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Phase Transitions

Interacting particles often lead to novel equil structure as parameters are varied:

T, P, conc, B, E, etc.

liquid → periodic crystal
liquid → glass
iron → spin-ordered ferromagnet or antiferromagnet
liquid xtal → nematic phase
He^4 → superfluid
metal → superconductor

Changes of one equil structure to another as parameter is varied called a "phase transition" between different phases. Some property, often called an "order parameter" must change from one phase to other, to distinguish the phases

sharpness of spots in X-ray diffraction
magnetization for ferromagnet
change in density (solid → liquid, liquid → gas)
superfluid order parameter is subtle, some complex #

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In big picture, physics deals with fundamental structure (particle physics, string theory) or how structure arises from known pieces (condensed matter physics, fluid dynamics, plasma physics, astrophysics, cosmology).

Most physicists work on emergent structure, few on fundamentals, one reason why thermal physics so important.

Show some slides:

water phase diagram — boiling water with ice

↳ but remember you can't boil water with boiling water

CO_2 phase diagram

steel-iron phase diagram

Terminology ...

Gibbs Free Energy Key To Understanding Phase Diagrams via Thermodynamics

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$$G = G(T, P, N) = U - TS + PV$$

$$dG = -S\,dT + V\,dP + \mu\,dN$$

Which ever phase has lower $\mu = \frac{G}{N}$, that is the stable phase that will be experimentally observed. Hard to calculate $\mu(T,P)$ for each phase from 1st principles because of interactions, often easier to use some exp't'l data and simple trends.

Two phases coexist when chemical potentials are equal:

$$\mu_1(T,P) = \mu_2(T,P) \quad \text{defines phase curve}$$

Three phases can only exist at an isolated point on the P–T plane

$$\mu_1(T,P) = \mu_2(T,P) = \mu_3(T,P) \Rightarrow \text{triple point}$$

Two identities give quick insight

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \qquad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$

slope of G vs T gives S

slope of G vs P gives V

$$\mu = \frac{G}{N}$$

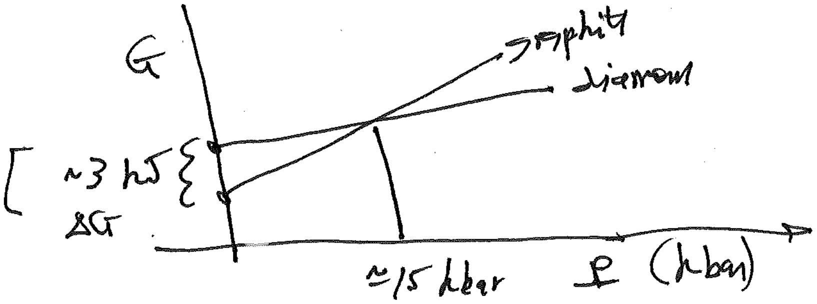
Example from Schroeder:

graphite ⟷ diamond conversion with increasing pressure

$V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$ expt tells us $V_{graphite} > V_{diamond}$ one mole diamond denser

$\Rightarrow \left(\frac{dG}{dP}\right)_{graphite} > \left(\frac{dG}{dP}\right)_{diam}$

$V_{graphite} \simeq 5.3\,cm^3$
$V_{diamond} = 3.4\,cm^3$

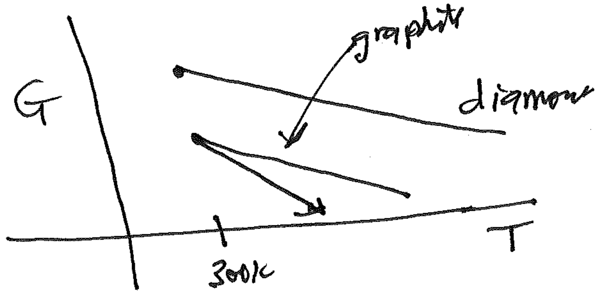


from Schroeder table
T=300K
P=1 bar

Explains why diamonds form ~ 50 km underground, 50 km reach ≅ 15 kbar

Similarly, $S = -\left(\frac{\partial G}{\partial T}\right)_{P,N}$ $S_{graphite} \simeq 5.7$ J/K
$S_{diam} \simeq 2.4$ J/K
p. 404-405 Schroeder

so $\left|\frac{\partial G}{\partial T}\right|_{graphite} > \left|\frac{\partial G}{\partial T}\right|_{diamond}$



increasing temperature for fixed pressure makes graphite more stable, won't create diamonds

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Clausius-Clapeyron eq. for phase boundaries.

$$\mu_1(T,P) = \mu_2(T,P)$$

This forces $P = P(T)$, so can diff. w.r.t T on both sides to get

$$\frac{\partial\mu_1}{\partial T} + \frac{\partial\mu_1}{\partial P}\frac{\partial P}{\partial T} = \frac{\partial\mu_2}{\partial T} + \frac{\partial\mu_2}{\partial P}\frac{dP}{dT}$$

But $\frac{\partial\mu_1}{\partial T} = \frac{1}{N}\left(\frac{\partial G}{\partial T}\right)_P \overset{\downarrow}{=} -\frac{S}{N} \overset{\downarrow}{=} -s$ = entropy per particle in phase 1

$\frac{\partial\mu_1}{\partial P} = \frac{1}{N}\left(\frac{\partial G}{\partial P}\right)_T = \frac{V}{N} = v$ = volume per particle in phase 1

so $\mu_1(T,P(T)) = \mu_2(T,P(T)) \Longrightarrow$

$$(-s_1) + v_1\frac{dP}{dT} = (-s_2) + v_2\frac{dP}{dT}$$

or $\boxed{\frac{dP}{dT} = \frac{s_2-s_1}{v_2-v_1}}$ Clausius-Clapeyron eq

$$= \frac{L/N}{T(v_2-v_1)} = \frac{L}{T(V_1-V_2)}$$

Let 2 = gas phase, 1 = liquid phase, $v_2 \gg v_1$ typically

$$v_2 - v_1 \simeq v_2 = \frac{V}{N} = \frac{kT}{P}$$

$$s_2 - s_1 = \frac{S_g - S_l}{N} = \frac{L/T}{N} = \frac{l}{T}$$ l = latent heat per particle

$$\frac{dP}{dT} = \frac{l/T}{kT/P} = \frac{lP}{kT^2}$$

For graphite-diamond system,

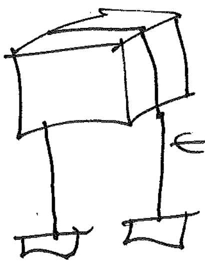
mole of diamond converts to mole graphite, $\Delta S = 3.4 \frac{J}{K}$

$\Delta V = 1.9 \cdot 10^{-6} m^3$

$$\frac{\Delta P}{\Delta T} = \frac{\Delta S}{\Delta V} = \frac{3.4}{1.9 \cdot 10^{-6}} \sim 18 \text{ bar}/K$$ slope of phase line

Can use Clausius-Clapeyron to predict what change in ΔT (or ΔP) is needed for given ΔP (or ΔT) to stay on phase line, e.g.

Can predict when pressure will cause ice to melt.



thin Cu wire

cut ice cube in half without breaking ice cube

Van der Waals model of gas to liquid transition.

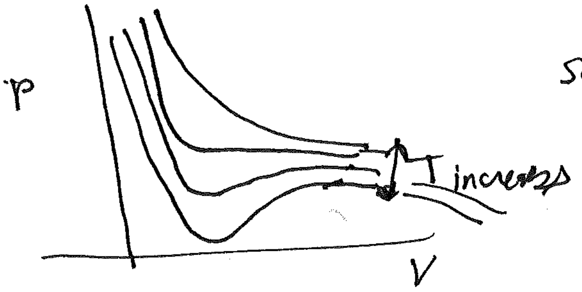
First principle study of phase transition quite hard, but numerous scientists have developed models that clarify main issues:

$a > 0, b > 0$ $$\left[P + a\left(\frac{N}{V}\right)^2\right]\left[V - Nb\right] = NkT$$ van der Waals 1873

assumes <u>homogeneity</u>

$b =$ finite volume of particles
$a =$ attraction between particles

One way to get insight, plot $P = P(V,T)$ for varying fixed T



See slide.

complicated behavior as T decreases. To understand this, let's calculate $G(T,P,N)$ for van der Waals equation

$$dG = -S\,dT + V\,dP + \mu\,dN$$

for fixed N, T, $dG = V\,dP \Rightarrow \left(\frac{\partial G}{\partial V}\right)_{N,T} = V\left(\frac{\partial P}{\partial V}\right)_{N,T}$

Right side known from van der Waals eq

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = -\frac{NkTV}{(V-Nb)^2} + \frac{2a^2N^2}{V^2}$$

Integrate both sides w.r.t. V, get

$$G = -NkT\ln(V-Nb) + \frac{(NkT)(Nb)}{V-Nb} - \frac{2aN^2}{V} + \underbrace{c(T)}_{\text{allowed by integration}}$$

Can plot G vs V for fixed T but more useful to plot

G(V) vs P(V) parametrically for fixed T