Introduction to thermodynamics & the "First Law"

Thermodynamics is the study of flow of heat/energy & how that can produce work

Developed principles before concept of atoms

Important note: major concept is "Equilibrium", where there does not seem to be much dynamics

a) lots happening at microscopic level

b) Mostly about changes between eq. states

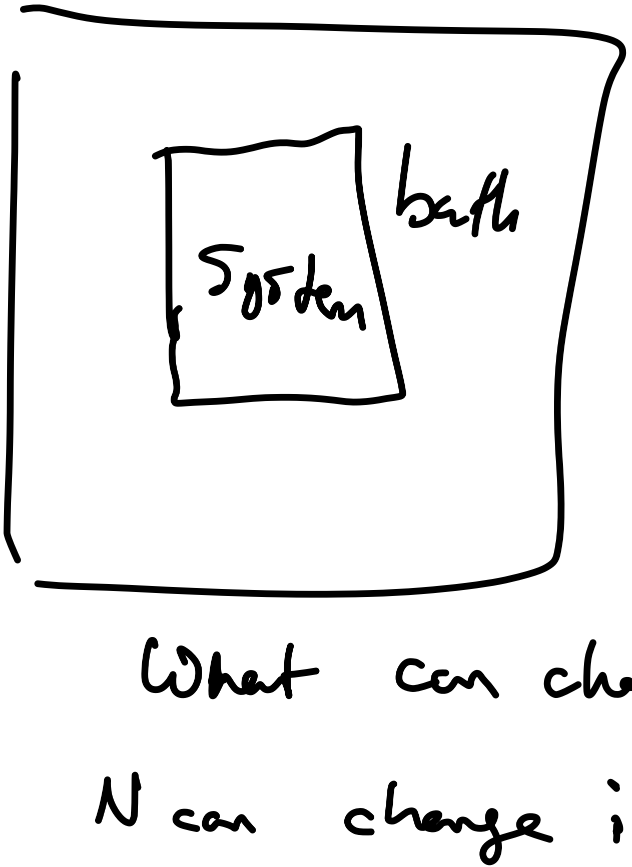
Key idea: dividing the universe into System & Surroundings ("Bath")

- System is what we are studying right now

- Bath is everything else, or everything else "locally"
- Boundary - imagine ideal situation boundary allows transmission of heat (or not), chemicals (or not)

Regarded as "thermodynamically negligible"

- "System - bath coupling" how do system & bath interact (via boundary)



System → N, V, E

Newtons equations (& QM)

say "isolated" system has constant energy

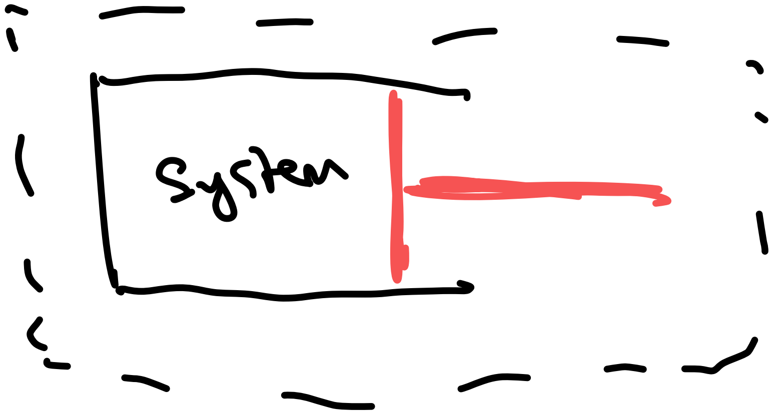
What can change?

N can change if we allow

- exchange of molecules
- chemical reactions

V can change - if we allow the box to change shape

Classically, we imagine a piston, because of engines



Or, heat can flow from system to bath, bath to system if not insulated

(will see this happens if at diff temperatures)

These allow changes of dN, dV, dq

There are different names for these different situations (unfortunately)

Allowed Changes!

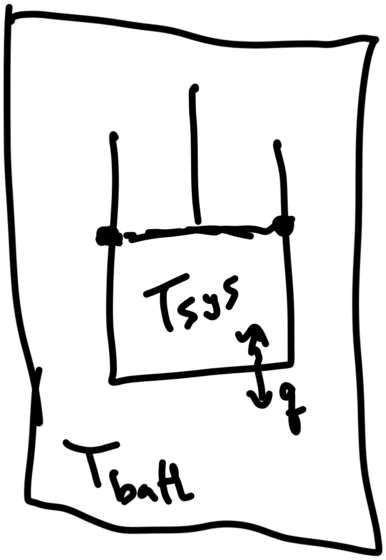
$dq = 0$ adiabatic – not passable through
$dq \neq 0$ diathermal – heat passes
"dia" – through
greek

$dN = 0$ closed
$dN \neq 0$ open (this is exchanging with surroundings)
(must also have diathermal)

$dV = 0$ isochoric – "same space"
$dU \neq 0$ isobaric – same pressure ("weight")

Equilibrium occurs when above processes stop and something balances inside & outside

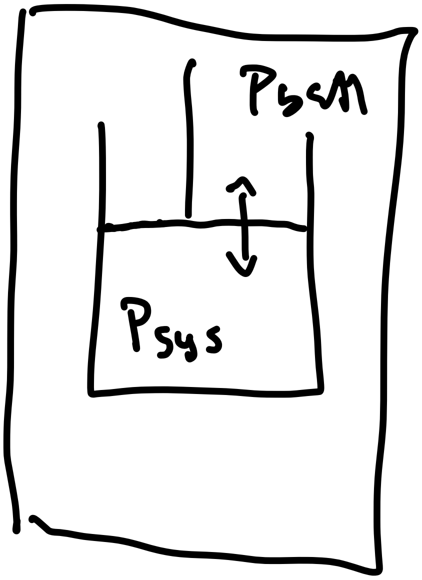
Diathermal Eq



$T_{bath} = T_{sys}$

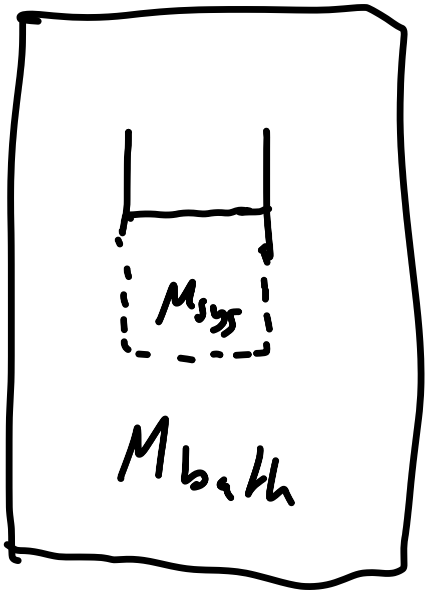
Heat flows until this

Isobaric Eq



$P_{sys} = P_{bath}$
volume adjusted

Open sys eq



$\mu_{sys} = \mu_{bath}$
after mc's flow
(also equal T)

T, P, μ [N/V] are what are called intensive variables - don't depend on system size - property of sys or bath

Extensive (Eg E, V, N) are proportional to system size

"What happen if copy system?".

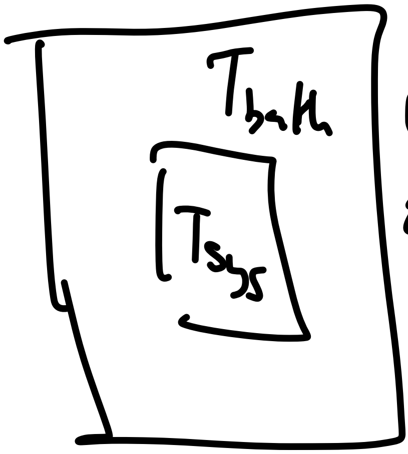
Extensive vars double

Changes of state

Discussed last time many ways to go from state A->B

One way is to go from A->B very slowly, so slowly that the system always equilibrates between our changes

These changes are called reversible because any one of the steps, we can go backwards and the system should follow



1) $T_{sys} = T_{bath} = T_{init}$

2) $T_{bath} \to T_{bath} + dT$

3) wait, $T_{sys} \to T_{sys} + dT$

$\updownarrow$ iterate

4) stop at $T_{final} = T_{sys} = T_{bath}$

Equations of State (EOS)

An EOS is a relationship between thermodynamic variables at equilibrium

If in one phase (solid liq gas)

Need 2 + num components to describe thermo state (more in Ch 6)

Eg $V(n,P,T)$ for isothermal, isobaric situation

or $P(n,V,T)$ for isothermal, isochoric

EOS example is $PV = nRT$ for ideal gas

$V = nRT/V$

$P = nRT/P$

(mistakes in ideal gas section)

First law of thermodynamics

In words - Energy neither created nor destroyed / Energy is conserved

This is for an isolated system & for the $\underbrace{\text{sytem + bath}}_{\text{universe}}$

big isolated system

Focusing on system, this means Energy flows in and out as it does work or you do work on the system (will discuss work more)

En eqs - for a system

$$d\mathcal{E} = đq + đw$$

(book also uses U)

$\mathcal{E} = K.E. + U$

Sign of đq & đW very important

Book version - both are things that if you increase, increase the energy

So - đq is heat into system

đw is work done on system

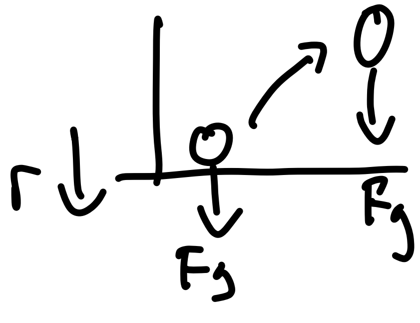
What is work

Work is the integrated change in a quantity against a "force"

Classical mechanics $w = -\int_{r_0}^{r_1} \vec{F} \cdot d\vec{r}$

if $\vec{F}$ & $\vec{R}$ in same direction $dw = -F\,dr$

eg



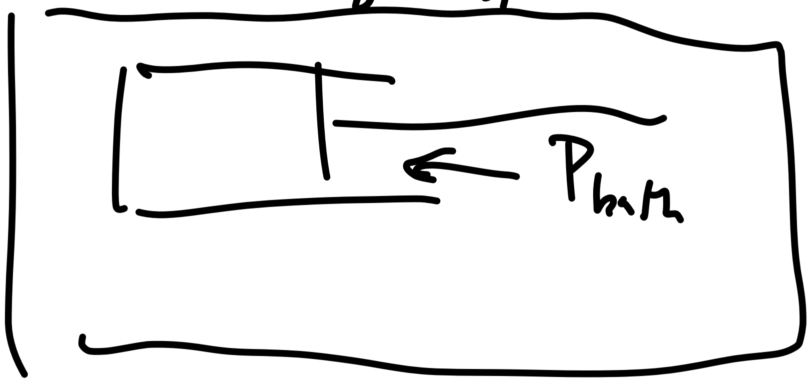
lift ball $w = -\int_0^{-h} F\,dr$

$= Fh = mgh = E_{final}$

Thermo example

$$dW = -P_{bath}\, dV$$

pressure from bath acts on system



so $dU < 0$ shrinking

is work done __on__ system

more next time!