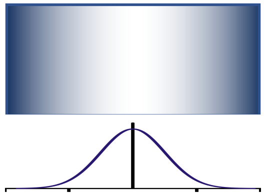
Lecture 2

FYS4715 2020

Statistical mechanics, diffusion, random walks

Thermodynamics

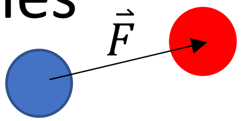
- Macroscopic
- Continuum matter
- Differentiable



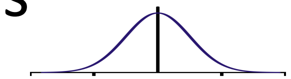
- Necessary relations based on some axioms
  - Always true for all matter
  - Necessary tool for theory
  - Always present in applications (engineering, chemistry, geoscience...)
- All properties of matter (ΔH_m, ΔS_v, c_V, λ, D) must be measured

Statistical physics

- Microscopic
- Discrete particles
- Mechanics

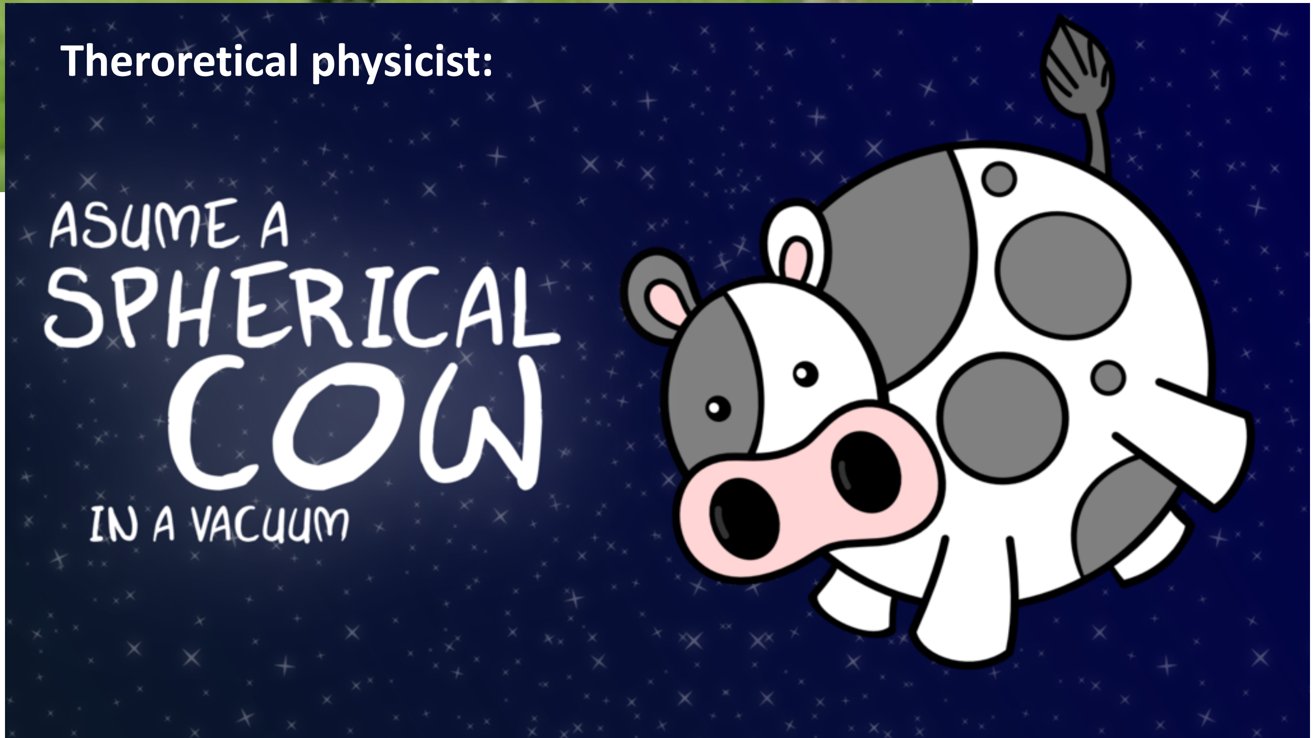


- Statistical behaviour of simplified models



- Bottom up explanation of thermodynamics
- Properties of model matter (ΔH_m, ΔS_v, c_V, λ, D) can be calculated and measured in simulation

How do cows move and interact in a meadow?



Model: Representation of a real phenomenon that is simple enough that you may do calculations.

Phenomenon: Diffusion

- Observations
  - Dissolved matter moves from high concentration to low concentration. (sugar in tea, smell of fart, ink in water).
    - After a long time: concentration is the same everywhere
    - What is diffused? “matter”, sugar, smelly molecules, ink
  - Hot metal in contact with cold metal: Temperature evens out.
    - After a long time: temperature is the same everywhere
    - What is diffused? **Heat**
    - **What is heat?**
- ”After a long time” = notion of equilibrium
- Only one direction of development -> equilibrium
- Irreversibility, arrow of time

A small detour...

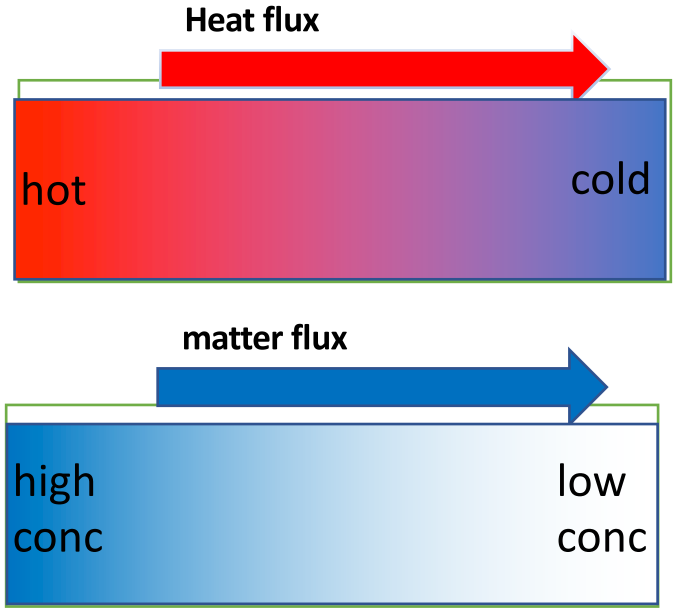
Heat, first physics definition

- **Heat** is energy in transfer to or from a system, by mechanisms other than work.
- Amount of heat transferred: J (Joule)
- Rate of heat transfer: W=J/s (Watt)
- Heat flux, Q, $[Q]=W/m^2$

Theory:
Relaxation to equilibrium by **diffusion**

Macroscopic explanation of diffusion:

Net transport of *energy* or *particles* until thermodynamic equilibrium is reached



- $\vec{J} = -D\nabla c$ *Matter flux is proportional to gradient of concentration*
- $\vec{Q} = -\lambda \nabla T$ Heat flux is proprtional to gradient of temperature
- What are «matter» and »heat»?

I. DIFFUSION AS A MIXING PROCESS

Diffusion equation:

$$J = -D_{12}\frac{\partial \rho}{\partial y} \tag{1}$$

Divergence theorem (continuity equation)

$$\frac{\partial \rho}{\partial t} + \nabla J = 0 \tag{2}$$

Combine the two to get the partial differential equation for diffusion:

$$\frac{\partial \rho}{\partial t} + D_{12}\frac{\partial^2 \rho}{\partial y^2} = 0 \tag{3}$$

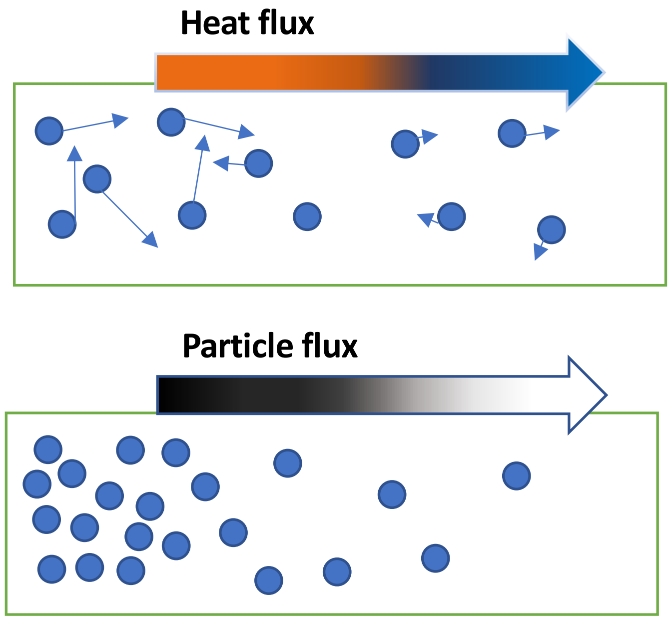
Starting with particles in $y = 0$ at time $t = 0$: $\rho(t = 0, y) = \delta(y)$, where δ is the Kroeneker delta function the diffusion equation has solution (you may easily verify this):

$$\rho(t, y) = \frac{1}{\sqrt{4\pi D_{12} t}} \exp(-\frac{y^2}{4D_{12}t}) \tag{4}$$

Theory:
Relaxation to equilibrium by diffusion

Microscopic explanation of diffusion:

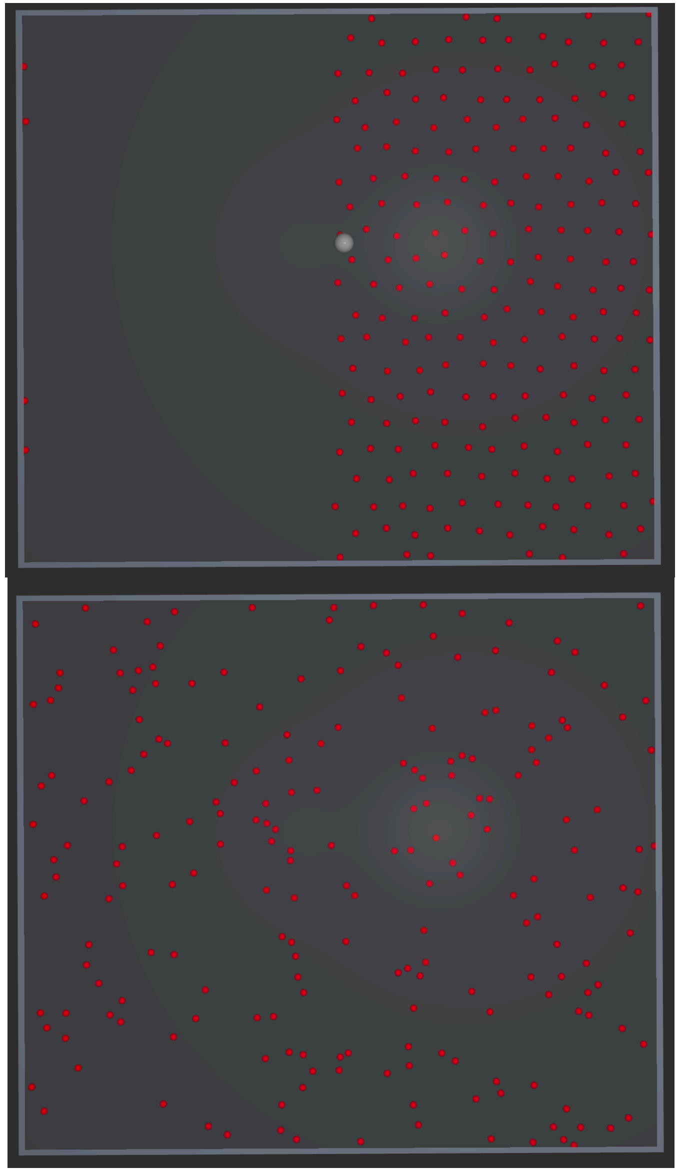
Net transport of *energy* or *particles* through random thermal motion and particle collisions until thermodynamic equilibrium is reached



- At any $T > 0\text{K}$, particles are in *thermal motion*
- Collisions between particles -> particle trajectory is a zigzag -- random *(diffusive particle)*

Models of diffusion

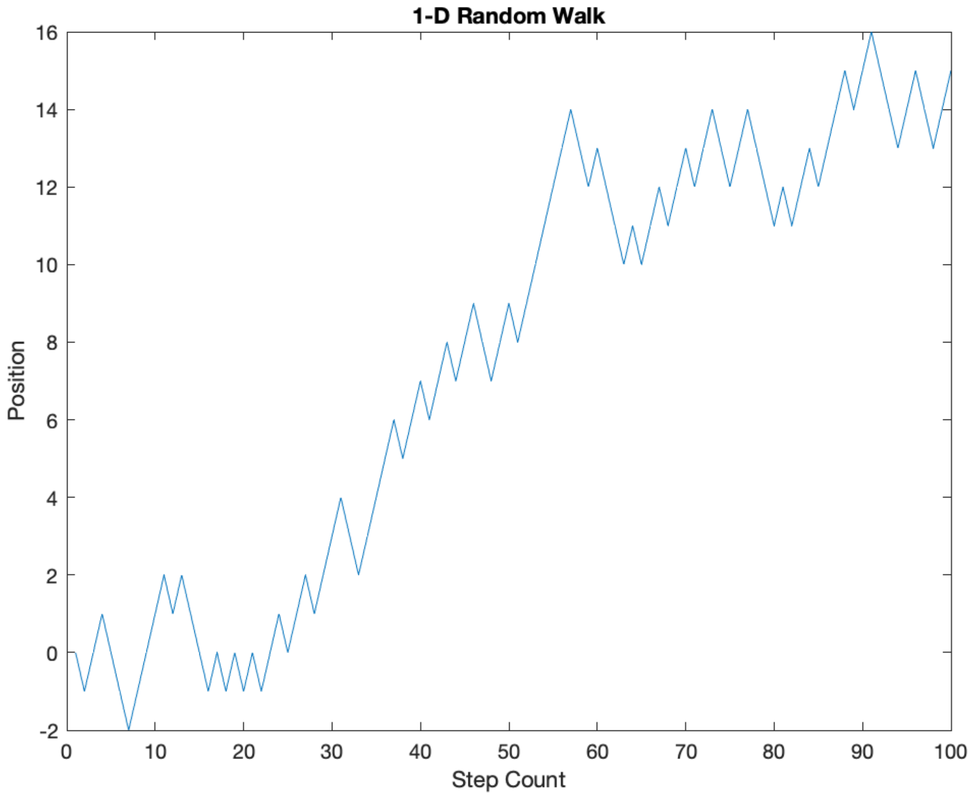
Gas particles moving randomly starting at one side.

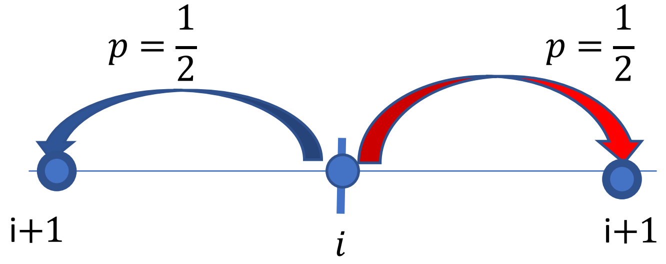


- Molecular dynamics: gas_2_sections_lampps.in
- Random walk: rw1d_vector.m, rw1d.m
- Algorithmic: gasboxalgo.m
- Ideal gas

- Reversible laws of motion
- Irreversible development: arrow of time
- Measure average property: distribution in box

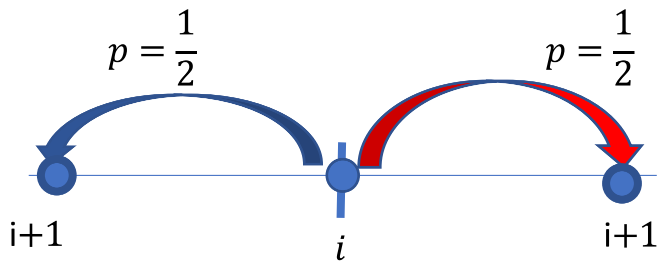
Random walk (RW)

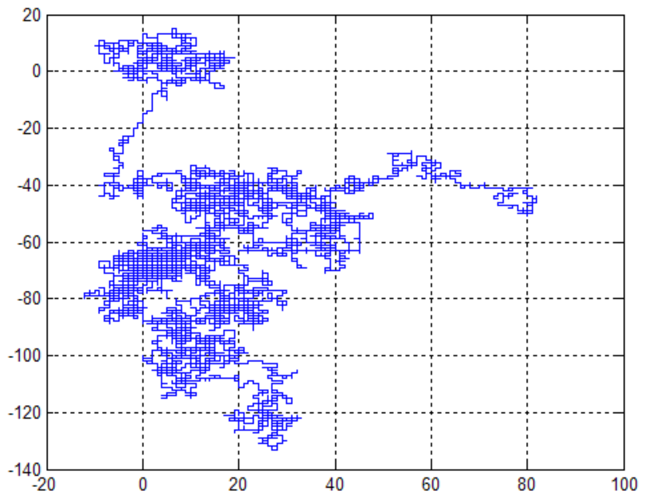


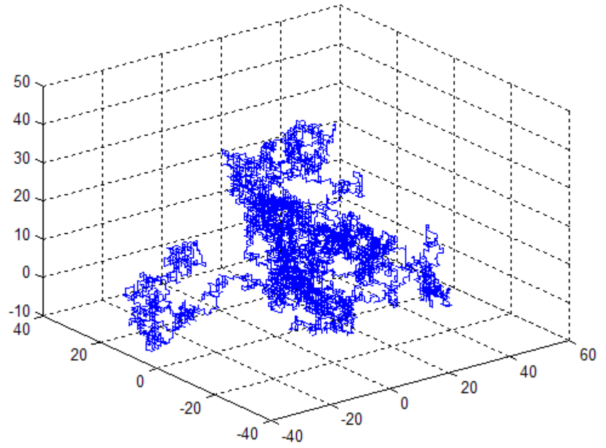



```
n = 100; % number of steps
P = zeros(n,1); %position(time) vector
P(1) = 0; % Starting value
for i=2:n
  R = rand;
  if R < 0.5
    S = -1;
  elseif R > 0.5
     S = 1;
  end
  P(i) = S+P(i-1);
end
plot(1:n,P)
ylabel('Position')
xlabel('Step Count')
title('1-D Random Walk')
```

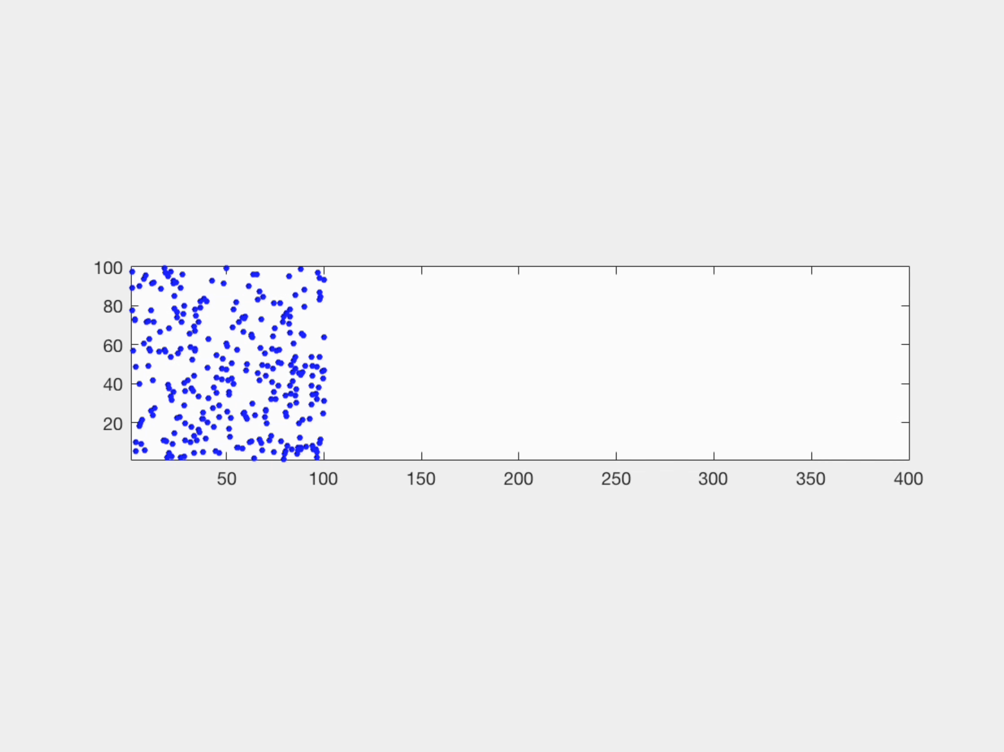
Random walk (RW)

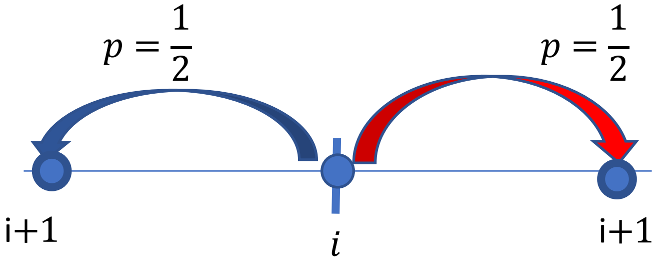






Random walk and diffusion





Exercise for tomorrow

- 2D RW in Matlab or Python
  - (live script or Jupyter notebook)

Ideal gas model

- Pressure = Force / Area
  - *[P]= [F]/[A]=N/m²*
- Newtonian mechanics
  - $\vec{F} = m\vec{a} = \frac{d\vec{p}}{dt}$
  - Used this to calculate pressure of ideal gas:

$$P_x = \frac{1}{A}\sum_i \frac{\Delta p_{x,i}}{\Delta t} = \frac{1}{A} N \frac{m\bar{v}_x^2}{2L} = \frac{N k_B T}{V} = \rho k_B T$$

- When forces at distance:
  - $P = \rho k_B T + \frac{1}{3V}\sum_{i<j} \vec{f}\left(\vec{r}_{ij}\right) \cdot \vec{r}_{ij}$
  - second term: virial

Statistical mechanics

- Model: MD (Atomify)
- micro x_i, m_i, v_i, f_{ij}, 10^{23}-> macro ρ, <v>, <v^2>, E_k,
- thermodynamics: P, T, c_P,H_v,... (stat + conservation laws)
- distributions: uniform, Gaussian, Poisson

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-x_0)^2}{2\sigma^2}}$$

- x->vx, x0->0, s
- <v>, <v^2>
- Model: ideal gas