Lecture 14
Recall from last lectures...

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

[Problem Set 4 #3 from a lattice model]

$$Q(N,V,T) = \frac{1}{N!}\left(q_{translations}\, q_{internal}\right)^N$$

$$= \frac{1}{N!}\left(\frac{V}{\lambda(T)^3}\, q_{int}(T)\right)^N$$

$$\Rightarrow \beta p = \left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} = \frac{N}{V} \qquad \Rightarrow \boxed{\beta p = \rho}$$

$$\uparrow$$
Ideal gas law

$$\left(\frac{\partial \ln Q}{\partial N}\right)_{T,V} = -\beta\mu = \ln \frac{V\, q_{int}(T)}{N\, \lambda(T)^3}$$

$$\Rightarrow \mu = k_B T \ln \frac{p_0 \beta \lambda(T)^3}{q_{int}(T)} + k_B T \ln \frac{p}{p_0}$$
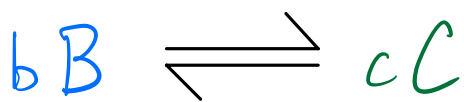
(our lattice model result but now with $\mu^{(0)}$ in terms of de Broglie)

Notice that the **essential** feature leading to these ideal forms was the factorization of the partition function into a product of single-particle partition functions. Fluctuations in particle 1's state are **decorrelated** from fluctuations in particle 2's state.

Decorrelated fluctuations are the essence of ideal systems   (ideal gases, ideal solutions, etc.)

A consequence of the ideal form of μ...

Chemical equilibrium

$$b B \rightleftharpoons c C$$

upper case: species name
lower case: stoichiometry

ΔN forward reactions takes

$$N_B \rightarrow N_B - b \Delta N \qquad N_C \rightarrow N_C + c \Delta N$$

How does the Gibbs free energy change as a result?

$$\frac{dG}{d\Delta N} = \left(\frac{\partial G}{\partial N_B}\right)_{T, p, N_c} \left(\frac{\partial N_B}{\partial \Delta N}\right) + \left(\frac{\partial G}{\partial N_c}\right)_{T, p, N_B} \left(\frac{\partial N_c}{\partial \Delta N}\right)$$

$$\Rightarrow \quad -b\mu_B + c\mu_c = 0 \quad \text{at equilibrium}$$

$$\Rightarrow \quad b\mu_B = c\mu_c$$

Aside:

$$G = E - TS + pV \qquad \qquad \left(\frac{\partial G}{\partial N_B}\right)_{T, p, N_c} = \mu_B$$

$$dG = dE - d(TS) + d(pV)$$

$$= TdS - pdV + \mu_B dN_B + \mu_c dN_c - TdS - SdT + pdV + Vdp$$

$$= -SdT + Vdp + \boxed{\mu_B}\, dN_B + \mu_c\, dN_c$$

Which, for an ideal solution implies

V_0: volume of lattice cell

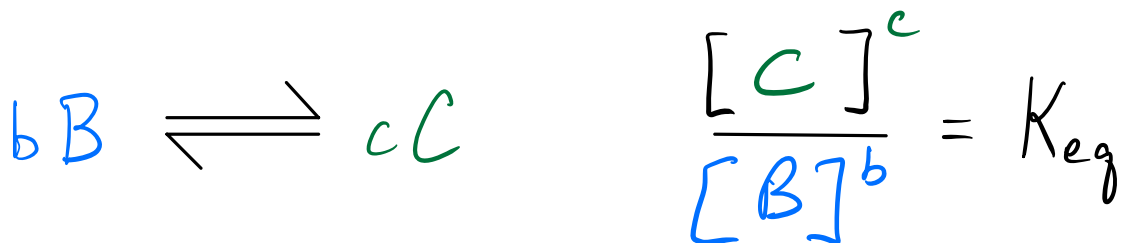ρ_B: density of B. $\frac{N_B}{V}$

$$b\left(k_B T \ln \rho_B V_0 + \mu_B^{(0)}\right) = c\left(k_B T \ln \rho_C V_0 + \mu_C^{(0)}\right)$$

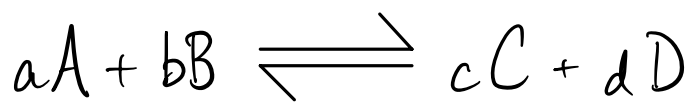$$\Rightarrow k_B T \ln \frac{\rho_B^b V_0^b}{\rho_C^c V_0^c} = c\mu_C^{(0)} - b\mu_B^{(0)} \equiv \Delta\mu_{rxn}^{(0)}$$

$$\Rightarrow \frac{\rho_C^c V_0^c}{\rho_B^b V_0^b} = e^{-\beta\Delta\mu_{rxn}^{(0)}}$$

$$\Rightarrow \frac{\rho_C^c}{\rho_B^b} = V_0^{b-c} e^{-\beta\Delta\mu_{rxn}^{(0)}} = K_{eq}(T)$$
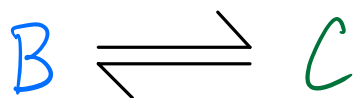
Law of mass action

$$bB \rightleftharpoons cC \qquad \frac{[C]^c}{[B]^b} = K_{eq}$$

We have the same story for

$$aA + bB \rightleftharpoons cC + dD$$

$$a\mu_A + b\mu_B - c\mu_c - d\mu_D = 0 \text{ at equilibrium}$$

$$\Rightarrow \frac{[C]^c [D]^d}{[A]^a [B]^b} = K_{eq}(T)$$

Crossovers (as a function of T)

$$B \rightleftharpoons C$$

$$\frac{\rho_C}{\rho_B} = e^{-\beta \Delta \mu^{(0)}} \text{ at equilibrium}$$

$$\left(\Delta \mu^{(0)} = \mu_c^{(0)} - \mu_B^{(0)} \right)$$

If $\rho_B + \rho_C = \bar{\rho}$ is fixed

$$\rho_C = \rho_C \frac{\bar{\rho}}{\rho_B + \rho_C} = \frac{\bar{\rho}}{1 + e^{\beta \Delta \mu^{(0)}}}$$

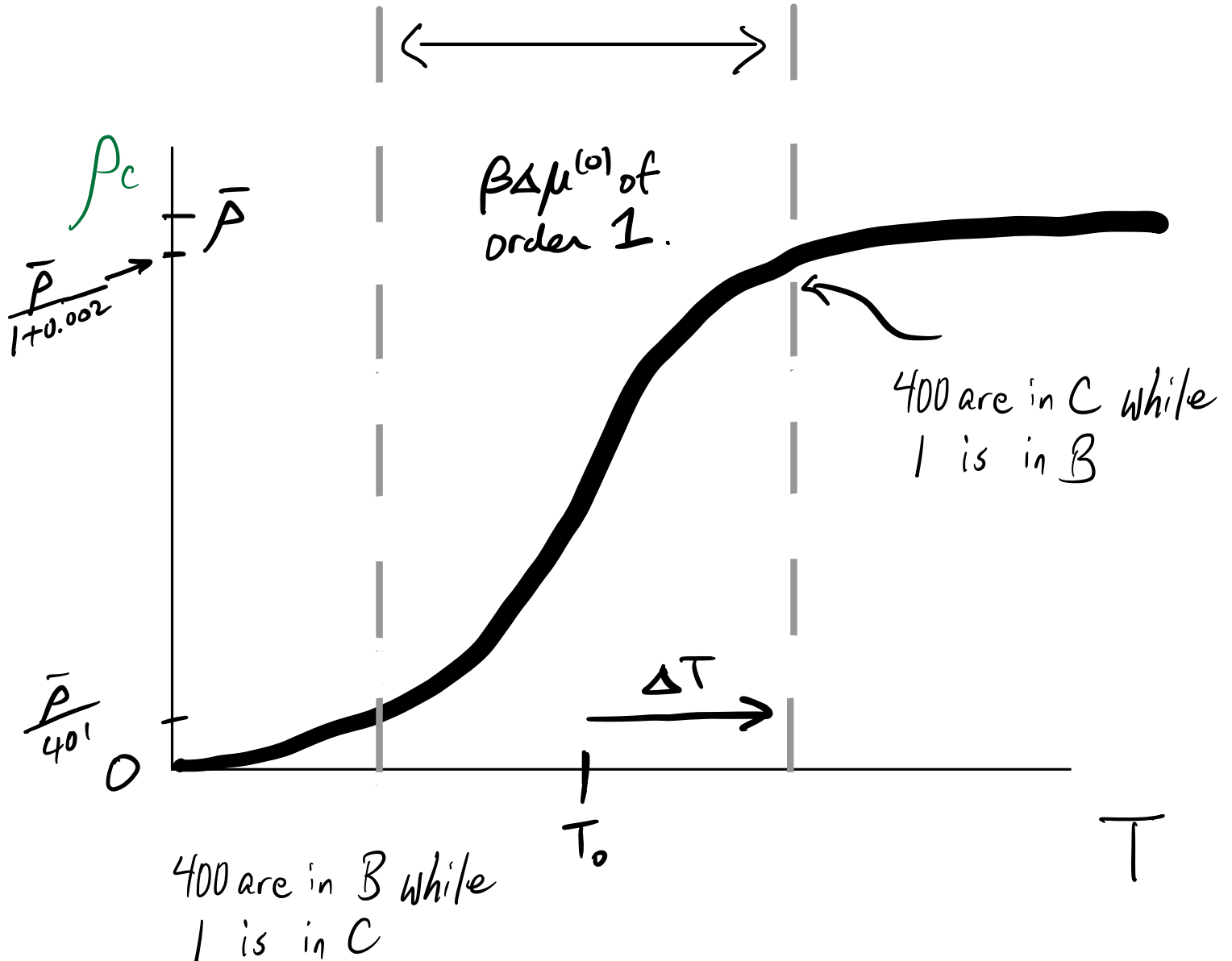$$G = E - TS + pV = (E + pV) - TS = H - TS$$

And $dG = -SdT + Vdp + \mu dN \Rightarrow \left(\dfrac{\partial G}{\partial N}\right)_{p,T} = \mu$

$\Rightarrow \Delta\mu^{(0)} = \Delta h^{(0)} - T\Delta s^{(0)}$

Both are positive and independent of T

At low T, $\rho_c = 0$; At high T, $\rho_c = \bar{P}$

How broad is this crossover?

$\beta\Delta\mu^{(0)}$ of order 1.

ρ_c

$\bar{P}$

$\dfrac{\bar{P}}{1+0.002}$

$\dfrac{\bar{P}}{40'}$

O

ΔT

T_0

T

400 are in C while 1 is in B

400 are in B while 1 is in C

Say between $e^{\beta\Delta\mu^{(0)}} = e^{-6} \approx 0.002$
$+ e^{\beta\Delta\mu^{(0)}} = e^{6} \approx 400$

What T causes $\Delta\mu^{(0)}$ to vanish? T_o

At $T = T_o$, $\rho_c = \dfrac{\bar{P}}{2}$, $e^{\beta\Delta\mu^{(0)}} = 1, \Delta\mu^{(0)} = 0$

$$\Delta\mu^{(0)} = \Delta h^{(0)} - T\Delta s^{(0)}$$

$\therefore \Delta\mu^{(0)} = 0$ at $T_o = \dfrac{\Delta h^{(0)}}{\Delta s^{(0)}}$

Let's consider the behavior at $T = T_o + \Delta T$
(near T_o when ΔT is small)

$$\beta\Delta\mu^{(0)} = \frac{1}{k_B T}\left(\Delta h^{(0)} - T\Delta s^{(0)}\right)$$

$$= \frac{1}{k_B(T_o + \Delta T)}\left(\Delta h^{(0)} - (T_o + \Delta T)\Delta s^{(0)}\right)$$

$$\approx -\frac{\Delta T \Delta s^{(0)}}{k_B T_o} + \mathcal{O}(\Delta T^2) \approx -\frac{\Delta h^{(0)}}{k_B T_o}\frac{\Delta T}{T_o}$$
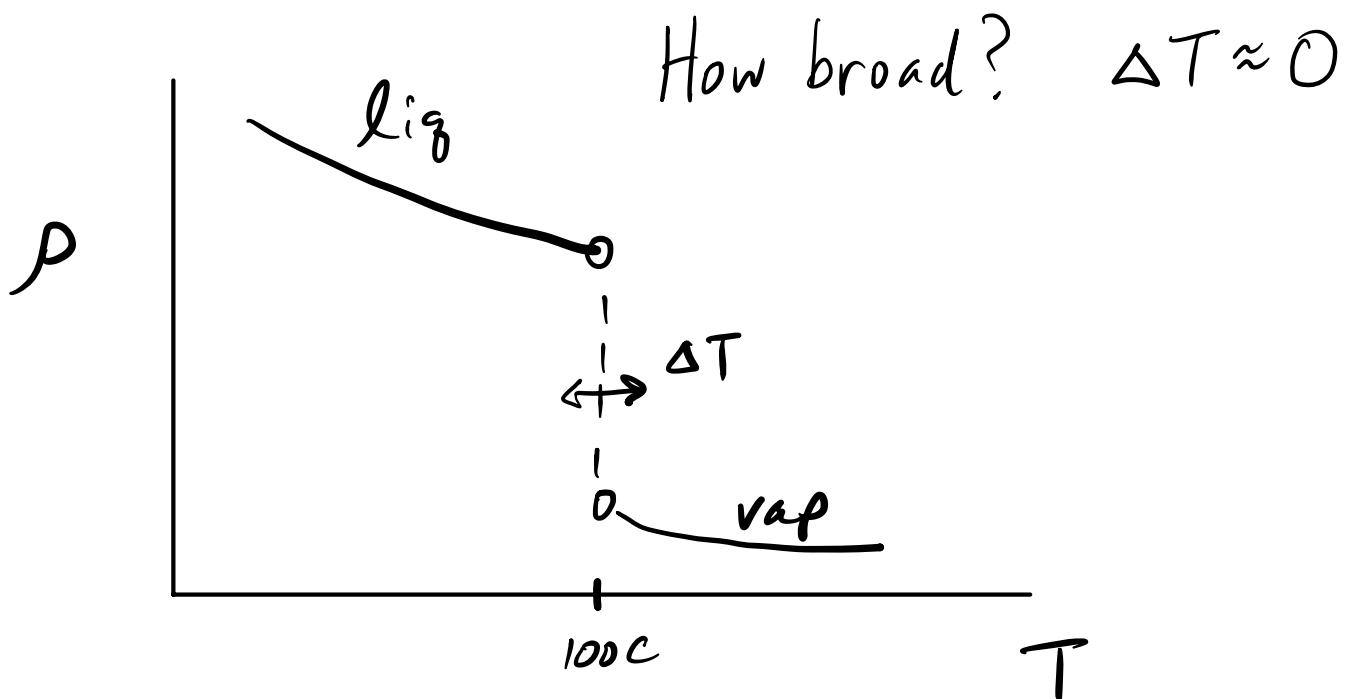
$\beta \Delta \mu^{(o)}$ spans ± 6 when $\frac{\Delta T}{T_0}$ spans $\pm 6 \frac{k_B T_0}{\Delta h^{(o)}}$

If the crossover is near room temperature (300K) and the reaction is very endothermic $(\Delta h^{(o)} = 600 k_B T_0)$

$\Rightarrow \quad \frac{\Delta T}{T_0}$ spans ± 0.01

$\Rightarrow \quad \Delta T \approx$ a few degrees C.

By contrast, for a liquid-vapor transition at fixed p,

How broad? $\Delta T \approx 0$

"Non-analytic" behavior defines a phase transition. What's so special about this?

$$P_{liq} = \frac{Q_{liq}}{Q}, \quad \text{where} \quad Q_{liq} = \int_{liq} dr^N \underbrace{e^{-\beta u(r^N)}}$$

↑ Smooth function at finite T

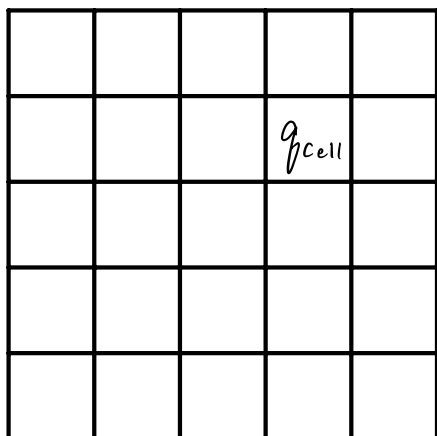Q_{liq} and Q are sums of smooth functions (of T)

⇒ They cannot be non-analytic!

What gives?

Strict phase transitions are only possible when $N \to \infty$ (thermodynamic limit)

We have employed lattice models...

We can divide a macroscopic system into many (M) uncorrelated subsystems.

Let q_{cell} = partition function for all fluctuations in a given cell (a smooth function of T)

$$\Rightarrow Q = q_{cell}{}^{M}$$

$$\Rightarrow -\beta A = \ln Q = M \ln q_{cell}$$

$$\Rightarrow \frac{A}{M},$$ the free energy per site is also smooth

$$\Rightarrow \text{No phase transitions}$$

Therefore, phase transitions must involve fluctuations which are <u>correlated</u> over <u>macroscopic</u> distances.

This motivates our exploration in the next lecture of the Ising model.