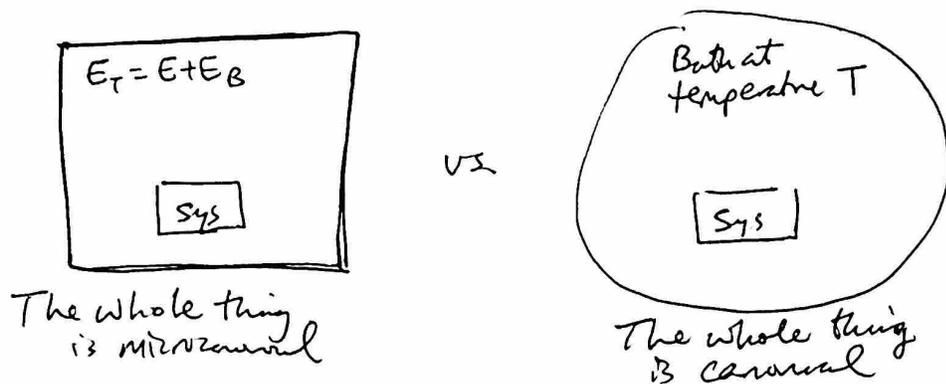


- Exam Logistics

- Last lecture: Ensemble equivalence.



As far as the system is concerned there is no difference.

On left, E_B settles into some value so that $\left(\frac{\partial \ln \Omega_B(E_B)}{\partial E_B}\right)_{N,V} = \frac{1}{T}$ which behaves like the T on the right as far as the system is concerned.

We rushed through an explicit calculation to show that we could equivalently set a constraint on E or fix its average through T .
(rigid)

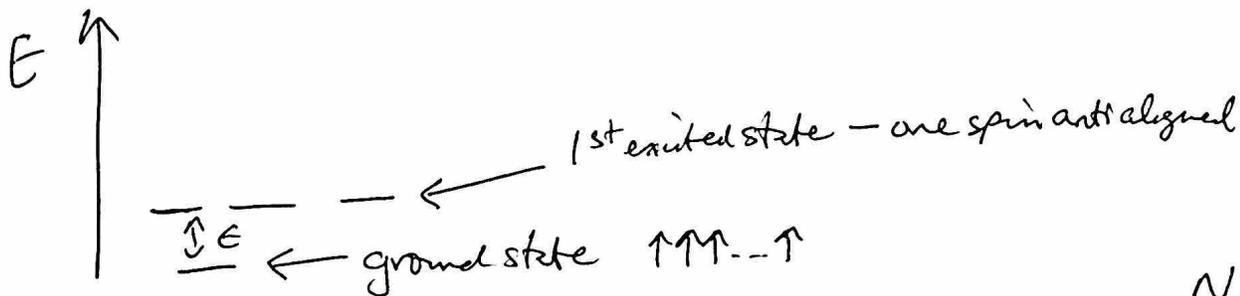
Noninteracting spins in an external field

$$\begin{array}{c} \uparrow \uparrow \downarrow \uparrow \downarrow \downarrow \dots \uparrow \\ S_1 S_2 \quad \quad \quad S_N \end{array} \quad S_i = \begin{cases} +1, & \text{aligned with field} \\ -1, & \text{anti-aligned} \end{cases}$$

$$v = \{S_1, S_2, S_3, \dots, S_N\} \quad E(v) = -\frac{\epsilon}{2} \sum S_i$$

We sought a relationship between T and the fraction of excited spins ($S_i = -1$ is excited)

Route 1 Microcanonical



Degeneracy of the n th excited state = $\Omega = N C_n = \frac{N!}{n!(N-n)!}$

$$\Rightarrow S = -N k_B \left[(1-f) \ln(1-f) + f \ln f \right], \text{ where } f = \frac{n}{N}$$

Fix the energy (equivalently fix f). What is the resulting T ? ^{"entropy of mixing"}

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_N = \frac{k_B}{\epsilon} \ln \frac{1-f}{f} \quad [\text{More work in last lecture notes}]$$

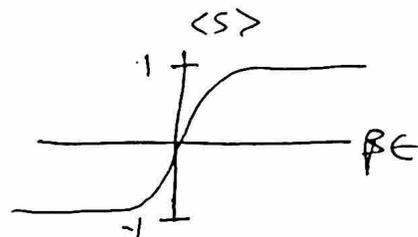
$$\Rightarrow \boxed{\frac{\epsilon}{k_B T} = \ln \frac{1-f}{f}}$$

Route 2 Canonical

$$\begin{aligned} P(s_1, \dots, s_N) &\propto e^{-\beta E(s_1, s_2, \dots, s_N)} \\ &= e^{\beta \frac{\epsilon}{2} s_1} e^{\beta \frac{\epsilon}{2} s_2} \dots e^{\beta \frac{\epsilon}{2} s_N} \quad \leftarrow \text{Factorized!} \\ &= p(s_1) p(s_2) \dots p(s_N) \end{aligned}$$

with $p(s) = \frac{e^{\beta \frac{\epsilon}{2} s}}{e^{\beta \frac{\epsilon}{2}} + e^{-\beta \frac{\epsilon}{2}}}$ and $\langle s \rangle = p(+1) + p(-1) (-1)$

$$\Rightarrow \langle s \rangle = \frac{e^{\beta \epsilon / 2} - e^{-\beta \epsilon / 2}}{e^{\beta \epsilon / 2} + e^{-\beta \epsilon / 2}} = \tanh\left(\frac{\beta \epsilon}{2}\right)$$



$$\Rightarrow \langle s \rangle = \frac{e^{\beta \epsilon} - 1}{e^{\beta \epsilon} + 1} \quad (*)$$

To compare with the microcanonical result,

$$\langle s \rangle = f(-1) + (1-f)(1) = 1-2f$$

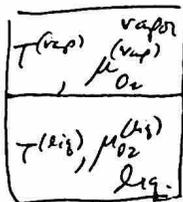
So (*) becomes $(1-2f)e^{\beta \epsilon} + (1-2f) = e^{\beta \epsilon} - 1$

$$\Rightarrow e^{\beta \epsilon} = \frac{1-f}{f} \Rightarrow \boxed{\frac{\epsilon}{k_B T} = \ln\left(\frac{1-f}{f}\right)}$$

SAME ANSWER!

For most of the rest of the course we will discuss phases - phase equilibria and phase transitions.

On your exam

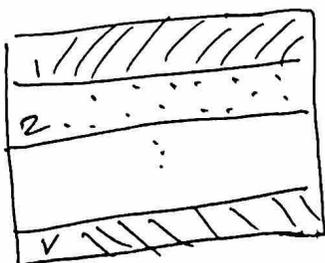


In equilibrium, how does $T^{(vap)}$ compare to $T^{(liq)}$?

how does $\mu_{O_2}^{(vap)}$ compare to $\mu_{O_2}^{(liq)}$?

Equality of $T + \mu_{O_2}$ allowed us to glue together two different statistical mechanical (lattice model) results to relate solute concentration in the liquid to the partial pressure in the vapor (Raoult's law).

What if I combine more phases together?



} v distinct phases. Can differ from each other by:
 $P, E, \text{ composition}$

Composition? Let there be r molecular species

$$x_1 = \frac{N_1}{N}, x_2 = \frac{N_2}{N}, \dots, x_r \text{ are the mole fractions} \quad \sum_{i=1}^r x_i = 1$$

Phase 1 might have large x_1 , while phase 2 has low, etc.

What must be the same between phases?

$$T, p, \mu_1, \mu_2, \dots, \mu_r$$

Constraints:

$$T^{(1)} = T^{(2)} = \dots = T^{(v)}$$

$$p^{(1)} = p^{(2)} = \dots = p^{(v)}$$

$$\mu_1^{(1)} = \mu_1^{(2)} = \dots = \mu_1^{(v)}$$

$$\mu_2^{(1)} = \mu_2^{(2)} = \dots = \mu_2^{(v)}$$

\vdots

$$\mu_r^{(1)} = \mu_r^{(2)} = \dots = \mu_r^{(v)}$$

$(v-1)$ $(2+r)$ equations.
of columns # of rows

How many total control variables?

$$T^{(1)}, T^{(2)}, \dots, p^{(1)}, p^{(2)}, \dots, \underbrace{x_1^{(1)}, x_2^{(1)}, \dots, x_{r-1}^{(1)}}_{\text{composition of phase \#1}}, x_1^{(2)}, x_2^{(2)}, \dots$$

There are $v(2+r-1)$ of these.

{ What happened to $x_r^{(1)}$? Why is N not a control variable? }

Let $f = \#$ of remaining controlled degrees of freedom

$$f = v(2+r-1) - (v-1)(2+r) = v(2+r) - v - v(2+r) + 2+r$$

$$\Rightarrow \boxed{f = 2+r-v} \quad \text{Gibbs phase rule.}$$

What scenarios are possible?

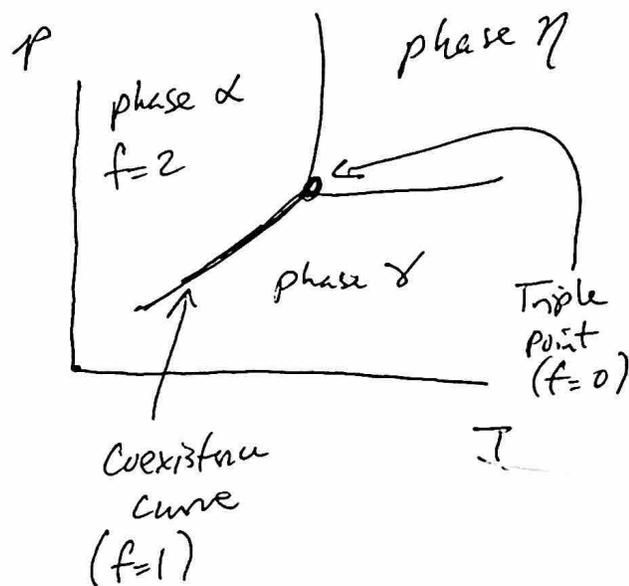
Start with one component ($r=1$)

1 phase $\Rightarrow f=2$. Can independently vary $T+p$

2 phases $\Rightarrow f=1$. $T+p$ are coupled together. $P_{\text{coex}}(T)$

3 phases $\Rightarrow f=0$. Unique $T+p$

4 phases? Not gonna happen.



Q. Though water had all of these different phases of ice, but how can that work if there are only 3 possible phases w/ $r=1$?

Many components ($r > 1$) can get very messy!

Simple case: oil/water ($r=2$)

2 phases $\rightarrow f=2$

$x_{\text{coex}}^{(1)}(T, p) \approx$ ~~some scribbles~~

$x = \frac{N_{\text{wet}}}{N}$

