prove it. An important property of the Poisson bracket in the last line is that

$$\{A, f(A)\} = 0$$

and the canonical state is just a function of H, so

$$\frac{\partial P_{\text{can}}}{\partial t} = -\{P_{\text{can}}, H\} \propto -\left\{e^{-\beta H}, H\right\} = 0$$

Therefore, the canonical state does not change under Hamiltonian dynamics.

0.1.1 Energy Fluctuations

Recall $P(E) = \frac{1}{Z}\Omega(E)e^{-\beta E}$ which increases strongly with E. Typically $\Omega(E) \sim E^f$ with $f \sim N$. Where does $P(E)$ have its maximum?

$$0 = \frac{\partial}{\partial E}\ln P(E) = \frac{\partial}{\partial E}\left[-\ln Z + \ln\Omega(E) - \beta E\right] = \frac{f}{E} - \beta$$

so

$$E_{\max} = \frac{f}{\beta} = f k_B T$$

Recall for the ideal gas, $f = \frac{3}{2}N$.

Next, how wide is the peak?

$$-\frac{1}{\sigma_E^2} = \left.\frac{\partial^2 \ln P}{\partial E^2}\right|_{E\to E_{\max}} = -\frac{f}{E_{max}^2} = -\frac{1}{f(k_B T)^2}$$

so

$$\sigma_E = \sqrt{f}k_B T$$

so the coefficient of variation is

$$\frac{\sigma_E}{E_{\max}} = \frac{\sqrt{f}k_B T}{f k_B T} = \frac{1}{\sqrt{f}} \sim \frac{1}{\sqrt{N}}$$

so again, the energy fluctuations scale such that at large N, they are small compared to the overall energy of the state.

Finally, let's link this to the Helmholtz free energy.

$$\begin{aligned}\ln P(E) &= -\beta E + \ln\Omega(E) - \ln Z \\ \ln Z &= -\beta E + \ln\Omega(E) - \ln P(E) \\ &= -\beta(\underbrace{E - TS}_{\text{Scales with } N}) - \overbrace{\ln \underbrace{P(E)}_{\text{width } \sim\sqrt{E},\text{ height } \sim\frac{1}{\sqrt{E}}}}^{\text{scales with } \ln E\sim\ln N}\end{aligned}$$

Therefore, for large N,

$$-k_B T\ln Z(T,V,N) = E - TS$$

The right-hand side would be the Helmholtz free energy if it was expressed in T, V, and N, and these are exactly the variables of $Z(T,V,N)$, so

$$F(T,V,N) = -k_B T\ln Z(T,V,N)$$

This is another super important equation in statistical mechanics. Alternatively we could write

$$e^{-\beta F} = Z = \int \mathrm{d}E\,\Omega(E)e^{-\beta E}$$

We can actually do even better than this, but to do it, we need a small excursion:

Excursion: Saddle Point Evaluation of Integrals

Here's a fun trick to approximate integrals. Suppose we have a function $f(x)$ that has a single maximum, and perhaps around that maximum we can Taylor expand into a parabola at x_m. Now suppose we want to integrate

$$I_N := \int \mathrm{d}x\, e^{Nf(x)}$$

approximately for large N. As long as $f(x)$ has a single peak, we can Taylor expand $f(x)$ around the maximum and replace $f(x)$ in the integral by that Taylor expansion. Naively, the function can diverge from that parabola arbitrarily far away from the point of expansion, but it turns out this doesn't matter:

$$\begin{aligned}I_N &\approx \int \mathrm{d}x\, e^{N\left[\underbrace{f(x_m)}_{\text{constant}}\underbrace{-\frac{1}{2}|f''(x_m)|(x-x_m)^2}_{\text{Gaussian}}+\ldots\right]} \\ &= e^{Nf(x_m)}\sqrt{\frac{2\pi}{N|f''(x_m)|}}\cdot\ldots \\ \ln I_n &= Nf(x_m) + \frac{1}{2}\ln\frac{2\pi}{N|f''(x_m)|} + \cdots\end{aligned}$$

and

$$\lim_{N\to\infty}\left(\frac{1}{N}\ln I_N\right) = f(x_m) = \max_x f(x)$$

We don't actually have to do any integral at all, we just need to find the maximum!

Now back to the main problem,

$$\begin{aligned} e^{-\beta F} = Z &= \int \mathrm{d}E\,\Omega(E)e^{-\beta E} \\ &= \int \mathrm{d}E\,e^{S(E)/k_B}e^{-\beta E} \\ &= \int \mathrm{d}E\,e^{-\beta(E-TS(E))} \\ &= N\int \mathrm{d}e\,e^{N(-\beta(e-Ts(e)))} \end{aligned}$$

What is

$$-\beta f = \lim_{N\to\infty}\left[\frac{1}{N}\ln e^{-\beta F}\right]?$$

where f is the specific free energy F/N.

From our saddle point evaluation, we can see that we just need the to find

$$-\beta f = \max_e\{-\beta(e-Ts(e))\} = -\beta\min_e\{e-Ts(e)\}$$

or

$$f = \min_e\{e-Ts(e)\}$$

The Legendre transform between the thermodynamic potentials $s(e)$ and $f(T)$ arises naturally as the saddle point approximation linking the partition functions $\Omega(E)$ and $Z(T)$! However, this is only valid for infinitely large systems, and this simple connection will not in general be true for finite systems, particularly computer simulations.