Phase Transitions, Part 2

Last time

Interactions

DNA unzipping

Today

Computer simulations

Ising model of magnetism

Next time

Mean-field theory

Real gases and liquids

Last time

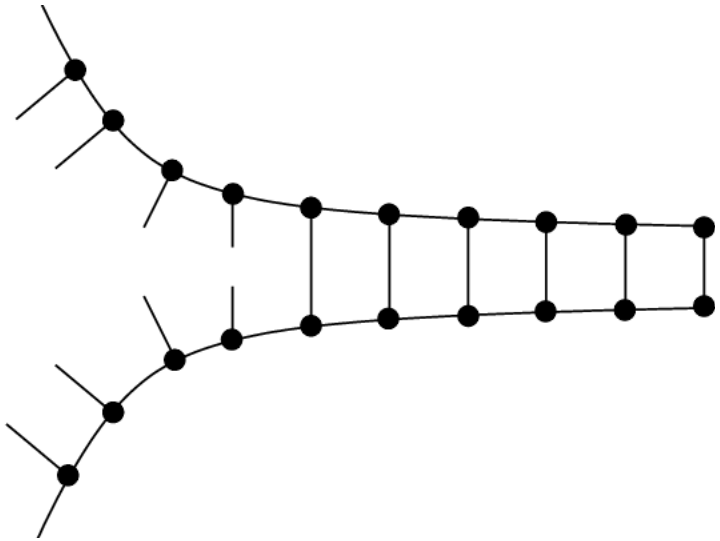
Phase transitions:

- Abrupt change in a physical property
- Require interactions between particles
- Only possible in thermodynamic limit



Simplest example:

- Unzipping of DNA
- Sharp transition above critical *T*
- Caused by interactions between links

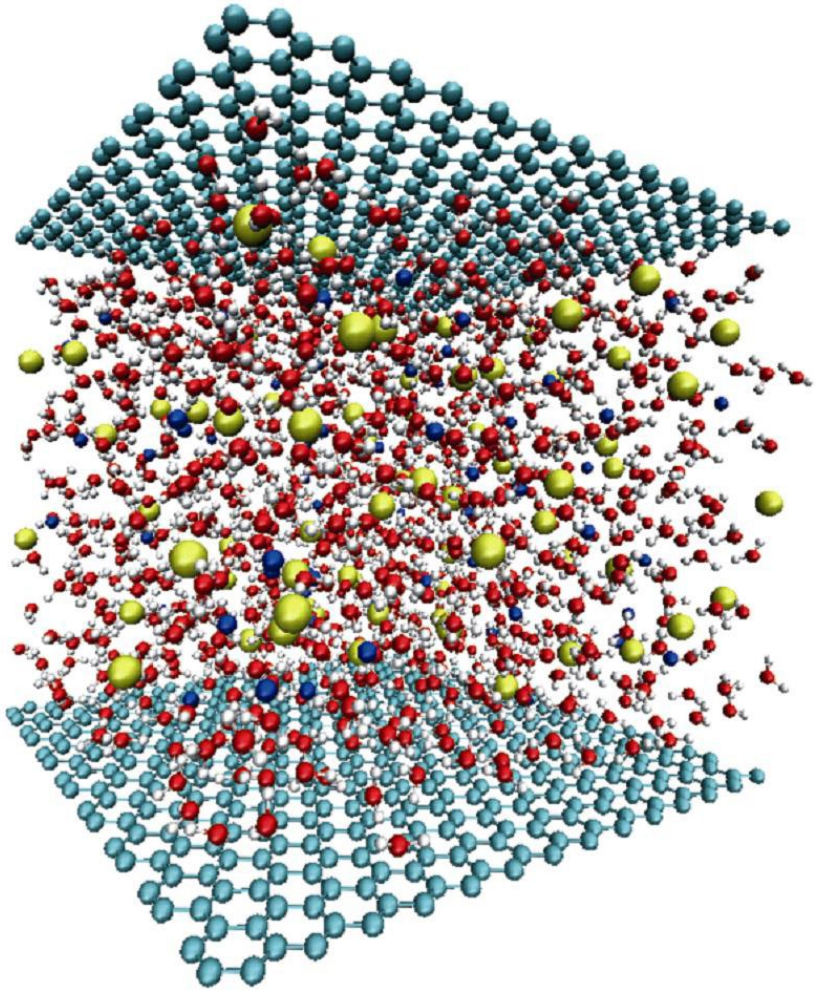


Today: Computer simulations

Unlike the DNA unzipping, most interacting systems cannot be solved exactly

That is, we cannot derive exact expressions relating macroscopic parameters, e.g., pressure as a function of temperature

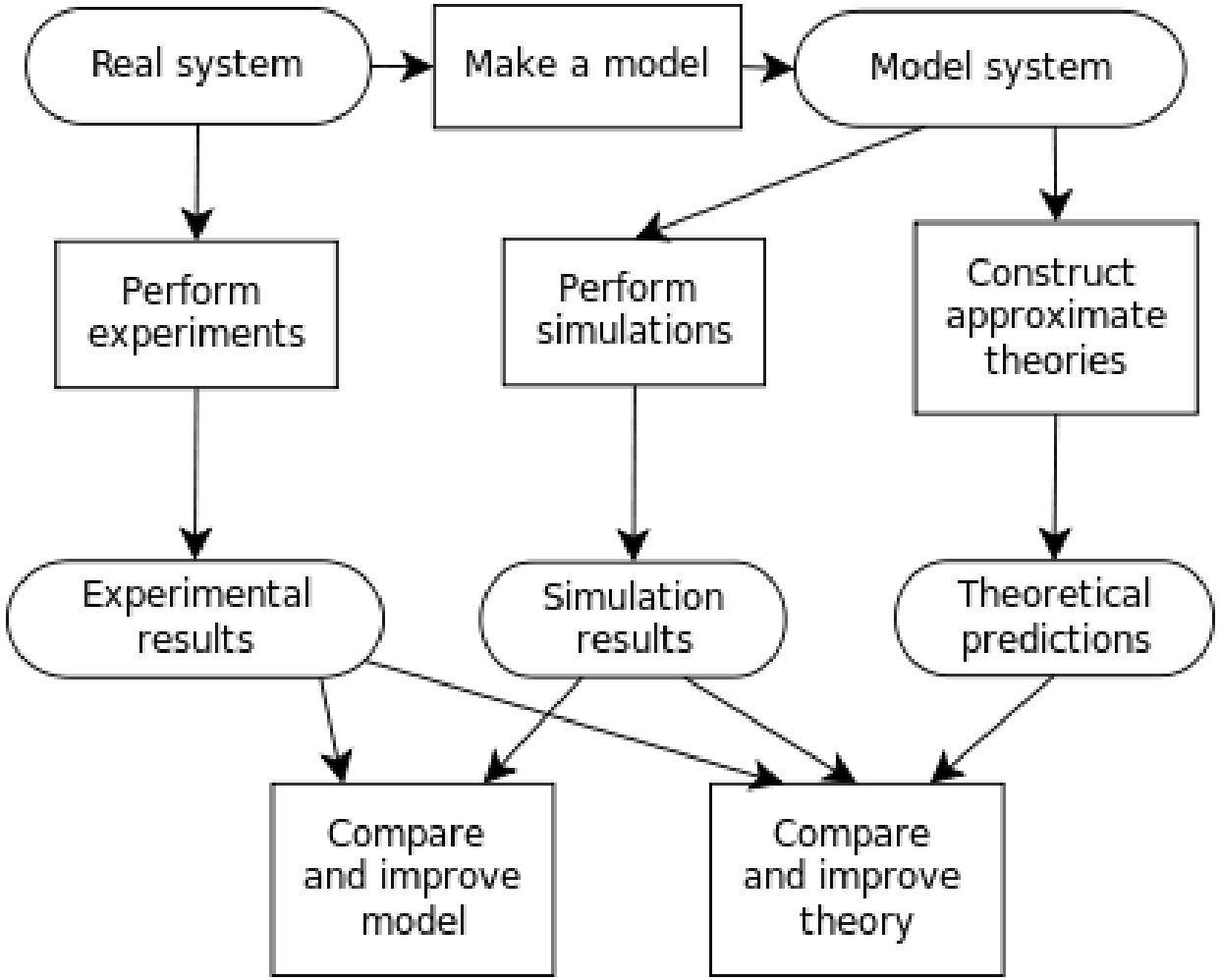
Instead, a powerful technique to gain better insight are *computer simulations*



Why use simulations?

- Need computers to study many-body systems of interacting particles
  - Fundamental laws of motion cannot be solved exactly except for a few special cases
- Provide experimentally unobservable microscopic insight into macroscopic properties and behavior
- Study experimentally inaccessible regimes:
  - Extreme conditions
  - Materials that have not yet been made
- Improve data analysis, e.g., X-ray and neutron diffraction, NMR
- Generate precise results that can be used to test a theory

Simulations bridge experiment and theory



http://en.wikipedia.org/wiki/Computer_simulation

Computer simulations and importance sampling

Calculating the thermodynamic average of quantity *X*:

$$\langle X \rangle = \frac{\sum_{j=1}^{\tilde{N}_{\text{trials}}} X_j e^{-\beta E_j}}{\sum_{j=1}^{\tilde{N}_{\text{trials}}} e^{-\beta E_j}}$$

Two options:

1. Generate configurations with equal probability, then weigh them by $e^{-\beta E}$
2. Generate configurations with probability $e^{-\beta E}$, then weigh them equally





Importance sampling!

Therefore, we want a computer to generate configurations with probability proportional to their probability at equilibrium

Monte Carlo simulations

Monte Carlo methods are probabilistic techniques to generate and sample configurations:

- Random trial moves
- Acceptance/rejection rules that ensure we eventually sample equilibrium configurations

Goal: Sampling configurations and evaluating properties at equilibrium, *not* dynamics



The method is named for the casinos of Monte Carlo

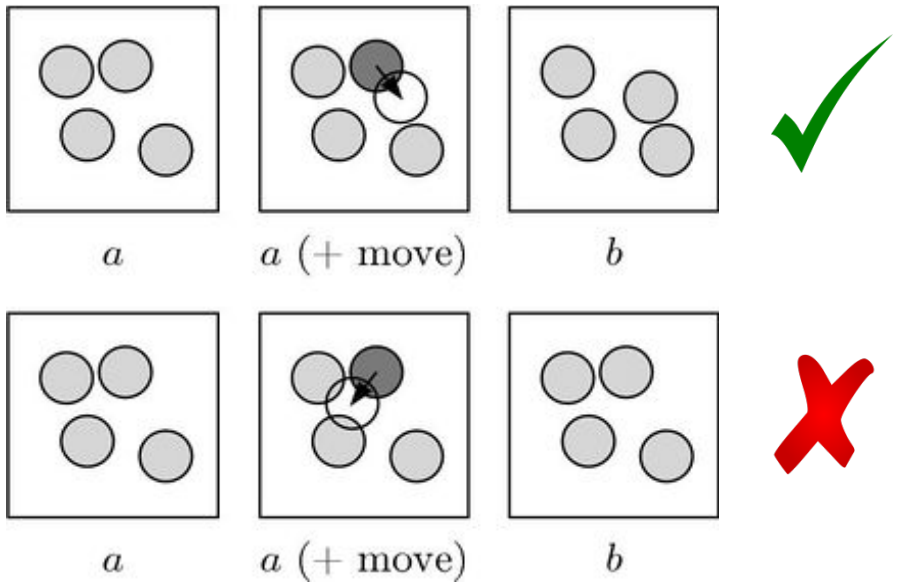
Metropolis Monte Carlo

Oldest and simplest Monte Carlo approach

Repeat two steps:

1. Choose a random particle, change its state randomly, calculate new energy
2. If energy went down, accept the move
   If energy went up, accept the move with probability $\exp(-\beta\Delta E)$

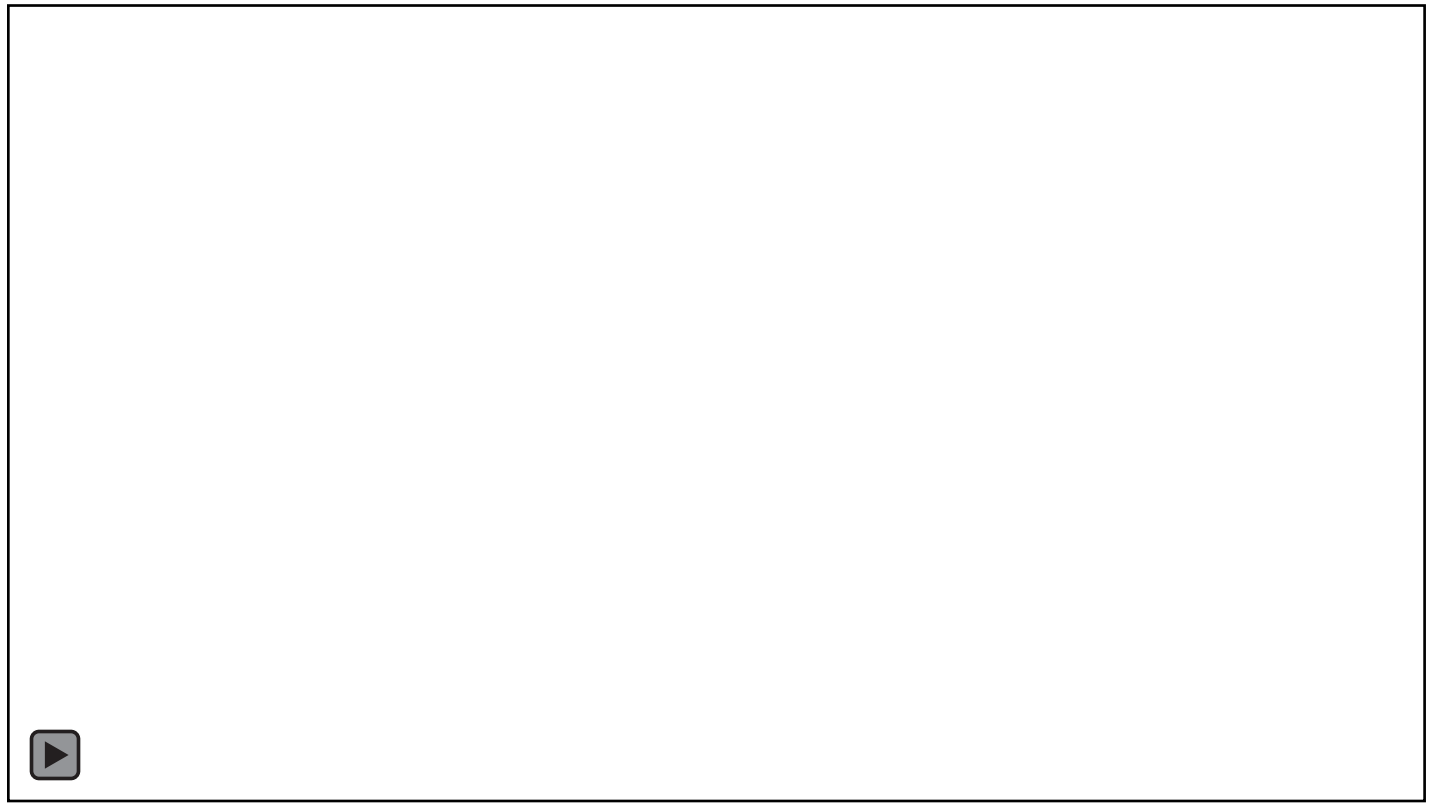
Eventually, this procedure samples the canonical ensemble (const. N,V,T), and the configurations can be used to calculate equilibrium properties



Ferromagnetic transition

If you heat a magnet above its Curie temperature, it loses its magnetism

This is a transition between the ferromagnetic and paramagnetic phases

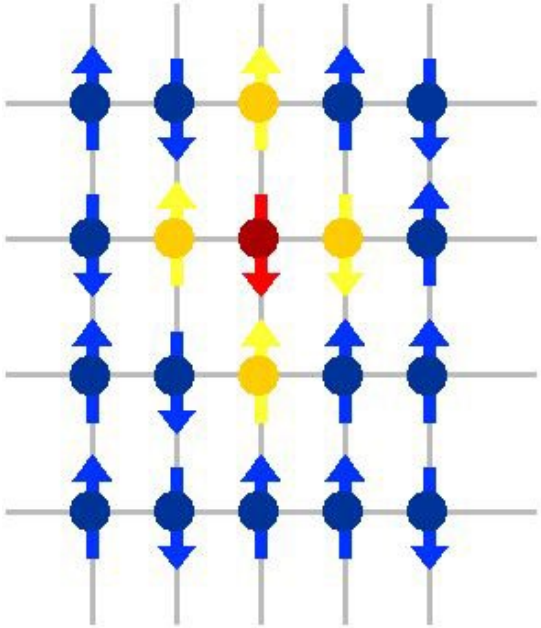


Minute Physics,
youtu.be/IlnZKSR73S0

Ising model of magnetism

The Ising model is a simple, but powerful, model of magnetism. Assumptions:

- Lattice of spins
- Each can only point up or down ($\sigma = \pm 1$)
- Interactions only with nearest neighbours



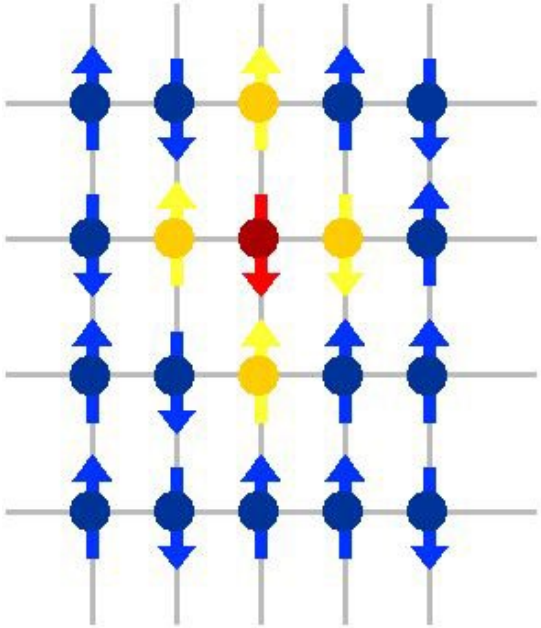
Total energy: $$E = -B\sum_i \sigma_i - J\sum_{\langle ij \rangle} \sigma_i \sigma_j$$

B: Applied magnetic field

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

Ising model of magnetism

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



The most important thing we want to know about a magnet is the net magnetisation as a function of *T*:

$$m = \sum_i \sigma_i$$

m is zero if spins randomly point up or down;
m is non-zero if one orientation is preferred

No exact solution in 3D → we'll first look at computer simulations

Periodic boundaries

A simulation cell has a high surface-area-to-volume ratio:

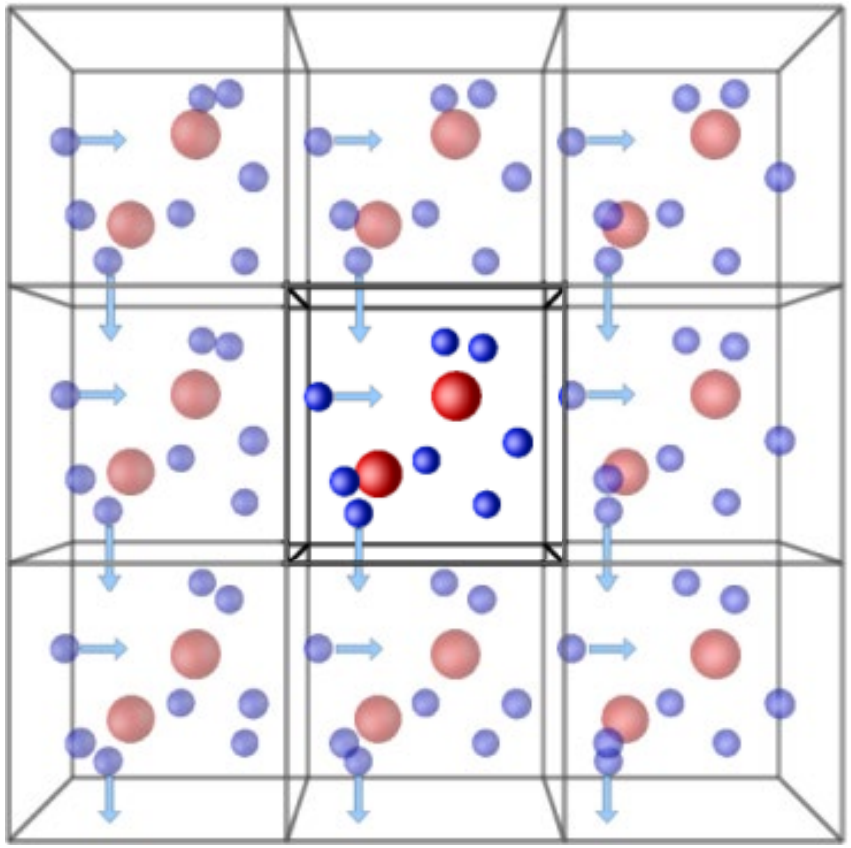
- Not representative of the bulk

Solution:

- Surround cell with virtual copies of itself (periodic boundary conditions)

Be careful:

- Cell needs to be large enough
- Need to avoid self-interactions and multiple interactions



Ising model: Simulation exercise

Interactive Monte Carlo simulation of the Ising model:

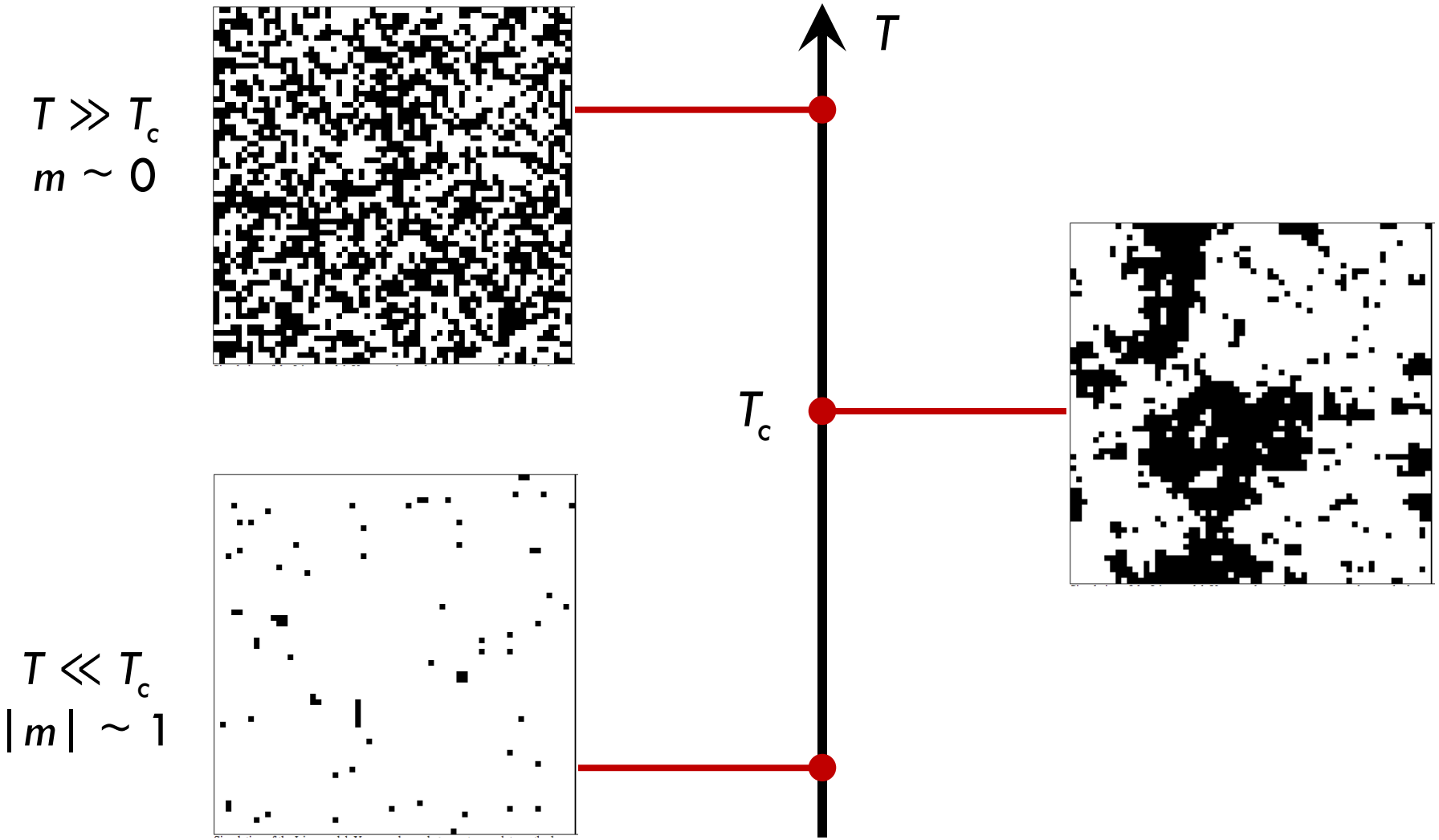
mattbierbaum.github.io/ising.js/

Run the simulation and consider these questions:

- Is the magnetisation constant at high temperature?
- Why is the ferromagnet disordered at high temperature?
- What happens to the spins at very low temperature?
- Why do nearby spins align at low temperature?
- How does the magnetisation change as the temperature decreases?
- At what temperature is the variation in the magnetisation greatest?

Mentimeter

Ising model: Phase behaviour



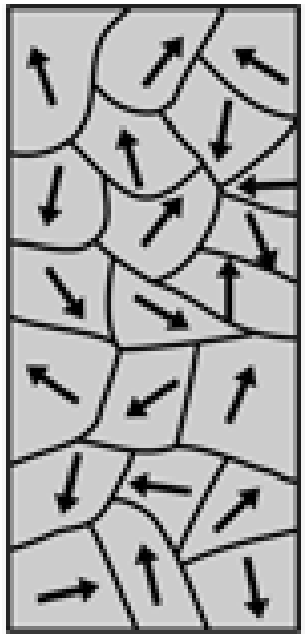
Magnetic domains

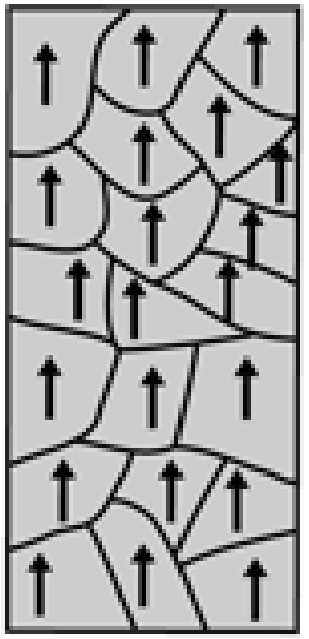
Does the Ising model predict that every piece of iron below the Curie temperature would have a net magnetisation?

In reality, spins will align within *magnetic domains*. If these are randomly oriented, the net magnetisation will be zero

Boundaries between domains are essentially grain boundaries

To magnetise a piece of iron, you can put it in a magnetic field to align the domains



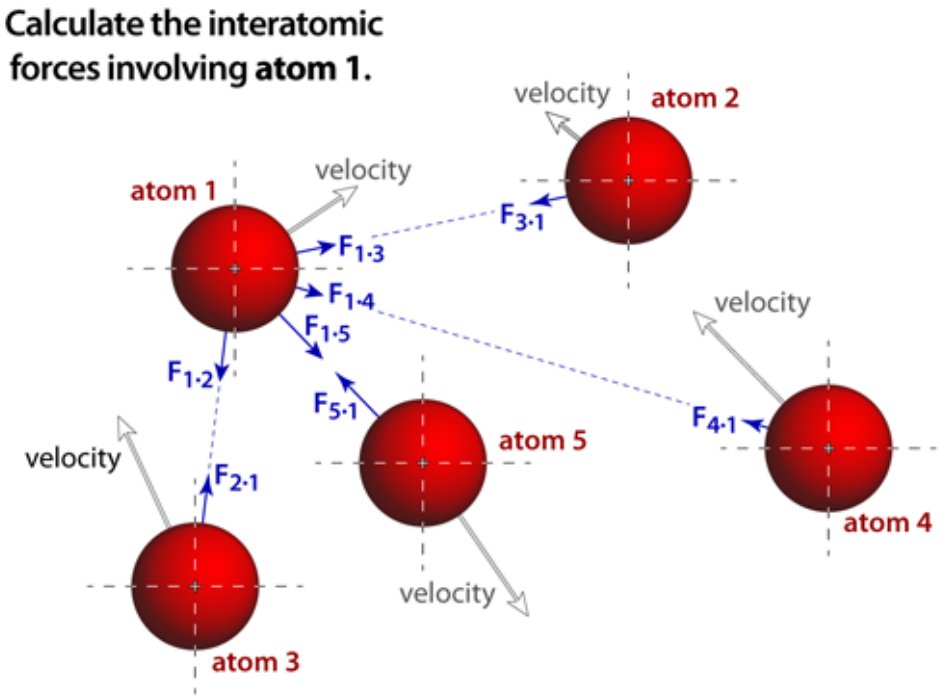


Molecular dynamics (MD)

We can also use computer simulations to predict the dynamics of phase transitions, or any other molecular process.

In *molecular mechanics*, we simulate the dynamics of atoms and molecules by numerically solving Newton's laws of motion for interacting particles

$$\mathbf{F}_i = m_i \mathbf{a}_i = -\frac{\partial U}{\partial \mathbf{r}_i}$$

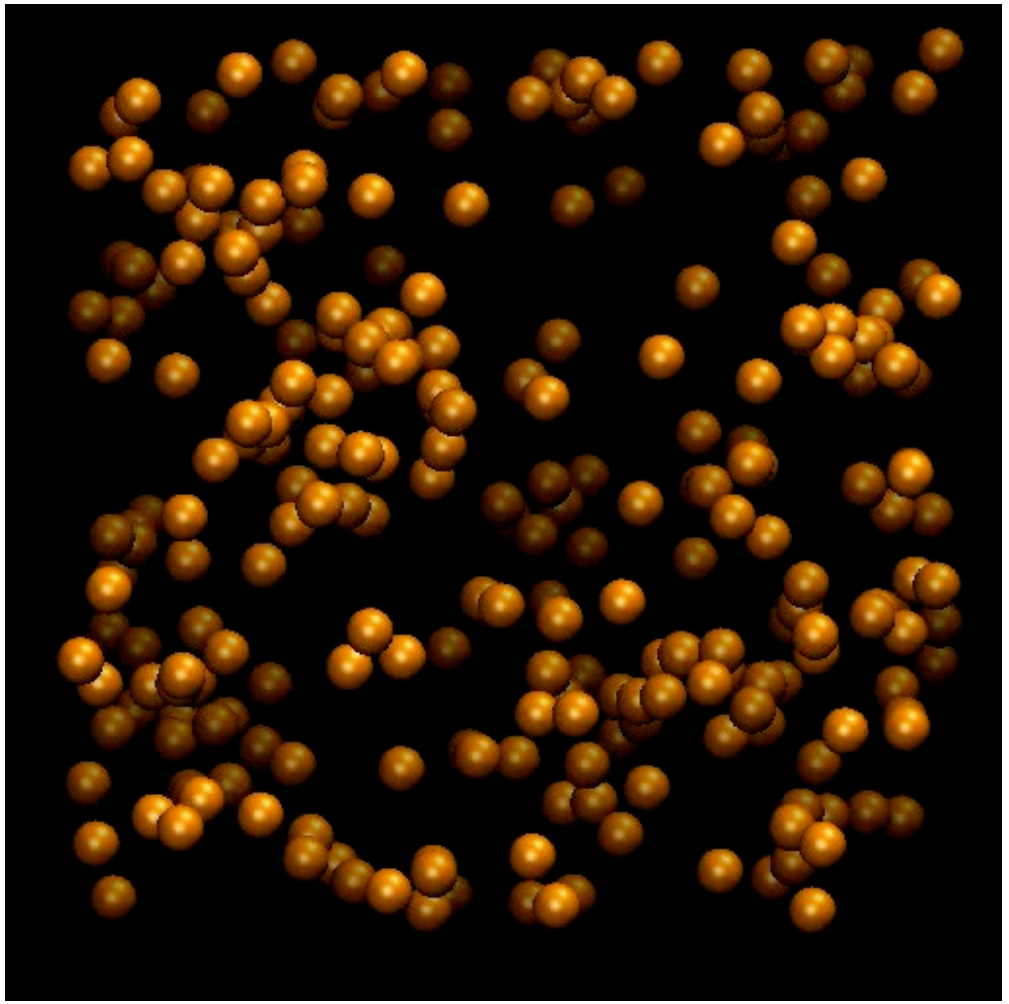


Example: MD simulation of condensation

Attractive particles (e.g., argon atoms) in a cell with fixed volume.

Initially in a gaseous state, they condense into a liquid droplet as T is decreased.

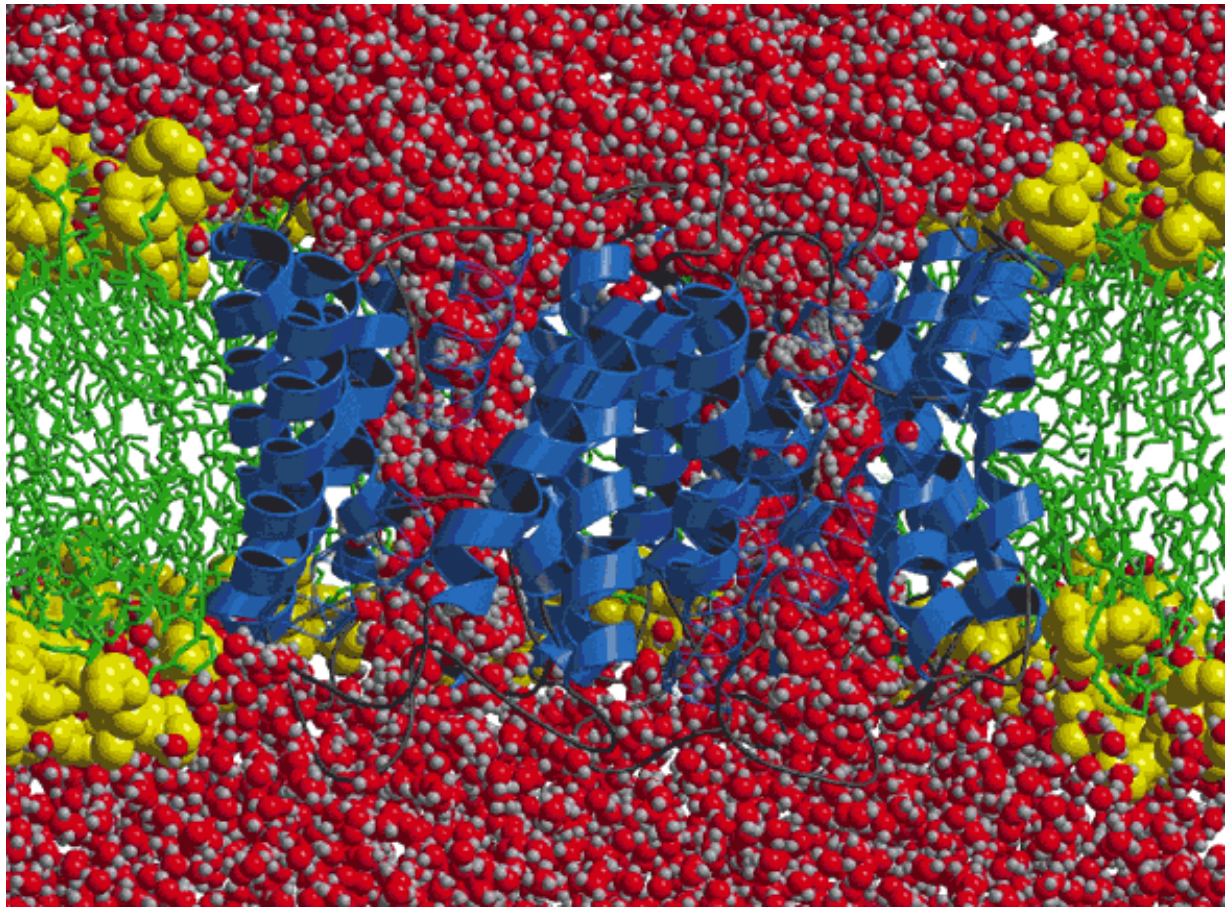
This is similar to what occurs in clouds.



MD simulation of biomolecules

For biomolecular dynamics, MD is the most-widely used simulation method

If you're interested, take CHEM3X23 (Computational Chemistry) next year



Interactive molecular dynamics

An excellent, interactive MD simulation is available online:

http://physics.weber.edu/schroeder/md/

Summary

Key points:

- Computer simulations are a powerful tool for testing theories and interpreting experiments
- The Ising model explains the ferromagnetic transition
- Importance sampling and Monte Carlo: way to generate configurations that accurately sample equilibrium distribution
- Molecular dynamics is a way to simulate the motion of molecules, including large biomolecules

Learning outcomes

You should be able to:

- Discuss the role of modelling, theory, and computer simulation in science
- Understand the assumptions and key results of the Ising model
- Explain the computational methods: Monte Carlo and molecular dynamics, and the types of information they can determine.

Next time

Next time, we will discuss mean-field theory, one of the most powerful approximation techniques, which will give us greater insight into phase transitions, including:

- the magnetic transition in the Ising model
- real (interacting) gases and their transition into liquids

Reading:

E&R (either book) 3.1–3.4, 7.1–7.2