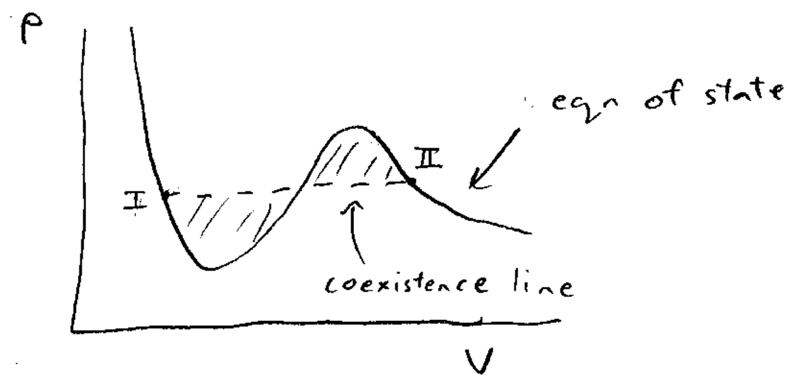
# Lecture 8

Still discussing phase transitions

Last time, described Maxwell construction

For liquid-gas transition




Argued that transition point set by $G(\mathrm{I}) = G(\mathrm{II}) \Rightarrow \int_{\mathrm{I}}^{\mathrm{II}} V\,dP = 0$

$\Rightarrow$ equal areas

- This is probably easier to see than I made it last time

Know that need $\mu_{\mathrm{I}} = \mu_{\mathrm{II}}$ for coexistence

and $G = \mu N$

so $G_{\mathrm{I}} = \mu_{\mathrm{I}} N = G_{\mathrm{II}} = \mu_{\mathrm{II}} N$

$G$ will be the same for any state on coexistence line

Today look at a different example of similar phenomenon: binary solution

Consider container, fixed $P, T$
two types of particles $A$ + $B$

If particles don't interact, they will mix

Recall from entropy of mixing, got

$$G = N_A \mu_A^o + N_B \mu_B^o + kT N_A \ln x_A + kT N_B \ln x_B$$

where $\mu_A^o$ = chem potential of $A$ in absence of mixing

$\mu_B^o$ = " $B$

$$x_A = \frac{N_A}{N} = \frac{N_A}{N_A + N_B}, \quad \text{sim for } B$$

With two species, have two chemical potentials

$$\mu_A = \frac{\partial G}{\partial N_A} \qquad \mu_B = \frac{\partial G}{\partial N_B}$$

also $\quad G = N_A \mu_A + N_B \mu_B$

Convenient to work with $\quad g = \frac{G}{N} = \frac{\text{Gibbs energy}}{\text{particle}}$

$$g = x_A \mu_A^o + x_B \mu_B^o + kT \left( x_A \ln x_A + x_B \ln x_B \right)$$

$$\mu_A = \frac{\partial g}{\partial x_A} \qquad \mu_B = \frac{\partial g}{\partial x_B}$$

Now, suppose $A$ + $B$ interact

Get additional energy $E_{int} = \lambda \frac{N_A N_B}{N}$

Adds to $G$, so

$$g \to x_A \mu_A^o + x_B \mu_B^o + kT(x_A \ln x_A + x_B \ln x_B) + \lambda x_A x_B$$

Assume $\lambda > 0$ : repulsive interaction

For small $\lambda$, not much effect

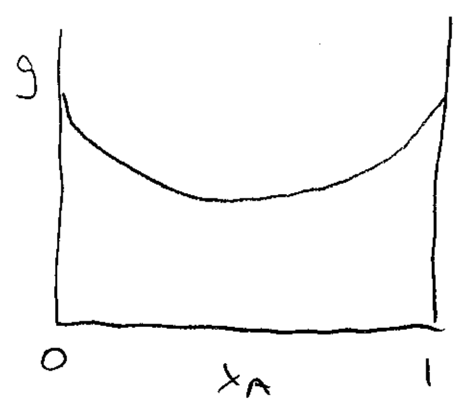
Large $\lambda$, expect species to separate
(like oil & water)

In fact, for any $\lambda > 0$, get phase transition at some $T$

See by plotting $g$ vs $x_A = 1 - x_B$

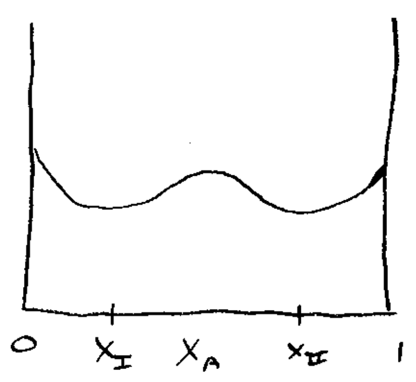
For simplicity, take $\mu_A^o = \mu_B^o$
(symmetric mixture)

High T:




Min at $x_A = x_B = \frac{1}{2}$
homogenous mixture

Low T:




Two minima, $x_I$ & $x_{II}$

$\Rightarrow$ Two phases,
one rich in A
other rich in B

Critical point where this occurs:

$$\left.\frac{\partial^2 g}{\partial x_A^2}\right|_{x_A=\frac{1}{2}} \to 0$$

Write $x$ for $x_A = 1 - x_B$

$$g(x) = x\mu_A^0 + (1-x)\mu_B^0 + kTx\ln x + kT(1-x)\ln(1-x) + \lambda x(1-x)$$

$$\frac{\partial g}{\partial x} = \underbrace{\mu_A^0 - \mu_B^0}_{=0 \text{ here, but doesn't matter}} + kT(\ln x + 1) + kT[-\ln(1-x) - 1] + \lambda - 2\lambda x$$

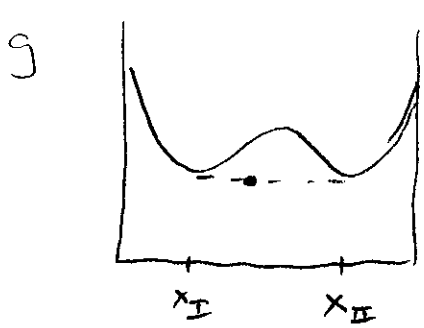
$$\frac{\partial^2 g}{\partial x^2} = kT\frac{1}{x} + kT\frac{1}{1-x} - 2\lambda = 0$$

At $x = \frac{1}{2}$: $2kT + 2kT = 2\lambda$

$$\boxed{T_c = \frac{\lambda}{2k}}$$

So for $T < T_c$, get seperation into components I, II

If $x_I < x < x_{II}$, equilibrium will be mixture of two phases




Here Maxwell construction = line tangent at $x_I$ + $x_{II}$

Free energy of mixture lies on line

$\Rightarrow$ less that free energy of homogenous system

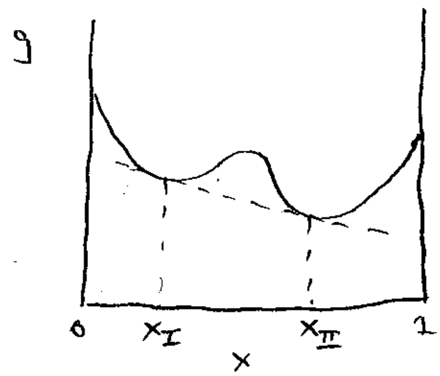
Here can get $x_I$ & $x_{II}$ by setting $\frac{\partial g}{\partial x} = 0$

$$\Rightarrow \quad kT \ln \frac{x}{1-x} = 2\lambda x$$

Solve numerically

But if $N_A \neq N_B$ or $\mu_A^0 \neq \mu_B^0$, more complicated

Looks like




Maxwell construction still works: find line tangent to curve at two points

Points where line intersects curve = $x_I$ & $x_{II}$

Ensures lowest possible free energy for mixture

You get to explore this further in homework

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Last topic for phase transitions:

Ginzburg-Landau theory

= "generic" theory for 2nd order phase transitions

Idea: phase transition reduces symmetry of system

- Liquid → solid: translation symmetry
- Ferromagnet: rotation symmetry
- BEC: gauge symmetry
- Liquid → gas: translation (due to inhomogeneity)

Can quantify symmetry with <u>order parameter</u>

- Liquid - solid: density correlation
- Ferromagnet: $\vec{M}$
- BEC: $\psi$
- Liquid - gas: $V_g - V_L$

Order parameter = zero above transition
$\neq$ zero below

Can often express order parameter as vector
Write as $\vec{M}$, thinking about magnet transition

Expect free energy minimized by $\vec{M}=0$ above
transition, $\vec{M}=0$ below

In 2nd order transition, $\vec{M}$ changes continuously
$\Rightarrow |\vec{M}|$ small near transition

$\Rightarrow$ Taylor expand in $|\vec{M}|$

Write Gibbs energy $G = G(T, \vec{M})$

$$\to G_0(T) + \alpha_2(T)\,|M|^2 + \alpha_4(T)\,|M|^4$$

No odd powers of $\vec{M}$, since $G$ should be independent of direction of $\vec{M}$

(overall symmetry of system)

Now, need $\alpha_2(T) < 0$ for $T > T_c$ (min at $\vec{M}=0$)

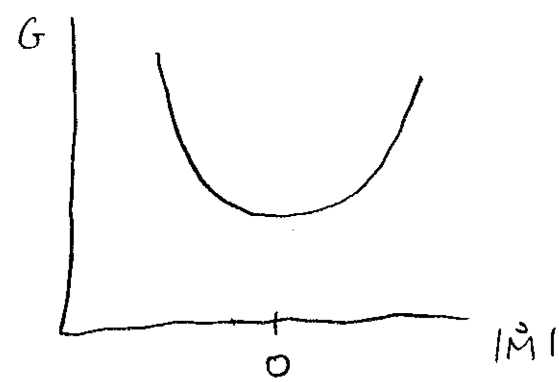
$> 0$ for $T < T_c$ (max at $\vec{M}=0$)

So write $\alpha_2(T) = a(T)(T-T_c)$

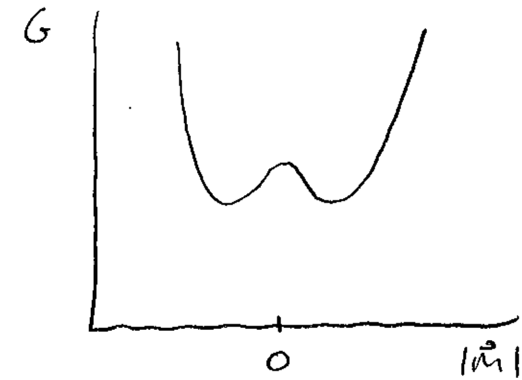
For system to be stable at $T<T_c$, need $\alpha_4(T) > 0$

So looks like:

$T > T_c$:




$T < T_c$:




Note, $\vec{M}$ a vector, so really get sphere of min $G$ when $T<T_c$

System picks direction of $\vec{M}$ spontaneously
"spontaneous symmetry breaking"

For $T<T_c$, get $|\vec{M}|$ from $\dfrac{\partial G}{\partial M} = 0$

$$= 2\alpha_2 |\vec{M}| + 4\alpha_4 |\vec{M}|^3 = 0$$

$$\boxed{|\vec{M}| = \sqrt{\frac{-\alpha_2}{2\alpha_4}} = \sqrt{\frac{a(T_c-T)}{2\alpha_4}}}$$

Shows how order parameter depends on T

Can also get heat capacity

$$C = -T\left(\frac{\partial^2 G}{\partial T^2}\right)$$

For $T > T_c$, $\vec{M} = 0$ and $C = -T\left(\frac{\partial^2 G_0}{\partial T^2}\right)$

For $T < T_c$,

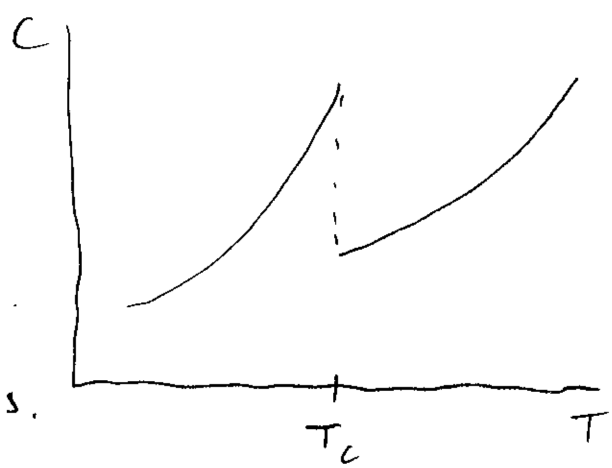
$$\begin{aligned} G &\simeq G_0 + a(T-T_c)M^2 + \alpha_4 M^4 \\ &\simeq G_0 + a(T-T_c)\frac{a(T_c-T)}{2\alpha_4} + \alpha_4 \frac{a^2(T_c-T)^2}{4\alpha_4^2} \\ &= G_0 - \frac{a^2}{4\alpha_4}(T-T_c)^2 \end{aligned}$$

So $C = -T\left[\frac{\partial^2 G_0}{\partial T^2} - \frac{a^2}{2\alpha_4}\right]$

See that C is discontinuous:

$$C(T_c-) - C(T_c+) = T_c \frac{a^2}{2\alpha_4}$$

Looks like:




Call "$\lambda$-point"

Observed in most 2nd order transitions.