

## Lecture 9

### Exam review:

- Have many thermodynamic variables ( $P, U, T, S, H, M, \mu, N, \dots$ )

Usually easy to determine which are relevant

- Eqn of state = relation between variables

- Can expand any relation into a differential

ie,  $T(P, \mu) \Rightarrow dT = \left(\frac{\partial T}{\partial P}\right)_{\mu} dP + \left(\frac{\partial T}{\partial \mu}\right)_{P} d\mu$

No constraint on choice of variables

- 1st & 2nd laws of thermo give special differential

$$dE = dQ - dW = TdS + YdX + \mu dN$$

Holds in addition to math expansion above

Note: also tells us about choice of indep variables:

Says that  $E$  can be expressed  $E(S, X, N)$

and  $T = \frac{\partial E}{\partial S}$ ,  $Y = \frac{\partial E}{\partial X}$ ,  $\mu = \frac{\partial E}{\partial N}$

also functions of  $(S, X, N)$

Eqn of state reduces # by one more

$\rightarrow$  typically, two variables needed to specify system.

(But not always: coexisting gas/liquid needs three)

- Free energies:

Various Legendre transforms of fund relation

change natural indep variables

- Appropriate free energy describes work stored & retrievable from system when natural variables held constant
- In equilibrium, appropriate free energy is minimized
- Applications we discussed:
  - Mixing / Gibbs paradox
  - Joule-Thompson effect
  - Phase transitions & Maxwell construction

Exam:

4 problems

two pretty easy

two a little harder

) expect average ~50%

Closed book, notes

I'll give you a couple formulas

Expect you to know everything on cheat sheet  
(remember to use corrected version)

Should know or be able to derive  
partial deriv relations

Be sure to show & explain work  
necessary for full or partial credit

# Statistical Mechanics

Goal: derive thermodynamics (macroscopic physics)  
from microscopic model

## Outline

- Conceptual/informal approach (Ch 1)
  - Formal classical theory (Ch 2-4)
  - Formal quantum theory (Ch 5-8)
  - Interacting systems (Ch 9-13)
- ↳ prob won't get to :

Think about microscopic picture

Consider system with  $N$  particles  
volume  $V$   
energy  $E$

From QM, know each particle has allowed  
energies  $\epsilon_i(V)$

Say  $n_i$  particles in level  $i$

Then  $E = \sum_i n_i \epsilon_i$  and  $N = \sum_i n_i$

(Since  $\epsilon_i$ 's discrete, only certain values of  $E$  allowed)  
But  $\epsilon_i$  so small,  $E$  appears continuous at macro level)

Say that  $\{n_i\}$  defines microstate

complete knowledge of particle distribution

$(N, U, E)$  define macrostate

In general, many different microstates have  
same macrostate

(Two eggs,  $\sim 10^{23}$  unknowns)

→ Basic postulate of stat mech:

For given macrostate, all microstates equally likely

Motivation: collisions cause microstate to  
constantly change. In fairly  
short time, sample most possible states.

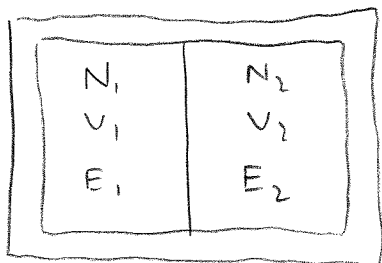
Define # of microstates  $\equiv \Omega(N, U, E)$

= very large number

Amazingly, all thermo properties can be derived  
from  $\Omega$ !

For instance:

Two systems with conducting wall:



System 1 has  $\Omega_1(N_1, U_1, E_1)$  states

System 2 has  $\Omega_2(N_2, U_2, E_2)$  states

But considered together,  $E_1$  &  $E_2$  aren't specified

Only know  $E_0 = E_1 + E_2$

Total # of states  $\Omega_0$

Consider  $\Omega_0(E_1, E_2) =$  # of states with  
 $E_1$  in sys 1, and  
 $E_2$  in sys 2

Simple combinatorics says

$$\Omega_0(E_1, E_2) = \Omega_1(E_1) \Omega_2(E_2)$$

Also require  $E_2 = E_0 - E_1$

Claim that in equilibrium,  $\Omega_0(E_1, E_2)$  will be  
as large as possible

$\Rightarrow$  if all microstates equally likely, then macrostate  
with largest  $\Omega$  is most likely

Observe that all systems tend to equilibrium,  
so equilibrium state must be most likely.

So, what value of  $E_1$  makes  $\Omega_0$  as  
large as possible?

$$\Omega_0 = \Omega_1(E_1) \Omega_2(E_2)$$

$$\left( \frac{\partial \Omega_0}{\partial E_1} \right)_{N_1, V_1} = \frac{\partial \Omega_1}{\partial E_1} \Omega_2(E_2) + \Omega_1(E_1) \frac{\partial \Omega_2}{\partial E_2} \underbrace{\frac{\partial E_2}{\partial E_1}}_{=-1} = 0$$

$$\text{So } \frac{1}{\Omega_1} \frac{\partial \Omega_1}{\partial E_1} = \frac{1}{\Omega_2} \frac{\partial \Omega_2}{\partial E_2}$$

$$\frac{\partial}{\partial E_1} (\ln \Omega_1) = \frac{\partial}{\partial E_2} (\ln \Omega_2)$$

So in equilibrium have  $\beta \equiv \left( \frac{\partial}{\partial E} \ln \Omega \right)_{N, V}$  same for both subsystems.

But from thermodynamics, already know that for equilibrium, temperatures must be equal

$\Rightarrow \beta$  related to  $T$

Further, know  $T = \left( \frac{\partial E}{\partial S} \right)_{N, V} \Rightarrow \frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N, V}$

Looks like  $\beta \propto \frac{1}{T}$  and  $\ln \Omega \propto S$

Constant of proportionality just  $k_B$ :

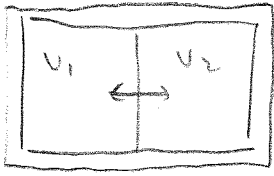
$$\boxed{S = k_B \ln \Omega}$$

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

So if we know  $\Omega(N, E, V)$ , get  $S(N, E, V)$

Further:

Suppose wall between systems is movable



Now have  $V_0 = V_1 + V_2$  fixed

But  $V_1$  &  $V_2$  can vary

By same reasoning as before, get

$$\Omega_0(E_1, V_1, E_2, V_2) = \Omega_1(E_1, V_1) \Omega_2(E_2, V_2)$$

Want  $\Omega_0$  maximized with respect to both  $E$  and  $V$

$$\frac{\partial \Omega_0}{\partial V_1} = 0 \Rightarrow \left( \frac{\partial \ln \Omega_1}{\partial V_1} \right)_{N_1, E_1} = \left( \frac{\partial \ln \Omega_2}{\partial V_2} \right)_{N_2, E_2}$$

But if  $S = k_B \ln \Omega$ , then

$$\left( \frac{\partial \ln \Omega}{\partial V} \right)_{N, E} = \frac{1}{k_B} \left( \frac{\partial S}{\partial V} \right)_{N, E}$$

From  $dE = TdS - PdV + \mu dN$ , have

$$0 = T \left( \frac{\partial S}{\partial V} \right)_{N, E} - P + 0$$

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

$$\left( \frac{\partial \ln \Omega}{\partial V} \right)_{N, E} = \frac{P}{k_B T}$$

So in equilibrium, pressures of subsystems equal

Finally, allow particles to flow from  $1 \leftrightarrow 2$

Then

$$\Omega_0(N_1, V_1, E_1, N_2, V_2, E_2) = \Omega_1(N_1, V_1, E_1) \Omega_2(N_2, V_2, E_2)$$

and

$$\left( \frac{\partial \Omega_0}{\partial N_1} \right)_{V_1, E_1} = 0 \Rightarrow \left( \frac{\partial \ln \Omega_1}{\partial N_1} \right)_{V_1, E_1} = \left( \frac{\partial \ln \Omega_2}{\partial N_2} \right)_{V_2, E_2}$$

$$\Rightarrow \left( \frac{\partial S}{\partial N} \right)_{V, E} \text{ is equal}$$

$$\text{But } \left( \frac{\partial S}{\partial N} \right)_{V, E} = - \frac{\mu}{T}$$

So  $\mu_1 = \mu_2$ , as expected

Conclude that identification  $S = k_B \ln \Omega$  makes sense

And from  $S$ , can get all other thermodynamic information.

That's all very general

Suppose further that we have non-interacting particles.

$$\text{Then } \Omega(N, V, E) \approx [\Omega(1, V, E)]^N$$

Since each particle distributed independently

Can reasonably expect  $\Omega(1, V, E) \propto V$

However many ways we can distribute a particle over one volume, should be twice as many for twice the volume.

$$\text{So } \Omega(N, V, E) \approx [\Omega_1(E) V]^N$$

$$\left( \frac{\partial (\ln \Omega)}{\partial V} \right)_{N, E} = \frac{\partial}{\partial V} [N \ln \Omega_1 + N \ln V]$$

$$= \frac{N}{V}$$

$$\frac{P}{kT} =$$

Therefore expect

$$\boxed{PV = NkT}$$

for non-interacting particles

Next lecture, calculate  $\Omega$  for real,  
make sure this is correct.