Theory 4. Statistical Physics.
Lecture 24.
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Last time: Photon gas, blackbody radiation
Ultraviolet catastrophe
Phonons: Einstein Model, Debye model
Virial expansion, start real gases & van der Waals eqn.

Today: van der Waals eqn.
Gibbs degeneracy & phase coexistence
Classification of phase transitions

Recall that the cumulant expansion is motivated by treating interactions as a series expansion in higher moments around well-defined (and idealized/exact) expectation values.

Can build intuition by studying virial expansion:

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots, \quad \text{or}$$

$$\frac{p}{k_B T} = \frac{N}{V}\left[1 + B_2(T)\frac{N}{V} + B_3(T)\left(\frac{N}{V}\right)^2 + \dots\right]$$

$V_m = \frac{V}{N}$.

[Can think of the expansion as manifestly intensive corrections to ideal gas law.]

Coefficients are temperature-dependent generally.

Using cluster expansion, can find explicit expressions for B_2 & B_3 (Kardar, Chap. 5.2.)

$$B_2 = -\frac{1}{2}\int d^3\vec{q}\left(e^{-\beta V(\vec{q})} - 1\right)$$

$$B_3 = \left[\int d^3\vec{q}\left(e^{-\beta V(\vec{q})} - 1\right)\right]^2$$
$$-\frac{1}{3}\left[3\int d^3\vec{q}_{12}\, d^3\vec{q}_{13}\, f(\vec{q}_{12}) f(\vec{q}_{13}) + \int d^3\vec{q}_{12}\, d^3\vec{q}_{13}\, f(\vec{q}_{12}) f(\vec{q}_{13}) f(\vec{q}_{12} - \vec{q}_{13})\right]$$

where $V(\vec{q})$ gives pairwise interactions of particles and $f(\vec{q}) = \exp(-\beta V(\vec{q})) - 1$.

A particularly well-motivated example of the virial expansion is the van der Waals equation of state for a realistic gas:

$$\left(p + \frac{a}{V_m^2}\right)\left(V_m - b\right) = RT \quad , \quad V_m = \frac{V}{n_{moles}}$$

[Interpretation: "a" is a constant to indicate intermolecular attraction
"b" is a constant that reflects the finite volume of molecular sizes.

We will not derive van der Waals equation (see Kardar, Chap. 5.3), but we can identify it as a virial expansion:

Use $V \to V_m$

$$p = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{RT}{V}\left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V^2}$$

$$\frac{pV}{RT} \doteq 1 + \frac{b}{V} - \frac{a}{RTV} + \frac{b^2}{V^2} + \frac{b^3}{V^3} + \ldots$$

So, van der Waals sets $B \equiv b - \frac{a}{RT}$
and $C \equiv b^2$.

How is the van der Waals equation of state different from ideal gas law?

First, recall that in (P, V) diagram, the ideal gas law has $P \propto \frac{1}{V}$, but here, as isotherms, the isotherms have a more interesting structure.

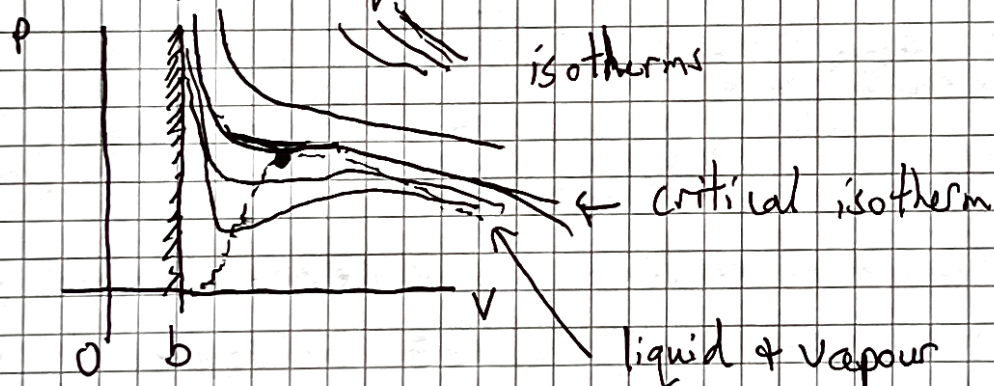
Use 1 mol. $\left(P + \frac{a}{V^2}\right)(V - b) = RT$

$$(PV^2 + a)(V - b) = RTV^2$$

$$PV^3 + aV - bPV^2 - ab = RTV^2$$

$$\Rightarrow PV^3 - (Pb + RT)V^2 + aV - ab = 0$$

Cubic in V.



How to analyze: keep T fixed, & consider which terms in cubic dominate for large or small T.

Crucially, at low enough T, the full cubic dependence of P on V is manifest.

We thus have $K_T \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ = isothermal compressibility where the $\left(\frac{\partial V}{\partial P}\right)_T$ goes positive and K_T is positive.

In practice, $\kappa_T > 0$ means that compressing the gas makes it bigger; negative work (even spontaneous) leads to energy available to amplify the fluctuation & an unstable system.

This denotes a critical isotherm:

$$\left(\frac{\partial p}{\partial V}\right)_T = 0 \quad \text{and} \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_T = 0$$

(See HW) Can solve & get $V_c = 3b$, $T_c = \frac{8a}{27Rb}$,

$p_c = \frac{a}{27b^2}$, $\frac{p_c V_c}{R T_c} = \frac{3}{8}$ for critical values.

(Analogy; roll a ball off a ski slope: if the transverse directions are negative gradient, it falls off the slope.)

More generally, we can explain the behavior of the system below the critical T_c by analyzing the Gibbs function (work done on system + heat): for T

We have $p = -\left(\frac{\partial F}{\partial V}\right)_T$ for F = Helmholtz fcn.

Recall $p = \frac{RT}{V-b} - \frac{a}{V^2}$ so $F = f(T) - RT \ln(V-b) - \frac{a}{V}$

then $G = F + pV = f(T) - RT \ln(V-b) - \frac{a}{V} + pV$.

Fix $T = 0.9 T_c$

Isobars.

At high p, the minimum favors small V + is stable.

At low p, the minimum favors large V and is stable.

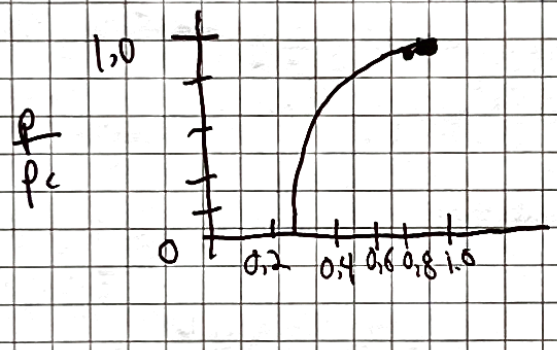
Transition from high to low ρ exhibits Gibbs degeneracy/ for some intermediate ρ. multivalued

As a result, for critical ρ_c, system is in coexistence of liquid & gas.

For $\rho > \rho_c$, system favors liquid state by ~~many~~ the ~~liquid~~ gas phase is still metastable.

Also, for $\rho < \rho_c$, the system favors gas state but may still be in liquid phase for a macroscopic time, again metastable.

Aside: (p, T) diagram for van der Waals gas.



See Fig. 26.6 of Blundell & Blundell.

Thus, in general, the analysis of free energy (Gibbs) can be used to understand the phase diagram of materials. In particular, ~~Ehrenfest~~ Ehrenfest classification & modern classification

First-order phase transition:

A first differential of G is discontinuous at T_c. (like entropy, volume)

and thus second differentials have spikes. (like heat capacity, compressibility).

This should be familiar from basic heat mechanics + study of latent heat.

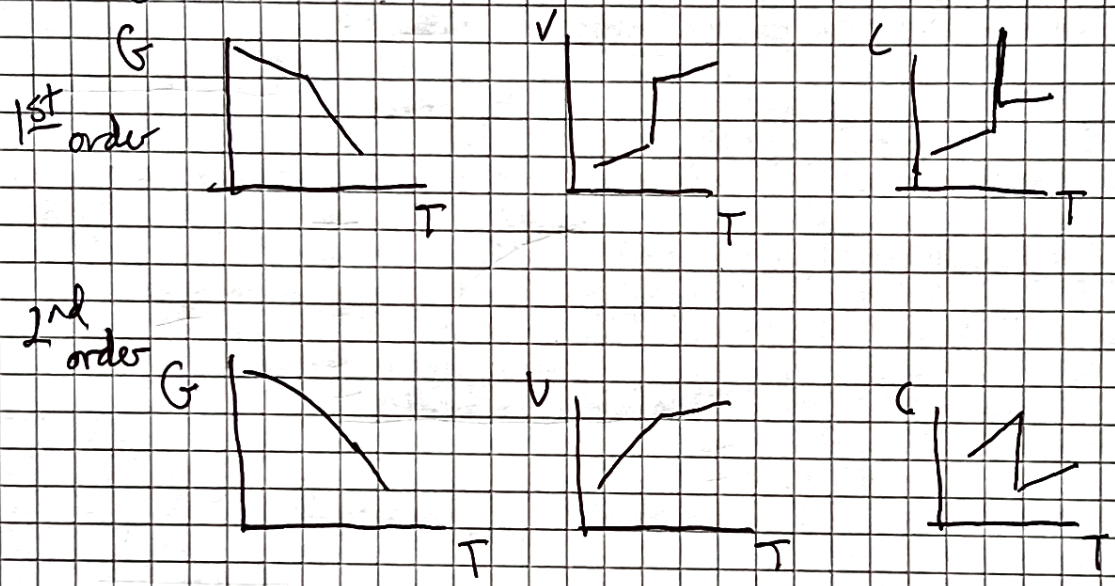
Ex: solid-liquid, solid-vapour, liquid-vapour.

Second-order phase transition:

The first differential is not discontinuous, but second diff. is. at T_c.

Ex: superconducting transition.

Cartoons:



Crucially, the behavior of materials near critical points falls into universality classes based on the strength of the phase transition. Intuitively, this is because the infinitesimal behavior near a critical point is still intensive across all scale dimensions, and so the scale of the system microscopically or macroscopically behaves the same. [See HW.] This is the essence of critical phenomena.

cf. Law of corresponding states