Mechanics - Lecture 11, 4/12/2022

[We'll spend at least half the 4/12 lecture finishing the material in the Lecture 10 notes.]

Final segment of this class is an introduction to some key aspects of Statistical Mechanics, including

- the microcanonical and canonical ensembles
- entropy and free energy
- Markov chain approach to sampling the canonical ensemble

Some comments on sources:

- One of the books on my syllabus - the one by David Chandler - is not available online; but a copy has been placed on reserve at Bobst Library (not the CIMS library, since the latter is still closed). It circulates for 4 hrs at a time, from the main Bobst circulation desk; the call # is QC174.8.C47 1987.

- Buhler's book is a little terse + lacking in examples; Tuckerman's book has *much* more detail + *many* more examples; Chandler's book lies in between (eg its Chapter 3 gives a great introduction to entropy + the microcanonical + canonical ensembles)

Orientation: goal of stat mech is to discuss "observable behavior" for systems too complex to describe in detail (answering questions about *macroscopic* quantities). We'll do this by using the language of *probability* even though no explicit source of randomness is assumed.

Why is this reasonable?

a) Recall Poincaré recurrence thm, proved as consequence of vol-preserving character of Hamiltonian flow. A vol-preserving flow can easily have very complicated orbits — even dense ones (consider irrational flow on a torus), though simpler behavior is also possible (e.g. rational flow on a torus) is periodic; so is the evolution of a pendulum at sufficiently low energy)

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

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

Note that "spatial average" is the avg of f wrt a very simple probability measure (the uniform one).

Two issues:

(i) Hamiltonian dynamics conserves H, so no region of phase space can be both invariant + indecomposable.

<u>Resolution</u>: The "shell" $\{x : H(x) \in [E, E+dE]\}$ meets these requirements (sort of) when dE is infinitesimal

(2) Is this shell <u>really</u> indecomposable? Hard to be sure, in practice. (It can fail; eg for particle constrained to move on a sphere, the geodesics are closed!). For physical systems we just assume it's true, unless there is reason to think otherwise.

We'll see soon (by considering a small system coupled to a "heat bath") that the uniform measure is not the only interesting one; the distribution with density

$$\rho = \text{const } e^{-\beta H}$$

is also of special interest (it defines the "canonical ensemble"; here β is essentially inverse temperature).

A minimal reqt for a prob distrn to be useful for stat mech is that it be <u>invariant</u> under the Hamiltonian flow. This occurs iff

$$(*)\quad \sum_j \frac{\partial H}{\partial p_j}\frac{\partial \rho}{\partial q_j} - \sum_j \frac{\partial H}{\partial q_j}\frac{\partial \rho}{\partial p_j} = 0$$

To see logic behind $(*)$, consider velocity vector field $\vec{v}$ of the Hamiltonian flow

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

i.e. $\vec{v}(q,p) = \left(\frac{\partial H}{\partial p_1}, \dots, \frac{\partial H}{\partial p_N}; -\frac{\partial H}{\partial q_1}, \dots, -\frac{\partial H}{\partial q_N}\right)$. A density ρ evolves by

$$(**)\quad \partial_t \rho + \operatorname{div}(\rho v) = 0$$

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

$\iff$ for any D, $\int_D \rho_t + \operatorname{div}(\rho v) = 0 \iff (**)$ holds).

So ρ is invariant $\iff \operatorname{div}(\rho v) = 0 \iff v\cdot\nabla\rho = 0$ (since $\operatorname{div} v = 0$) $\iff (*)$ holds.

A suff't condn for $(*)$ is that ρ be a fn of H, since $\rho = G(H(q,p)) \Rightarrow v\cdot\nabla\rho = G'(H)\, v\cdot\nabla H = 0$

[We'll stick to

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

(the microcanonical ensemble) and

$$(b)\quad \rho = \text{const}' \, e^{-\beta H}$$

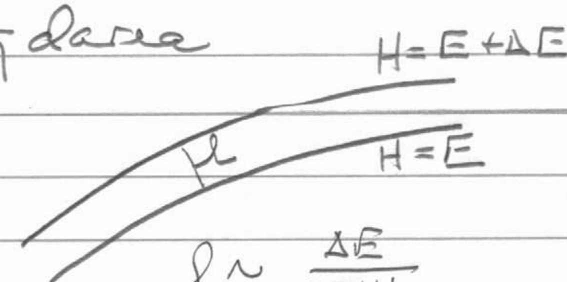
(the canonical ensemble) in these introductory lectures.]

An important note about (a): This ρ is concentrated on the surface $H=E$, but it is not a constant times surface area. Rather, it is a constant times

$$(\text{surface area}) / |\nabla H| ,$$

since (by "the method of shells")

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



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

(The essential hypothesis here is that all pts in the shell are equally likely.)

When to use the microcanonical ensemble?
Ans: for a system that's truly isolated (a very ideal situation).

<u>Example 1</u>: A 1D particle with mass m on $[0,L]$ with periodic bc

$$H = p^2/2m \qquad (p \in \mathbb{R})$$

Phase space $= [0,L] \times \mathbb{R}$; given E,

$$\{H=E\} = \{q \in [0,L],\ p = \sqrt{2mE}\}$$
$$\cup \{q \in [0,L],\ p = -\sqrt{2mE}\}.$$

$$1/|\nabla H| = (|p|/m)^{-1}$$

$\Rightarrow$ surface measure on $\{H=E\}$ weighted by $\dfrac{m}{\sqrt{2mE}} = \left(\dfrac{m}{2E}\right)^{1/2}$

Note that "the number of possible states"

$$\Omega(E) = 2L \cdot \left(\frac{m}{2E}\right)^{1/2}$$

depends on E!

[The physics books discuss this as "a particle in a box", with the particle reflecting at $x=0$ or $x=L$. It's the same calculation.]

Example 2: N identical particles in $[0,L]^3$ with mass m and periodic bc.

Now $\{H=E\}$ leaves $q_1, \cdots, q_N \in [0,L]^3$ unrestricted and requires

$$H = \sum_{i=1}^{N} \frac{|p_i|^2}{2m} = E$$

Evidently $\nabla_{p_i} H = \frac{p_i}{m}$ so $|\nabla H| = \frac{1}{m}(|p_1|^2 + \cdots + |p_N|^2)^{1/2}$

$$= (2mE)^{1/2}/m$$

$$= \left(\frac{2E}{m}\right)^{1/2}$$

$\Rightarrow$ surface measure on sphere of radius $(2mE)^{1/2}$ weighted by $\left(\frac{m}{2E}\right)^{1/2}$

Except: if particles are interchangeable then we must divide by $N!$ to avoid counting the same config'n many times.

Now the "number of possible states" is

$$\Omega(N,E) = \frac{L^{3N}}{N!}\left(\frac{m}{2E}\right)^{1/2} \cdot \text{area of sphere of radius } (2mE)^{1/2} \text{ in } \mathbb{R}^{3N}$$

Recall that

$$\text{Area of sphere of radius } R \text{ in } \mathbb{R}^m = \frac{2\pi^{m/2}}{\Gamma\left(\frac{m}{2}\right)} R^{m-1}$$

(check: $m=2 \Rightarrow$ this is $2\pi R$ since $\Gamma(1)=1$) so

$$\Omega(N,E) = \frac{L^{3N}}{N!}\left(\frac{m}{2E}\right)^{1/2} \frac{2\pi^{3N/2}}{\Gamma\left(\frac{3N}{2}\right)} (2mE)^{\frac{3N-1}{2}}$$

With Stirling's formula

$$\Gamma\left(\frac{3N}{2}\right) = \left(\frac{3N}{2}-1\right)! \simeq e^{-3N/2}\left(\frac{3N}{2}\right)^{3N/2}$$

this simplifies to

$$\Omega(N,E) = \frac{L^{3N}}{N!} \cdot \frac{1}{E} \cdot \left(\frac{4\pi m E}{3N}\right)^{3N/2} e^{3N/2}$$