recap ·

thermodynamics ; framework for relating macroscopic properties, processes relating to work, heat

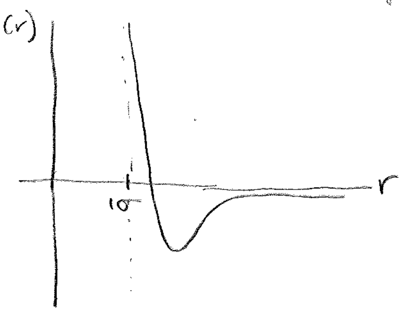
stat mech : microscopic info $\Rightarrow$ macroscopic properties (1st principles)

pictures worth 1000 words $\rightarrow$ illustrate basic concepts w/ MD simulation

explore equilibrium, arrow of time

experiment on your own! compadre.org/stpbook
(thermal physics)

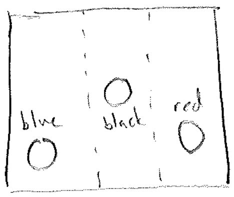
simulation system: N particles, closed container (fixed V)
- $\rightarrow$ no external forces (like gravity)
- $\rightarrow$ motion given by solving $\vec{F} = m\vec{a}$ for each particle
- $\rightarrow$ assume Lennard-Jones potential, only depends on r



$$f = -\frac{du}{dr}$$

- $\rightarrow$ don't need 10^{23} particles, small as 100 enough to illustrate macroscopic phenomena
- $\rightarrow$ use periodic boundary conditions to avoid boundary effects (pac-man)

Approach to equilibrium (Three Parts MD)



"gas molecules"
color = portion of the box
particles start in the middle (random)
, assigned random velocities ($v_{cm} = 0$)
• $t = 0$, remove walls
• PBC → NOT bouncing off walls

(1) What do you expect?

(2) N = 100

- what is "final" state?
- arrow of time?
- how long?

(3) N = 1000

- what is final state?
- how long?
- exactly evenly distributed?

Why is there an arrow of time?

→ We started in a very special <u>microstate</u>
→ if we start in a more probable microstate (even distribution) arrow of time not as clear

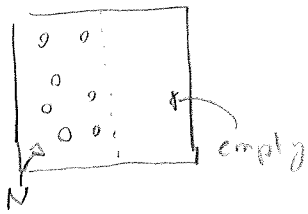
non-equilibrium "special" microstate ⟶ more probable microstate

direction of time

ponder this concept, we will leave it vague for now (need new tools to properly address)

Probabilistic model (not MD)

- simplified model with same behavior
- no forces, velocities
- each step, choose particle at random and move to other side



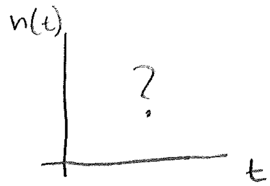
Plot $n(t)$, particles in left half $\left[\begin{array}{l} N \text{ total} \\ N-n \text{ right half} \end{array}\right]$

- each particle has <u>equal</u> chance to move

$$\Rightarrow P(\text{left} \to \text{right}) = \frac{\#\text{ particles on left}}{\text{total }\#\text{ particles}} = \frac{n}{N}$$

- before we begin, what do we expect?

(run beforehand)



- # on left decreases
- flucuations
- eventually # becomes equal on both sides

- let's try for different values of $N = \{16, 32, 64, 128, 512, 1024\}$
  - equalibrium? how do you know?
  - how does equillibrium behavior change with N?

→ equillibrium: approach mean value, independent of time

→ ratio of flucuations decrease w/increasing N

- small $N = 8$ – do we ever see return to intial state?

likely, after 250 time steps when I ran it last

→ do you expect this for large N?
how long do you think it would take?

microstates:

Count particles in each half:

N = 2

microstate	n	# of microstates $W(n)$	probability $P(n)$
L L	2	1	1/4
L R, R L	1	2	1/2
R R	0	1	1/4

Take aways

- average values of macroscopic quantities become independent of time

  → system has reached equilibrium

  → macroscopic quantities exhibit fluctuations about averge value

- relative fluctuations decrease w/increasing N

- why is there an arrow of time?

  - could study dynamics ..

  - note in equilibrium, independent of time

    → time is irrelevant

  - counting # ways particles can be distributed tells us about equilibrium

    (doesn't tell about approach, but will tell us about arrow of time)

TABLE DISCUSSED HERE

Microstate - arrangement of particles

Macrostate - specified by macroscopic quantities, here n

note: in equilibrium particles are equally likely to be on either side

$$\left.\begin{matrix} L\ L \\ L\ R \\ R\ L \\ R\ R \end{matrix}\right\} \text{all equally probable}$$

are all the macrostates equally probable? No!

consider $N=4$:

microstate	n	$W(n)$	$P(n)$
LLLL	4	1	1/16
RLLL	3		
LRLL	3		
LLRL	3		
LLLR	3	4	4/16
RRLL	2		
RLRL	2		
RLLR	2		
LRRL	2		
LRLR	2		
LLRR	2	6	6/16
RRRL	1		
RRLR	1		
RLRR	1		
LRRR	1	4	4/16
RRRR	0	1	1/16

- all microstates equally probable
  - → one state w/all on left
  - → most probable state $n=2$

<u>takeaway</u>: equillibrium macrostate corresponds to <u>most probable</u> microstate

(here $n = N/2$)

observations

- macrostate that gives least amount of info about microstate is most probable

ex : $N=4$ microstate LLLL $p = 1/16$ particle #1 on left!

microstate LRLR
LLRR
⋮
RRLL

$p = 6/16$ 50% chance particle #1 on left

"more random"

→ isolated system evolves in time ⇒ more random

stop 3/30

- a system in a nonuniform macrostate changes in time on average to approach the most random macrostate where it is in equilibrium

independent of dynamics!

in MD example, energy conserved.. what's changing?

entropy ⇒ must be connected to # microstates

⇒ entropy of isolated system increases or stays the same when internal constraint removed

2nd law of thermodynamics!