

Lecture 12

Last time, introduced ensemble theory
= well-defined way to think about
averaging over unknown microstates

Idea: imagine repeating measurements many times
using many identically prepared systems.

Think about averaging over those measurements.

Of course, it's possible that the one system
we do have tends to sample all possible
microstates as time goes on.

If so, then time-average of our system
= ensemble average.

Call systems like this ergodic

Many systems seem empirically to be ergodic
but not all

and hard to predict from microscopic model

Ensemble average is conceptually safer

Classically, describe ensemble by $\rho(q, p)$
= phase space density

= density of systems w/ momenta $\{p_i\}$
& coords $\{q_i\}$

Ensemble average of $f(p, q)$

$$\langle f \rangle = \frac{\int f(p, q) \rho(p, q, t) \, dw}{\int \rho(p, q, t) \, dw}$$

$$dw = d^{3N} q \, d^{3N} p$$

In general, ρ changes in time

if $\frac{\partial \rho}{\partial t} = 0$, say ensemble is stationary

Expect that equilibrium system should be described by stationary ensemble.

A little more classical mechanics:

Poisson brackets

$$[A, B] = \sum_i \left(\frac{\partial A}{\partial q_i} \frac{\partial B}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial B}{\partial q_i} \right)$$

$$A = A(p, q) \quad B = B(p, q)$$

General property

$$\frac{dA}{dt} = \left(\frac{\partial A}{\partial t} \right)_{p, q} + [A, H]$$

Hamiltonian H

Special property of ρ : $\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right)$

= 0

"Liouville's theorem"

$$\text{So } \frac{\partial \rho}{\partial t} = - [\rho, H]$$

\Rightarrow for stationary ensemble, $[\rho, H] = 0$

General way to achieve $[\rho, H] = 0$

is to make

$$\rho = \rho(H(p, q))$$

$$= \rho(E)$$

Since then

$$[\rho, H] = \sum_i \left(\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right)$$

$$= \sum_i \left(\frac{\partial \rho}{\partial H} \frac{\partial H}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial H} \frac{\partial H}{\partial p_i} \frac{\partial H}{\partial q_i} \right)$$

$$= 0$$

So, any ensemble in which the density of states depends only on the energy will be stationary.

Different choices for energy dependence define different ensembles.

Simplest is micro-canonical ensemble

Define

$$\rho(p, q) = \begin{cases} 1 & \text{if } E - \frac{\Delta}{2} \leq H(p, q) \leq E + \frac{\Delta}{2} \\ 0 & \text{otherwise} \end{cases}$$

for some small nonzero Δ

Now connect to thermodynamics:

) Ensemble represents different microstates you could get if you prepared system again in same way.

Specifically

$$\omega = \int \rho \, d\omega$$

= volume of phase space occupied by ensemble

Any one system could be anywhere in that volume

) In Ch 1, took $S = k_B \ln \Omega$

$\Omega = \#$ of microstates system could be in

Refine here a bit:

$\Omega \rightarrow \#$ of microstates you might get if you prepared system again in same way

Reasonable to expect $\Omega \propto \omega$

$$\text{or } \Omega = \frac{\omega}{\omega_0}$$

where $\omega_0 =$ volume of one state in phase space

Should be clear that $\omega_0 \sim$ quantum mechanics

Classically, $\omega_0 = 0$

In QM, know $\Delta q \Delta p \geq \frac{\hbar}{2}$

so expect $\omega_0 \sim \hbar$ per degree of freedom.

Turns out

$$\omega_0 = h^{3N}$$

To get this factor, compare a few classical & quantum calculations.

Example 1: Ideal Gas

Calculate
$$\omega = \int_{E-\frac{\Delta}{2}}^{E+\frac{\Delta}{2}} \dots \int d^{3N} q d^{3N} p$$

with
$$H = \frac{p^2}{2m}$$

Do q integrals immediately to get V^N
system volume V

Leaves

$$\int \dots \int d^{3N} p = (2m)^{3N/2} \int \dots \int d^{3N} y$$

$$E - \frac{\Delta}{2} \leq \sum_{2m} p_i^2 \leq E + \frac{\Delta}{2} \quad Y_1^2 \leq \sum y_i^2 \leq Y_2^2$$

for $y_i = \frac{p_i}{\sqrt{2m}}$

$$Y_1 = \sqrt{2m(E - \frac{\Delta}{2})} \approx \sqrt{2mE} - \sqrt{\frac{m}{2E}} \frac{\Delta}{2}$$

$$Y_2 = \sqrt{2m(E + \frac{\Delta}{2})} \approx \sqrt{2mE} + \sqrt{\frac{m}{2E}} \frac{\Delta}{2}$$

$$= (2m)^{3N/2} [V_{3N}(Y_2) - V_{3N}(Y_1)]$$

V_{3N} = volume of $3N$ -hypersphere

We figured that out already

$$V_{3N}(Y) = \frac{\pi^{3N/2}}{(3N/2)!} Y^{3N}$$

$$V_{3N}(Y_1 + \delta) - V_{3N}(Y_1 - \delta) \approx \frac{\partial V_{3N}}{\partial Y} 2\delta$$

$$= \frac{\pi^{3N/2}}{(3N/2)!} 3N Y^{3N-1} 2\delta$$

$$= \frac{2\pi^{3N/2}}{(3N/2-1)!} (2mE)^{\frac{3N-1}{2}} \cdot \sqrt{\frac{m}{2E}} \Delta$$

$$= \frac{(2\pi mE)^{3N/2}}{(3N/2-1)!} \cdot \frac{2}{\sqrt{2mE}} \cdot \sqrt{\frac{m}{2E}} \Delta$$

$$= \frac{\Delta}{E} \frac{(2\pi mE)^{3N/2}}{(3N/2-1)!}$$

and thus $\omega = \frac{\Delta}{E} V^N \frac{(2\pi mE)^{3N/2}}{(3N/2-1)!}$

Compare to result of counting quantum states:

$$\Gamma = \frac{\Delta}{E} \left(\frac{V}{h^3} \right)^{3N} \frac{(2\pi m E)^{3N/2}}{(3N/2 - 1)!}$$

see that $\Gamma = \frac{\omega}{\omega_0}$ for $\boxed{\omega_0 = h^{3N}}$

which is what we wanted to determine.

Example 2: 1D harmonic oscillator

$$H = \frac{p^2}{2m} + \frac{1}{2} m \Omega^2 q^2$$

Know solutions $q = A \cos(\Omega t + \phi)$

$$p = -m\omega A \sin(\Omega t + \phi)$$

$A =$ amplitude

Then $E = \frac{p^2}{2m} + \frac{1}{2} m \Omega^2 q^2 = \frac{1}{2} m \omega^2 A^2$

defines ellipse in phase space

$$\frac{q^2}{A^2} + \frac{p^2}{m^2 \Omega^2 A^2} = 1$$

axes $a = A$ $b = m\Omega A$

Area enclosed by ellipse = $\pi ab = \pi m \Omega A^2$

$$= \pi m \Omega \left(\frac{2E}{m\Omega^2} \right)$$

$$= \frac{2\pi E}{\Omega}$$

= volume in phase space = ω

Now compare to quantum theory:

eigenstates $\epsilon_n = (n + \frac{1}{2}) \pm \hbar \omega$

So # of states with energy $< E$

$$\approx \frac{E}{\pm \hbar \omega} = \frac{2\pi E}{h \omega}$$

$$= \frac{\omega}{h}$$

Again see that reference volume of phase space is h per degree of freedom.

On strength of these examples, argue that general result is

$$S = k_B \ln \frac{\omega}{h^{3N}}$$

$$\omega = \int p \, dq$$

= phase space volume

Fundamental result for micro-canonical ensemble.

Basic method:

Given classical Hamiltonian, calculate

$$\omega = \text{phase space volume near energy } E$$

Gives S & thus all thermo

Unfortunately, micro-canonical ensemble is
limited usefulness

Usually, calculating ω is quite difficult

Also, in practice don't usually prepare systems
with definite energy E .

More often, have definite temperature T

Seem physically better to set up ensemble accordingly

\Rightarrow canonical ensemble, Ch 3

Will discuss a length, but make point now:

main reason to choose ensemble is mathematical
convenience.

System with definite T has, in practice, a
definite E . So both ensembles should
($\&$ do) give equivalent results.