Exam review:

- Have many thermodynamic variables ($P, U, T, S, W, M, \mu, N, \text{etc.}$)
  Usually easy to determine which are relevant

- Eqn of state = relation between variables

- Can expand any relation into a differential
  i.e., $T(P, \mu)$:
  $$dT = \left( \frac{\partial T}{\partial P} \right)_\mu dP + \left( \frac{\partial T}{\partial \mu} \right)_P d\mu$$
  No constraint on choice of variables

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

  $$dE = dQ - dW = TdS + Y dX + \mu dN$$
  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

  -> 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 cheatsheet (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)

Think about microscopic picture

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

From QM, know each particle has allowed energies $\varepsilon_i(U)$

Say $n_i$ particles in level $i$

Then $E = \sum n_i \varepsilon_i$ and $N = \sum n_i$

(Since $\varepsilon_i$'s discrete, only certain values of $E$ allowed)

But $\varepsilon_i$ 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 eqns, $\sim 10^{23}$ 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 $\Omega (N, U, E)$

= very large number

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

For instance:

Two systems with conducting well:

<table>
<thead>
<tr>
<th></th>
<th>$N_i$</th>
<th>$V_i$</th>
<th>$E_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$N_1$</td>
<td>$V_1$</td>
<td>$E_1$</td>
</tr>
<tr>
<td>2</td>
<td>$N_2$</td>
<td>$V_2$</td>
<td>$E_2$</td>
</tr>
</tbody>
</table>
System 1 has \( \mathcal{N}_1(N_1, U_1, E_1) \) states
System 2 has \( \mathcal{N}_2(N_2, U_2, E_2) \) states

But considered together, \( E_1 + E_2 \) aren't specified
Only know \( E_0 = E_1 + E_2 \)
Total \# of states \( \mathcal{N}_0 \)

Consider \( \mathcal{N}_0(E_1, E_2) = \# \) of states with
\( E_1 \) in sys 1, and
\( E_2 \) in sys 2

Simple combinatorics says
\[ \mathcal{N}_0(E_1, E_2) = \mathcal{N}_1(E_1) \mathcal{N}_2(E_2) \]
Also require \( E_2 = E_0 - E_1 \)

Claim that in equilibrium, \( \mathcal{N}_0(E_1, E_2) \) will be
as large as possible

\( \Rightarrow \) if all microstates equally likely, then macrostate
with largest \( \mathcal{N} \) is most likely

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

So, what value of \( E_1 \) makes \( \mathcal{N}_0 \) as
large as possible?
\[ \Sigma_0 = \Sigma_1 (E_1) \Sigma_2 (E_2) \]

\[ \left( \frac{\partial \Sigma_0}{\partial E_1} \right)_{N,V} = \frac{\partial \Sigma_1}{\partial E_1} \Sigma_2 (E_2) + \Sigma_1 (E_1) \frac{\partial \Sigma_2}{\partial E_2} \left( \frac{\partial E_2}{\partial E_1} \right) = 0 \]

So \[ \frac{1}{\Sigma_1} \frac{\partial \Sigma_1}{\partial E_1} = \frac{1}{\Sigma_2} \frac{\partial \Sigma_2}{\partial E_2} \]

\[ \frac{\partial}{\partial E_1} (\ln \Sigma_1) = \frac{\partial}{\partial E_2} (\ln \Sigma_2) \]

So in equilibrium have \[ \beta = \left( \frac{\partial E}{\partial S} \ln \Sigma \right)_{N,V} \] same for both subsystems.

But from thermodynamics, already know that for equilibrium, temperatures must be equal \[ \Rightarrow \beta \text{ related to } T \]

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 \[ \ln \Sigma \propto S \]

Constant of proportionality just \( k_b \):

\[ S = k_b \ln \Sigma \]

\[ \beta = \frac{1}{k_b T} \]

So if we know \( \Sigma (N,E,V) \), get \[ S (N,E,V) \]
Suppose wall between systems is movable

\[ \text{Now have } U_0 = U_1 + U_2 \text{ fixed} \]

But \( U_1 + U_2 \) can vary

By same reasoning as before, get

\[ S_0 (E_1, U_1, E_2, U_2) = S_1 (E_1, U_1) + S_2 (E_2, U_2) \]

Want \( S_0 \) maximized with respect to both \( E \) and \( U \)

\[ \frac{\partial S_0}{\partial U_1} = 0 \implies \left( \frac{\partial \ln S_1}{\partial U_1} \right)_{N,E_1} = \left( \frac{\partial \ln S_2}{\partial U_2} \right)_{N,E_2} \]

But if \( S = k_B \ln S \), then

\[ \left( \frac{\partial \ln S}{\partial U} \right)_{N,E} = \frac{1}{k_B} \left( \frac{\partial S}{\partial U} \right)_{N,E} \]

From \( dE = TdS - PdU + \mu dN \), have

\[ 0 = T \left( \frac{\partial S}{\partial U} \right)_{N,E} - P + \mu \]

\[ \left( \frac{\partial S}{\partial U} \right)_{N,E} = \frac{P}{T} \]

\[ \left( \frac{\partial \ln S}{\partial U} \right)_{N,E} = \frac{P}{k_B T} \]

So in equilibrium, pressures of subsystems equal
Finally, allow particles to flow from $1 \rightarrow 2$

Then

$$\mathcal{S}_2 (N_1, U_1, E_1, N_2, U_2, E_2) = \mathcal{S}_1 (N_1, U_1, E_1) \mathcal{S}_2 (N_2, U_2, E_2)$$

and

$$\left( \frac{\partial \mathcal{S}_2}{\partial N_1} \right)_{U_1, E_1} = 0 \Rightarrow \left( \frac{\partial \ln \mathcal{S}_1}{\partial N_1} \right)_{U_1, E_1} = \left( \frac{\partial \ln \mathcal{S}_2}{\partial N_2} \right)_{U_2, E_2}$$

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

But \( \left( \frac{\partial \mathcal{S}}{\partial N} \right)_{U, E} = - \frac{\mu}{k} \)

So \( \mu_1 = \mu_2 \), as expected

Conclude that identification \( S = k_0 \ln \mathcal{S} \) makes sense

And from \( S \), can get all other thermodynamic information.

That's all very general

Suppose further that we have non-interacting particles.

Then \( \mathcal{S}_2 (N, U, E) \approx \left[ \mathcal{S}_1 (1, U, E) \right]^N \)

Since each particle distributed independently.
Can reasonably expect $S_2(N, V, E) \propto V$

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

So $S_2(N, V, E) \propto [S_1(1, E) V] N$

$$\left( \frac{\partial (\ln Z)}{\partial V} \right)_{N, E} = \frac{1}{\partial V} \left[ N \ln Z_1 + N \ln V \right]$$

$$= \frac{1}{Z}$$

$$\frac{p}{kT} = \text{Therefore expect } \boldsymbol{pV = NkT}$$

for non-interacting particles

Next lecture, calculate $S_2$ for real, make sure this is correct.