Mechanics - Lecture 11, 4/18/2018

Fresh start: 3 lectures introducing some central elements of statistical mechanics. Main sources: Chapter 5 of the book by Chorin + Hald, + Chapter 3 of the book by Bühler.

Orientation: goal of stat mech is to consider "typical behavior" (and typical fluctuations), for systems too complex to describe in detail. We'll do this by describing things probabilistically — though no explicit source of randomness is assumed.

Why is this reasonable?

a) Recall the "recurrence thm", proved as consequence of vol-preserving property of Hamiltonian flow in phase space. Vol pres flow can easily have very complicated orbits — even dense ones. (A key example is irrational flow on a torus) — though there can also be simpler behavior such as periodic orbits (example: rational flow on a torus; or, 2D systems such as a pendulum)

b) Birkhoff's ergodic thm — true once agn for vol preserving flow $\varphi_t(x)$ with a finite-volume invariant set D — says that if D is "indecomposable" (not decomposable into 2 invt regions, each of pos measure) then

$$\underbrace{\lim_{T\to\infty} \frac{1}{T}\int_0^T f(\varphi_t(x_0))\,dt}_{\text{time avg}} = \underbrace{\frac{1}{|D|}\int_D f\,dx}_{\text{spatial avg}}$$

and "spatial averaging" amounts to expected value wrt a very special prob. distribution (the uniform one).

Two issues:

1) The Hamiltonian is conserved (for Hamiltonian dynamics), so no region of phase space is ever indecomposable

2) Are orbits dense in the surface H = const? Hard to know, in most cases.

Ans to (1) is easy; we can focus on infinitesimal shell $\{X : H(X) \in [E, E + \partial E]\}$.

Proving (2) is hard, so usually we assume orbits are dense unless there's reason to think otherwise (eg due to an additional cons. law).

Q: What probability distrns are of interest?
A: At least, they should be invariant under the flow (assumed Hamiltonian).

What does this mean? Well, in fluid dynamics an initial density $\rho_0(x)$ evolves under flow with velocity $u(x) = \frac{d}{dt}\Big|_{t=0} \varphi_t(x)$ by

$$\partial_t \rho + \operatorname{div}(\rho u) = 0, \quad \rho\Big|_{t=0} = \rho_0$$

[proof: for any region D,

$$\frac{d}{dt} \int_D \rho(t,x)\, dx = -\int_{\partial D} \rho\, u \cdot n$$

$$\Rightarrow \int_D \partial_t \rho + \operatorname{div}(\rho u)\, dx = 0$$

true for all $D \Rightarrow \partial_t + \operatorname{div}(\rho u) = 0$.

Note: we have assumed there is transport only, with no diffusion!].

So ρ is invt iff $\mathrm{div}(\rho u) = 0$. If $\mathrm{div}\, u = 0$ (ie if flow is vol preserving) then ρ is invt iff $u \cdot \nabla \rho = 0$.

This calcn applies in Hamiltonian "phase space" $(q_1, \ldots, q_N, p_1, \ldots, p_N)$ with $\vec{u} = \left(\frac{\partial H}{\partial p_1}, \ldots, \frac{\partial H}{\partial p_N}, -\frac{\partial H}{\partial q_1}, \ldots -\frac{\partial H}{\partial q_N}\right)$

How to find such ρ? Any fn of H is invariant! (Of course, to be a measure it must be nonneg + integrate to 1). In fact:

if $\rho = G(H(q,p))$ then

$$u \cdot \nabla \rho = G'(H)\, u \cdot \nabla H.$$

and we showed $u \cdot \nabla H = 0$ before (this was the pf that $H =$ const along trajectories).

Two key examples:

a) $$\rho = \begin{cases} \text{const} & \text{for } H(q,p) \in [E, E+dE] \\ 0 & \text{otherwise} \end{cases}$$

in the limit $dE \to 0$

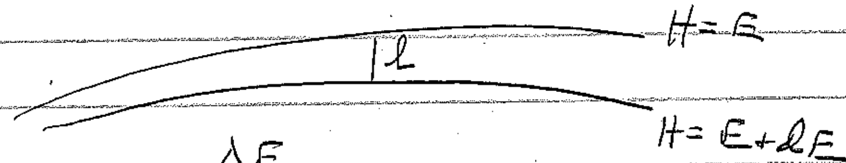
(this is the <u>microcanonical</u> distrn)

b) $\rho = \text{const} \cdot e^{-\beta H(q,p)}$

(as we'll see, β is essentially 1/temp; this is the <u>canonical</u> distrn)

<u>Note</u> abt (a): the microcanonical distrn is concentrated on the surface $H = E$, but it is usually <u>not</u> a const times surface area. Rather, it is a constant times (surface area)$/|\nabla H|$, since (by "method of shells")

$$\int_{E<H<E+\Delta E} f \, d\mathrm{vol} \simeq \Delta E \cdot \int_{H=E} \frac{f}{|\nabla H|} \, d\mathrm{area}$$



$$\frac{\Delta E}{l} \approx |\nabla H|$$

$$\text{so } l \simeq \frac{\Delta E}{|\nabla H|}.$$

<u>Central concept</u> of (a): it assumes all pts in shell $E < H(x) < E + \Delta E$ are are equally likely.

The microcanonical distrn can be useful, but for most practical purposes the canonical one is more relevant.

1st pass: a quick (but not very physical) way to see its importance uses the information-theoretic notion of the entropy of a prob distrn. (In Bühler this is §3.6; in Chaikin + Hald it's §5.3).

Working with discrete prob distrns, for simplicity, let's discuss prob distrns $p_1, \dots, p_n$ on a finite set $\{1, \dots, n\}$. The (information theoretic) entropy is

$$S = -\sum_i p_i \ln p_i$$

(cont's analogue would be $-\int \rho \ln \rho \, dq \, dp$ where $\rho = \rho(q,p)$ is a prob density on phase space).

Question: what's so special about $p \ln p$?
Ans (due to Shannon, I think):

with n states, $S = S(p_1, \dots, p_n) = -\sum p_i \ln p_i$ has these properties:

(1) for each n, it is a cont's fn of n vars

(2) Let $S_n = S(1/n, \dots, 1/n)$ be the entropy assoc to the uniform distrn on n pts. Then S_n is monotonically increasing in n.

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

$k_0 \quad k_1 \quad k_2 \quad k_3 \quad k_M$. $\qquad 1 = k_0 \le k_1 \le \dots \le k_M = n$.

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

Then

$$S(p_1, \dots, p_n) = S(q_1, \dots, q_M) + q_1 S\left(\frac{p_1}{q_1}, \dots, \frac{p_{k_1}}{q_1}\right) + q_2 S\left(\frac{p_{k_1+1}}{q_2}, \dots, \frac{p_{k_2}}{q_2}\right) + \cdots$$

Moreover, S is the only such fn (up to a mult. constant). Interptn: "entropy" represents "uncertainty":

(1) $\Leftrightarrow$ entropy depends cont'sly on probabilities

(2) $\Leftrightarrow$ more states, each equally likely $\Rightarrow$ more uncertainty

(3) $\Leftrightarrow$ uncertainty is additive; sum of that inherent in a particular grouping + averages of uncertainties of the groupings.

Note that $p \to -p \ln p$ is <u>concave</u>, so

$$\max_{\substack{\sum' p_j = 1 \\ p_j \geq 0}} -\sum' p_j \ln p_j$$

is a concave maximization. The optimum is achieved when $p_1 = \cdots = p_n = 1/n$, by method of Lagr mult, since

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

No surprise – a localized prob. density carries lots of info, a uniform one carries none.

More interesting: canonical distrn arises by maximizing entropy subject to constraint on avg H

$$\max_{\substack{\sum' p_j = 1 \\ \sum' p_j H_j = U}} -\sum' p_j \ln p_j \quad \Rightarrow \quad p_j = Z e^{-\beta H_j} \text{ for some } \beta$$

Pf is agn method of Lagr mult:

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

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

$$\Rightarrow \quad p_j = Z e^{-\beta H_j}$$ renaming the constants

Thus: canonical distrn is the max-entropy distrn consistent with a given value of $\mathbb{E}[H]$.

Well, that's nice, but it isn't very physical (why should $\mathbb{E}[H]$ be specified? why should entropy be maximized?) Answer is: we should use canonical distrn when we're observing a (possibly small) system that's in equilibrium with a much larger one (a "reservoir"). To explain, I'll follow Bühler §3.2–3.3

Discn is fundamentally about probability, not dynamics, so we'll focus on a discrete "coin-flipping" example involving no dynamics:

$$\text{state} = X = (s_1, \ldots, s_N), \quad \text{each } s_i = \pm 1$$

$$\text{Hamiltonian} = H(X) = \sum_{i=1}^{N} s_i$$

(if s_i reports coin flip by $+1$ = heads, -1 = tails, then H reports the # of heads in N flips).

We'll assume all states are equally likely (cf earlier discn of microcanonical distrn), so we're using a fair coin.

Let $\Omega(E)$ = # of ways of getting $H = E$. (Up to normalization, this is the "measure" of the assoc set in phase space, using counting measure.) By CLT, $s_1 + \cdots + s_N$ is approx Gaussian as $N \to \infty$, with mean 0 + variance N, so

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

when E is not too large (at most $\sim \sqrt{N}$) and N is large. Evidently: due to redundancy (many ways to get same result) $H = E$ is vastly more likely if E is near 0 than if E is far from 0.

It is convenient to discuss

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

(abusing notation – this is different from the "informational entropy" discussed earlier). This is the "<u>microcanonical entropy</u>." Note that if we break system into 2 indep parts, # states is multiplicative but "entropy is additive", as I now explain.

$$\underbrace{s_1 \circ \circ \circ \circ \circ \circ}_{\text{group } A} \underbrace{\circ \circ \, s_N}_{\text{group } B}$$

group A state X_A Hamiltonian H_A

group B state X_B Hamiltonian H_B

$$H(X) = H_A(X_A) + H_B(X_B) = \sum_{j=1}^{N} s_j$$

when $X = (X_A, X_B)$.

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

<u>Ans</u>: want $\max_{E_A} \Omega_A(E_A) \cdot \Omega_B(E - E_A)$

(by independence), or equivalently (taking log)

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

If N is large we can treat E_A as cont's var $\Rightarrow$ max when

$$S_A'(E_A^*) = S_B'(E - E_A^*)$$

Convention: $S_A'(E_A^*) = \beta = \frac{1}{T}$ (β = inverse temperature).

(Units: entropy is nondim'l here, so T has units of energy. If we measured temp in degrees we would need a conversion factor — Boltzmann's const k_B, giving $\beta = \frac{1}{k_B(\text{temp})}$.)

Recall our discn using central limit thm:

$$\Omega_A(E) = \text{const} \cdot e^{-E_A/2N_A}$$

$$\Rightarrow S_A(E) = \frac{-E_A^2}{2N_A} + \text{const}$$

$$\Rightarrow S_A'(E) = -E_A/N_A$$

so the most likely state has

$$\frac{-E_A}{N_A} = \frac{-E_B}{N_B} \qquad E_A + E_B = E.$$

Another question: given that $H(X) = E$, find

a) the conditional probability of event X_A?
b) the prob that $H(X_A) = E_A$?

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

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

since if X_A is fixed then X_B must have $H_B(X_B) = E - H_A(X_A)$ and all states with this property are equally likely

Ans to (b):

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

<u>Now here's the main pt.</u> Suppose we're interested in considering a <u>small</u> system (in mechanics: one particle) as part of a much larger system (eg many interacting particles). We'll model this by keeping system A fixed but taking size of B to ∞ (B is "the reservoir").

Let's revisit our formula for cond prob with this in mind:

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

Use lin approxn of entropy

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

so

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

$$\text{with } \beta = S_B'(E)$$

Evidently: holding E fixed, but focusing on system A and dropping the cond expectation notation,

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

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

This is the canonical distrn!

Simple arithmetic reveals that under this distrn,

$$\langle H \rangle = \frac{1}{Z} \sum_X H(X)\, e^{-\beta H(X)} = -\frac{\partial}{\partial\beta} \ln Z$$

and $$\text{var}(H) = \langle H^2 \rangle - \langle H \rangle^2 = + \frac{\partial^2}{\partial\beta^2} \ln Z$$