Lecture 4

micro and macro
irreversibility, equilibrium and entropy

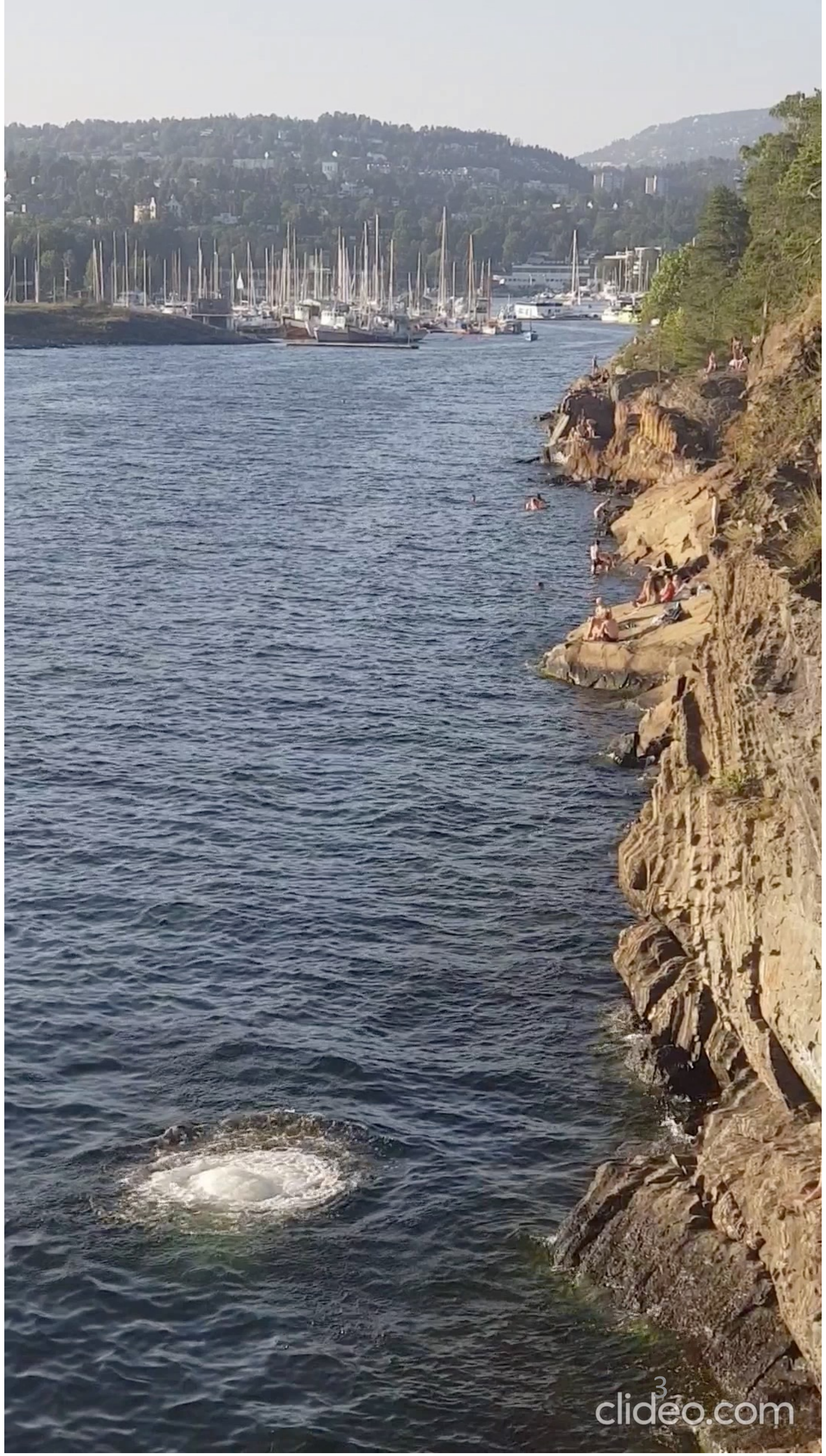
Fys2160

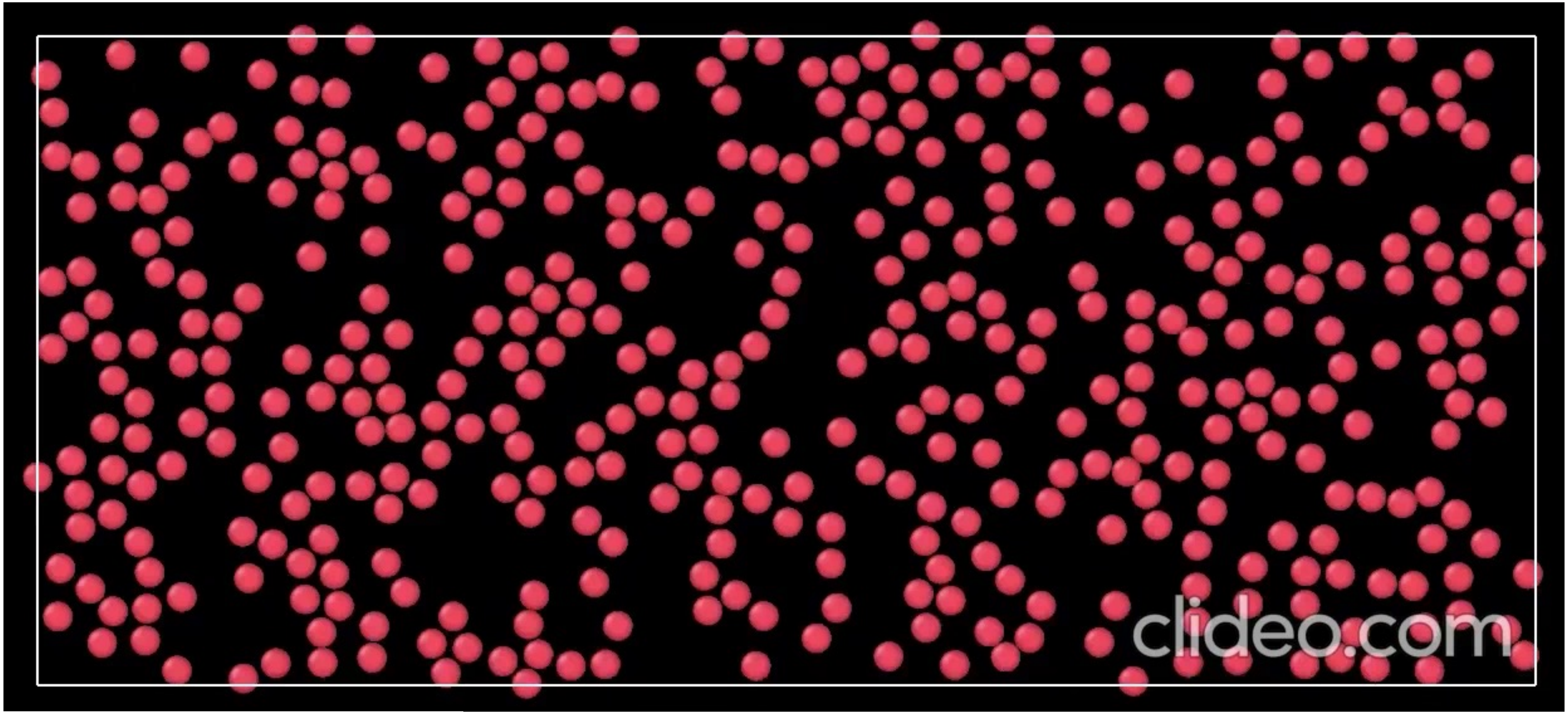
30.08.2023

Tuesday 5 Sept:

- Bring your laptops!
- We will install and test Lammps
- https://lammps.sandia.gov/doc/Install.html

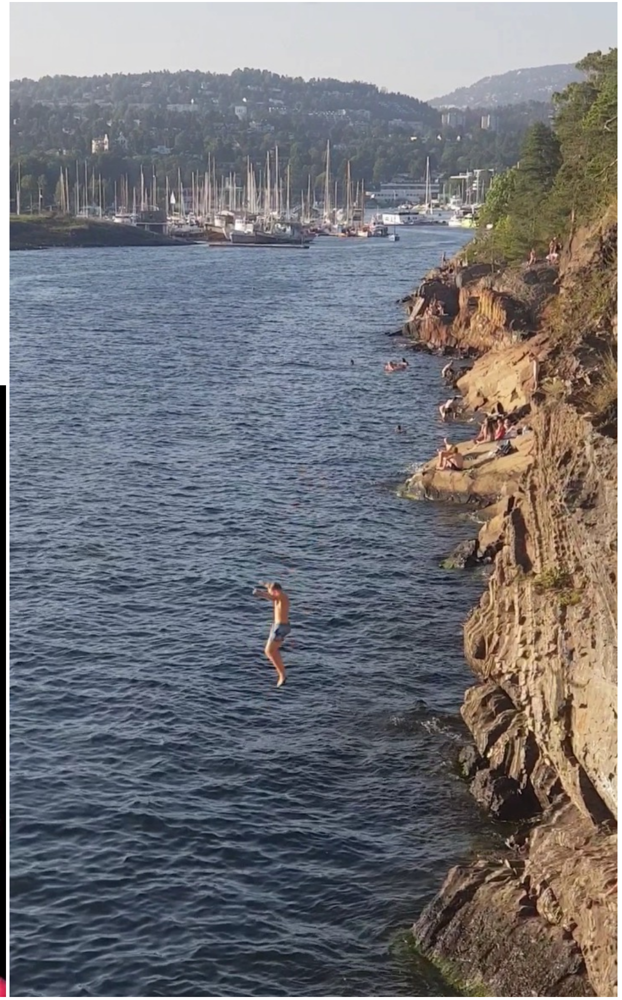
Reversible
or
irreversible



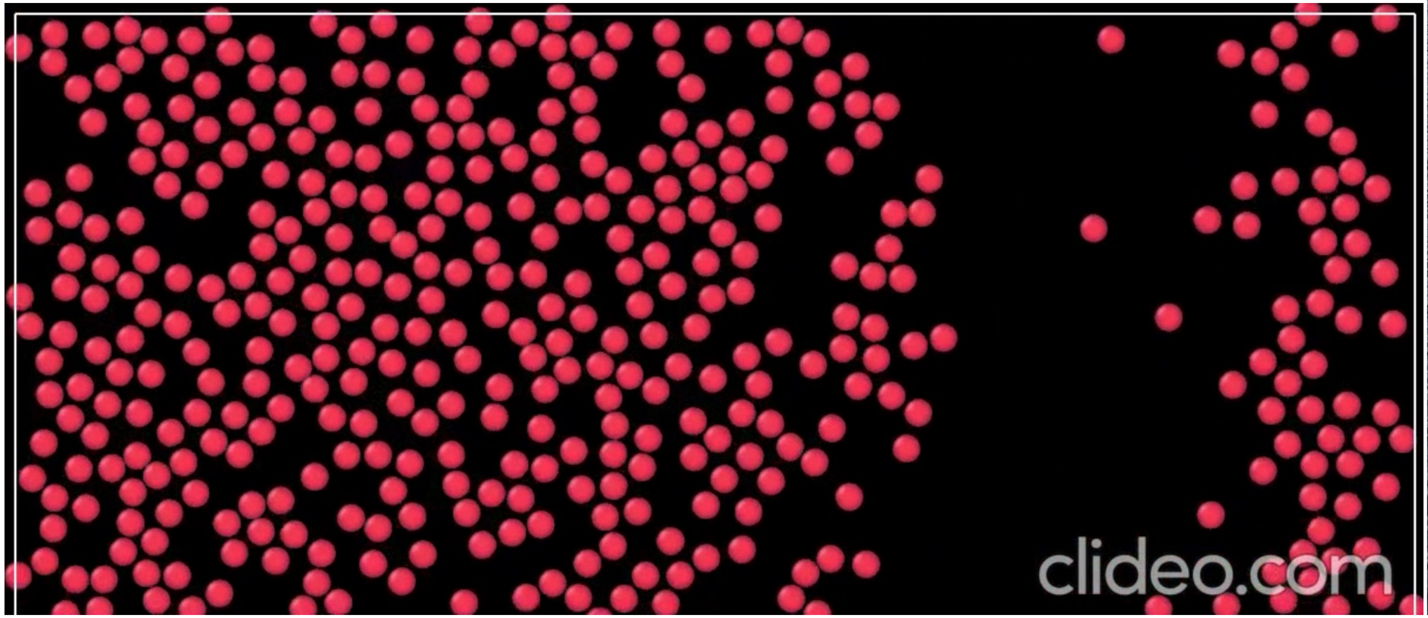


- Particle dynamics:
    - Newtons law of motion
    - Elastic collisions (no friction, no loss of energy)
    - => Reversible
    - => Possible evolution
- Why does it never happen?

- One body: reversible motion (My son can be shot from the water up to Pantern)
- Multibody systems:
  - reversible laws of motion (beads CAN move all to one side)
  - irreversible collective dynamics (it will never happen)



- Macro definition of equilibrium:
  - Homogeneous particle distribution
- Micro definition of equilibrium?



New concept: Microstates and macrostates

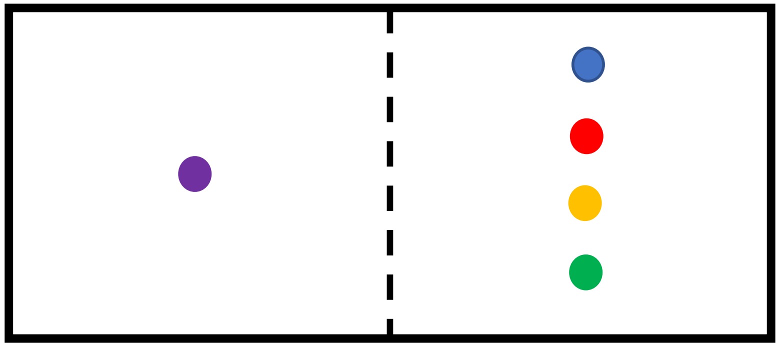
- What is the most likely outcome of tossing 3 coins?
  (ordered sequence without replacement)
- Microstates: state of all coins
  - heads: s_i=1, tails: s_i=0
  - all microstates are equally likely
- Macrostate: sum of states
  - $n=\Sigma_i s_i$ (= 0,1,2,3)
- Which is the most likely macrostate
  - 8 = 2^3 possible microstates
  - Probabilities:

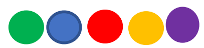
i: 1	2	3	n
0	0	0	0
1	0	0	1
0	1	0	1
0	0	1	1
1	1	0	2
1	0	1	2
0	1	1	2
1	1	1	3

n=0: P=1/8
n=1: P=3/8
n=2: P=3/8
n=3: P=1/8

Microstates and macrostates

- Box with left and right side
- Example: $N = 5$
- Particles can be distinguished (i=1, 2,.. 5)
- Particle state s_i:
  - left: s_i=1
  - right: s_i=0
- Macrostates $n=\Sigma_i\, s_i$ (= 0,1,2, ..5)
- List the possible microstates of n=1

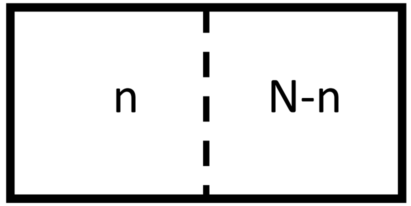




- 00001
- 00010
- 00100
- 01000
- 10000

5 microstates => multiplicity **Ω**(N,n) of macrostate n=1 is **Ω**(5,1) = 5

Multiplicity of macrostates



n=0	n=1	n=2	n=3	n=4	n=5
00000	00001	00011	11100	11110	11111
	00010	00101	11010	11101	
	00100	01001	10110	11011	
	01000	10001	01110	10111	
	10000	00110	11001	01111	
		01010	10101		
		01100	10011		
		10010	01101		
		10100	01011		
		11000	00111		
Ω(5,0)=1	**Ω**(5,1)=5	**Ω**(5,2)=10	**Ω**(5,3)=10	**Ω**(5,4)=5	**Ω**(5,5)=1

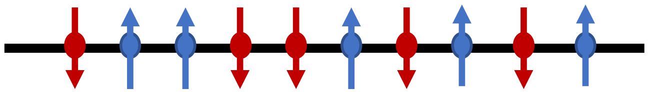
General formula for multiplicity: $\Omega(N,n) = \frac{N!}{(N-n)!n!}$ $\Omega(5,2) = \frac{5!}{3!2!} = 10$

Number of possible microstates: $\Omega_t = \sum_{n=0}^{5} \Omega(n) = 32(= 2^5)$

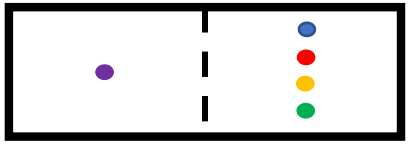
Probability of macrostates: $\mathrm{P(N,n)} = \Omega(N,n)/2^N = \frac{2^{-N}N!}{(N-n)!n!}$

Two-state models

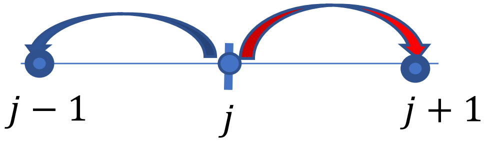
paramagnet



two-sided box



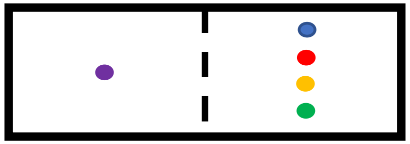
random walk



and many others…

- System: ***N*** spins, particles, steps, coins
  - **Isolated**
  - **Independent** (no interaction between spins/particles, no correlation between successive steps)
  - **Distinguishable** (the order matters)
  - **Equal probability of states** $s_i = \pm 1$ (up/down, left/right, head/tail)

two-sided box, N=5

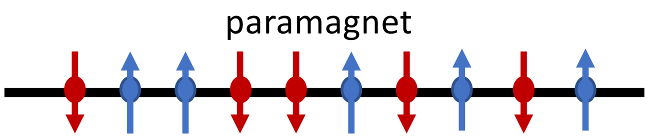


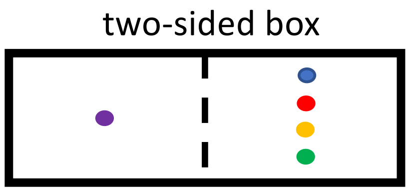
What are the macro-states? n = number of atoms on left side 0,1,2,3,4,5

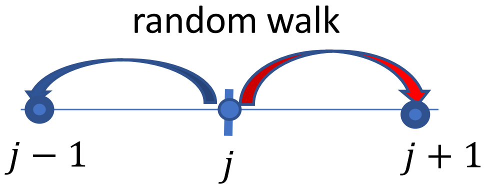
What is a microstate? A particular ordering of atoms

How many microstates? $2^N=2^5=32$

Two-state models







and many others...

Microstates:

- All possible combinations of ordering the N atoms/particles/steps...
- Total number = 2^N

Multiplicity of macrostate n in two-state model?

- All possible combinations of ordering the N atoms/particles/steps given that exactly n are in one state.
- $\Omega(N,n) = \frac{N!}{(N-n)!n!}$

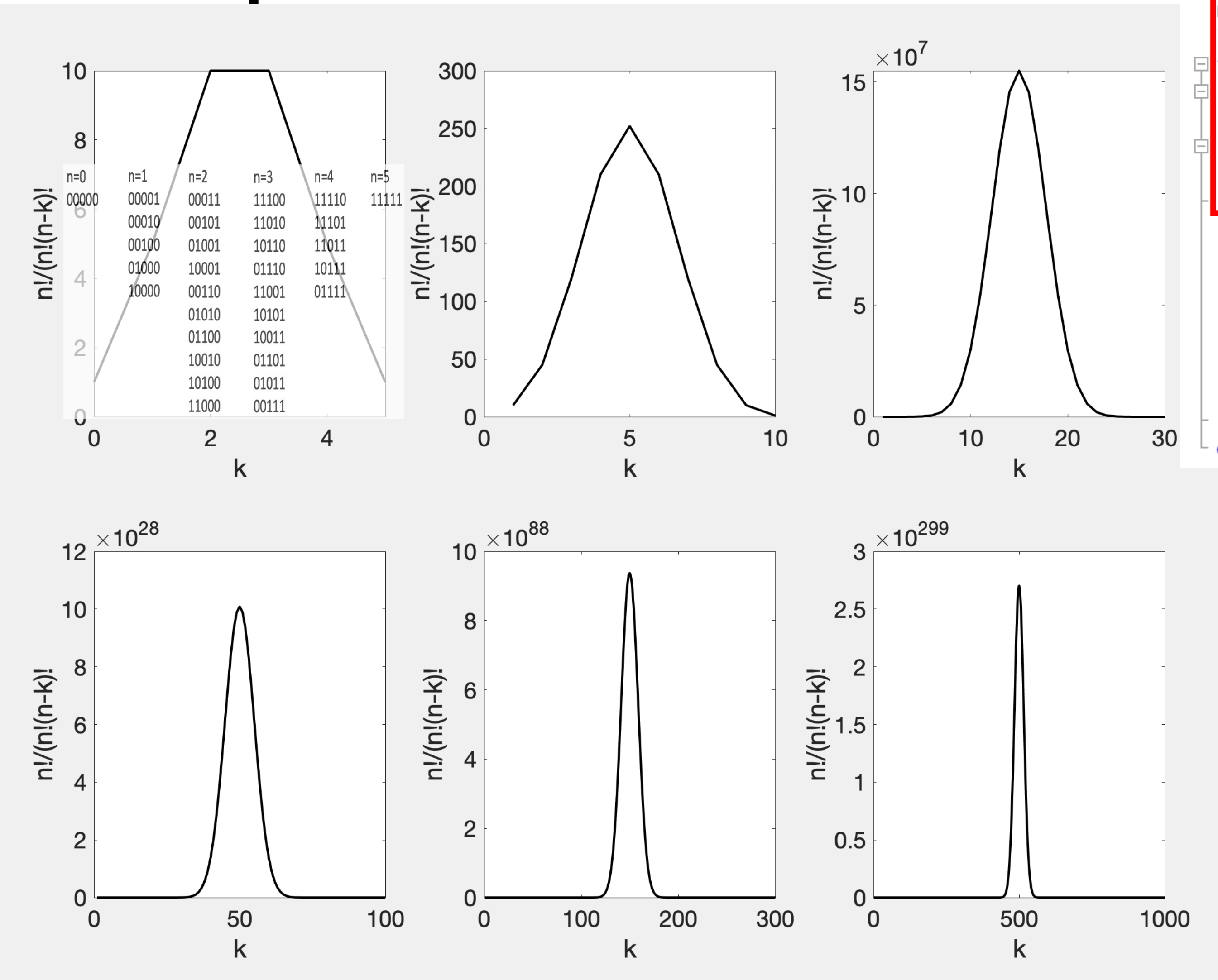
n=0	n=1	n=2	n=3	n=4	n=5
00000	00001	00011	11100	11110	11111
	00010	00101	11010	11101	
	00100	01001	10110	11011	
	01000	10001	01110	10111	
	10000	00110	11001	01111	
		01010	10101		
		01100	10011		
		10010	01101		
		10100	01011		
		11000	00111		

Fundamental assumption of statistical mechanics?

- In an isolated system in thermal equilibrium, all a microstates are equally probable
- Probability of macrostate n?

$$\mathrm{P(n,N)} = \Omega(N,n)/2^N = \frac{2^{-N}N!}{(N-n)!\,n!}$$

Sharpness of distribution

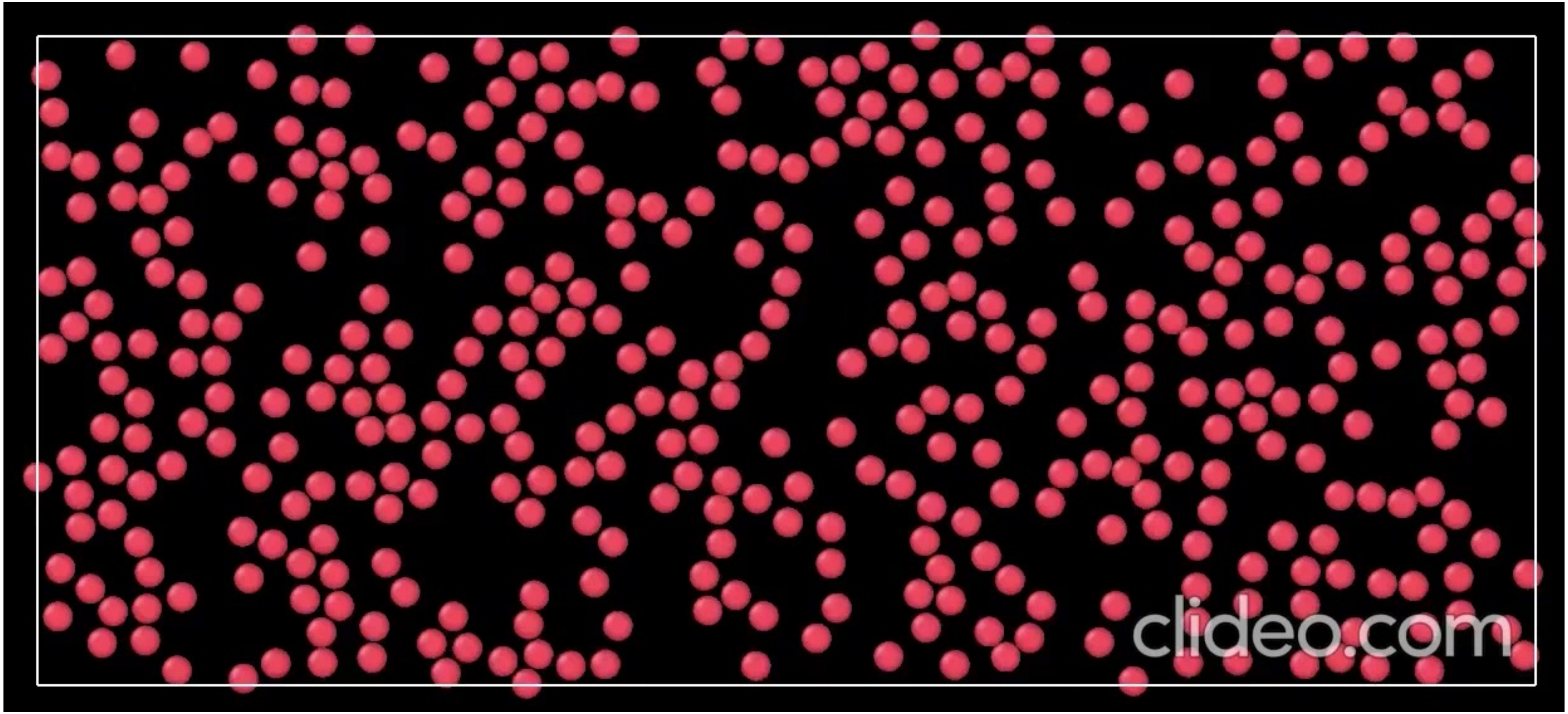


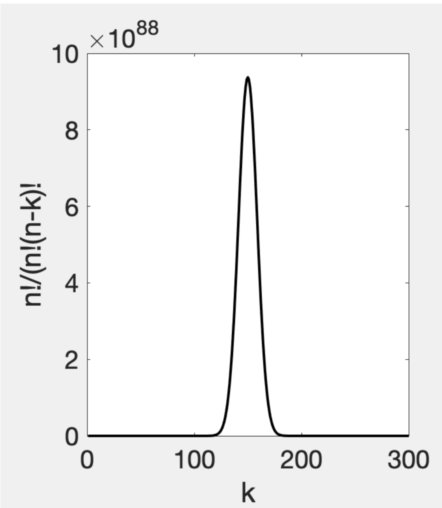

```
n=[5 10 30 100 300 1000];
l=1;
for i=1:2
    for j=1:3
        nk=1;
        for k=1:n(l)
            nk(k)=nchoosek(n(l),k);
        end
        subplot(2,3,l)
        plot(nk,'k','LineWidth',2)
        xlabel('k','FontSize',20)
        ylabel('n!/(n!(n-k)!','FontSize',20)
        ax1 = gca; % current axes
        ax1.FontSize = 20;
        l=l+1;
    end
end
```

What happens when $q \rightarrow 10^{23}$?

$$\Omega(N,k) = \frac{N!}{k!(N-k)!}$$

We need an approximation for *N!* when *N>>1*





- Particle dynamics:
  - Newtons law of motion
  - Reversible
  - Possible evolution
- Why does it never happen?

Relaxation to equilibrium by diffusion

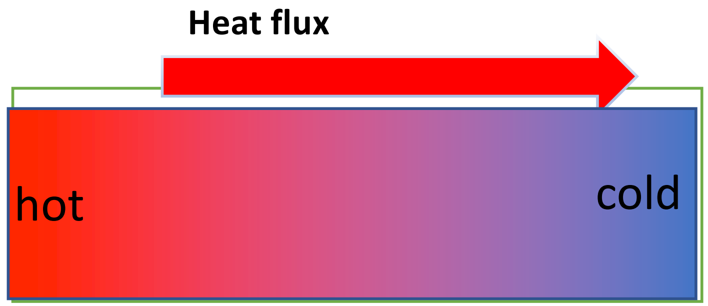
Macroscopic explanation of diffusion:

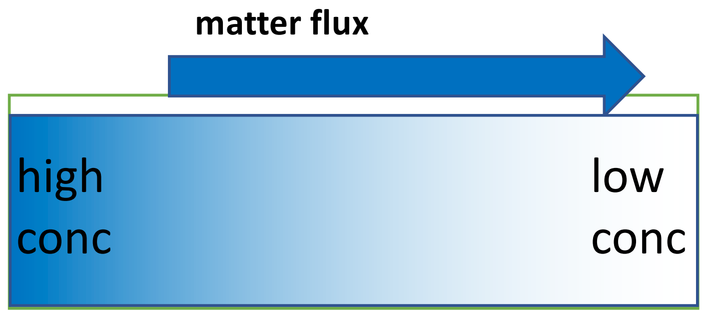
Net transport of *energy* or *particles* until thermodynamic equilibrium is reached

- $\vec{J} = -D\nabla c$ *Matter flux is proportional to gradient of concentration*

- $\vec{Q} = -\lambda\nabla T$ Heat flux is proprtional to gradient of temperature

- What are the equilibrium conditions?



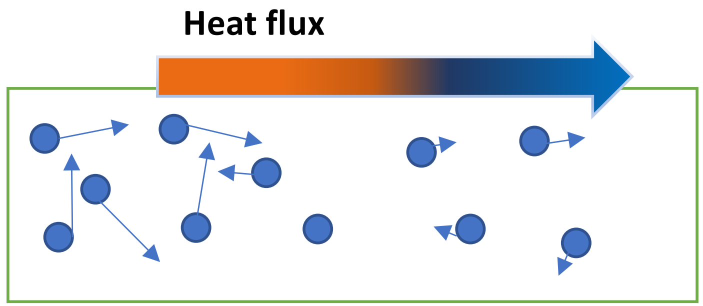


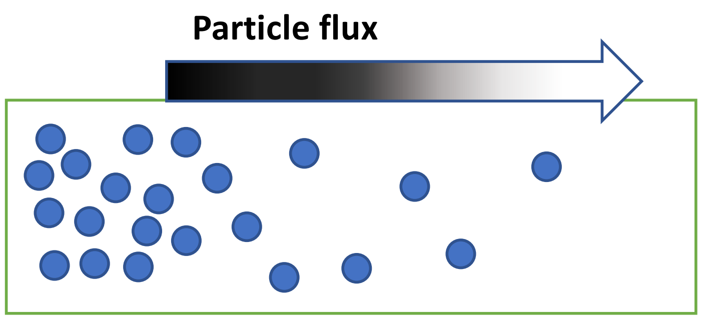
Relaxation to equilibrium by diffusion

Microscopic explanation of diffusion:

Net transport of *energy* or *particles*

- through random thermal motion and particle collisions
- until the most likely states are reached





- At any $T > 0\mathrm{K}$, particles are in *thermal motion*

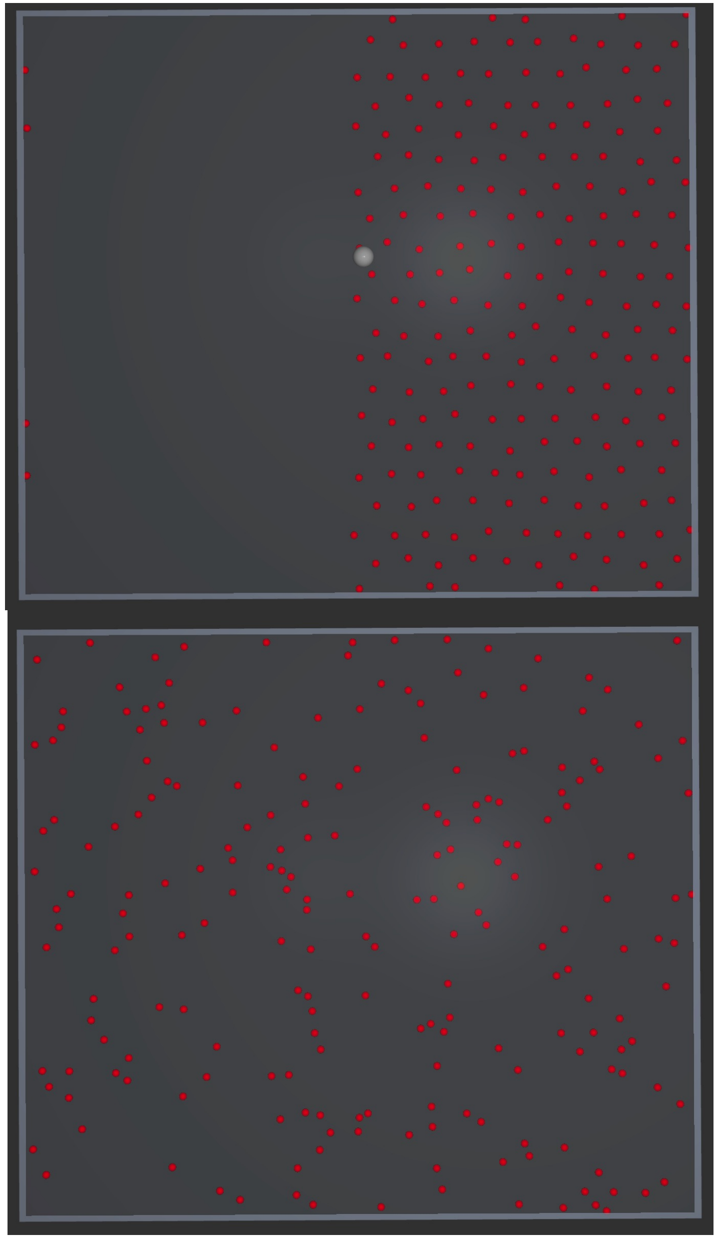
- Collisions between particles -> particle trajectory is a zigzag -- random *(diffusive particle)*

Microscopic models of diffusion

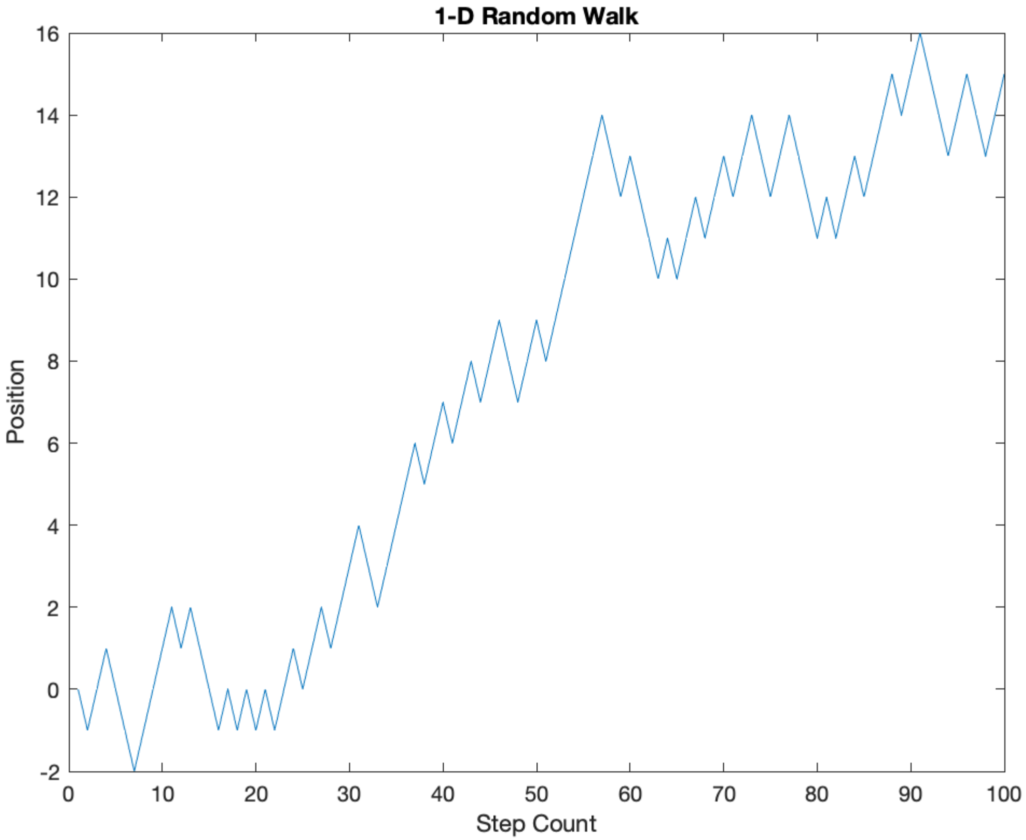
1. Random walk
2. Algorithmic
3. MD (soon)

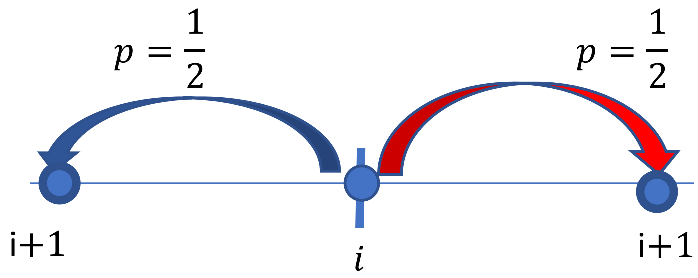
- Reversible laws of motion
- Irreversible development: arrow of time
- Measure average property: distribution in box (right/left)

Gas particles moving randomly starting at one side.



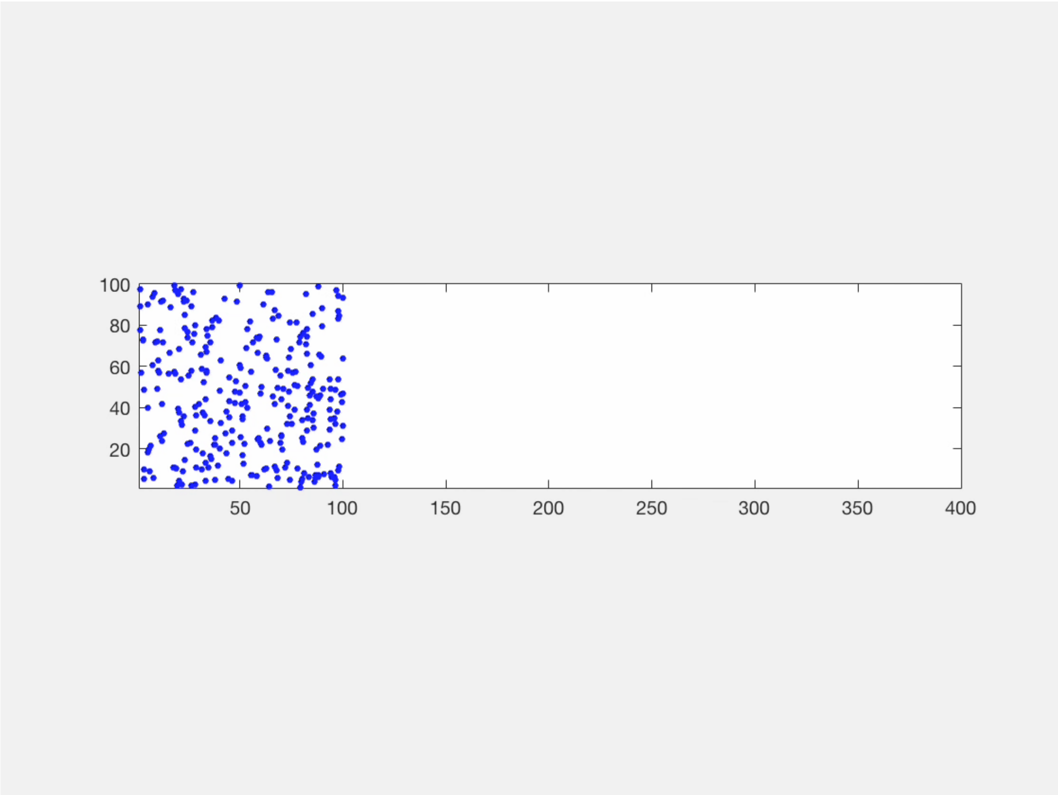
Random walk (RW)

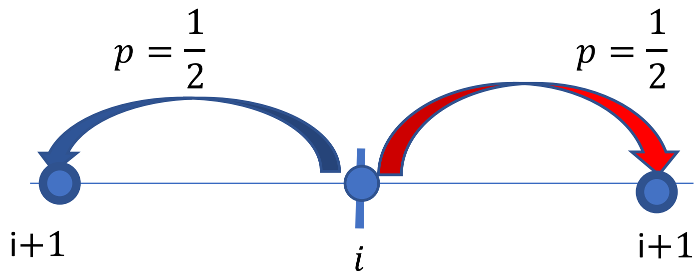




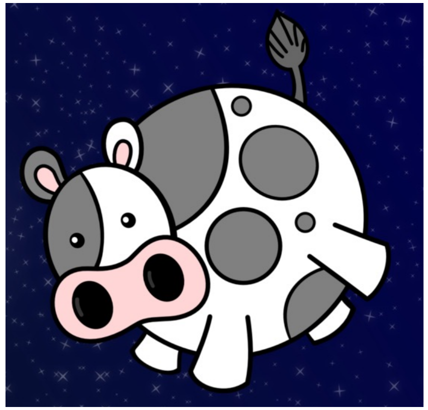

```
n = 100; % number of steps
P = zeros(n,1); %position(time) vector
P(1) = 0; % Starting value
for i=2:n
  R = rand;
  if R < 0.5
    S = -1;
  elseif R > 0.5
     S = 1;
  end
  P(i) = S+P(i-1);
end
plot(1:n,P)
ylabel('Position')
xlabel('Step Count')
title('1-D Random Walk')
```

Random walk and diffusion

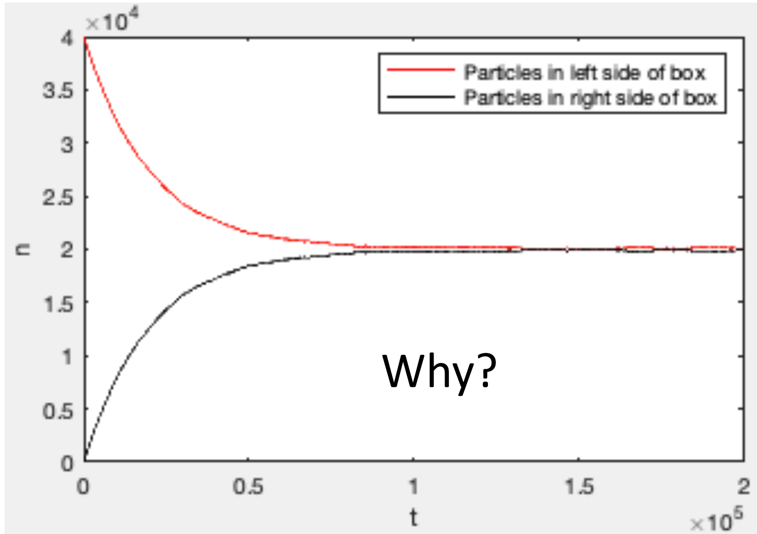


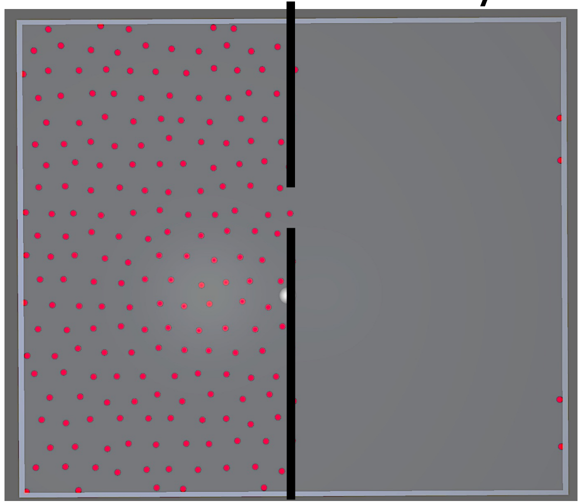


Algorithmic model



- How can we simplify?
- Positions: only left and right
- N particles in total
- n particles on left side
- Initially: $n = N$
- Every timestep:
  - pick a random number r
  - if $r < n/N$ move particle to right, else to left

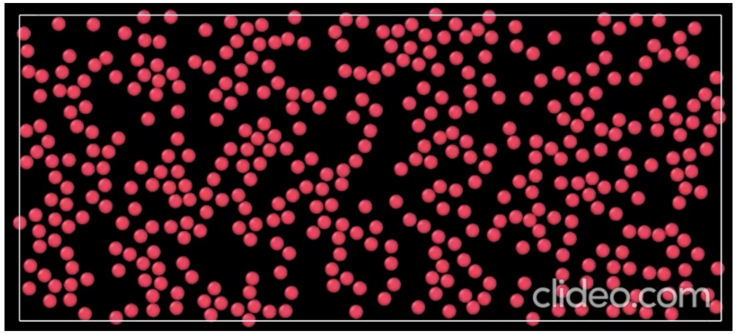


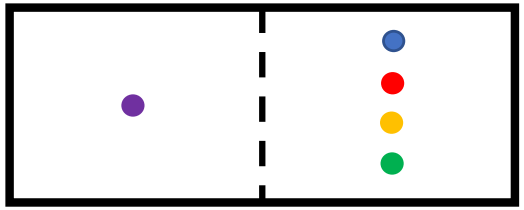


```
N = 40000;
nstep = 5*N;
n = zeros(nstep,1);
n(1) = N; % Initial number on left side
for i = 2:nstep
    r = rand(1,1);
    if (r<n(i-1)/N) %If r is smaller than fraction of particles on left side
        n(i) = n(i-1) - 1; % Move atom from left to right
    else
        n(i) = n(i-1) + 1; % Move atom from right to left
    end
end
figure(1), plot((1:nstep),n,'r',(1:nstep),N-n,'k')
xlabel('t'),ylabel('n')
legend('Particles in left side of box','Particles in right side of box')
```

Irreversibility & equilibrium

- $\vec{J} = -D\nabla c$, equilibrium: $\nabla c = 0$
- 2 box system:
  - $c_1 = c_2$ highest multiplicity
  - $\mathrm{P(n, N)} = \Omega(n, N)/2^N = \frac{2^{-N} N!}{(N-n)!n!}$
  - equilibrium is the most probable state





- Next: Equilibrium between two sub-systems that each have multiplicities => general multiplicity formulation of equilibrium.

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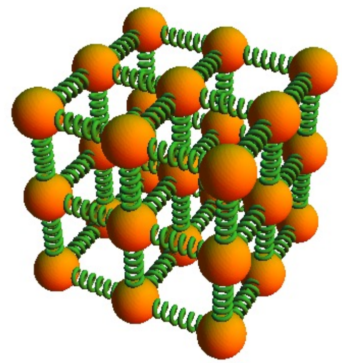
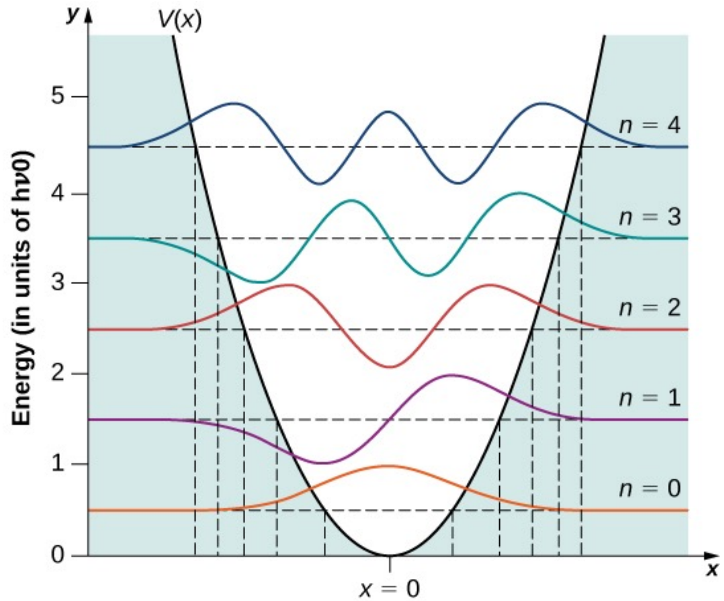
Einstein crystal



- N independent and localized (distinguishable) quantum harmonic oscillators
- Each quantum oscillator has a discrete spectrum of energy levels, $n = 0,1,2...$ (not two-state)

$$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

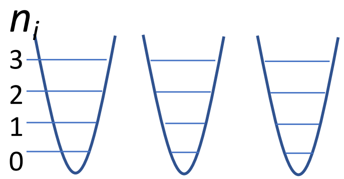
- Microstates: $\{n_1, n_2, \ldots n_{N-1}, n_N\}$
- Macrostate = total energy:
  - $U_N = \sum_{i=1}^{N} \epsilon_{n_i} = \sum_{i=1}^{N} n_i\, \hbar\omega + \frac{N}{2}\hbar\omega$
  - $q = \frac{U_N - \frac{N}{2}\hbar\omega}{\hbar\omega} = \sum_{i=1}^{N} n_i$
  - defined by (N,q)

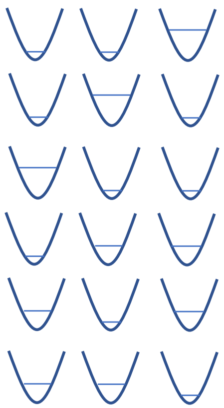


Einstein crystal

Multiplicity $\Omega(N,q)$ of a macrostate with N oscillators and q units of energy distributed between them. Trick: map to two-state system.

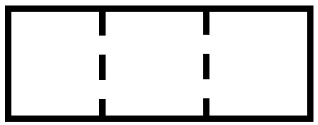
N oscillators
q energy units
n_i energy units in oscillator i





0	0	2
0	2	0
2	0	2
0	1	1
1	0	1
1	1	0

N boxes, N-1 walls
q balls
n_i balls in box i



```
   |    |oo
   |oo  |
oo |    |
   | o  | o
o  |    | o
o  | o  |
```

Two-state model:

$$\Omega(N,k) = \frac{N!}{k!\,(N-k)!}$$

Number of digits: *N' = N-1+q* (= wall + balls)

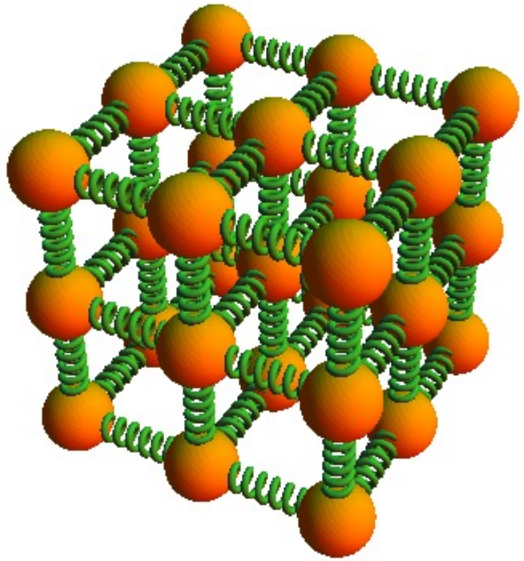
Number of states: *k' = q*

N' – k' = N - 1 + q – q = N - 1

Number of ways of combining *(N-1)-walls* and *q* balls:

$$\boldsymbol{\Omega(N,q) = \frac{(N-1+q)!}{q!\,(N-1)!}}$$

Physical interpretation of Einstein crystal



- In the metal block: what does N correspond to?
- In the metal block: what does q correspond to?
- Temperature?

coupled Einstein crystals

$$\Omega_A(N_A, q_A) = \frac{(N_A - 1 + q_A)!}{q_A!\,(N_A - 1)!}$$

$$\Omega(N_B, q_B) = \frac{(N_B - 1 + q_B)!}{q_B!\,(N_B - 1)!}$$

Composite system:

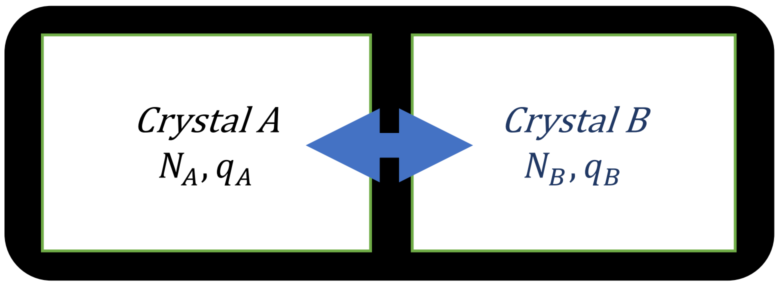
$$q = q_A + q_B, \qquad N = N_A + N_B$$

N_A, N_B, q fixed, but energy can be «transferred» between A and B

Multiplicity of a macrostate of the composite systems

$$\boldsymbol{\Omega_t = \Omega_A(N_A, q_A) \cdot \Omega_B(N_B, q_B)}$$

Towards thermal equilibrium: $q_A/N_A = q_B/N_B$



Probability of throwing a 5 twice is 1/6 * 1/6 = 1/36

What do we call such "energy transfer"?

Einstein crystal heat simulation

- Conduction law?
- Compared to experiment?

Equilibrium between two systems

- *N, q=q$_A$+q$_B$, (N,q)* constant
- Multiplicity $\Omega_{tot} = \Omega_A \Omega_B$ is maximum in equilibrium

$$\frac{\partial \Omega_{tot}}{\partial q_A} = 0$$

$$\frac{\partial(\Omega_A \Omega_B)}{\partial q_A} = \Omega_A \frac{\partial \Omega_B}{\partial q_A} + \Omega_B \frac{\partial \Omega_A}{\partial q_A} = 0$$

$$\frac{-1}{\Omega_B}\frac{\partial \Omega_B}{\partial q_B} + \frac{1}{\Omega_A}\frac{\partial \Omega_A}{\partial q_A} = 0$$

$$\boxed{\frac{\partial \ln \Omega_B}{\partial q_B} = \frac{\partial \ln \Omega_A}{\partial q_A}}$$

Entropy: $S = k \ln \Omega(N, V, U)$

Total entropy is maximized in equilibrium!

Thermal eq.: $\frac{\partial S_A}{\partial q_A} = \frac{\partial S_B}{\partial q_B}$, $\frac{1}{T} \equiv (\frac{\partial S}{\partial q})_N$

$$T_A = T_B$$

$$\frac{q_A}{N_A} = \frac{q_B}{N_B}$$

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