Mechanics - Lecture 12 - 4/19/2022

[We'll start on 4/19 with the Lecture 11 notes.]

Big picture: (1) We discussed this for the *microcanonical ensemble*, which uses the simple hypothesis that all pts on the set $H = E$ are equally likely; so the assoc prob distrn is "uniform measure on $\{E < H < H + dE\}$", i.e. the one s.t.

$$\mathbb{E}[f(q,p)] = \frac{1}{Z_E}\int_{H=E} \frac{f(q,p)}{|\nabla H|}\,dq\,dp.$$

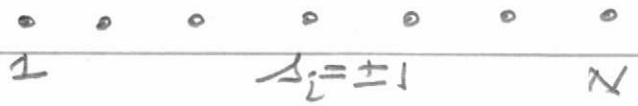
where Z_E is the normalization

$$Z_E = \int_{H=E} \frac{dq\,dp}{H=E}.$$

(2) But usually we observe a *very limited* system (eg a single particle) that's interacting with the rest of some larger system! We need a *different* prob distrn for this. It is the *canonical distribution*, in which any energy E is permitted but likelihood is weighted by $e^{-\beta E}$; here β is a constant, representing *inverse temperature*.

(3) Explaining the canonical ensemble is mostly about *counting*; we have no further use of the Hamiltonian eqns of motion. Therefore it can be done just as well for discrete systems as for continuous ones. This is a little easier, since "counting the no of states with energy E" is about actual counting rather than integration. I'll follow Buhler's book (§3.2 + 3.3) and take this approach. (Tuckerman's book has the analogous ideas done directly in a continuous setting.)

Let's focus on the following very simple discrete system:



The "state" (a pt in phase space) is

$$s = (s_1, \dots, s_N), \quad \text{each } s_i = \pm 1$$

and the Hamiltonian is $H(s) = \sum_{i=1}^{N} s_i$.

(The famous 2D Ising model, which is a favorite example of a system with a phase transition, is not so different: there the "spins" s_{ij} are on a 2D lattice and

$$H = -J \sum_{\text{neighbors}}' s_\alpha s_\beta + B \sum' s_\alpha .)$$

In the microcanonical ensemble we treat each $s = (\pm 1, \cdots, \pm 1)$ as equally likely. Viewing s_i as a coin flips, the statistics of H is very familiar: $H = \sum' s_i$ reports the # of heads − # tails for N flips. By Central Limit Thm, $s_1 + \cdots + s_N$ is approx Gaussian as $N \to \infty$, with mean 0 and variance N; so

$$\Omega(E) \underset{\text{defn}}{=} \text{number of states with } H = E$$

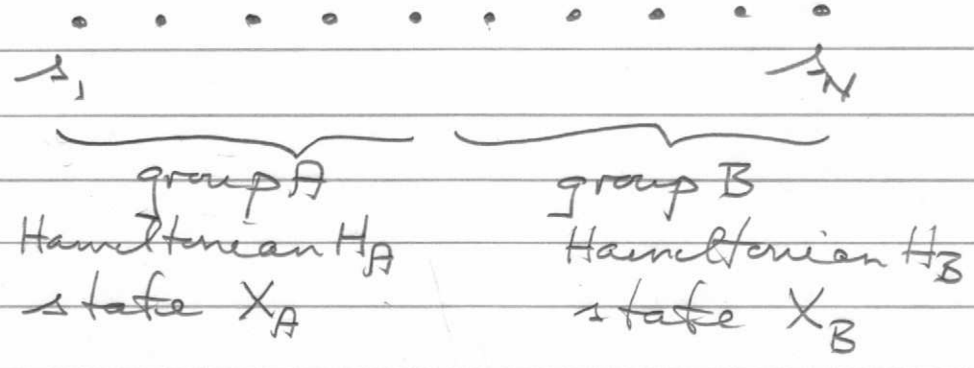
$$\simeq C_N e^{-E^2/2N}$$

when E is reasonably close to 0 & N is large. (While the exact formula is different from our calulation for N particles in Lecture 11, it shares the feature that $\Omega(E)$ depends very strongly on E.)

It is convenient to introduce

$$S(E) = \ln \Omega(E)$$

which is called entropy. Obviously it measures the size of $\Omega(E)$ — and therefore our uncertainty about the state if we know only that $H = E$ — but so does $\Omega(E)$ itself. To see why $\ln \Omega(E)$ is useful, we do some warmup calculations involving what happens when we break the system into two parts



(X_A = list of s_j in group A, $H_A(X_A)$ = their sum, etc). Note that if $X = (X_A, X_B)$ is state of entire system then $H(X) = H(X_A) + H(X_B)$ $= \sum_{j=1}^{N} s_j$.

Question 1: Given that $H(X) = E$, what is the most likely value of $E_A = H(X_A)$?

Ans: We want E_A that

$$\underset{E_A}{\text{maximizes}} \; \Omega_A(E_A) \cdot \Omega_B(E - E_A)$$

(since the A + B systems are independent). Taking log:

$$\max_{E_A} \; S_A(E_A) + S_B(E - E_A).$$

If N is large we can treat E_A as a cont's variable; then

$$\text{max is when } S_A'(E_A^*) = S_B'(E - E_A^*).$$

Defining the temperature T of a system by

$$S'(E) = \frac{1}{T},$$

we see that the answer to Question 1 was: The most likely situation is when the two subsystems have the same temperature.

Note: we'll often be more interested in $S'(E)$ than in T. So it is convenient to work with

$$\beta = \frac{1}{T} = S'(E) .$$

(Here entropy is nondimensional so T has units of energy. If we measure temp in degrees we need a conversion factor; that's Boltzmann's constant, usually written k_B, and then $S'(E) = \beta = 1/k_B\cdot(\text{temp})$.)

<u>Question 2</u>: Given that $H(X) = E$, find

a) the conditional probability of event X_A?

b) the probability that $H_A(X_A) = E_A$?

Ans to (a):

$$\text{Prob}(X_A \mid H=E) = \frac{\Omega_B(E - H_A(X_A))}{Z(E)}$$

where

$$Z(E) = \sum_{\substack{\text{all states} \\ X_A \text{ of system } A}} \Omega_B(E - H_A(X_A))$$

[In fact, if X_A is fixed then X_B must have $H_B(X_B) = E - H_A(X_A)$ and all states with this energy are equally likely.]

Ans to (b):

$$\text{Prob}\left(H(X_A)=E_A \mid H=E\right) = \frac{\Omega_A(E_A)\,\Omega_B(E-E_A)}{Z(E)}$$

OK, now we're ready to think about a small system in equilibrium with a much larger one (a "heat bath"). We model this by keeping the size of A fixed but sending the size of B to ∞. (B is "the reservoir").

Start by rewriting answer to Question 2(a):

$$\text{Prob}\{X_A \mid H=E\} = \frac{1}{Z(E)}\, e^{S_B(E-E_A)}$$

where $E_A = H_A(X_A)$.

Use linear approx of entropy

$$S_B(E-E_A) \approx S_B(E) - S_B'(E)\,E_A$$

to see that

$$\text{Prob}\{X_A \mid H=E\} \simeq c_E\, e^{-\beta E_A}$$

where $\beta = S_B'(E)$

Evidently: holding E fixed, but focusing on system A and dropping the conditional probability notation,

$$\text{Prob of state } X_A = \frac{1}{Z(\beta)} e^{-\beta H_A(X_A)}$$

$$\text{where } Z(\beta) = \sum_{\substack{\text{states } X_A \\ \text{of system } A}}' e^{-\beta H_A(X_A)}.$$

This is the canonical distribution.

An important note: dropping A from our notation (since we're now only thinking about system A),

The probability that $H(X) = E$ under the canonical distribution is

$$\frac{1}{Z(\beta)} e^{-\beta E} \Omega(E) = \frac{1}{Z(\beta)} e^{[S(E) - \beta E]},$$

so the most likely value of E is the one that minimizes $E - \frac{1}{\beta} S(E) = E - TS(E)$. This is the "free energy". (Evidently:

a value E becomes more likely <u>either</u> because it is lower ($\Rightarrow e^{-\beta H}$ is larger) <u>or</u> because it is achievable many different ways (larger entropy).

Bottom line: at finite temperature the most likely value of H is determined by minimizing the <u>free</u> <u>energy</u>