Statistical Mechanics:
from the microscopic to the macroscopic

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Macroscopic laws: phases of water

- Phenomena that are directly observable are Macroscopic.
- For example, water at ambient pressure freezes at $0°C$ and boils at $100°C$.
- Liquid water, vapor and ice all have very different properties, and yet one can easily transition between these states, simply by changing the temperature
  - A gas fills the entire volume available.
  - A liquid is incompressible, but flows.
  - A solid is rigid, and moves only as a whole.
- Melting ice is exactly at $0°C$, and boiling water is exactly at $100°C$.

Macroscopic laws: gasses

- The state of a (ideal) gas is entirely characterized by three quantities:
  - p: pressure
  - T: temperature
  - n: density
- Ideal gas law:

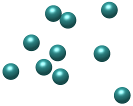
$$p = \frac{k_B}{\mu} nT$$

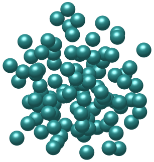
- Energy density:

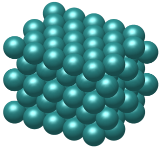
$$e = \frac{3}{2} k_B T$$

Microscopic Theories: phases of water

- Understand macroscopic laws from first principles: Microscopic theories.
- Freezing and boiling: ordering transitions.



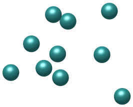




  - Gases expand because the molecules are far apart.
  - Liquids are jammed, but molecules can still move around each other.
  - Solids are constrained by the rigid pattern of their molecules.

Microscopic Theories: gasses

- Ideal gas: non-interacting molecules.



- We will discuss later how this predicts the laws discussed earlier.

What is Statistical Mechanics?

- Statistical mechanics: understanding how the macroscopic properties follow from the microscopic laws of nature ("first principles").

The arrow of time

- Microscopic dynamics are reversible.
- Consider the motion of a point particle, which follows the laws of (conservative) Newtonian mechanics. If time is reversed, the motion still satisfies the same laws of Newtonian mechanics.
- In fact, Newtonian mechanics has a recurrence time: any (bounded, conservative) mechanical system will return arbitrarily close to its original state in finite time.

The arrow of time

- Yet, many macroscopic phenomena are irreversible.
- Friction: the law of friction is not invariant under time reversal.
- The expansion of a gas in a container.
- How can reversible microscopic dynamics give rise to irreversible macroscopic phenomena?

The thermodynamic limit

- One mole $\approx\ 6.02 \times 10^{23}$.
- Rough estimate of the recurrence time for a mechanical system containing 10^{23} particles: $\approx 10^{10^{23}}$ s. (Time since the big bang: $\approx 10^{17}$ s.)
- Whereas a finite number of microscopic particles behaves reversibly, an infinite number of microscopic particles does not.
- Fundamental tool of statistical mechanics: the thermodynamic limit, in which the number of particles $\to \infty$.

Putting the Statistics in Statistical Mechanics

- To understand these infinite interacting particles, we use probability theory.
- Simple example: the ideal gas:
  - Each particle is a point, and no two particles interact.
  - Probability distribution: Gibbs distribution

$$p(\mathbf{x},\mathbf{v}) = \frac{1}{Z} e^{-\beta H(\mathbf{x},\mathbf{v})}, \quad \beta := \frac{1}{k_B T}$$

    where $H(\mathbf{x},\mathbf{v})$ is the energy of the configuration where the particles are located at $\mathbf{x} \equiv (x_1, \cdots, x_N)$ with velocities $\mathbf{v} \equiv (v_1, \cdots, v_N)$.

The ideal gas

- The energy is the kinetic energy:

$$H(\mathbf{x}, \mathbf{v}) = \frac{1}{2} m \sum_{i=1}^{N} v_i^2.$$

- Denoting the number of particles by N and the volume by V, we have

$$Z = \int d\mathbf{x} d\mathbf{v} \; e^{-\beta H(\mathbf{x},\mathbf{v})} = \int d\mathbf{x} \int d\mathbf{v} \; e^{-\frac{\beta m}{2}\mathbf{v}^2} = V^N \left(\frac{2\pi}{\beta m}\right)^{\frac{3}{2}N}.$$

- The average energy is

$$\mathbb{E}(H) = \frac{1}{Z} \int d\mathbf{x} d\mathbf{v} \; H(\mathbf{x}, \mathbf{v}) e^{-\beta H(\mathbf{x},\mathbf{v})} = -\frac{\partial}{\partial \beta} \log Z = \frac{3N}{2\beta} = \frac{3}{2} N k_B T.$$

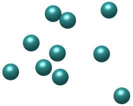
- The ideal gas law can also be proved for this model.

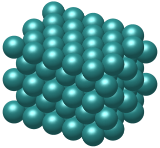
Hard sphere model

- The ideal gas does not form a liquid or a solid phase.
- In order to have such phase transitions, we need an interaction between particles.
- Hard sphere model: each particle is a sphere of radius R, and the interaction is such that no two spheres can overlap.
- Parameter: density.

Hard sphere model

- We expect, from numerical simulations, to see two phases: a gaseous phase at low density and a crystalline one at high density.





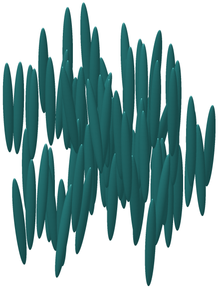
- In the gaseous phase, the particles are almost decorrelated: they behave as if they did not interact.
- In the crystalline phase, they form large scale periodic structures: they behave very differently from the ideal gas.

Hard sphere model

- The gaseous phase is very well understood.
- The crystalline phase is much more of a mystery: we still lack a proof that it exists at positive temperatures!
- Open Problem: prove that hard spheres crystallize at sufficiently low temperatures.
- Even at zero temperature, it was only proved that they crystallize in 2005, and that proof is computer-assisted.
- This is very difficult: even tiny fluctuations in the positions of the spheres could destroy the crystalline structure.

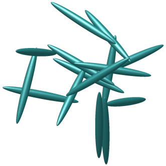
Liquid crystals

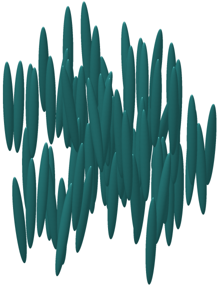
- Phase of matter that shares properties of liquids (disorder) and crystals (order).
- Nematic liquid crystals: order in orientation, disorder in position.

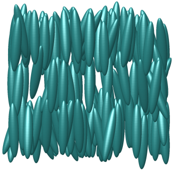


Liquid crystals

- Model: hard cylinders, expected phases: gas, nematic, smectic, ...







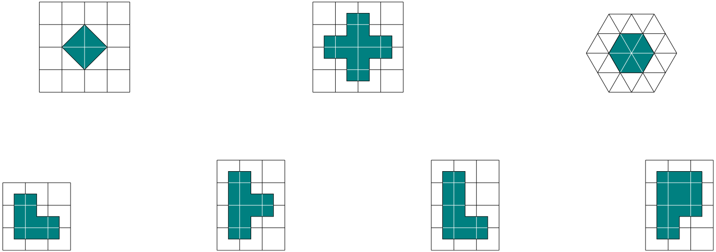
- Here again, the gas phase is well understood, but neither the nematic nor the smectic have yet been proved to exist.

Continuous symmetry breaking

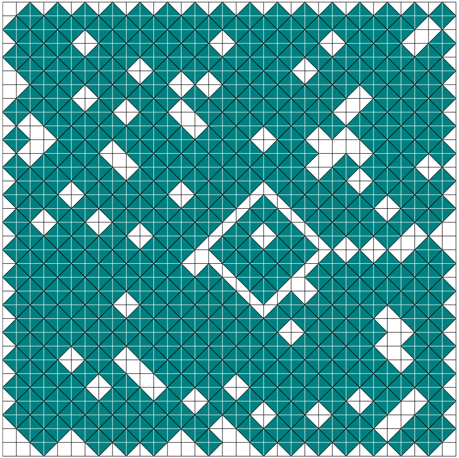
- Difficulty for both the hard spheres and liquid crystals: breaking a continuous symmetry (translation for the hard spheres, rotation for the liquid crystals).
- Continuous symmetries cannot* be broken in one or two dimensions.
- Continuous symmetry breaking can, so far, only be proved in very special models.

Lattice models

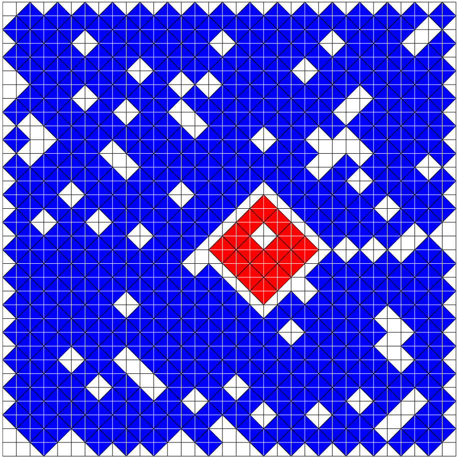
- Many examples:



Hard diamond model



Hard diamond model

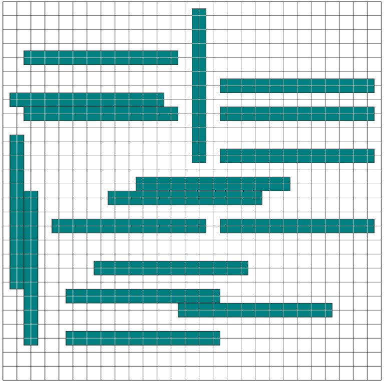


Hard diamond model

- Idea: treat the vacancies as a gas of "virtual particles".
- Can prove crystallization for a large class of lattice models.

Hard rods on a lattice

- Model: rods of length k on $\mathbb{Z}^2$.



Hard rods on a lattice

- Can prove that, when $k^{-2} \ll \rho \ll k^{-1}$, the system forms a nematic phase.
- For larger densities, one expects yet another phase, in which there are tiles of horizontal and vertical rods.
- Open Problem: generalization to 3 dimensions.

Conclusion

- Statistical Mechanics establishes a link between Microscopic theories and Macroscopic behavior.
- (In equilibrium) it consists in studying the properties of special probability distributions called Gibbs Measures.
- Even simple models pose significant mathematical challenges.
- Still, much can be said about lattice models, even though there are many problems that are still open!