Lecture 15

Recall from last lectures...

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

[Problem Set 4 #3 from a lattice model]

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

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

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

↑ Ideal gas law

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

$$\Rightarrow \mu = k_B T \ln \frac{p_o \beta \lambda(T)^3}{q_{\text{int}}(T)} + k_B T \ln \frac{p}{p_o}$$

(our lattice model result but now with $\mu^{(o)}$ 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

$$bB \rightleftharpoons cC$$

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:

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

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

$$= TdS - pdV + \mu_B dN_B + \mu_C dN_C - TdS - SdT + pdV + Vdp$$

$$= -SdT + Vdp + \mu_B dN_B + \mu_C dN_C$$

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

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

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

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

Crossovers (as a function of T)

$$B \rightleftharpoons C$$

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

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

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

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

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

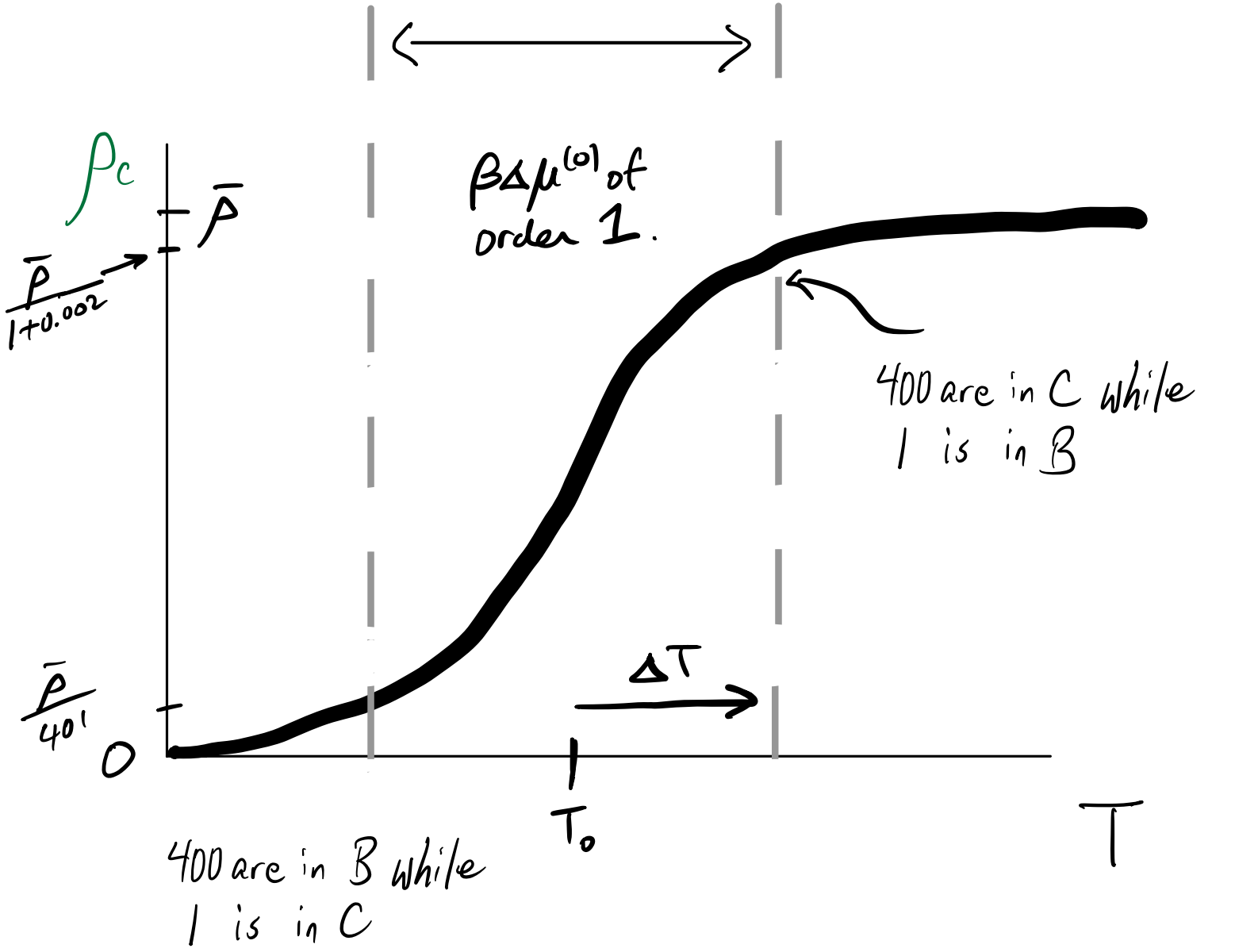
And $dG = -SdT + Vdp + \mu dN \Rightarrow \left(\frac{\partial G}{\partial N}\right)_{p,T} = \mu$

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

Both are positive and independent of T

At low T, $\rho_c = 0$; At high T, $\rho_c = \frac{\bar{\rho}}{1+e^{-\Delta s^{(0)}/k_B}}$

How broad is this crossover?



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

What T causes $\Delta\mu^{(0)}$ to vanish? T_0

At $T = T_0$, $\rho_c = \frac{\bar{\rho}}{2}$, $e^{\beta\Delta\mu^{(0)}} = 1$, $\Delta\mu^{(0)} = 0$

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

$$\therefore \Delta\mu^{(0)} = 0 \quad \text{at} \quad T_0 = \frac{\Delta h^{(0)}}{\Delta s^{(0)}}$$

Let's consider the behavior at $T = T_0 + \Delta T$
(near T_0 when ΔT is small)

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

$$= \frac{1}{k_B(T_0+\Delta T)}\left(\Delta h^{(0)} - (T_0+\Delta T)\Delta s^{(0)}\right)$$

$$\approx -\frac{\Delta T \Delta s^{(0)}}{k_B T_0} + \mathcal{O}(\Delta T^2) \approx -\frac{\Delta h^{(0)}}{k_B T_0}\frac{\Delta T}{T_0}$$

$\beta \Delta\mu^{(0)}$ spans ± 6 when $\frac{\Delta T}{T_0}$ spans $\pm 6 \frac{k_B T_0}{\Delta h^{(0)}}$

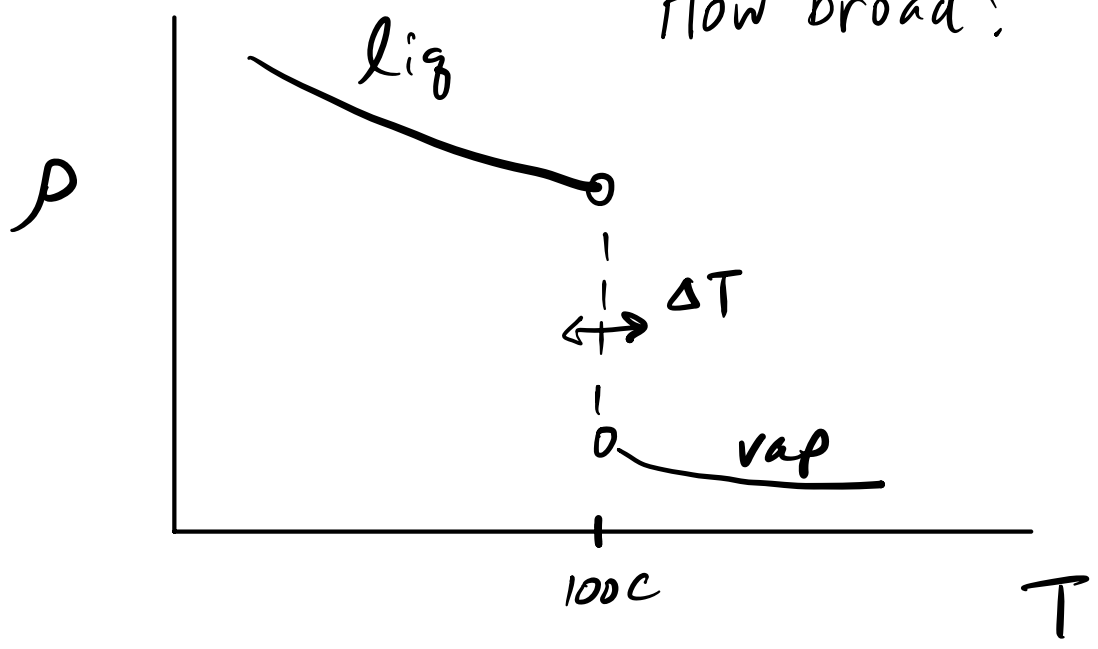
If the crossover is near room temperature (300K) and the reaction is very endothermic ($\Delta h^{(0)} = 600 k_B T_0$)

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

$\Rightarrow$ $\Delta T \approx$ 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

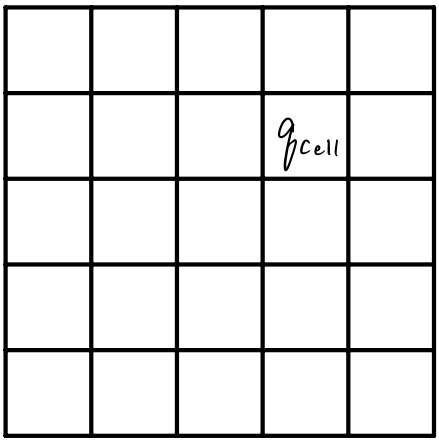
Q_{liq} and Q are sums of smooth functions (of T)

$\Rightarrow$ 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

$\Rightarrow$ 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.