Phase Transitions, Part 1

Last time

Defects in solids

Today

Interactions

DNA unzipping

Next time

Computer simulations

Ising model of magnetism

Progress so far…

So far, we have only looked at single phases and non-interacting particles

- E.g., ideal gas, Einstein solid

For non-interacting particles:

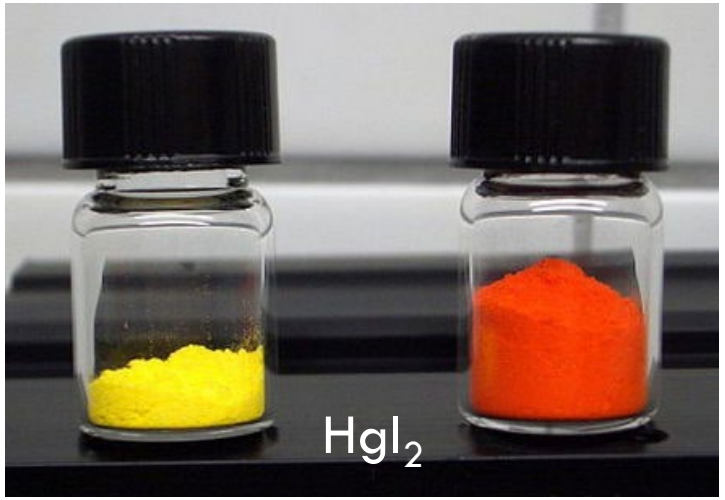
$$Q = \begin{cases} q^N & \text{(distinguishable)} \\ \frac{q^N}{N!} & \text{(indistinguishable)} \end{cases}$$

$$E_n = nE_1$$
$$S_n = nS_1$$
$$G_n = nG_1$$
$$\text{etc.}\ldots$$

As a result, we have so far almost always only considered q, the molecular partition function

Today: Phase transitions











Phase transitions

A *phase* can be defined as a state whose properties change **continuously**

E.g.: ice, liquid water, water vapour

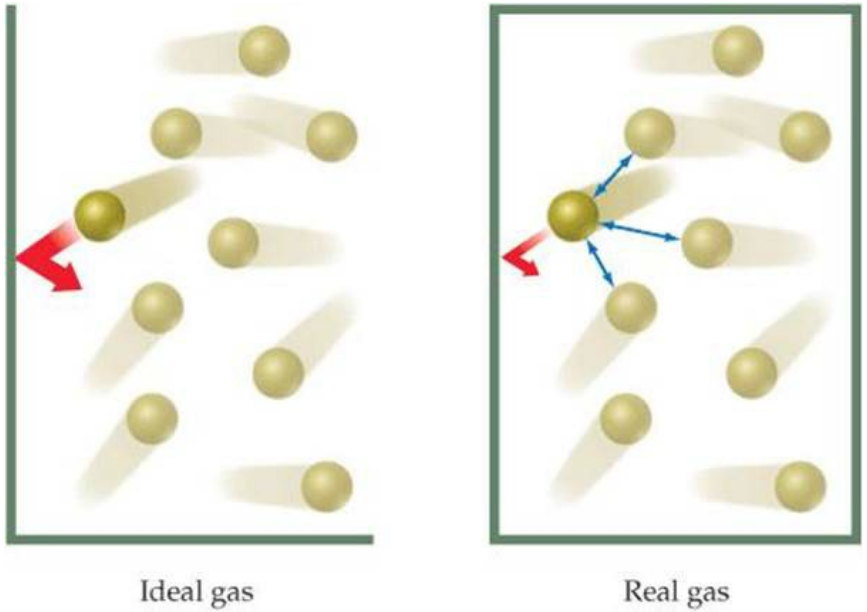
A *phase transition* is an **abrupt** change in a physical property

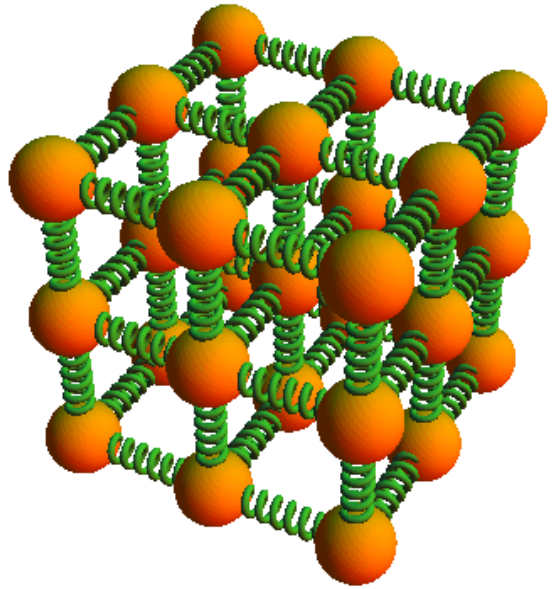
E.g.: water is liquid at $T < 100$ °C and gaseous at $T > 100$ °C; it's density changes discontinuously at $T = 100$ °C



Phase transitions require interactions

Phase transitions occur **because of interactions** between particles





Compressed real gases liquefy once the molecules can't avoid each other

At low *T*, atoms in solids vibrate collectively and Einstein model fails

Statistical mechanics of interacting particles

So far, we only considered non-interacting particles, which gave us the *molecular* partition function:

$$q = \sum_{i=1}^{N} e^{-\beta \varepsilon_i}$$

Sum over *N* states of each molecule, indexed *i*, with energy ε_i

Among many non-interacting molecules, there will be many in each possible state. Therefore, the expectation value of any observable coincides with the *ensemble average* of the ensemble consisting of many copies of a molecule.

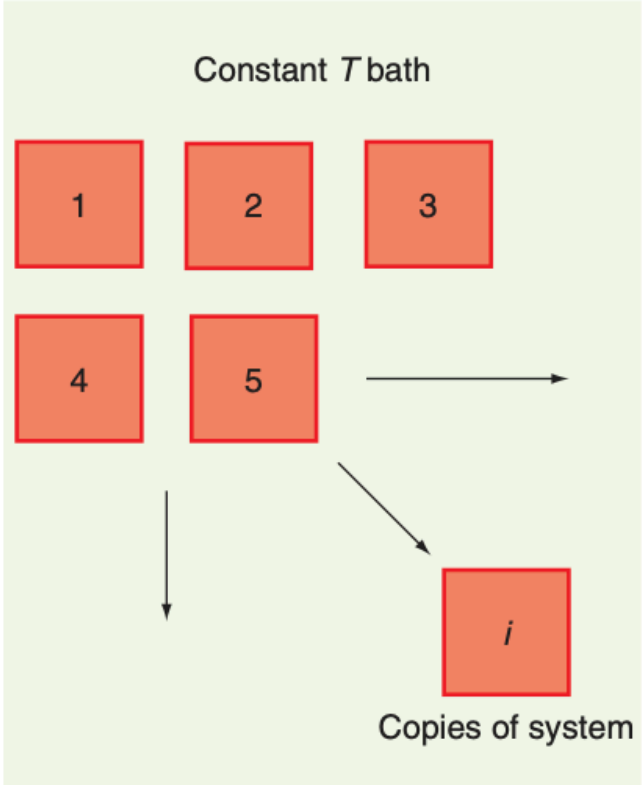
But this reasoning no longer works for interacting molecules.

Statistical mechanics of interacting particles

With interactions, we can no longer consider each molecule separately.

Solution: Instead of considering an ensemble of molecules, we consider an (imaginary) ensemble consisting of many copies of the entire system.

The *canonical ensemble* is one in which each system has the same N, V, and T.



Statistical mechanics of interacting particles

The *canonical partition function* follows from analogous arguments to those we used to derive the molecular partition function from the ensemble of molecules:

$$q = \sum_{i=1}^{N} e^{-\beta\varepsilon_i} \longrightarrow Q = \sum_{j=1}^{\tilde{N}} e^{-\beta E_j}$$

Sum over N states of *each molecule*, indexed i, with energy ε_i

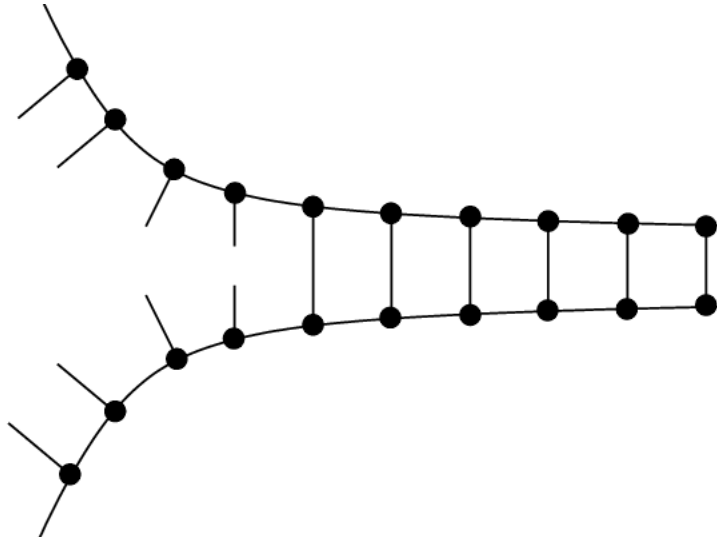
Sum over $\tilde{N}$ states of the *entire system*, indexed j, with energy E_j
NB: The total energy E_j depends on *all* the degrees of freedom of *all* molecules in the system

Unzipping of DNA

At high temperature, DNA unzips

Can also be achieved by applying a force to the two ends

(unrelated to enzymatic unzipping during replication)



Model:

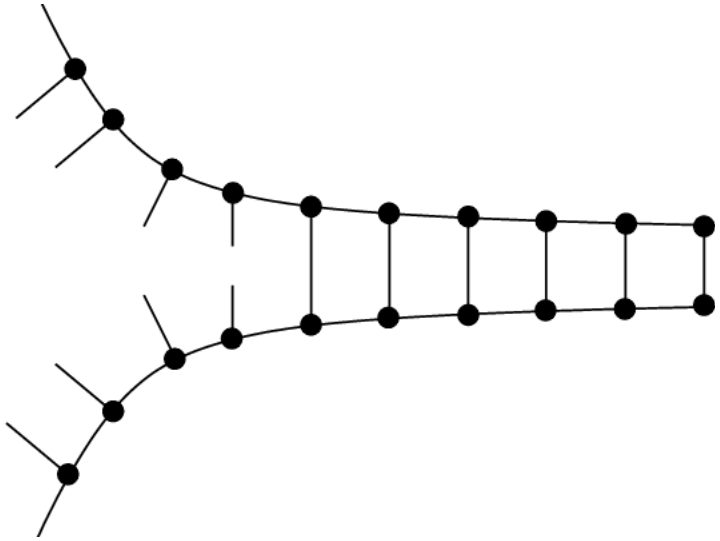
- Each open link has energy ε and orientational degeneracy g
- Zipper can only unzip from the left: link s can only open if all links to the left (1, 2, …, s-1) are already open

→ Interactions! Links are not independent

Mentimeter

Unzipping of DNA

To predict the phase transition, we need to calculate the expected number of open links $\langle s \rangle$ as a function of T. For that, we need to find the partition function



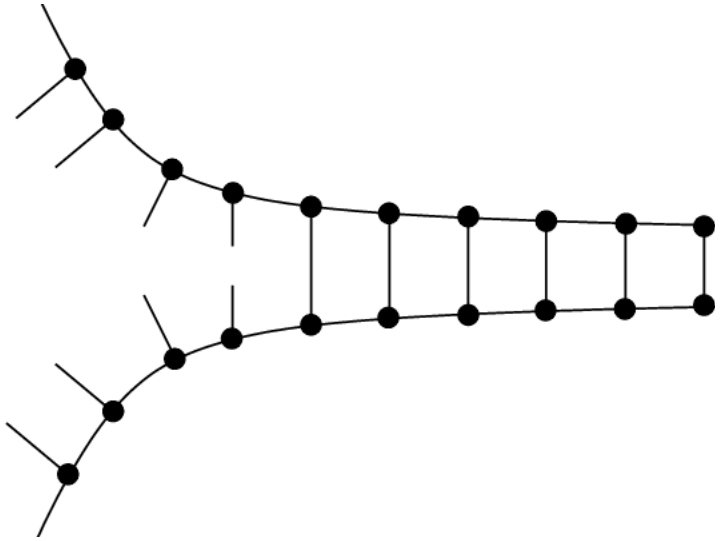
$$Q = \sum_{s=0}^{N-1} g(s) e^{-\beta E(s)} = \sum_{s=0}^{N-1} g^s e^{-\beta s \varepsilon}$$

$$= \sum_{s=0}^{N-1} x^s \quad \text{where} \quad x = g e^{-\beta \varepsilon}$$

$$= \frac{1 - x^N}{1 - x}$$

Unzipping of DNA

$$Q = \frac{1 - x^N}{1 - x}$$



Expectation value of number of open links:

$$\langle s \rangle = \sum_{s=0}^{N-1} s\, p_s = \sum_{s=0}^{N-1} s\, \frac{g^s e^{-\beta s \varepsilon}}{Q} = \sum_{s=0}^{N-1} \frac{s\, x^s}{Q}$$

To evaluate this, we note that $sx^s = x\frac{d}{dx}x^s$

$$\langle s \rangle = \sum_{s=0}^{N-1} \frac{1}{Q} x \frac{d}{dx} x^s = \frac{1}{Q} x \frac{d}{dx} \sum_{s=0}^{N-1} x^s = \frac{1}{Q} x \frac{d}{dx} Q$$

Now it's standard algebra to evaluate: $\langle s \rangle = \frac{N x^N}{x^N - 1} - \frac{x}{x - 1}$

Unzipping transition

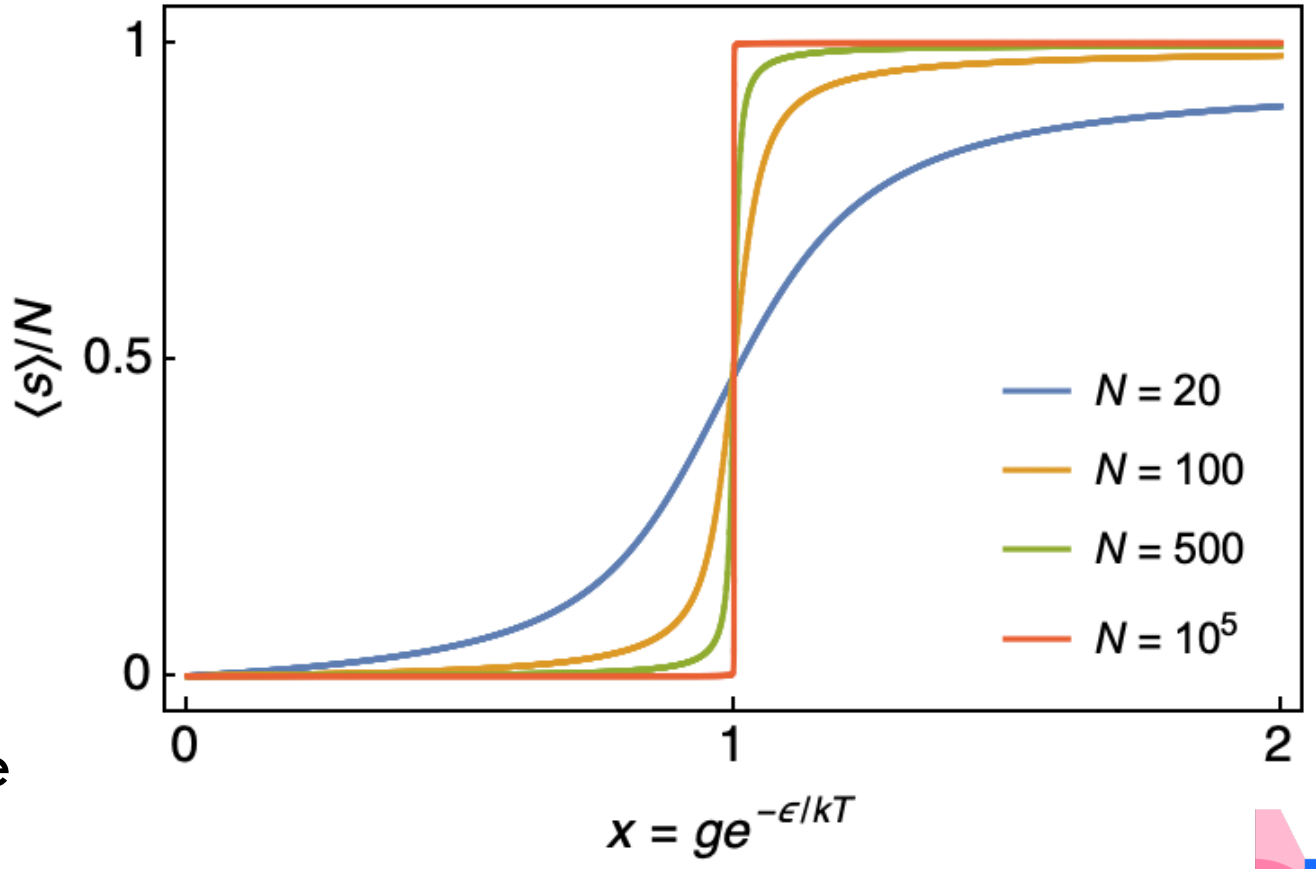
$$\langle s \rangle = \frac{N x^N}{x^N - 1} - \frac{x}{x - 1}$$

Fraction unzipped is:

$$\frac{\langle s \rangle}{N} = \frac{x^N}{x^N - 1} - \frac{x}{N(x - 1)}$$

Abrupt transition from fully zipped to fully unzipped at $x=1$, i.e., at critical temperature

$$T_c = \varepsilon / k \ln g$$

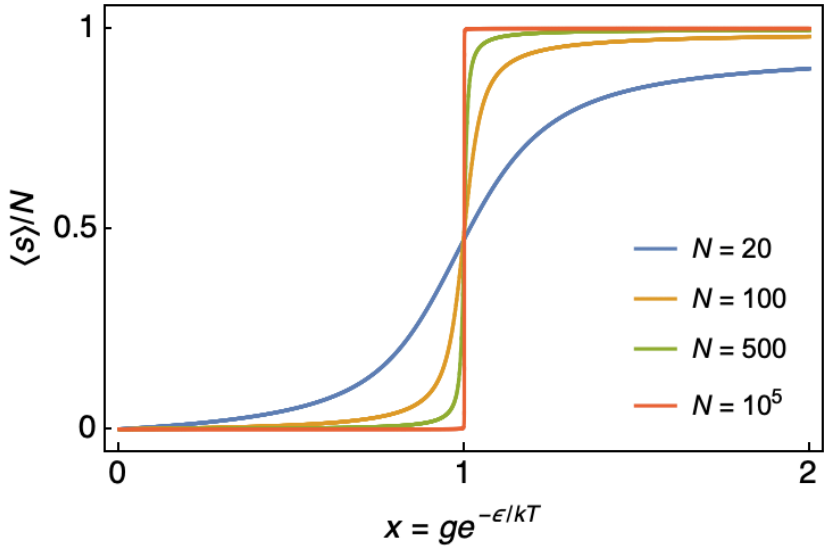


Mentimeter

Phase transitions only in thermodynamic limit

The partition function seems to be a continuous function of *T*:

$$Q = \sum_{s=0}^{N-1} g^s e^{-s\varepsilon/kT}$$



Discontinuities can only appear as $N \longrightarrow \infty$

General fact: **Phase transitions can only occur in the thermodynamic limit**

Indeed, we can *define* a phase as a state whose properties vary smoothly

Phase transitions only in thermodynamic limit

Even common phase transitions stop being sharp when there are few particles



Gold nanoparticle: solid or liquid?

There is no longer a sharp melting temperature

Summary

Key points:

- With interacting particles, we need to consider the canonical partition function Q of the entire system, which is calculated using an imaginary ensemble of copies of the entire system
- Phases are states that change continuously with external parameters
- Phase transitions are caused by interactions between particles
- Sharp phase transitions can only occur in the thermodynamic limit; otherwise, all thermodynamic functions are continuous
- In DNA there is an unzipping transition

Learning outcomes

You should be able to:

- Understand the meaning of the canonical partition function.
- Average over the canonical ensemble of simple systems to calculate the expectation value of a property of the system.
- Define and understand the cause and conditions under which a phase change can occur.
- Predict the phase behaviour near a phase transition, including how it depends on the size of the system.

Next time

The DNA zipper is one of very few models where a phase transition can be demonstrated exactly.

Next time, we will look at more realistic cases, including the Ising model of magnetism, and explore how computer simulations can help us identify phase transitions and other thermodynamic processes.