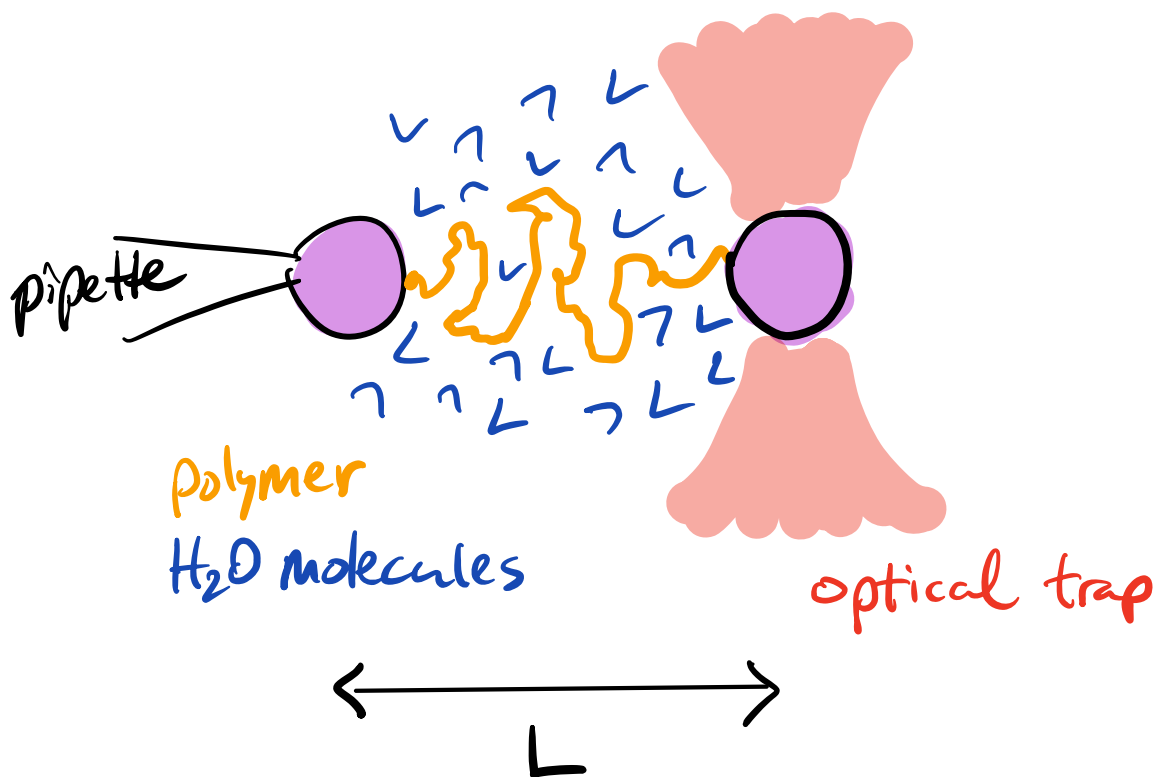
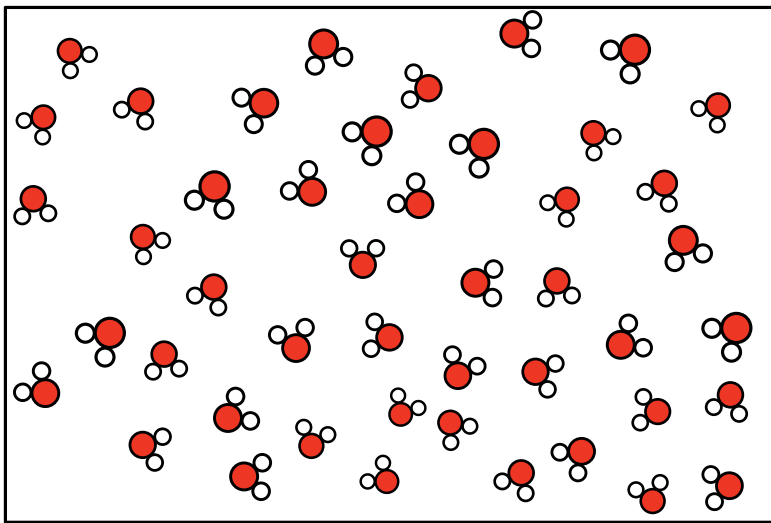


# Lecture 12

Recall from last lectures...

We have been discussing the likely values of macrostates when we don't measure all the microscopic degrees of freedom.



In thermodynamic equilibrium, the macroscopic coordinate has an effective energy (a free energy) such that lower-free-energy states are more probable.

$$-k_B T \ln P(m) = \mathcal{F}(m)$$

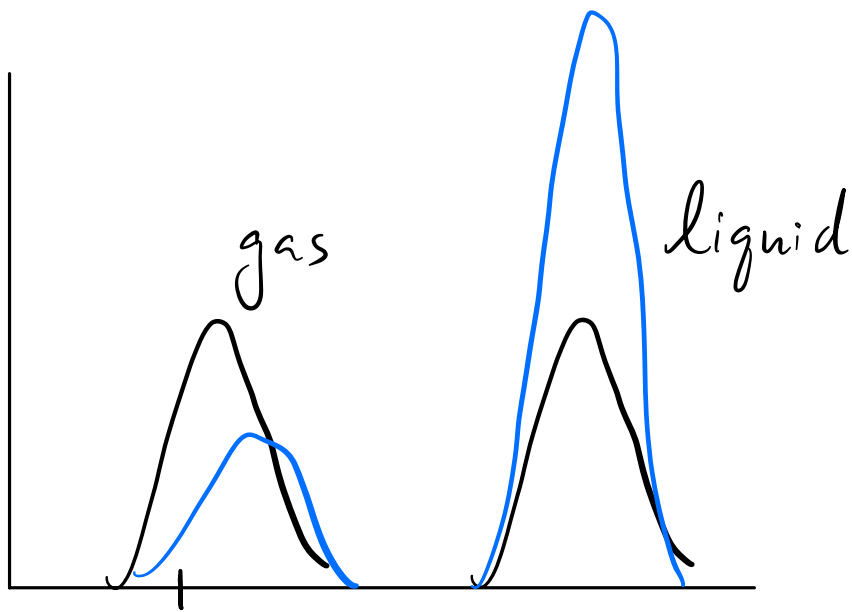
Degree(s) of freedom you measure  $\nearrow$   $\nwarrow$  Free energy for  $m$ .

Furthermore, if we set some mixture of global constraints and exponential biases (e.g.,  $N, V, T$ ), we could compute the typical value of a macrostate (e.g.  $\langle E \rangle$ ).

$$\langle E \rangle = \sum_E E \underbrace{P(E)}$$

$\uparrow$

Must  $P(E)$  be dominated by a single  $E^*$  in the thermodynamic limit?

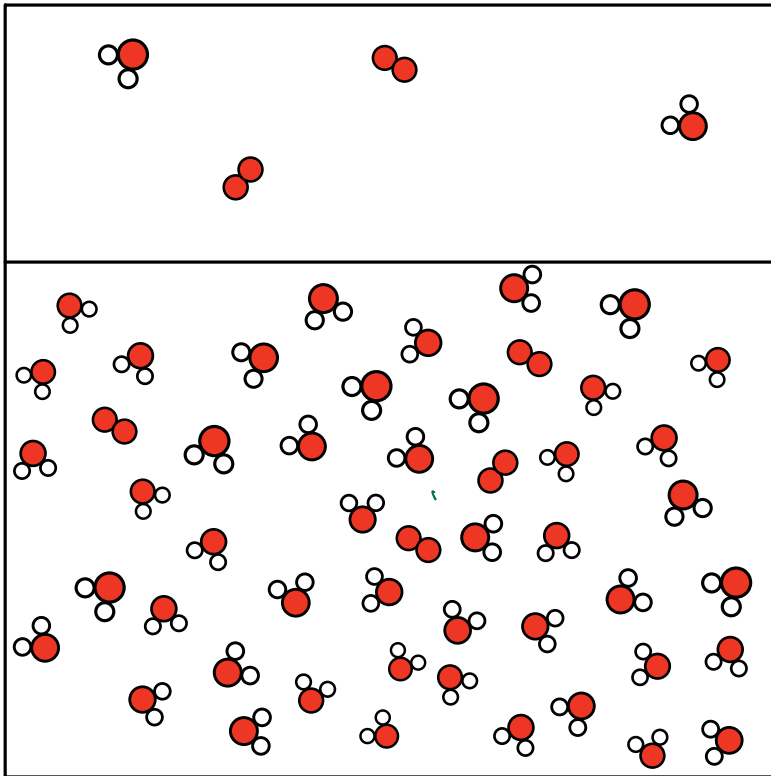


$E$

There can exist a special value of  $T$  where the two effects balance and  $P(E)$  is profoundly multimodal, even in the thermodynamic limit!

What is a practical consequences of such a multimodal distribution?

# Phase coexistence!



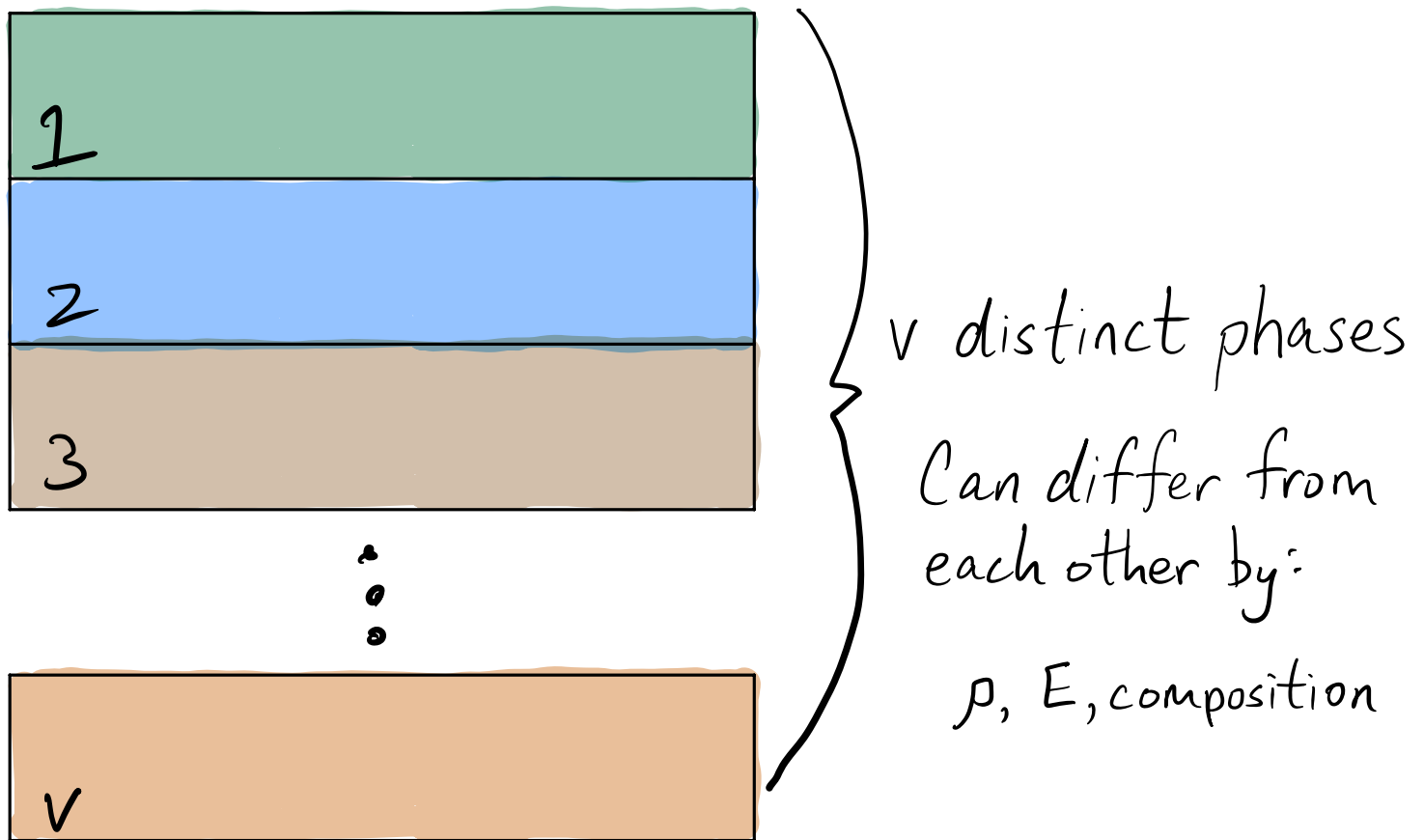
Vapor phase

Liquid phase

In equilibrium,  $T^{(\text{vap})} = T^{(\text{liq})}$

$$\mu^{(\text{vap})} = \mu^{(\text{liq})}$$

How many phases can possibly coexist?



Composition? Let there be  $r$  molecular species

$$N_1 \text{ of species 1} \Rightarrow x_1 = \frac{N_1}{N} \quad (\text{mole fraction})$$

$$N_2 \text{ of species 2} \Rightarrow x_2 = \frac{N_2}{N}$$

$$\vdots$$
$$x_r$$

In equilibrium, what must be the same between phases?

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

How many total degrees of freedom characterize the  $v$  phases? (if we were not necessarily in equilibrium)

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

$$x_1^{(1)}, x_1^{(2)}, \dots, x_1^{(v)}$$

⋮

$$x_{r-1}^{(1)}, x_{r-1}^{(2)}, \dots, x_{r-1}^{(v)}$$

Composition of  
phase #1

$$\text{dof} = v(2+r-1)$$

What happened to  $x_r^{(1)}$ ?

$$\sum_{i=1}^r x_i^{(1)} = 1$$

So  $x_r^{(1)}$  cannot vary independently of  $\{x_1^{(1)}, x_2^{(1)}, \dots, x_{r-1}^{(1)}\}$

Why was there no  $N$  on the list?

We were listing intensive quantities

How many constraints on these degrees of freedom does equilibrium impose?

Constraints:

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

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

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

⋮

$$\mu_{r-1}^{(1)} = \mu_{r-1}^{(2)} = \dots = \mu_{r-1}^{(v)}$$

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

How many equations?

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

Number of  
Columns

Number of  
Rows

Let  $f$  = Number of remaining degrees of freedom

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

$$f = \cancel{2v} + \cancel{rv} - v - \cancel{2v} + 2 - \cancel{rv} + r$$

$$f = 2 + r - v$$

Gibbs Phase Rule

What scenarios are possible?

Start with one component ( $r=1$ )

One phase ( $v=1$ )  $\Rightarrow f=2$  Can independently vary both  $p$  &  $T$ .

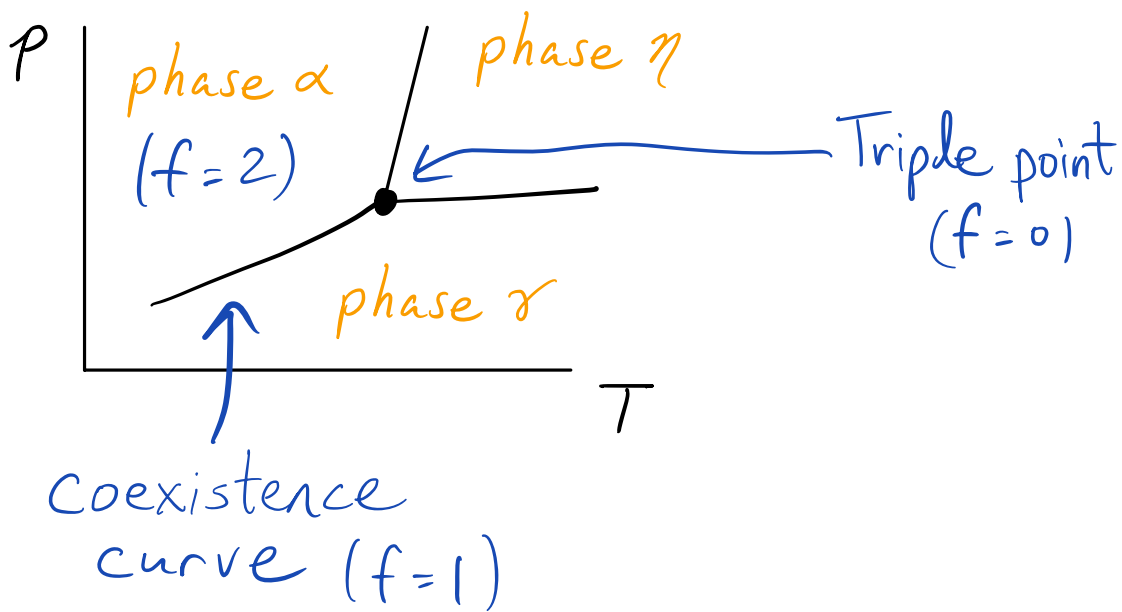
Two phases ( $v=2$ )  $\Rightarrow f=1$   $p$  &  $T$  are coupled.

Only possible along  $p_{\text{coex}}(T)$   $\leftarrow$  coexistence curve

Three phases ( $v=3$ )  $\Rightarrow f=0$  Unique  $p$  &  $T$ .

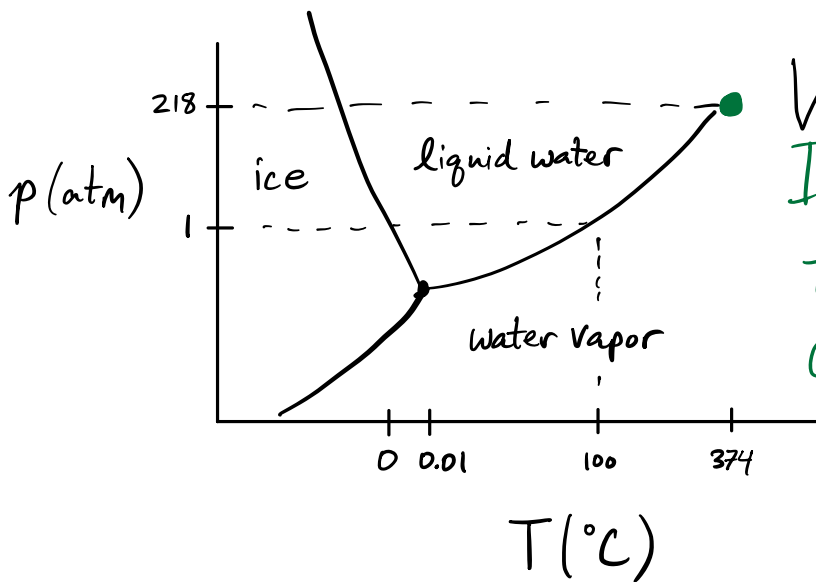
Four phases ( $v=4$ )  $\Rightarrow f=-1$  Not gonna happen!





I thought water had all of these different phases of ice, so how can it be that there are only 3 possible phases with  $r=1$ ?

The Gibbs Phase Rule is limiting coexisting phases.



What's up with this?  
Is it a liquid or a vapor to the right of the critical point?

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

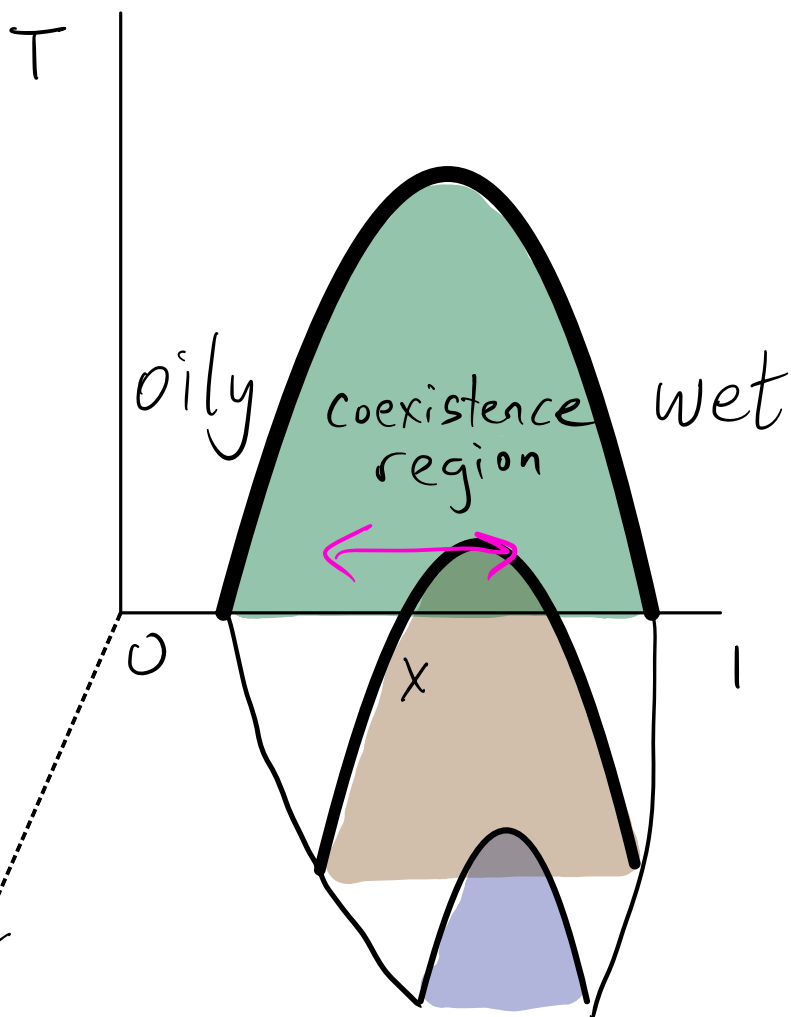
Simple case: oil/water ( $r=2$ )

$$f = 2 + r - v \quad v = 2 \Rightarrow f = 2$$

Coexistence between 2 phases is 2 dimensional

$$\text{mole fraction of H}_2\text{O: } x^{(1)} = \frac{N_{\text{H}_2\text{O}}}{N} \equiv x$$

$$\text{mole fraction of oil: } x^{(2)} = \frac{N_{\text{oil}}}{N} \equiv (1-x)$$



Varying relative amounts of the coexisting phases

Remember, the conditions for being in equilibrium in a coexistence region is that each phase must have equal chemical potential for all components

We used a lattice model to find how  $\mu$  depends on  $T$  and  $p$  for an ideal gas ...

$$\mu(T, p) = \mu^{(0)}(T) + k_B T \ln\left(\frac{p}{p_0}\right)$$

[ Problem Set 4 #3 ]

Let's see this another way...