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

step 3/30

- a system in a nonuniform macrostate changes in time on average to approach the most random macrostate when 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!

More observations

(1) in equilibrium macroscopic observables not constant, but fluctuate about a mean value

e.g. $n(t)$ depends on time, but not $\bar{n}$

→ fluctuations become smaller with larger N

(2) approach to equilibrium doesn't matter

e.g. $n(t) \to \bar{n}$ no matter how we start

history independent

(3) we need a statistical approach!

can describe system by specifying microstate

e.g. position of every gas atom in room

but this doesn't help, and is intractable

→ want to know info on macroscopic properties

$N \sim 10^{23}$

→ averages more meaningful

→ fluctuations small!

(4) we assumed all microstates were equally probable

(microstates of isolated system equally probable in equilibrium)

⇒ this is a key assumption!; we will make it much more explicit when we lay out framework for stat mech

Thermodynamics

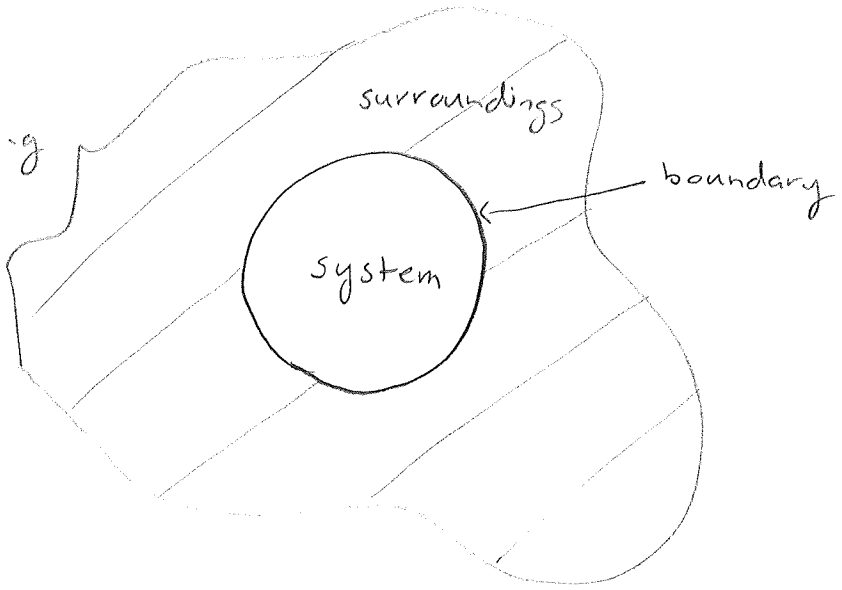
TLDR:

- energy is conserved
- entropy increases

These statements are deceptively simple!
We will spend the next few classes unpacking them, being very careful about definitions

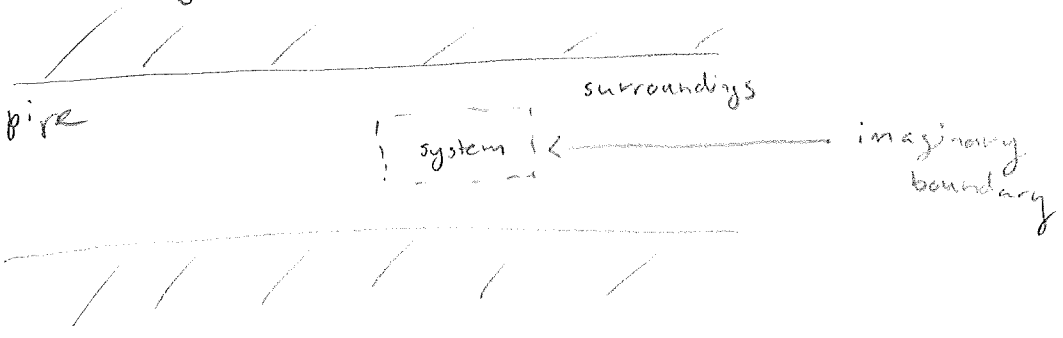
Definitions

We begin by selecting the system; this is something we have to choose.



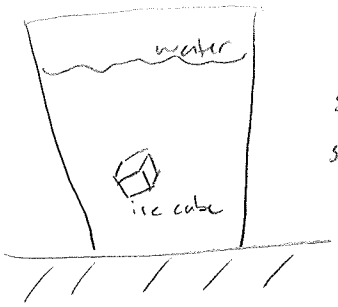
ex: chunk of steel, helium balloon, etc

NB: boundary does not have to be real

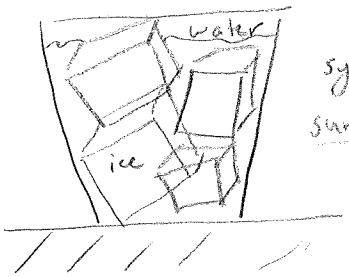


- could consider a small section of flowing liquid for example

ex:



system: ice
surroundings: water



system: ice + water
surroundings: air in room

- choice of system depends on question of interest!

Definition: open system: exchange matter w/ surroundings

closed system: cannot exchange matter w/ surroundings

recall: last class we spent time using simulations to explore equilibrium

↖ macroscopic properties time-independant

How do we know? Not necessarily straightforward!

→ need to have confidence we have waited "long enough"

→ ex: pour hot coffee over glass of ice

at first temperature varies everywhere

→ not in equilibrium

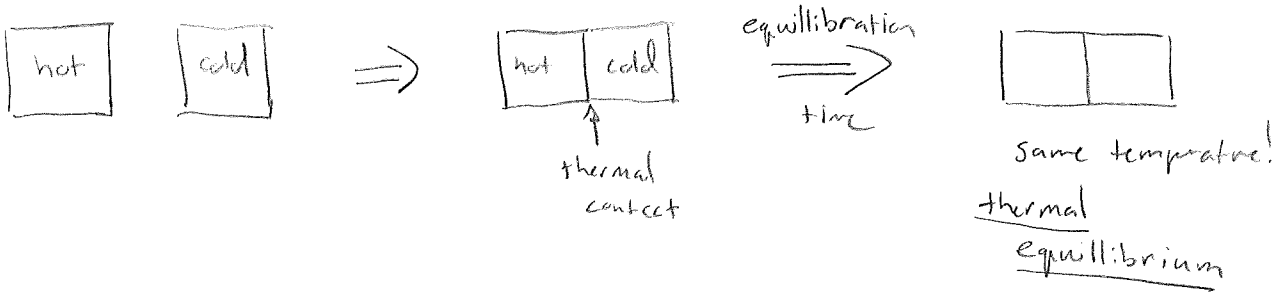
ice melts, all becomes same temperature

→ equilibrium

NB: we must be confident our system is in equilibrium to proceed applying thermodynamic rules

Temperature

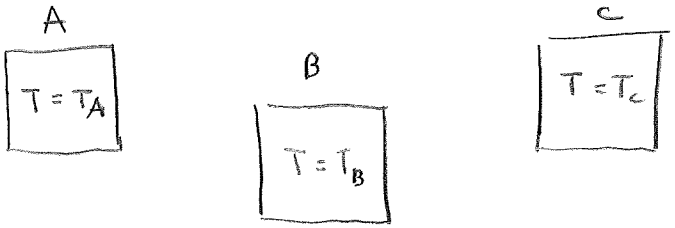
Definition?



note: we assumed this was a conducting wall, so that energy transfer was possible

We will also encounter insulating walls, which do not allow energy transfer (a thermos!)

0th law of thermodynamics: temperature is transitive



if $T_A = T_B$
$T_B = T_C$
$T_C = T_A$

OR

if A & B are in thermal equilibrium, B & C are in thermal equilibrium
C & A are in thermal equilibrium

- this is an emperical fact
- many properties are NOT transitive

ex: NYC is 1200 km from Chicago (as the crow flies)
Dallas, TX is 1200 km from Chicago

Dallas is not 1200 km from NYC! (its 2200 km)

How do we measure temperature?

thermometer: body whose macroscopic properties change in a well-defined way w/ temperature

ex: alcohol thermometer

alcohol expands w/ increasing temperature, narrow tube makes this easy to see

calibration / scale?

ideal gas scale (K)

$T \propto P$ ⇒ choose T so that $T(P=0) = 0$

⇒ triple point $T = 273.16$

(historically, gave 100K between melting and freezing)

celsius $T_{celsius} = T_K - 273.15$

(only different by shifting zero)

Pressure equation of state

$P = f(T, \rho)$ pressure is determined by T, $\rho = N/V$ (simple fluid, single species)

→ this is all you need to know, then can determine everything about relationships between macroscopic properties

e.g. If I raise temperature, how does pressure change?

→ Historically, determined empirically

"Boyles law" PV = constant (fixed T)

"Charles law" $V \propto T$ (fixed P)

→ stat mech allows us to calculate theoretically

Here, we just state it

$$\boxed{PV = NkT}$$

Boltzmann constant $k \equiv 1.38 \times 10^{-23}$ J/K

IDEAL GAS (point particles, no interactions)

$\left(R = N_A k \quad PV = nRT\right)$

Note: real gases only satisfy this at low density, more generally

$$\left(P + \frac{N^2}{V^2}a\right)(V - Nb) = NkT$$ ← van der Waals eqn of state

$\frac{N^2}{V^2}a$: interparticle interactions

Nb: finite molecular size