Phase Transitions, Part 3

Last time

Computer simulations

Ising model of magnetism

Today

Mean-field theory

Real gases and liquids

Next time

Thermodynamics of phase transitions

Chemical potential

Phase diagrams

So far…

Phase transitions:

- Are sharp changes in a macroscopic parameter
- Require intermolecular interactions
- Occur in the thermodynamic limit (otherwise, the partition function is continuous)

Interacting systems are difficult to study:

- Configuration space is enormous and exact solutions usually impossible
- Computer simulations (e.g., importance-sampling Monte Carlo) can help
- Still, it can be hard to extract intuitive explanations from simulations

Today

Today: mean-field theory, an *approximate* way of including interactions

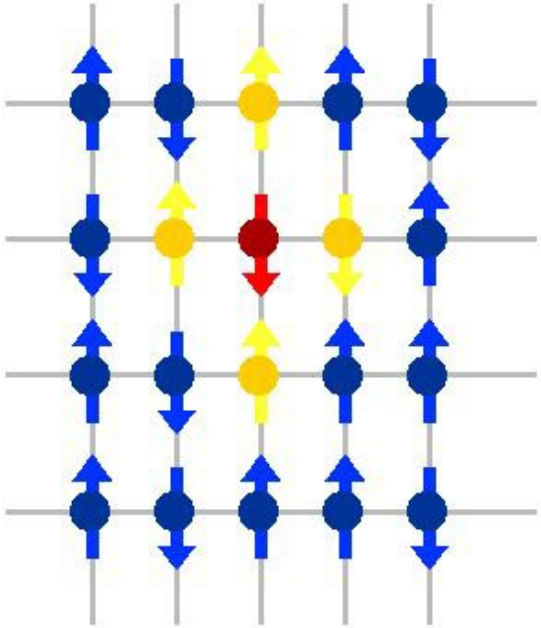
- The approximation is sometimes crude, but it can give important qualitative insight
- In particular, mean-field theory will allow us to predict phase transitions

We'll look at two systems:

- Ising model of the ferromagnetic-paramagnetic transition
- van der Waals model of the real gas, and the gas-liquid transition

Recap: Ising model of magnetism

- Lattice of spins, each pointing up or down ($\sigma = \pm 1$)
- Interactions only with nearest neighbours



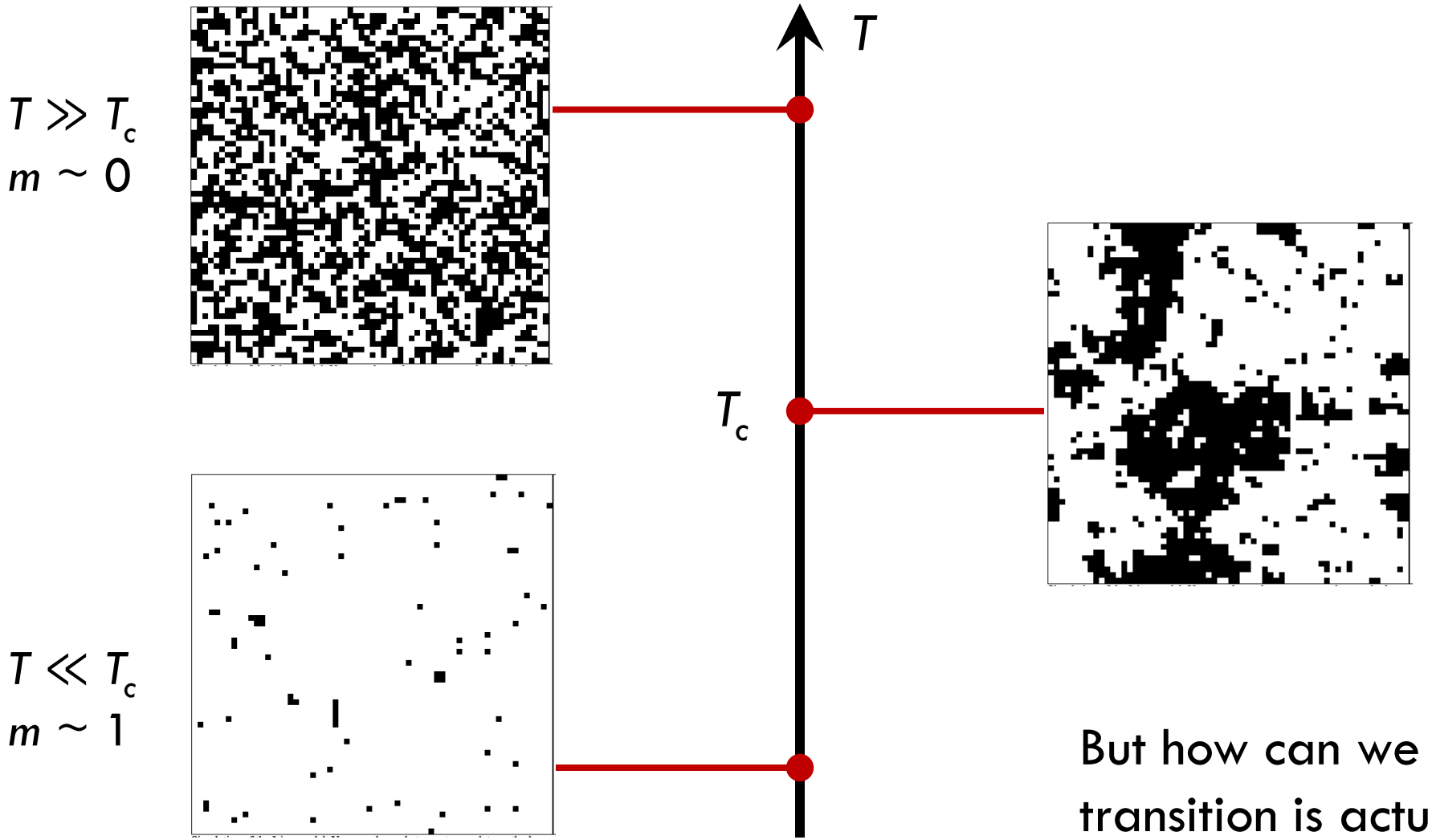
Total energy: $$E = -B\sum_i \sigma_i - J\sum_{\langle ij \rangle} \sigma_i \sigma_j$$

B: Applied magnetic field

J: Interaction between nearest-neighbour spins (denoted $\langle ij \rangle$)

The most important thing is the net magnetisation: $$m = \sum_i \sigma_i$$

Ising model: Phase behaviour

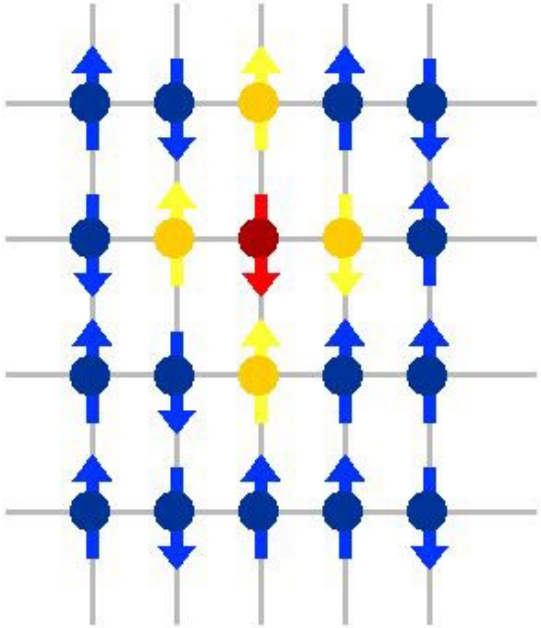


But how can we be sure the transition is actually sharp?

Non-interacting Ising model

We start with the easier, *non-interacting* Ising model:

$$E = -B \sum_i \sigma_i$$



Because there are no interactions, we can treat each spin separately.

$$q = e^{\beta B} + e^{-\beta B}$$

$$p_\uparrow = \frac{e^{\beta B}}{e^{\beta B} + e^{-\beta B}}$$

$$p_\downarrow = \frac{e^{-\beta B}}{e^{\beta B} + e^{-\beta B}}$$

Non-interacting Ising model

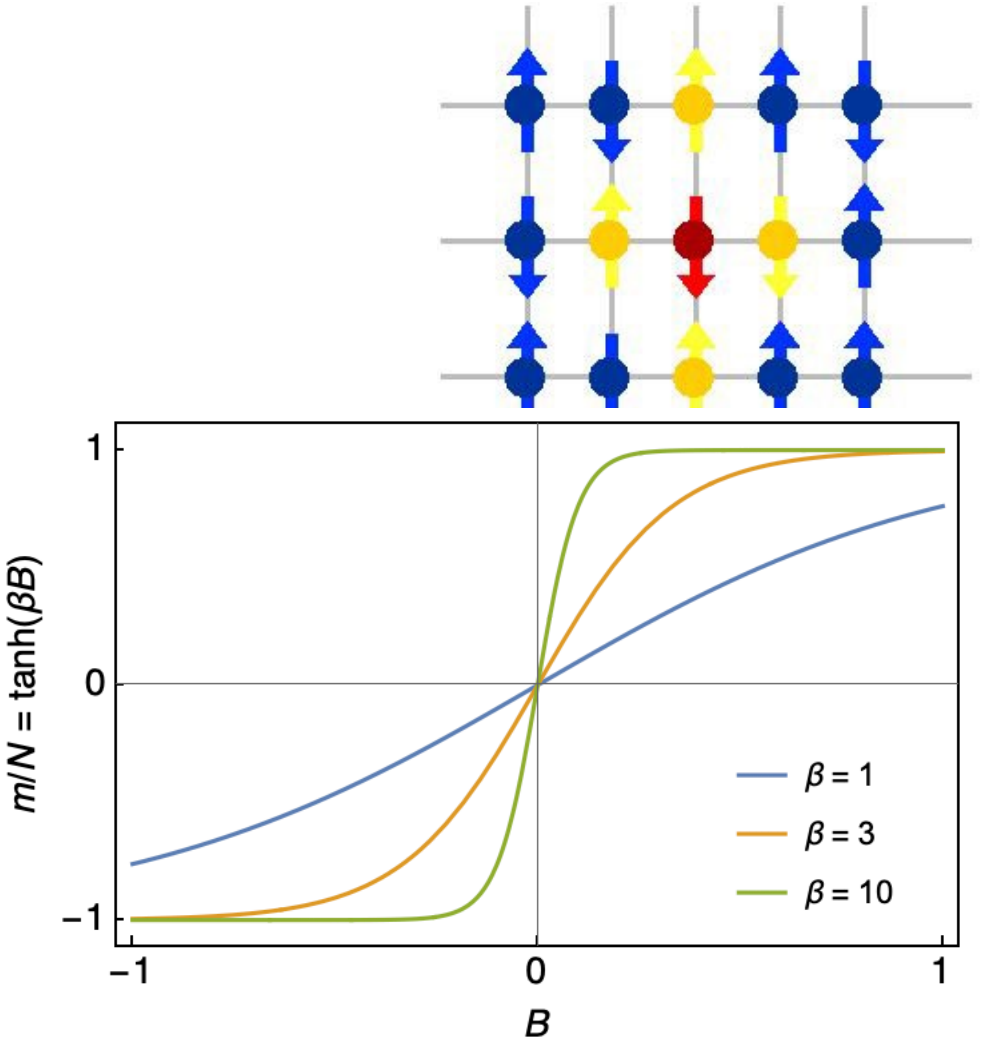
The net magnetisation is then

$$m = \sum_i \sigma_i = N_\uparrow - N_\downarrow$$

$$= N\left(\frac{e^{\beta B}}{e^{\beta B}+e^{-\beta B}} - \frac{e^{-\beta B}}{e^{\beta B}+e^{-\beta B}}\right)$$

$$= N\frac{e^{\beta B}-e^{-\beta B}}{e^{\beta B}+e^{-\beta B}}$$

$$= N\tanh(\beta B)$$



Mean-field Ising model

The idea of mean-field theory is to approximate all the individual interactions a single particle experiences with an **average** interaction

$$E = -B\sum_i \sigma_i - J\sum_{\langle ij\rangle} \sigma_i\sigma_j \quad \longrightarrow \quad E = -B\sum_i \sigma_i - J\sum_i \sigma_i\langle\sigma\rangle d$$

d: number of nearest neighbors of each spin

This now looks like a non-interacting model:

$$E = -(B + J\langle\sigma\rangle d)\sum_i \sigma_i$$

Mean-field Ising model

$$E = -(B + J\langle\sigma\rangle d)\sum_i \sigma_i$$

Specialising to the case of no applied field, $B = 0$, and noting that $\langle\sigma\rangle = m/N$:

$$E = -\frac{Jmd}{N}\sum_i \sigma_i$$

This is the same as the non-interacting model with "field" Jmd/N

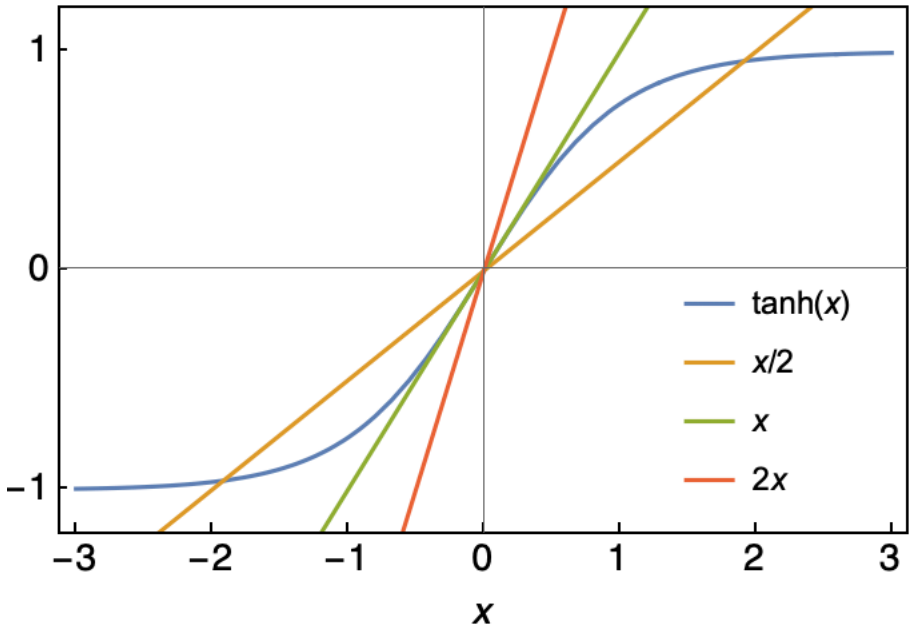
Using the non-interacting result, we get

$$\frac{m}{N} = \tanh\left(\beta J d \frac{m}{N}\right)$$

Mean-field Ising model

$$\frac{m}{N} = \tanh\left(\beta J d \frac{m}{N}\right) \xrightarrow{x = \beta J d m/N} \frac{kT}{Jd} x = \tanh(x)$$

This is a funny equation with x on both sides. Let's solve it graphically:



High T: One solution ($x = 0$, i.e., $m = 0$), unmagnetized phase

Low T: Three solutions! Two non-zero solutions are the magnetic phases (spin-up/spin-down). ($x = 0$ is free-energy maximum)

$T_c = Jd/k$ (corresponding to $m = 1$)

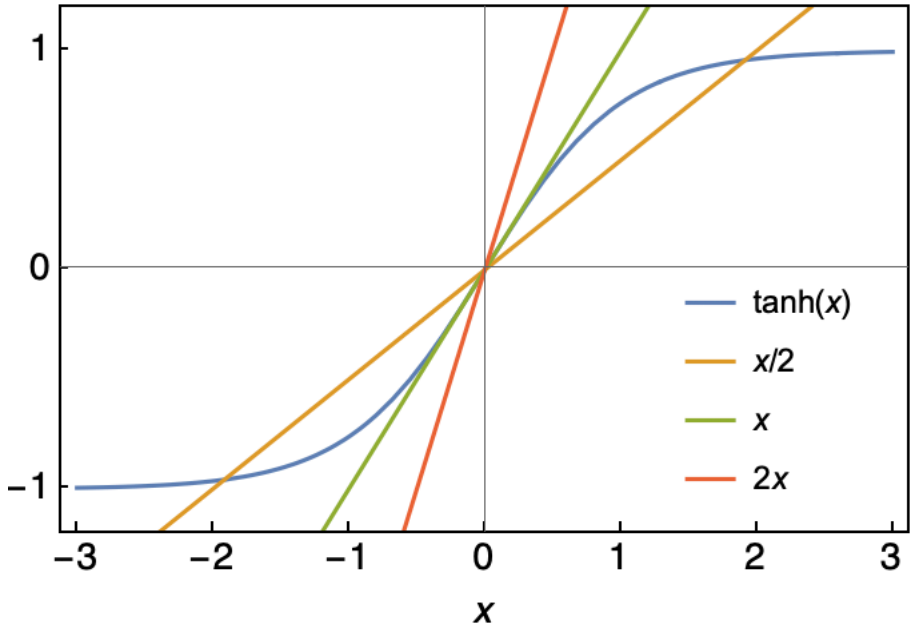
Mean-field Ising model

Mean-field theory explains important phenomena in magnetism:

- Sudden transition from magnetised phase to unmagnetised phase as the Curie temperature T_c is crossed
- Both spin-down and spin-up are equally likely solutions

Limitations:

- Mean-field theory is an approximation, so numerical predictions are incorrect

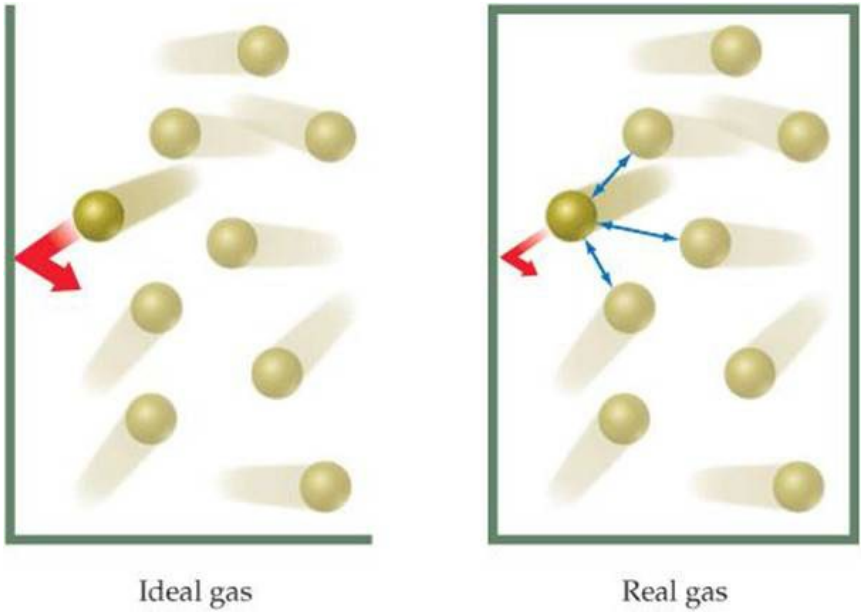


Real gases

Real gases involve interactions between molecules

Oldest real-gas equation of state is the van der Waals equation

$$\left(p + \frac{aN^2}{V^2}\right)(V - Nb) = NkT$$



Importantly, it predicts the gas-to-liquid phase transition

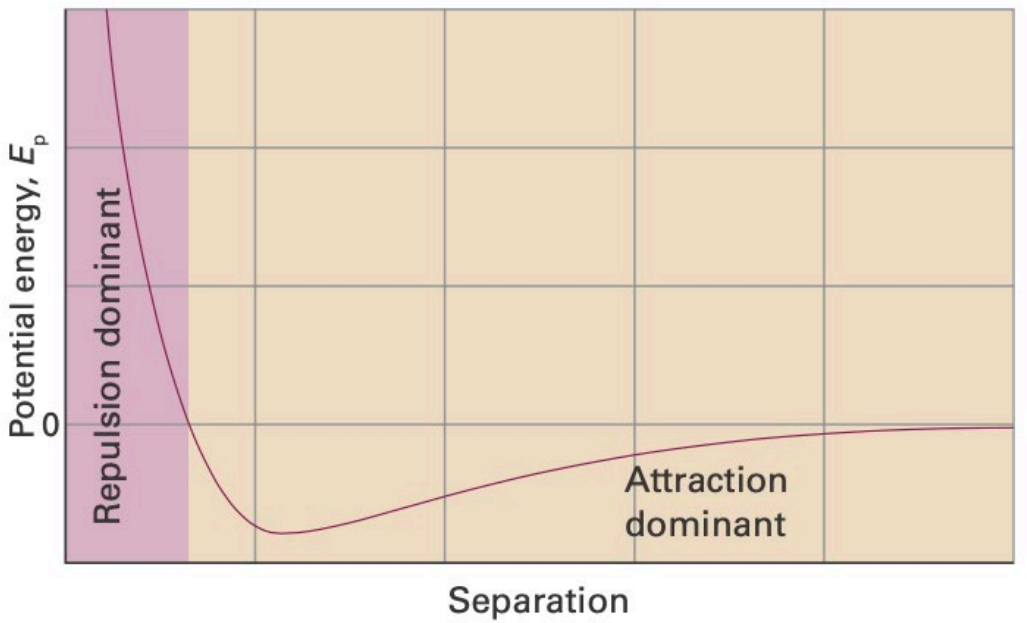
We can derive it using mean-field theory!

Interactions in gases

Molecules interact in two ways:

- Repulsive when very close (they can't overlap)
- Attractive at medium distances (van der Waals attraction)





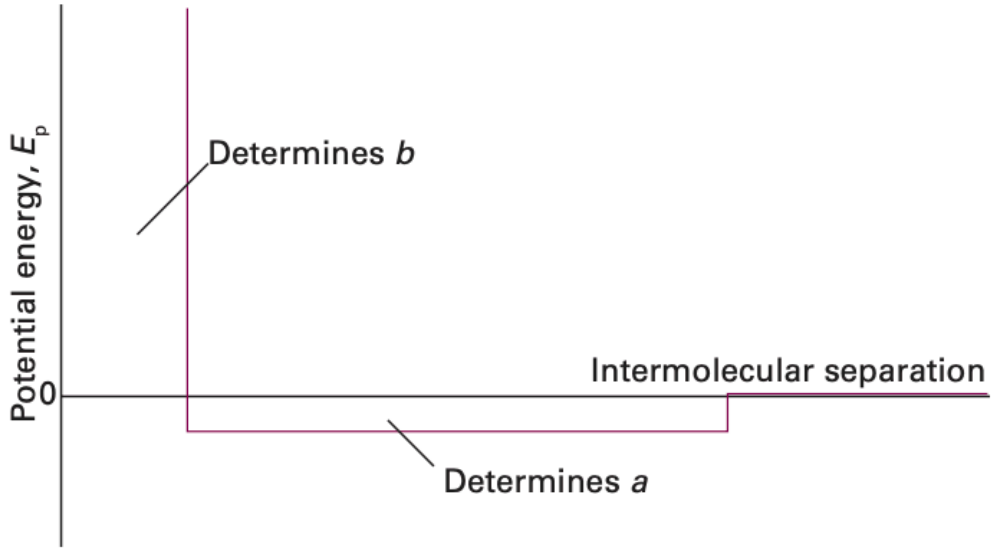
Note:

- At low pressures, molecules are far apart. This means weak interactions, i.e., gas becomes ideal

Excluded volume

The precise form of the intermolecular interaction is not important (or, usually, known)

Let's approximate it as shown on the right



The infinite wall at small *r* explains why the vdW equation replaces *V* with *V* – *Nb*

Nb is the "excluded volume" of all the molecules

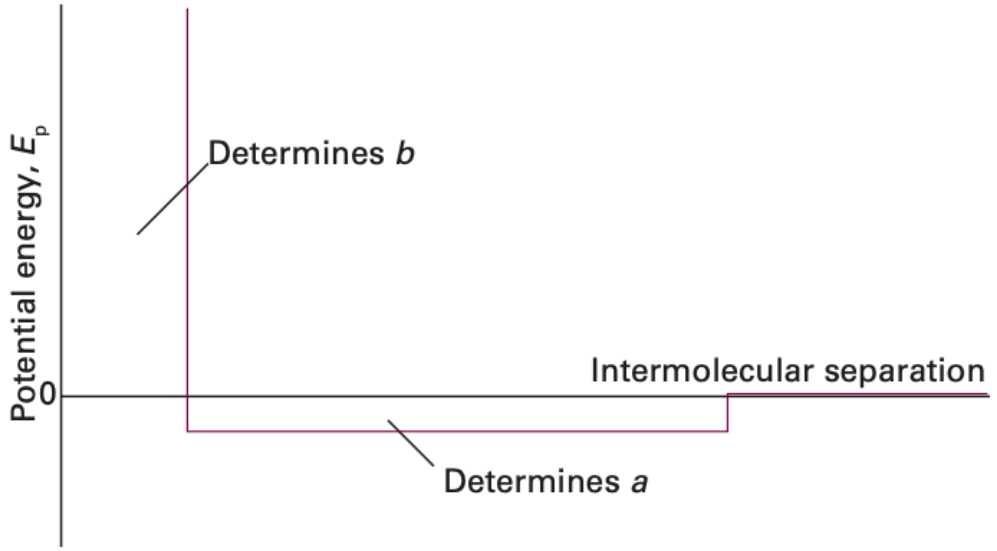
$$\left(p + \frac{aN^2}{V^2}\right)(V - Nb) = NkT$$

Attractive potential

The pressure correction comes from the attractive potential

It's too hard to add up all the pairwise interactions

Instead, we consider the point of view of one molecule and assume the other molecules are evenly distributed in the remaining volume



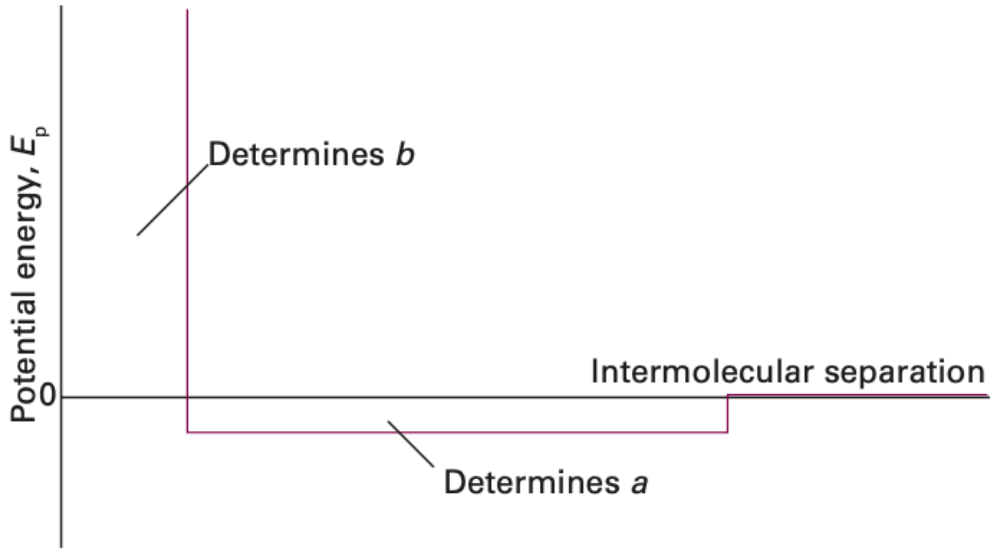
Mean-field approximation!

$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = NkT$$

Attractive potential

Per molecule, the potential energy is proportional to the density of nearby molecules (i.e., how many are in its radius of attraction)

$$U_{\text{pot,mol}} = -a\frac{N}{V}$$



Total potential energy:

$$U_{\text{pot}} = -a\frac{N^2}{V}$$

Attractive potential

$$U_{\text{pot}} = -a\frac{N^2}{V}$$

First law says $dU = TdS - pdV$

Therefore: $p = -\left(\frac{\partial U}{\partial V}\right)_S \quad \Longrightarrow \quad p_{\text{pot}} = -\frac{d}{dV}\left(-a\frac{N^2}{V}\right) = -\frac{aN^2}{V^2}$

Adding this (negative) pressure to the non-interacting equation gives the vdW equation of state:

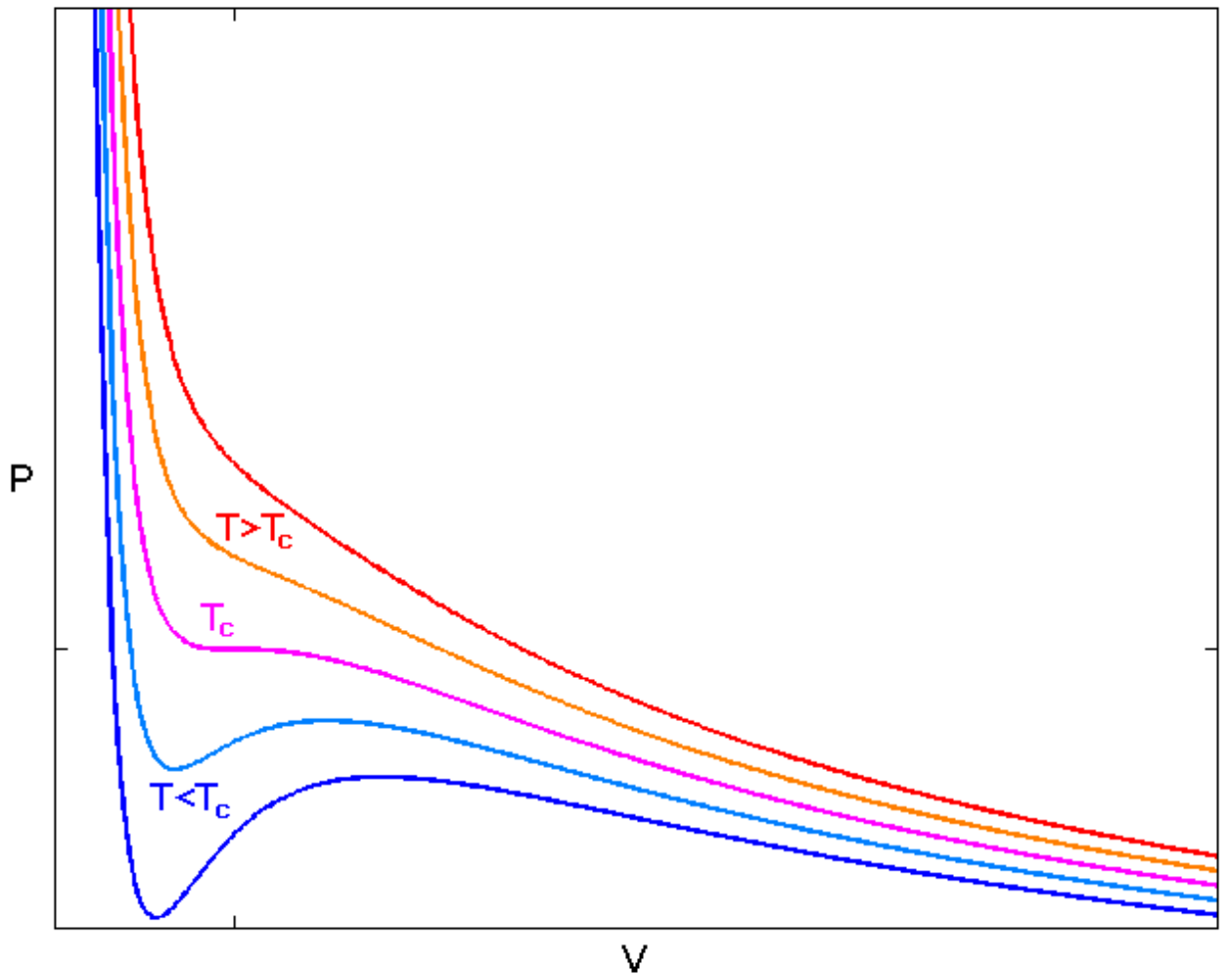
$$p = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

Mentimeter

van der Waals isotherms

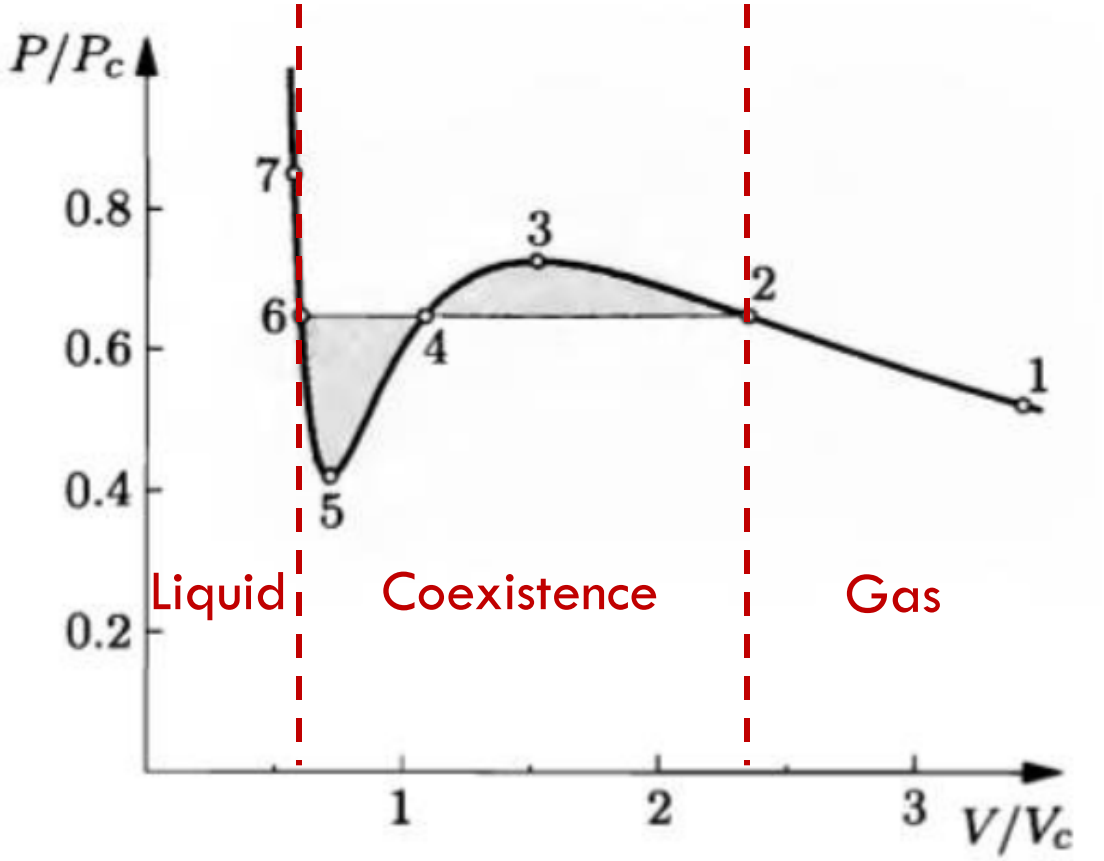
We can plot the pressure as a function of volume

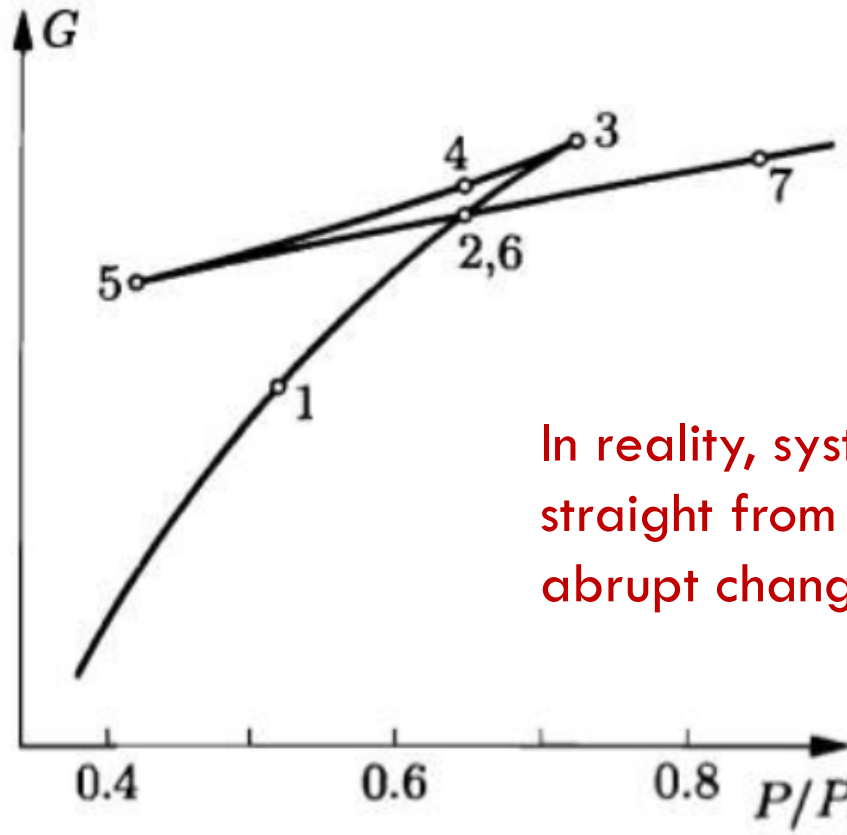
Below a certain temperature (T_c), there are regions where it seems, unphysically, that compressing the gas would cause its pressure to drop



Liquid-gas phase transition

The true equilibrium at given T and p is determined by the Gibbs free energy

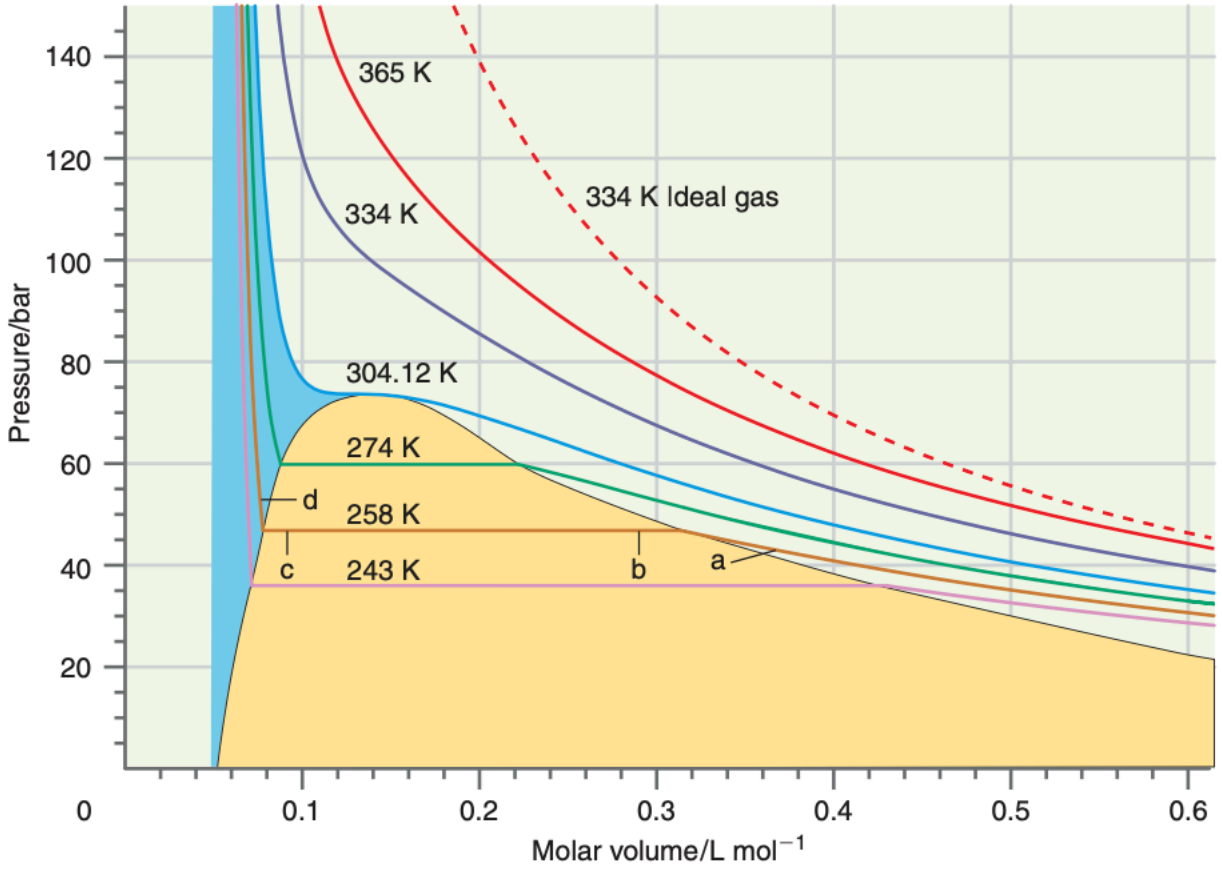


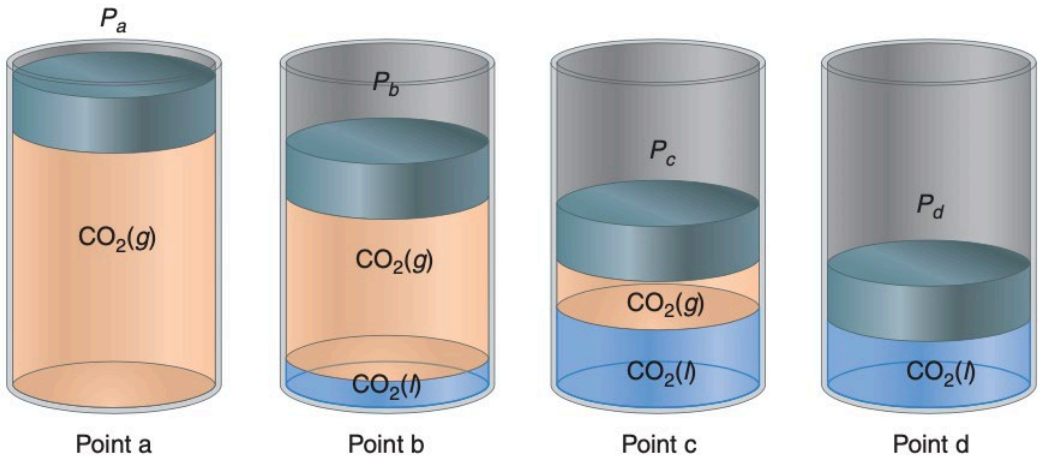


In reality, system will go straight from 2 to 6, an abrupt change in volume

Liquid-gas phase transition

Complete phase diagram of van der Waals fluid:





van der Waals model

The van der Waals model explains important qualitative features of fluids:

- Discontinuous transition from gas to liquid (if below T_c)
- Coexistence of liquid and gas at certain volumes
- Super-critical fluid above T_c (more on this next time)

Limitations:

- The van der Waals equation is not particularly accurate. There are better equations for real gases
- Mean-field approach is an approximation; in real fluids, molecules tend to clump at high pressure

Summary

Key points:

- Mean-field theory idea: replace interactions with an average
- Mean-field theory predicts abrupt phase transitions in both the Ising model of magnetism and the van der Waals fluid
- The van der Waals equation corrects the ideal gas law to account for excluded volume and intermolecular attraction
- Below a critical temperature, gases can be compressed into liquids

Learning outcomes

You should be able to:

- Explain the approximations and assumptions in mean field models
- Understand the predictions of a mean-field theory applied to the Ising model of magnetism and the van der Waals fluid
- Use the van der Waals equation to more accurately quantify the behaviour of non-ideal fluids
- Relate these models to phase diagrams of these systems

Next time

Next time, we will continue looking at phase transitions, from a more thermodynamic perspective:

- Phase diagrams
- Critical phenomena

Reading:

E&R (either book) 6.4, 8.1–8.5

Appendix: Gibbs energy of vdW fluid

At a given temperature and pressure, the true equilibrium state of a system is determined by its Gibbs free energy. To calculate G for a van der Waals fluid, let's start with the thermodynamic identity for G:

$$dG = -S\,dT + V\,dP + \mu\,dN. \tag{5.53}$$

For a fixed amount of material at a given, fixed temperature, this equation reduces to $dG = V\,dP$. Dividing both sides by dV then gives

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = V\left(\frac{\partial P}{\partial V}\right)_{N,T}. \tag{5.54}$$

The right-hand side can be computed directly from the van der Waals equation (5.52), yielding

$$\left(\frac{\partial G}{\partial V}\right)_{N,T} = -\frac{NkTV}{(V-Nb)^2} + \frac{2aN^2}{V^2}. \tag{5.55}$$

To integrate the right-hand side, write the V in the numerator of the first term as $(V - Nb) + (Nb)$, then integrate each of these two pieces separately. The result is

$$G = -NkT\ln(V-Nb) + \frac{(NkT)(Nb)}{V-Nb} - \frac{2aN^2}{V} + c(T), \tag{5.56}$$

where the integration constant, $c(T)$, can be different for different temperatures but is unimportant for our purposes. This equation allows us to plot the Gibbs free energy for any fixed T.

From Schroeder, *Introduction to Thermal Physics*