

Lecture 13

Last time, presented microcanonical ensemble
 set of identically prepared systems
 such that

$\rho(p, q) =$ density of systems
 near p, q

$$= \begin{cases} 1 & \text{if } |H - E| \leq \frac{\Delta}{2} \\ 0 & \text{else} \end{cases}$$

Describes systems prepared
 with definite E

Canonical ensemble generally more useful

Describes systems prepared with definite T

To develop, start with different problem:

What is distribution of energies w/in a system?

Suppose N particles, total energy E

Label individual particle states by r

State r has energy ϵ_r

Define $n_r =$ # of particles in state r

Require $\sum_r n_r = N$

$$\sum_r n_r \epsilon_r = E$$

Now, set $\{n_r\}$ defines state of system
 up to interchanges of particles

For QM, that's good

Exchanging identical particles doesn't change state

But let's assume for now particles are distinguishable
(Thinking about classical systems)

Then each set $\{n_r\}$ corresponds to

$$W\{n_r\} = \frac{N!}{n_1! n_2! \dots} \quad \text{different states of system}$$

We want to know $P_r =$ fraction of particles
in state r

Define $\langle n_r \rangle =$ micro-canonical ensemble
average of n_r

All states in ensemble equally likely, so

$$\Rightarrow \langle n_r \rangle = \frac{\sum_{\{n_r\}} n_r W\{n_r\}}{\sum_{\{n_r\}} W\{n_r\}}$$

Sum is over all sets $\{n_r\}$ satisfying
 $E + N$ constraints

This average can, in fact, be evaluated,

But math is pretty hard...

tricky complex integrals

Seems more useful to skip

See in text, ps 47-51

* Theory students should read!

Instead, consider something similar,

$$n_r^* = \text{most probable value of } n_r \text{ in ensemble}$$

Reasonable to expect $n_r^* \approx \langle n_r \rangle$

Eventually, I'll give an argument to verify this

But first get n_r^* ;

Again, all states equally likely

so $\{n_r^*\} = \text{set with largest } W\{n_r\}$

Same as set with largest $\ln W$.

$$\ln W = \ln N! - \sum_r \ln n_r!$$

$$\approx N \ln N - N - \sum_r (n_r \ln n_r - n_r)$$

$$= N \ln N - \sum_r n_r \ln n_r$$

$$\text{since } \sum n_r = N$$

Want to maximize $\ln W$

but have constraints $\sum n_r = N$

$$\sum n_r \epsilon_r = E$$

Use method of Lagrange multipliers

$$\text{Maximize } \ln W - \alpha \sum_r n_r - \beta \sum_r n_r \epsilon_r$$

and pick α, β so that constraints obeyed

$$\text{Set } \frac{\partial}{\partial n_s} (N \ln N - \sum_s n_s \ln n_s - \alpha \sum_s n_s - \beta \sum_s n_s \epsilon_s) = 0$$

picks out $s=r$ terms in sums

$$-\ln n_r - n_r \left(\frac{1}{n_r}\right) - \alpha - \beta \epsilon_r = 0$$

$$\ln n_r = - (1 + \alpha + \beta \epsilon_r)$$

$$\text{So } n_r^* = e^{-(1+\alpha)} e^{-\beta \epsilon_r}$$

$$= C e^{-\beta \epsilon_r}$$

$$C = e^{-(1+\alpha)}$$

Then C & β determined by

$$\sum n_r^* = N \text{ and } \sum n_r^* \epsilon_r = E$$



$$\sum C e^{-\beta \epsilon_r} = N$$

$$C = \frac{N}{\sum e^{-\beta \epsilon_r}}$$

$$\text{So } n_r^* = N \frac{e^{-\beta \epsilon_r}}{\sum e^{-\beta \epsilon_r}}$$

$$P_r \approx \frac{n_r^*}{N} = \frac{e^{-\beta \epsilon_r}}{\sum e^{-\beta \epsilon_r}} \equiv \frac{e^{-\beta \epsilon_r}}{Q}$$

$$Q = \sum e^{-\beta \epsilon_r} = \text{"partition function"}$$

$$\text{and } E = \frac{-\sum \epsilon_r e^{-\beta \epsilon_r}}{\sum e^{-\beta \epsilon_r}} = -\frac{\partial}{\partial \beta} \ln \sum e^{-\beta \epsilon_r}$$

$$E = -\frac{\partial}{\partial \beta} \ln Q$$

In principle, solve \uparrow for β
gives P_r as desired

Connect to thermodynamics:

$$E = -\left(\frac{\partial}{\partial \beta} \ln Q\right)_{N,V}$$

Expect β , $\ln Q$ are thermo quantities

Look for derivative relation of this form

Find:

$$E = A + TS \quad A = \text{Helmholtz free energy}$$

$$dA = -SdT - PdV + \mu dN$$

$$\text{so } S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}$$

$$E = A - T\left(\frac{\partial A}{\partial T}\right)_{N,V}$$

$$= -T^2 \frac{\partial}{\partial T} \left(\frac{A}{T}\right)_{N,V}$$

$$= \left[\frac{\partial (A/T)}{\partial (1/T)} \right]_{N,V}$$

$$\text{Suggests } \beta \propto \frac{1}{T} \quad \ln Q \propto -\frac{A}{T}$$

Constant of proportionality turns out to be, again, Boltzmann's constant;

$$\beta = \frac{1}{k_B T}$$

$$A = -k_B T \ln Q$$

So in fact, if we know temperature, can get immediately

$$P_r = \frac{e^{-\epsilon_r/k_B T}}{Q} = \frac{e^{-\epsilon_r/k_B T}}{\sum_r e^{-\epsilon_r/k_B T}}$$

"Boltzmann distribution"

Can check $\beta = \frac{1}{k_B T}$ with quick example

1D harmonic oscillator, $N=1$

$$\epsilon_r = r h \nu \quad \text{if we define } E=0 \text{ at } V(0) + \frac{1}{2} h \nu$$

$$\text{So } Q = \sum_{r=0}^{E/h\nu} e^{-\beta r h \nu}$$

Consider limit $E \gg h \nu$

$$Q \rightarrow \sum_{r=0}^{\infty} (e^{-\beta h \nu})^r = \frac{1}{1 - e^{-\beta h \nu}}$$

$$E = -\frac{\partial}{\partial \beta} \ln Q = \frac{\partial}{\partial \beta} \ln (1 - e^{-\beta h \nu}) = \frac{h \nu}{1 - e^{-\beta h \nu}}$$

* move earlier

But since $E \gg h \nu$

Must have $e^{-\beta h\nu} \approx 1$
 $= 1 - \beta h\nu$ by Taylor exp.

$$\text{So } E = \frac{h\nu}{\beta h\nu} = \frac{1}{\beta} \Rightarrow \beta = \frac{1}{E}$$

But from problem 4.2 (Pathria 1.8)

already got $E = NkT = kT$

$$\Rightarrow \beta = \frac{1}{k_B T} \quad \text{as claimed } \checkmark$$

Now, could raise some objections to this calculation:

1) n_r 's are integers, and generally not large ones
 So does setting $\frac{\partial}{\partial n_r} = 0$ really make sense?

2) Even if we calculated P_r as $\frac{\langle n_r \rangle}{N}$,

any given system will have integer n_r

So n_r fluctuates a lot around mean

Fix: interpret r as referring to group of many states with nearby energy (same # in each group)

Include enough states so that $n_r \gg 1$

Nothing in argument required fact that r referred to single state, so result doesn't change.

Actually, could use different # of states in each group as long as we account for that.

Say g_i states in group i

Then

$$P_i = \frac{\langle n_i \rangle}{N} = \frac{g_i e^{-\beta E_i}}{\sum g_i e^{-\beta E_i}}$$

More general way to express Boltzmann relation

This is probably the single most important result we'll see in this class:

Prob to be in state $r \propto e^{-E_r/kT}$

Useful in many situations.

In particular, go back now to idea of canonical ensemble

= Ensemble of states at temperature T

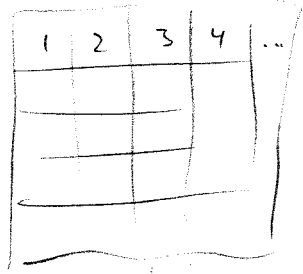
From stat mech point of view, best definition of T is from Boltzmann relation

ie, have $T = \left(\frac{\partial E}{\partial S} \right)_{N, V}$

but if we don't have definite E , hard to interpret.

Do know that T is same for systems in equilibrium,

So imagine ensemble of similar systems, all in thermal equilibrium with each other:



Say \mathcal{N} systems

Total energy E

$$\Rightarrow \text{average energy } U = \frac{E}{\mathcal{N}}$$

Ask: what is probability that system r has energy E_r ?

Equivalent to Boltzmann problem:

Account for ways to distribute fixed energy into \mathcal{N} boxes

Doesn't matter whether boxes are particles, groups of states, or whole systems.

Answer is same:
$$P_r = \frac{e^{-E_r/kT}}{Q}$$

Note that here, none of the problems with derivation apply:

- Can take $\mathcal{N} \rightarrow \infty$, so each system configuration r can have large n_r
- Systems are distinguishable, no issue with identical particles

So, define canonical ensemble as set of systems with

$$\rho(p, q) = \rho(H(p, q)) = \frac{e^{-\beta H(p, q)}}{Q}$$

$$Q \propto \int e^{-\beta H(p, q)} dw$$

But include two quantum corrections:

Divide Q by $h^{3N} = \omega_0$

So Q is analogous to # of states available

Also divide by $N!$

Account for indistinguishability of particles, in classical limit

$$\text{So } Q(N, V, T) = \frac{1}{N! h^{3N}} \int e^{-\beta H(p, q)} dw$$

Since $A = -kT \ln Q,$

if we can calculate Q , we get all of thermo.

See examples next time