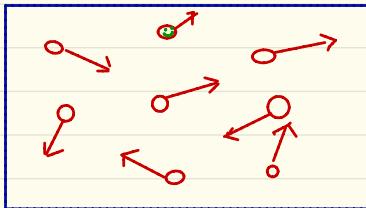


Lecture 1 - Problem + Postulates

1

Many microscopic variables \rightarrow small set of macro quantities

Gas/liquid of N particles



T, V, N

Microscopic chaos of activity

Condition of any particle given by position \vec{r} + momentum \vec{p} .

$\rightarrow 6N$ total DOFs!

Yet to completely specify state of system,
only have to specify three things:

N : # molecules in box

V : volume of box

T : temperature of box

How does $6N \rightarrow 3$?

- ① Molecules move fast relative to our ability to observe them
 - we observe only time-averages
 - Only linear combinations of DOFs that are time-independent are observable

② gas molecules are tiny

- we observe macro systems on length scales
 >> molecular scale

myriad of
molecular
coordinates \Rightarrow thermodynamics
equilibrium, time-
invariant states.

All those "hidden" DOFs are still important.
Contribute to internal energy U of the system

$$U \rightarrow \left\{ \begin{array}{l} \text{composite of all} \\ \text{contributions of } 6N \\ \text{DOFs.} \end{array} \right.$$

This internal energy is the central actor of thermodynamics. Very useful to us.

We focus first on simple, homogeneous macroscopic systems.

Characterized by extensive variables. Variables that scale with system size.

Eg. Combine two identical systems, extensive variables will double

volume V , # molecules N , internal energy U , all extensive

Key undergirding concept of thermodynamics
is conservation of energy

Direct consequence of time-reversal symmetry
of the universe.

All physical laws ($F = ma$, $H \Psi = E\Psi$) are
invariant to $t \rightarrow -t$.

Symmetry \rightarrow conservation law

Took a long time for this concept to emerge,
and various forms of energy have had to be
invented to maintain consistency:

- kinetic
- gravitational potential
- electric potential
- elastic
- chemical
- mass-energy

Intuitive, but mysterious. Take it as an
observed fact.

If is possible to exchange energy between
its many forms, but not to create or
destroy. Basis of energy balances in
engineering.

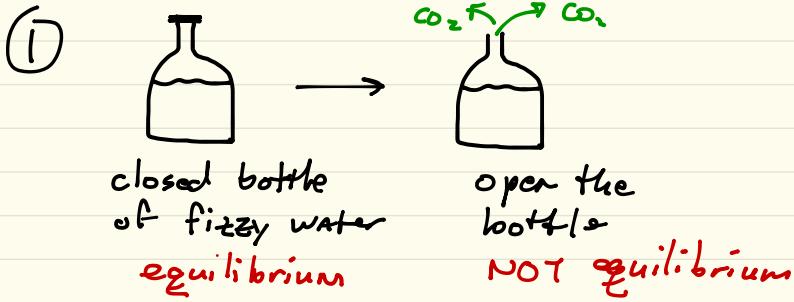
Summed up in:

4

Postulate 1 - There exists "equilibrium states" of simple systems that are completely characterised by the extensive variables U, V, N_i

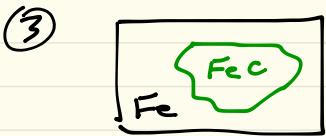
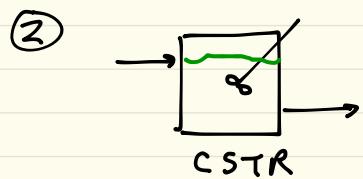
Completely characterized \rightarrow All other macro properties determined

Pop quiz \rightarrow equilibrium or not?



I think so!

Batch reactor?



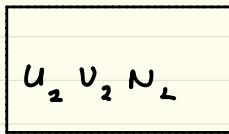
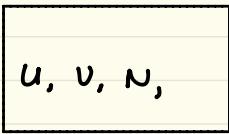
not "simple"

macroscopically inhomogeneous, BUT as long as we observe macro properties on scales \gg inhomogeneities + timescales \ll composition changes, then equilibrium

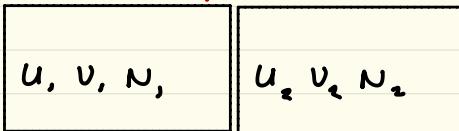
simple systems

5

4



↓
composite system

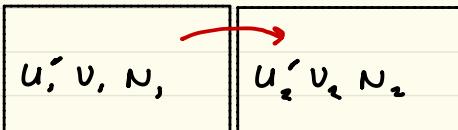


independently,
at equilibria

NOT at
equilibrium

Imagine walls are permeable to energy ("heat") and impermeable to particles and to volume change. Is new combination at equilibrium? Probably not. Energy/heat flows across boundary until a new equilibrium is achieved.

heat



$$U'_1 + U'_2 = U_1 + U_2$$

Eventually achieves a new equilibrium, which we know/shall see is determined by $T_1 = T_2$.

Are they in equilibrium along the way? In general no.

If we allow energy exchange to happen very slowly, can imagine a quasi-static process,

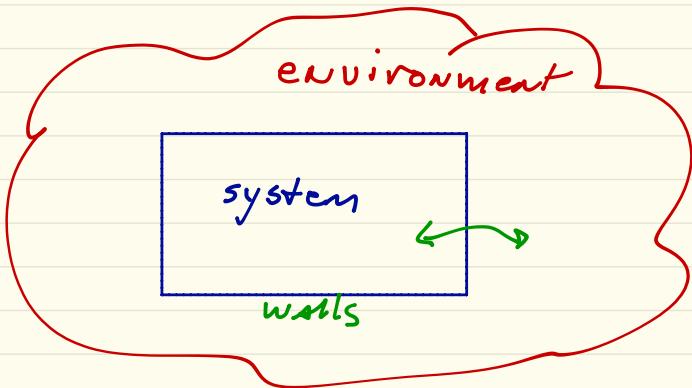
One in which each sub-system is in equilibrium each step along the way.

Can we go back the other way? Generally, NO! Sportaneous changes go in one direction. Hmm... energy is conserved but there seems to be a directionality to processes.

But not always no. There is a subset of quasi-static processes called reversible, that can go backwards. Will learn more later.

System + environment

In these examples, implicit that there is a system we are interested in and an environment it communicates with.



7

thermal

This movement of energy across a wall is called heat.

diathermal wall - permeable to heat

adiabatic wall - impermeable to heat

The existence of adiabatic walls means we can control the transfer of thermal energy to a system.

How else can we change the energy of a system?



Can do work on the system eq by moving a wall.

Externally can measure mechanical work using

$$W = - \int F_{ext}(x) dx = - \int P_{ext}(V) dV$$

ext. force · displacement $P = \frac{F}{A}$ $V = xA$

its external
F, P + matter

If walls are adiabatic, must have

$$\Delta U = W$$

or for infinitesimal changes, $dU = \delta W$

If diathermal, then both heat and work can influence energy:

$$\text{d}U_{\text{sys}} = \text{d}Q + \text{d}W$$

Conservation of energy considering heat & work

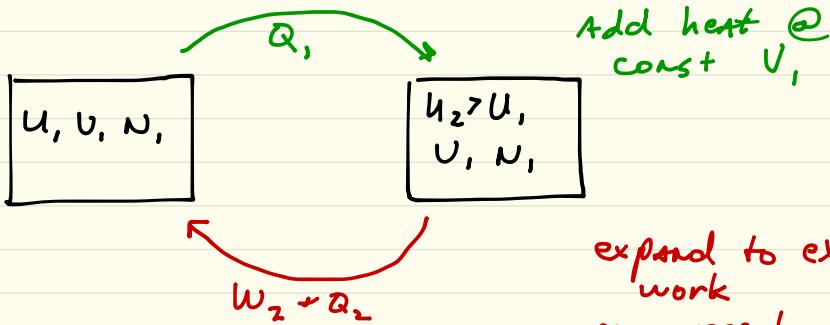
$\text{d}Q > 0$ energy as heat flows into system

$\text{d}W > 0$ work done on system

ΔU is an exact differential, only depends on start + end points of systems

$\text{d}Q, \text{d}W$ are inexact, depend on paths.
fluxes, not state fluxes

ex



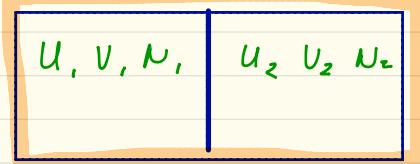
expand to extract
work
compress to reject
heat

System ends up where it started, $\Delta U_{\text{sys}} = 0$

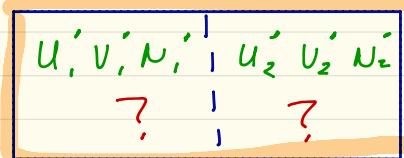
$-Q_1 = W_2 + Q_2$ not conserved

isolated

Often faced w/ 4 different problems:
Bring two simple systems into communication with each other, what happens?



constrained



unconstrained

Could allow U, V, and/or N to cross boundary. First law can't tell us — any final state with $U_1' + U_2' = U_1 + U_2$ is ok.
Need help!!

Postulate 2 - There exists a thermodynamic state function **entropy** that is a function of the extensive parameters and that assumes a maximum value when a constraint is removed.

This $S(U, V, N)$ function is the **fundamental equation**. — It contains all thermodynamic information.

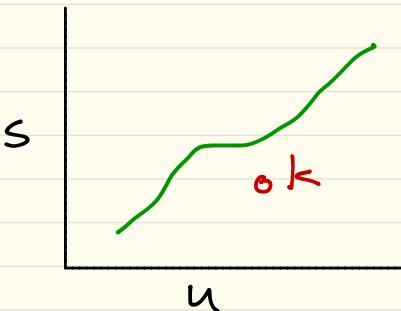
U, V, N , all determined by maximizing S over their allowable values

Postulate 3 - Entropy is additive over subsystems. It is continuous, differentiable, and monotonically increasing in U .

$$S = S_1(U_1, V_1, N_1) + S_2(U_2, V_2, N_2)$$

$$\left(\frac{\partial S}{\partial U}\right)_{V, N} > 0$$

homogeneous order 1



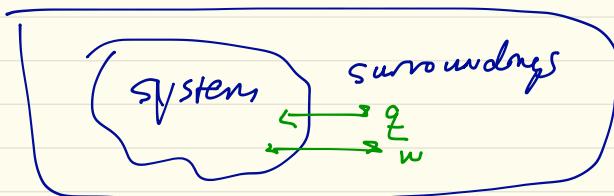
From this, clear that $S(U, V, N) \leftrightarrow U(S, V, N)$

Postulates 2+3 \Rightarrow "2nd Law of Thermodynamics"

Postulate 4 - S vanishes in the state in which $\left(\frac{\partial U}{\partial S}\right)_{V, N} = 0$.

$\left(\frac{\partial U}{\partial S}\right)_{V, N} = 0 \rightarrow S=0$ "3rd Law of Thermodynamics"

Clausius: Die Energie der Welt ist konstant. Die Entropie der Welt strebt einem Maximum zu.



CONSERVE energy,

$$\Delta U_{sys} + \Delta U_{sur} = 0$$

no

yes

