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]

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

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

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

$$\uparrow$$
Ideal gas law

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

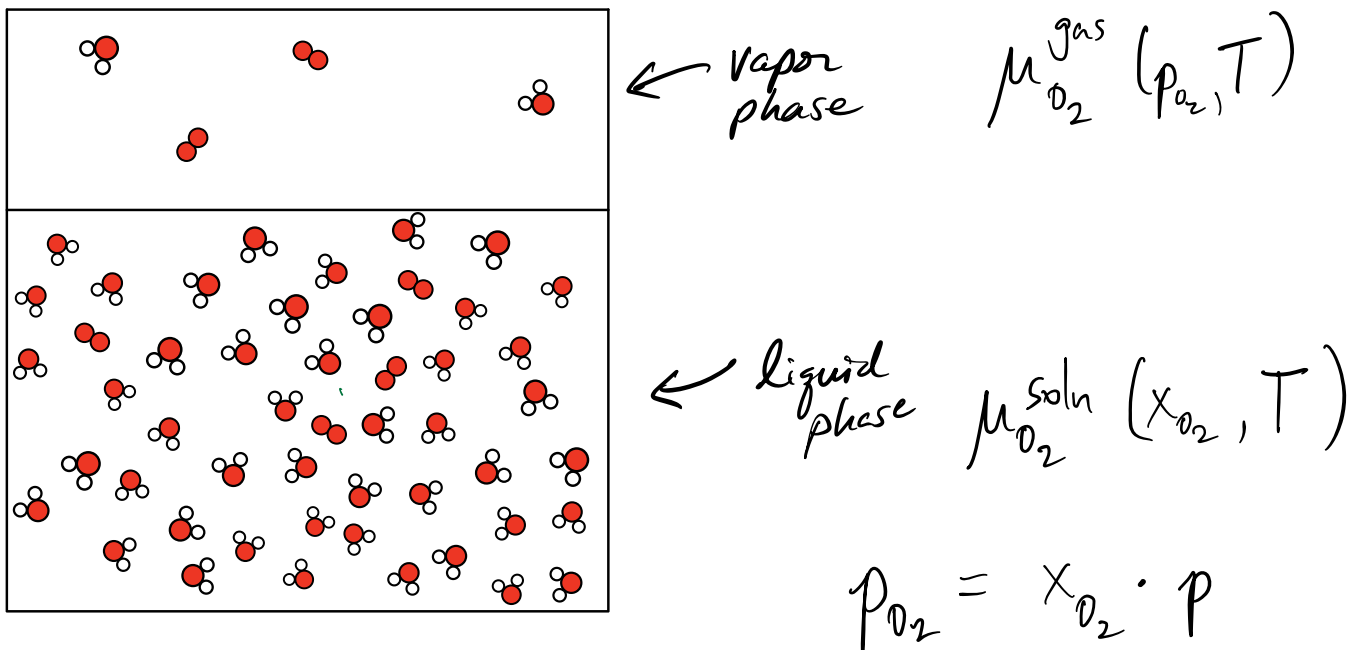$$\Rightarrow \mu = k_B T \ln \frac{p_0 \beta \lambda(T)^3}{q_{\text{int}}(T)} + k_B T \ln \frac{p}{p_0}$$

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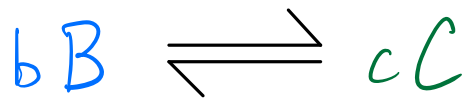
Decorrelated fluctuations are the essence of ideal systems (ideal gases, ideal solutions, etc.)

Consequences of the ideal form of μ...

① Partitioning between phases - Raolt's Law

vapor phase $\mu_{O_2}^{gas}(p_{O_2}, T)$

liquid phase $\mu_{O_2}^{soln}(x_{O_2}, T)$

$$p_{O_2} = x_{O_2} \cdot P$$

② 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?

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

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

$$\Rightarrow \qquad b\mu_B = c\mu_C$$

Which, for an ideal solution implies

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

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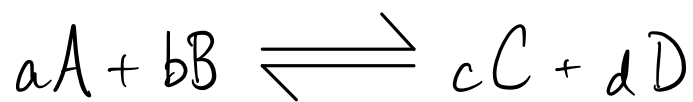
$$\Rightarrow \frac{\rho_C^c V_0^c}{\rho_B^b V_0^b} = e^{-\beta\Delta\mu_{rxn}^{(0)}}$$

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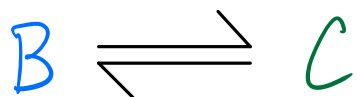
Law of mass action

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

We have the same story for

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

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

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

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

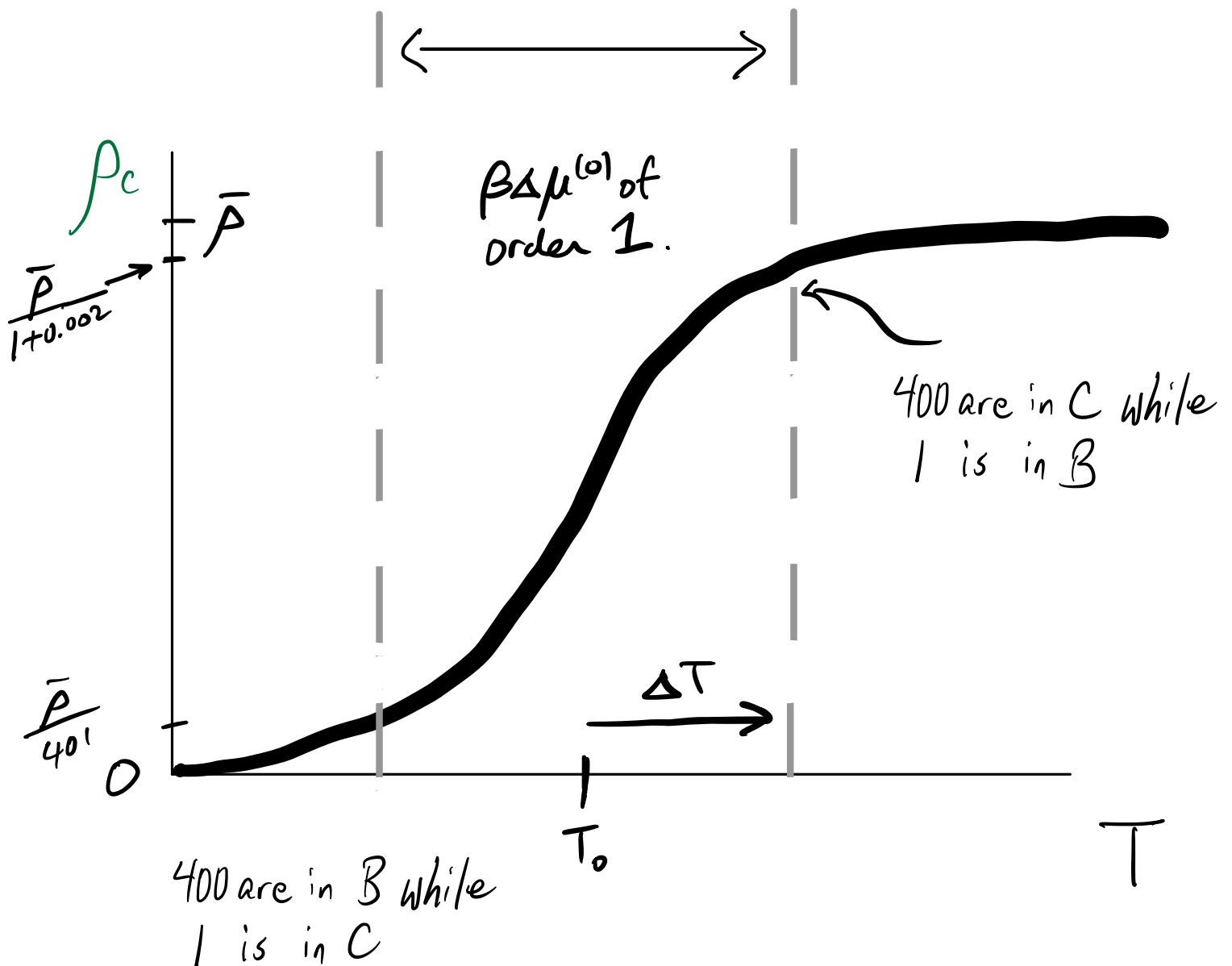$$\rho_C = \rho_C \frac{\bar{\rho}}{\rho_B + \rho_C} = \frac{\bar{\rho}}{1 + e^{\beta \Delta \mu^{(0)}}}$$

$(\Delta\mu^{(0)} > 0)$

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

$\bar{P}$

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

$\frac{\bar{P}}{40!}$

O

400 are in C while 1 is in B

ΔT

T_0

400 are in B while 1 is in C

T

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

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

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

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

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

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

lowercase indicates
per particle/rxn

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

Both are positive and independent of T

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

Let's consider the behavior at $T = T_0 + \Delta T$

(near T_0 when ΔT is small)

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

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

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

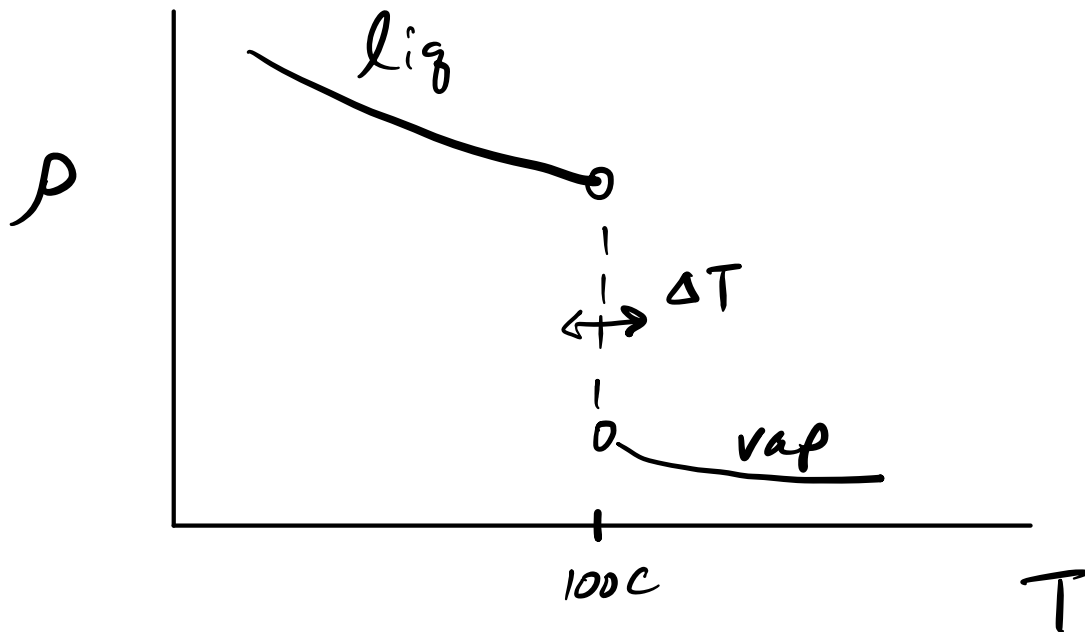$$\approx -\frac{\Delta h^{(0)}}{k_B T_0} \frac{\Delta T}{T_0}$$

$\beta\Delta\mu^{(0)}$ 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 $(\Delta h^{(0)} = 600 k_B T_0)$

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

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

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

How broad? $\quad \Delta T \approx 0$

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

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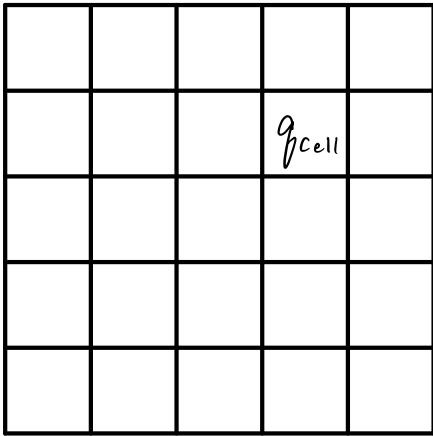
↑

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)

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

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

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

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

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.