

Thermodynamics = phenomenological description of macroscopic systems in thermal equilibrium. □

\* no assumptions about the underlying structure (e.g., atoms) or dynamics  $\Rightarrow$  highly universal but limited in scope

"Thermodynamics has something to say about everything, but does not tell us everything about anything."

Statistical Mechanics = microscopic approach based on probabilistic concepts to understand macroscopic properties of systems with large # of DOF.

\* As you learned in your undergrad SM/Thermal Physics course, SM is more fundamental - you can derive TD from 1<sup>st</sup> principles, and can go well beyond what TD can.

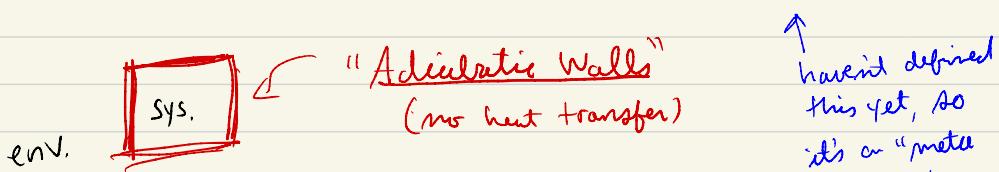
\* Nevertheless, I find it useful to start with a quick recap (3-4 lectures) of classical TD (i.e., where we follow the path of Joule, Kelvin, Clausius, Carnot, and others by using a combination of empirical observations and clever idealized thought experiments to deduce the laws of TD.)

Side remark: Why cover the historical (i.e., phenomenological) development of TD if SM gives a rigorous/fundamental derivation?

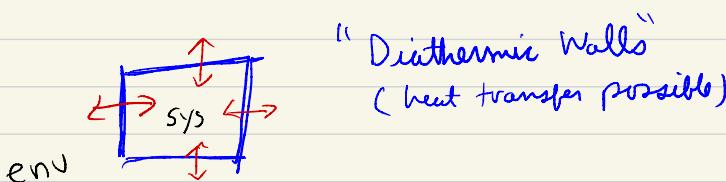
- 1) Nice example of viewing complex system as "black box" and still being able to construct a predictive theory based on empirical observations (precursor of more modern examples like Landau-Ginzburg theory of Superfluids)
- 2) It will make you appreciate the SM derivation of TD!

- \* Pretend we are 18<sup>th</sup> century physicists. Newtonian mechanics rules the day w/ many successes, but is unable to describe simple processes like heating up a container of gas. (need new concepts like heat + temperature)
- \* We want to fix this. How do we proceed?
- \* Part of N's genius was clever idealizations (point particles, frictionless motion, etc.) that are never exactly realized in Nature, but allow a clearer view of the underlying laws of Nature.
- \* Let's try to do the same for thermal processes/properties.

"Heat" is the new complication. So let's first imagine an idealized system that is 100% isolated from the environment with no exchange of heat possible



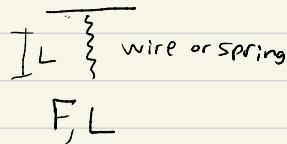
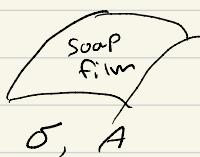
vs



\* The next idealization is the notion of equilibrium.

≡ when macroscopic properties not changing over observation time (fuzzy/imprecise notion.  
e.g., glass is technically a flowing fluid over timescales of  $\sim 10^3$  years)

Macroscopic properties: We can carry over some concepts from Mechanics & EM, e.g.



or  $(\vec{H}, \vec{M})$  magnetic etc.  
 $(\vec{E}, \vec{P})$  dielectric

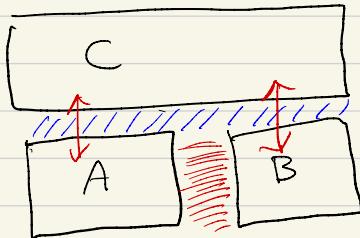
BUT we are clearly in need of new concepts  
(Temperature, Heat, + Entropy being the "big" ones)  
to describe thermal properties.

\* Let's follow our 18<sup>th</sup>-19<sup>th</sup> century predecessors and rely heavily on phenomenology based on experimental observation to introduce these new concepts systematically.

↙ empirical observation

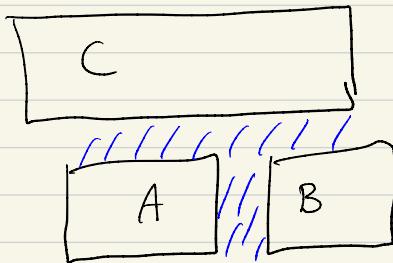
\* 0<sup>th</sup> Law: If 2 systems A & B are separately in equilibrium with C, then they are in equil. with each other. ( $\Rightarrow$  temperature)

\* Physically, this means nothing changes if we go from

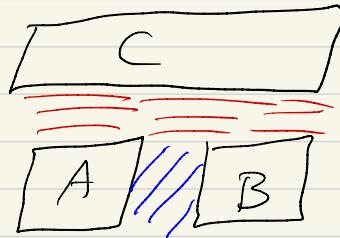


||| = diathermic wall  
≡ = adiabatic wall

↓ to



or



\* Transitivity of thermal equil. implies a new property that is a measure of equilibrium (temperature)

\* let's see this mathematically

\* let  $\{C_1, C_2, \dots\} \equiv \text{TD "coordinates" (i.e.- macroscopic properties) for C}$

$$\{A_1, A_2, \dots\} = \text{" " for A}$$

$$\{B_1, B_2, \dots\} = \text{" " for B}$$

equilibrium of A+C:  $f_{AC}(A_1, A_2, \dots, C_1, C_2, \dots) = 0 \quad (1)$

parameters of A+C are not independent of each other by virtue of the fact that they are in equilibrium.

i.e., there is a constraint represented by  $f_{AC}(A_1, \dots, C_1, \dots) = 0$

\* likewise, equilibrium of B+C  $\Rightarrow f_{BC}(B_1, B_2, \dots, C_1, C_2, \dots) = 0 \quad (2)$

(Note:  $f_{AC} + f_{BC}$  are not the same function in general!)

\* Now imagine taking eq. (1) and solving for one particular coordinate, say  $C_1$ . Repeat using eq. (2)

$$(1) \Rightarrow C_1 = F_{AC}(A_1, A_2, \dots, C_2, \dots)$$

$$(2) \Rightarrow C_1 = F_{BC}(B_1, B_2, \dots, C_2, \dots)$$

$$\therefore \boxed{F_{AC}(A_1, A_2, \dots, C_2, \dots) = F_{BC}(B_1, B_2, \dots, C_2, \dots)} \quad (3)$$

\* OK, so eq. (3) is the mathematical statement of the 1<sup>st</sup> part of the 0<sup>th</sup> Law (i.e., that A+B are in equil. w/ C)

\* But the 2<sup>nd</sup> part of the 0<sup>th</sup> Law (transitivity feature) that A+B are then in equil. w/ each other



A+B are in equil.:

$$\boxed{f_{AB}(A_1, A_2, \dots, B_1, B_2, \dots) = 0} \quad (4)$$

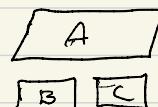
\* But eq. (3) has to contain the same information as eq. (4), which only refers to  $\{A, A_2, \dots\}$  &  $\{B, B_2, \dots\}$ .

$$F_{AC}(A_1, A_2, \dots, C_1, \dots) = F_{BC}(B_1, B_2, \dots, C_1, \dots)$$

∴ Must be possible to cancel out the dependence on  $C_2, C_3, \dots$



$$\boxed{\Theta_A(A_1, A_2, \dots) = \Theta_B(B_1, B_2, \dots)}$$



\* Repeating the argument now with

$$\Rightarrow \Theta_A(\{A_i\}) = \Theta_B(\{B_i\}) = \Theta_C(\{C_i\})$$

(Remark: the functions  $\Theta_A, \Theta_B$  etc. are different, in general, but they take the same # value at eq.)

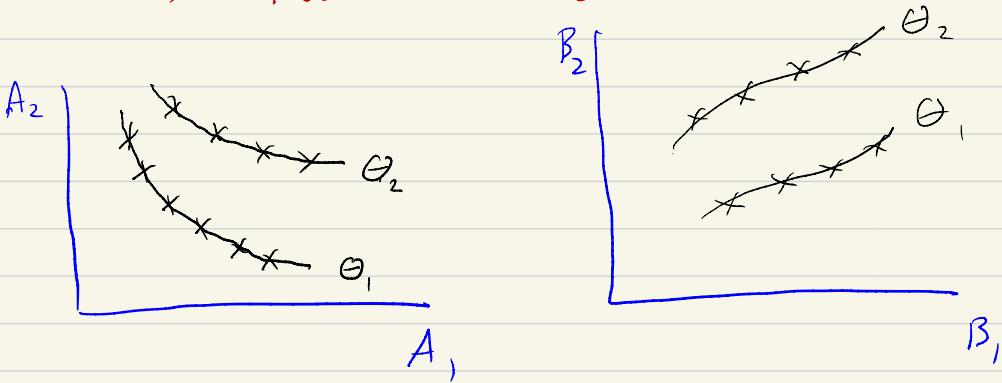
\* The function  $\Theta_A(\{A_i\})$  is called the equation of state (EOS)

\* Thermal equilibrium between systems is marked by all EOS functions having the same value  $\Theta$

$$\Theta_A(\{A_i\}) = \Theta_B(\{B_i\}) = \Theta \quad (= \text{"empirical temperature"})$$

↓

Leads to the notion of isotherms. For drawing purposes, let's pretend the TD coordinate space for  $A+B$  are 2 dim (i.e.,  $\{A_1, A_2\} + \{B_1, B_2\}$ )



\* In general, an isotherm  $\Theta = \Theta_A(\{A_i\})$  specifies a surface of  $N-1$  dim. where  $N = \# \text{ of TD coords}$  needed to specify the system.

### Ideal Gas temperature Scale

So far have not assigned a prescription to define different numerical  $\Theta$ -values (i.e., define a Temp. scale)