Lecture 14

Start by clearing up some confusions from last time

Wanted to calculate distribution of energy over particles in system

Use micro-canonical ensemble:

Set of systems w/ energy E

Label systems $S_1, S_2 \ldots$

Describe each system by energy distribution $\{n_r\}$
$= \{n_1, n_2 \ldots\}$ $\quad n_r =$ # particles in state r

For distinguishable particles, each set $\{n_r\}$ corresponds to $W\{n_r\} = \frac{N!}{n_1! n_2! \ldots}$ different systems S_i

Calculation last time found the largest $W\{n_r\}$
$\Rightarrow$ most probable distribution in ensemble $\{n_r^*\}$

So we really solved for a set of occupation numbers all at once

Clearly this set satisfies
$$\sum_r n_r^* = N$$
$$\sum_r \varepsilon_r n_r^* = E$$
since it is a member of ensemble

Source of confusion is fact that we actually maximized
$$\ln W = \ln N! - \sum_r \ln n_r$$

= sum of functions of each n_r

When $f(x_1, x_2, ..) = f_1(x_1) + f_2(x_2) + ..$,

make sense to talk about maximizing f

w/ respect to x_1 alone

But in our case, constraints $\sum n_r = N$, $\sum n_r \varepsilon_r = E$

mean that n_r's actually are related

$\Rightarrow$ need to consider entire set $\{n_r^*\}$ together

which Lagrange multiplier method accomplishes.

So, find $n_r^* = \dfrac{e^{-\beta \varepsilon_r}}{\sum_r e^{-\beta \varepsilon_r}}$ with $\beta = \frac{1}{k_B T}$

(Remember, can calculate $\langle n_r \rangle$ as well, and get same result)

Last time, I said $Q = \sum_r e^{-\beta \varepsilon_r}$

should have said $Q_1 = \sum_r e^{-\beta \varepsilon_r}$

and result I got in class was right,

Helmholtz free energy $\boxed{A = -NkT \ln Q_1}$

Now, what this is all leading to is

the canonical ensemble

Micro-canonical: set of systems w/ same energy

Canonical: set w/ same temperature

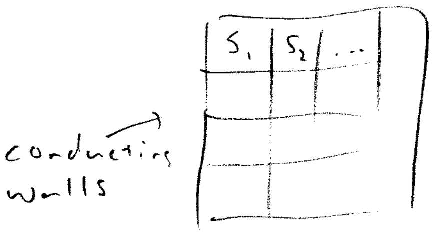
But we don't really have a microscopic definition of temperature to use

Best handle is Boltzmann distribution

Consider this way:

Know that systems in equilibrium have same T

So imagine systems in ensemble to be in equilibrium with each other



Suppose $\mathcal{N}$ systems in ensemble

Total energy $\mathcal{E}$

Then what is distribution of energy over systems?

Same problem as Boltzmann:

particles → systems

argument works same way

Now r labels states of system = N-particle states

n_r = # of systems in state r

E_r = energy of system in state r

Get $P_r = \dfrac{n_r^*}{\mathcal{N}} = \dfrac{\langle n_r \rangle}{\mathcal{N}} = e^{-\beta E_r} \Big/ \sum_r e^{-\beta E_r}$

= prob to find system w/ energy E_r

In fact, argument works better:

- Systems are certainly distinguishable (unlike particles)
- Can take $\mathcal{N} \to \infty$

  So all n_r's $\to \infty$

  - Stirling's approximation valid
  - Don't expect fluctuations to be significant

So, define canonical ensemble by

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

$$= \rho(H(p,q)) \quad \text{depends only on energy}$$

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

where $Q_N = \sum_r e^{-\beta E_r}$ = partition function

where $\{E_r\}$ = possible energies for system of N particles

vs $\{\varepsilon_r\}$ = possible energies for individual particle

Connection to thermo is

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

$$A = -kT \ln Q_N$$

Then for instance

average system energy

$$U = \langle E_r \rangle = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \text{weighted average}$$

$$= -\frac{\partial}{\partial \beta} \ln Q_N = \left(\frac{\partial (A/T)}{\partial (1/T)} \right)_{N,V}$$

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

$$= kT \frac{\frac{\partial Q_N}{\partial V}}{Q_N}$$

$$= kT \frac{\sum_r -\beta \frac{\partial E_r}{\partial V} e^{-\beta E_r}}{Q_N}$$

$$= -\frac{\sum_r \frac{\partial E_r}{\partial V} e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$$

So $P = \left\langle -\frac{\partial E_r}{\partial V} \right\rangle$

and $P dV = -\sum_r \underbrace{P_r}_{\text{probabilities}} dE_r = -dU$

where dU = change in average energy of system as V changed but P_r's held fixed

Makes sense!

What about entropy?

Have: $A = E - TS$ $\quad E \to U$, average

so $S = \frac{1}{T}(U - A)$

$$= k_B \beta \left[\frac{1}{Q_N} \sum_r E_r e^{-\beta E_r} + \frac{1}{\beta} \ln Q_N \right]$$

Express in terms of $P_r = \frac{e^{-\beta E_r}}{Q_N}$

= prob system has energy E_r

$$\ln P_r = \ln e^{-\beta E_r} - \ln Q_N$$
$$= -\beta E_r - \ln Q_N$$

$$\Rightarrow E_r = -\frac{1}{\beta}(\ln P_r + \ln Q_N)$$

So $$S = k_B \beta \left[\frac{1}{Q_N}\left(-\frac{1}{\beta}\right) \sum_r e^{-\beta E_r} \ln P_r + \frac{1}{Q_N}\left(-\frac{1}{\beta}\right) \sum_r e^{-\beta E_r} \ln Q_N + \frac{1}{\beta} \ln Q_N \right]$$

$$= -k_B \left[\frac{1}{Q_N} \sum_r e^{-\beta E_r} \ln P_r + \frac{1}{Q_N} \ln Q_N \underbrace{\sum_r e^{-\beta E_r}}_{Q_N} - \ln Q_N \right]$$ Cancel

$$\boxed{S = -k_B \sum_r P_r \ln P_r = -k_B \langle \ln P_r \rangle}$$

So entropy is determined by set of P_r's

Closest connection yet between entropy + randomness:

If we knew for sure that system in microstate r_0

Then $P_{r_0} = 1$ other P_r's $= 0$

$S = 1 \ln 1 = 0$ no entropy

If system in one of two possible states:

say $P_{r_1} = \frac{1}{2}$ $P_{r_2} = \frac{1}{2}$

$S = \left(-\frac{1}{2}\ln\frac{1}{2} - \frac{1}{2}\ln\frac{1}{2}\right)k_B = k_B \ln 2 > 0$

Say system is equally likely to be in one of Ω possible states:

$$S = -k_B \sum_r \frac{1}{\Omega} \ln \frac{1}{\Omega} = \frac{k_B \ln \Omega}{\Omega} \sum_r = k_B \ln \Omega$$

= Definition of entropy from microcanonical ensemble!

So $S = -k_B \sum_r P_r \ln P_r$

is just generalization of prior definition to case where all states not equally likely

Quite general:

foundation of information theory

Using canonical ensemble:

Basic job is to calculate $Q_N(V,T) = \sum_r e^{-\beta E_r}$

Often the case that many system states r have same energy E_r

Let i lable group of g_i states with energy E_i

Then $Q_N = \sum_i g_i e^{-\beta E_i}$

$P_i = \dfrac{g_i e^{-\beta E_i}}{Q_N}$ = prob to find system with energy E_i

vs $P_r = \dfrac{e^{-\beta E_r}}{Q_N}$ = prob to find system in a particular state r

Usually, allowed energies E_i are closely spaced

Take $Q_N \rightarrow \int g(E)\, e^{-\beta E}\, dE$

$g(E)$ = density of states

$g(E)dE$ = # of states between E + $E+dE$

Then $P(E)\,dE = \dfrac{g(E)\, e^{-\beta E}\, dE}{Q_N}$ = prob to find system with energy between E & $E+dE$

For classical systems, can also express of phase space integral

$$Q_N \propto \int e^{-\beta H(q,p)} \, d\omega$$

To count states, should normalize this by $\omega_0 = h^{3N}$

And to handle fact that particles are indistinguishable, divide by $N!$

Then
$$\boxed{Q_N(V,T) = \frac{1}{N!\,h^{3N}} \int e^{-\beta H(p,q)} \, d\omega}$$

or
$$\boxed{Q_N(V,T) = \int g(E)\, e^{-E} \, dE}$$

↳ Here quantum corrections in $g(E)$

Next time, see some examples.

But can say now what makes canonical ensemble better

Microcanonical:
$$\Omega = \frac{1}{N!\,h^{3N}} \int_{|H-E|<\frac{\Delta}{2}} d\omega \qquad \left(\text{or } \Sigma \propto \int_{H<E} d\omega\right)$$

Canonical
$$Q = \frac{1}{N!\,h^{3N}} \int e^{-\beta H} \, d\omega$$

For Ω, need to integral over complicated N-dimensional region

For Q, integrate over all phase space

Don't need to deal with boundary

For instance, if particles don't interact,

$$H = \sum_{i=1}^{N} H_i(\vec{p}_i, \vec{q}_i)$$

$$Q_N = \frac{1}{N! h^{3N}} \int e^{-\beta H} d\omega$$

$$= \frac{1}{N! h^{3N}} \int e^{-\beta H_1} d^3p_1 d^3q_1 \int e^{-\beta H_2} d^3p_2 d^3q_2 \cdots$$

$$= \frac{1}{N! h^{3N}} \left[\int e^{-\beta H_1} d^3p_1 d^3q_1 \right]^N$$

$$= \frac{1}{N!} Q_1^N \quad \text{for } Q_1 = \frac{1}{h^3} \int e^{-\beta H} d^3p\, d^3q$$

"single particle partition function"

Q_1 is what we encountered last time.

So N-particle problem reduces to single particle integral. Big improvement!