Thermodynamics

I. The Zeroth Law and Related Concepts

What Zeroth Law gives us...

- temperature and thermometers
- Why we know two systems are in thermal equilibrium even they never meet each other (through a third party or many thermometers working at different places)

Related Concepts

- System and surrounding, and how they interact (thermal contact, and more)
- Equilibrium (thermodynamic)
- State variables & State functions

Zeroth Law

If each of two systems is in thermal equilibrium with a third, then they are in thermal equilibrium with one another.

↖ This is the formal statement.

In plain language,

If systems A and B are at the same temperature, and B and C are at the same temperature, then A and C are at the same temperature.

i.e. when two systems are put into thermal contact (& wait for some time) and achieve equilibrium, they have one quantity (temperature) in common.

- Thermodynamics is based on daily life experience/observations
- No need to mention what are the stuff in the systems
  - gases, liquids, solids ...
  - Don't need to refer to atoms/molecules

    this is statistical mechanics' job!
  - Don't need to refer to microscopic models of matter

    e.g. an array of atoms forming a solid with a Hamiltonian that carries quadratic (harmonic) and third order (anharmonic) terms

Make thermodynamics work for macroscopic systems of any kind!

systems with many stuff!

Einstein (1949)[†]:

"... A theory is more impressive the greater the simplicity of its premises, ... Therefore, classical thermodynamics has made a deep impression on me. It is the only physical theory of universal content which I am convinced, ..., will never be overthrown."

[†] Holton and Elkana, "Albert Einstein, Historical and Cultural Perspectives", (Princeton Univ. Press)

Simple but deep!

- System + (what's not the system)

what we focus on

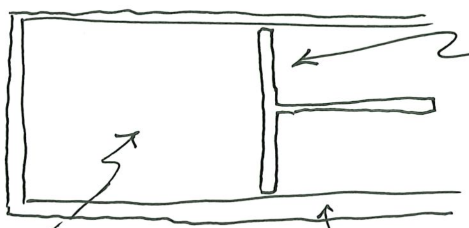
(what's not the system): surrounding (could do something to affect the system)

could do something:

- Add/Take something called "Heat" [+]
- "Do work" on the system
- Add/Take matter to/from system

to affect the system: depends on nature of boundary

- A standard physicist's system



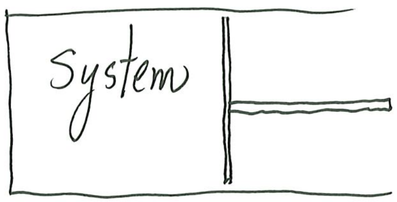
Gas

piston can be rigid (not moving) (block work done)
OR piston can move (work done on/by system)
— mechanical

walls can insulate heat (block thermal contact)
OR walls can allow thermal contact
— thermal

[+] These are thermal interaction, mechanical interaction, chemical interaction, respectively.
All these amount to adding/substracting ENERGY to system, that will change the STATE of system.

- Equilibrium
  - From experience/observations
  - After something is done on a system [heat in, piston in a bit, ...] and let's wait [don't care how long it will take], system will settle into an equilibrium state



- Bulk parameters (things you can see) NOT changing in time

  e.g. P, V, T, N (amount of matter)
- these state variables are uniform (the same) throughout the system
- System's equilibrium state is characterized by these (few) state variables!

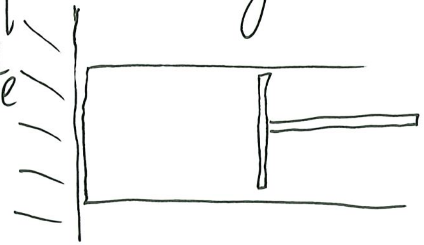
Meaning

Start:

at equilibrium

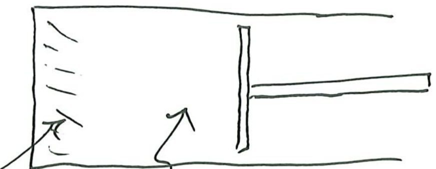
fixed N

hot plate



Just begin touching the "bottom" of system with a hot plate

Zoom in



"hotter" still not knowing hot plate is there

NOT HAVING a uniform temperature in system

System is NOT in an equilibrium state

System is OUT OF Equilibrium

We need to wait and let system to adjust to another equilibrium state

- State variables (e.g. p, V, T, N) are related through

<u>equation of state</u> [ideal gas for example: $pV = NkT$]

$pV = RT$ (1 mole)

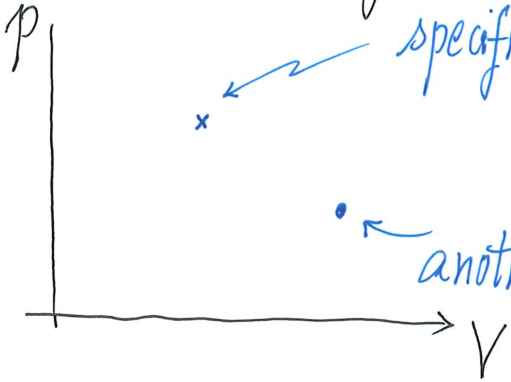
a key property of the system

$\Rightarrow$ <u>Not all state variables are independent</u>

but still free to make the choice

- <u>State Diagram / Indicator Diagram</u>

e.g. PV diagram



specifies (p, V) ← eq. of state gives T

← thus specifies an equilibrium states

key concept!

another equilibrium state

$\boxed{\text{None equilibrium states CANNOT be dotted on to indicator diagram!}}$

∵ Don't have well-defined p, V, T

- Later, will see there are other quantities U, S, F, G, H that have a certain value depending only on the equilibrium state.

  F ← Helmholtz free energy, G ← Gibbs free energy, H ← Enthalpy

They are often called <u>State Functions</u>. In principle, p, V, T are also state functions, as their values are specified by the equilibrium state of the system. (OR $U, S, \ldots$ can also be state variables.) But p, V, T were the bulk quantities easier to observe (and they helped establish the subject), they are often taken to be the state variables.

- Back to zeroth law
  - Referring to $\underbrace{\text{systems}}$ in $\underbrace{\text{thermal contact}}_{\text{allows heat}^{+}\text{ in/out [no work done, no matter added]}}$

wait → bulk properties in systems settled → equilibrium

They have a common property called Temperature.

+ Historically, heat was taken to be something unrelated to work [Newtonian mechanics]. We still use quantities such as HEAT capacities (there are tables to look up values for different materials).

A few words on Temperature Scales

- Any thing that has $\underbrace{\text{a property changing}}_{\text{e.g. height of mercury/alcohol in thermometers}}$ with hotness will do

- But will be nice to have a construction that people can follow to make a thermometer and will agree on the measurement results

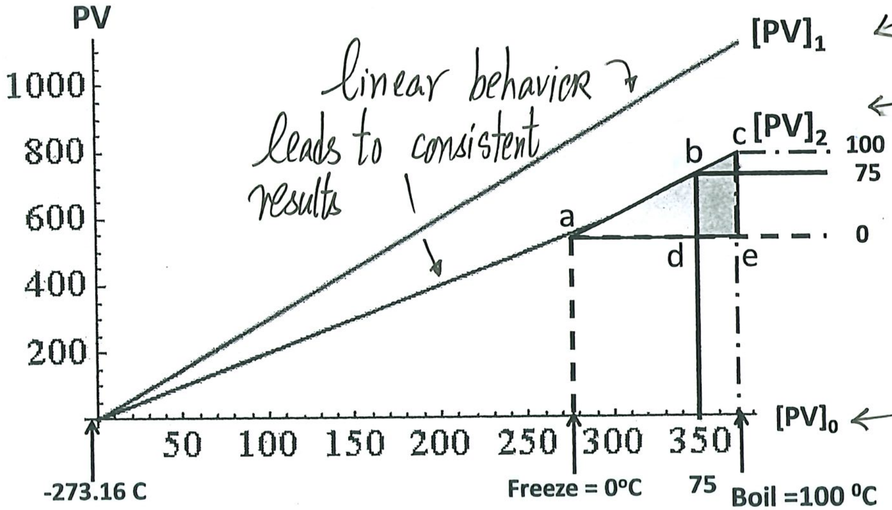
- Gas Thermometers

  - Take a gas (doesn't matter which gas). calibrate [PV] against selected phenomena [$\underbrace{\text{ice melts}}_{\text{call it } 0°C}$ and $\underbrace{\text{water boils}}_{\text{call it } 100°C}$ at sea level]

    thus 100 divisions

- Follow the recipe, different thermometers will agree on the results!

Figure taken from Shankar, "Fundamentals of Physics I"



yet another thermometer

another thermometer [different gas, different size] (more gas)

1st thermometer [using its [PV] (call it $[PV]_0$)] to fix a temperature scale

- experimentally based
- dilute gas [condition when different real gases behave like ideal gas]

Magical Moment in Physics

Extrapolating lines of Different Gases to low [PV] (down in temperature), Lines converge and meet at one point (this is the absolute zero T = 0 K) [Kelvin]

- A rare occasion in physics!
  - You define a measurement scale for practical reasons

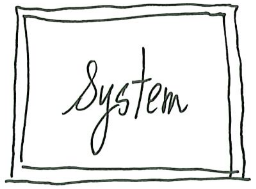
    hotter vs colder? at equilibrium?
  - Then discover a behavior of NATURE

    ↳ there is a lowest possible[+] temperature 0 K (zero Kelvin)

    [Advertisement: There is a microscopic reason (stat. mech.)]

[+] There is No negative K.

Remarks on Systems

- 

  Isolated System

  adiabatic walls

  [Walls do not allow thermal, mechanical, chemical interactions with outside/surrounding]

- Open System

  Can exchange (in/out) energy (heat OR work) AND matter with outside

- Closed System in Thermodynamics

  Can exchange (in/out) energy (heat OR work) but NOT Matter

Remark: In Statistical Mechanics, we also use a system that can exchange heat but with fixed Volume (thus no work done) and no exchange on Matter

Beyond (P,V) in (P,V,T)

- For our gas/fluid system, we have P, V specifying equilibrium state
- Other systems
  - Wire under tension [Tension $\mathcal{T}$ and extension (or length $\mathcal{L}$)]

    "funny T" (not the temperature)
  - Paramagnetic Materials [Applied magnetic induction B_0 and total magnetic dipole moment of the system $\mathcal{M}$]

    can be magnetized by applying an external field

The Goal remains the same

- General relations among state variables, and state functions
- Stat Mech: Calculate quantities from microscopic starting point

This sets the stage for $\underbrace{\text{the 1}^{\text{st}}\text{ law}}_{\text{accounting both work and heat as Energy}}$