Mechanics – Lecture 13 – 4/26/2022

[Most of 4/26 will be spent on the Lecture 12 notes, but we'll continue with these notes if there is time.]

Bottom line concerning the canonical distribution:

- any state can occur (any energy) but probabilities are weighted by $e^{-\beta H}$
- average of any $f(q,p)$ in this distr'n is

$$\mathbb{E}[f] = \frac{1}{Z_\beta}\int f\, e^{-\beta H(q,p)}\, dq\, dp$$

$$= \frac{1}{Z_\beta}\int e^{-\beta E}\underbrace{\left[\int_{H=E} \frac{f}{|\nabla H|}\, d(\text{Area})\right]}_{\substack{\text{we called this}\\ \Omega(E) \text{ in}\\ \text{Lecture 11, viewing}\\ \text{it as "the number}\\ \text{of states with } H=E\text{"}}} dE$$

where Z_β (the partition function) is the normalization needed for $\mathbb{E}[1] = 1$:

$$Z_\beta = \int e^{-\beta H}\, dq\, dp = \int e^{-\beta E}\, \Omega(E)\, dE,$$

The expected energy + variance of energy have simple expressions in terms of Z_β:

$$\partial_\beta Z_\beta = -\int H(q,p)\, e^{-\beta H}\, dq\, dp$$

$$= -Z_\beta\, \mathbb{E}[H]$$

so

$$-\frac{d}{d\beta}(\ln Z_\beta) = \mathbb{E}[H]$$

Similarly

$$\frac{d^2}{d\beta^2}(\ln Z_\beta) = \frac{d}{d\beta}\left(\frac{-\int H e^{-\beta H}}{Z_\beta}\right)$$

$$= \frac{1}{Z_\beta}\int H^2 e^{-\beta H} - \frac{1}{(Z_\beta)^2}(\partial_\beta Z_\beta)^2$$

$$= \mathbb{E}[H^2] - (\mathbb{E}[H])^2$$

$$= \text{variance of } H$$

Let's return to the examples we considered in Lecture 10:

Example 1: a 1D particle in $[0,L]$ (with periodic bc, or reflecting at the boundaries).

$$H = \frac{p^2}{2m}, \quad \text{phase space is } [0,L]\times\mathbb{R}$$

$$\mathbb{E}[f] = \int f(q,p)\, e^{-\beta p^2/2m}\, dq\, dp$$

$$Z_\beta = L \int_{-\infty}^{+\infty} e^{-\beta p^2/2m}\, dp$$

$$= L\sqrt{\frac{2m\pi}{\beta}} \qquad \left(\text{using } \int_{-\infty}^{+\infty} e^{-\alpha y^2} = \sqrt{\frac{\pi}{\alpha}}\right)$$

<u>Example 2</u>: N 3-dimensional particles in $[0,L]^3$ (but let's take them to be <u>distinguishable</u> this time)

Now $\quad H = \sum_{i=1}^{N} \frac{|p_i|^2}{2m}$; each $q_i \in [0,L]^3$, each $p_i \in \mathbb{R}^3$

Going directly to Z_β:

$$Z_\beta = \left(L^3 \int_{\mathbb{R}^3} e^{-\beta|p|^2/2m} \right)^N$$

$$\ln Z_\beta = N \cdot \left[\log Z_\beta^{\text{one particle}}\right]$$

We could easily get a formula for the one particle partition fn (it's like Example 1 but in $\mathbb{R}^3$). But more interesting: we observe that

expected H for N particles = N times expected H for one particle

variance of H for N particles = N times variance for 1 particle

(just like independent random vars!)
so relative size of energy fluctuations

is
$$\frac{\text{st dev}}{\text{mean}} = \text{const}\cdot\frac{\sqrt{N}}{N} \longrightarrow 0 \quad \text{as } N \to \infty.$$

Thus: as $N \to \infty$ (for N indep copies of a single system) the fluctuations of energy become negligible + the canonical distrn resembles the microcanonical one.

You may have heard the term "entropy" used in what appears to be an entirely different context, namely the

<u>entropy of a probability distribution</u>

$= -\int \rho \ln \rho$ for a cont's distrn with density ρ

or

$= -\sum p_j \ln p_j$ for a discrete distrn with $p_j = $ prob of atom j.

What's so special about this functional? Well, in the discrete setting with n states, and writing $\tilde{S}(p_1, \dots, p_n) = -\sum p_i \ln p_i$, it has the properties

(1) for each n, $\tilde{S}$ is a cont's fn of n vars

(2) the entropy assoc the uniform distr

on n pts, $\tilde{S}_n = \tilde{S}_n(1/n, \cdots, 1/n)$ is monotonically increasing in n

(3) If we partition $(1, \cdots, n)$ into M bins

$$k_0 = 1 \quad k_1 \quad k_2 \quad \cdots \quad k_M = n$$

+ set $q_1 = p_1 + \cdots + p_{k_1}$, $q_2 = p_{k_1+1} + \cdots + p_{k_2}$, etc
Then

$$\begin{aligned}\tilde{S}(p_1, \cdots, p_n) = \tilde{S}(q_1, \cdots, q_M) &+ q_1 \tilde{S}\left(\frac{p_1}{q_1}, \cdots, \frac{p_{k_1}}{q_1}\right) \\ &+ q_2 \tilde{S}\left(\frac{p_{k_1+1}}{q_2}, \cdots, \frac{p_{k_2}}{q_2}\right) \\ &+ \cdots\end{aligned}$$

(Moreover: $\tilde{S}$ is the only such function, up to mult by a constant.) Interpretation: $\tilde{S}$ represents "uncertainty" [evidently, (3) asserts a certain additivity of this notion of uncertainty].

Note that $p \to -p \ln p$ is concave, so

$$\max_{\substack{\sum p_j = 1 \\ p_j \geq 0}} -\sum_{j=1}^{n} p_j \ln p_j$$

is a concave maximization. Optimum is at $p_1 = \cdots = p_n = 1/n$ by method of Lagr mult, since

$$\frac{\partial}{\partial p_j}\left[\sum p_j \ln p_j - \lambda \sum p_j\right] = 0 \Rightarrow 1 + \ln p_j = \lambda$$
for each j

No surprise here – the uniform distrib is the one that gives the least information.

<u>The canonical distrib arises by maximizing entropy subject to a constraint on the avg H.</u>

<u>In other words:</u>

$$\max \; -\sum_j' p_j \ln p_j \implies p_j = Z e^{-\beta H_j}$$
$$\sum_j' p_j = 1 \qquad \text{for some } \beta.$$
$$\sum_j' p_j H_j = U$$

Proof is again by method of Lagr mult:

$$\frac{\partial}{\partial p_j}\left[\sum' p_j \ln p_j - \lambda \sum' p_j - \mu \sum' p_j H_j\right] = 0$$

$$\implies \ln p_j = \lambda + \mu H_j - 1$$

$$\implies \quad p_j = Z e^{-\beta H_j} \quad \text{after renaming the constants.}$$

(Is this useful? Well, not so much I guess. But it provides intuition about the character of the canonical distribution.)