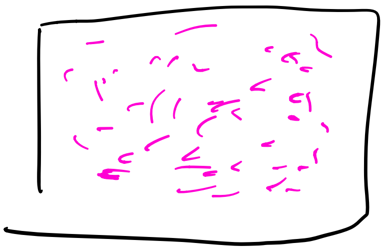
1) Thermodynamics of irreversible processes

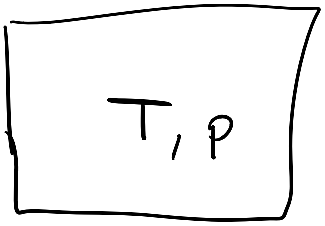
Basic idea is to generalise the familiar concepts of equilibrium thermodynamics to non-equilibrium systems

The power of thermodynamics clearly lies in its macroscopic nature



microscopically:

$\sim 10^{27}$ molecules in a room



macroscopically:

Temperature T

pressure p

Equilibrium:

⇒ Complex many body systems can be characterized by few macroscopic properties

We will investigate under what circumstances the same holds for non-equilibrium systems

- Equilibrium thermodynamics
- Entropy production in irreversible (non-equilibrium) processes
- Linear transport phenomena

1.1 Equilibrium thermodynamics (reminder)

We will follow the formulation of thermodynamics due to H.B. Callen ('60) based on a description in terms of extensive macroscopic variables.

Q: What means extensive?

A: additive under composition

So if we consider so called „simple" systems

$\hat{=}$ homogenous, isotropic, chemically inert

we have the following extensive macroscopic variables

U	V	N_i
internal energy	volume	particle numbers

will be collectively labeled as

$$X_i \in \{U, V, N_1, N_2 \dots\}$$

Now except for the volume V those extensive macroscopic quantities are related to conserved quantities

→ well suited for non-equilibrium description

Based on the variables X equilibrium thermodynamics follows from the following four postulates

Postulates:

I) Existance of equilibrium state which is completely characterized by the values of $\{X_i\}$

Q: What are these states?

A: microcanonical ensembles

II) Existance of a thermodynamic fundamental relation, that defines an entropy $S(X_i)$ for each equilibrium state with the properties

- $S(X_i)$ is extensive

- if the system is divided into sub-systems (labeled (A)) characterized by $\{X_i^{(A)}\}$ the entropy

$$S(X_i) = \sum_{\underline{A}} S(X_i^{(A)})$$

is maximal wrt free variations of $\{X_i^{(A)}\}$

iii) $S(X_i)$ is continuously differentiable wrt $\{X_i\}$ and monotonically increasing as a function of U

iv) $S(X_i) = 0$ for all states with $\left(\frac{\partial U}{\partial S}\right)_{V,N_i} = 0$

Based on the postulates all information on thermodynamic properties of a system are contained in „thermodynamic fundamental relation"

$$S = S(\{X_i\})$$

in the simplest case (one species)

$$S(U,V,N)$$

Differentiation of S characterizes change of equilibrium state under allowed changes of X_i

„Gibbs fundamental relation"

$$dS = \sum_i \frac{\partial S}{\partial X_i}\, dX_i$$

Since S and X_i are extensive the quantities

$$y_i = \frac{\partial S}{\partial X_i}\bigg|_{\{X_j\}_{j\neq i}}$$

are intensive, their functional dependence on X_i

$$\boxed{y_i = \frac{\partial S}{\partial X_i}\left(\{X_i\}\right)}$$

is called an Equation of State (EoS)

Specifically for "simple" systems

$$dS = \frac{\partial S}{\partial U}\bigg|_{V,N} dU + \frac{\partial S}{\partial V}\bigg|_{U,N} dV + \sum_i \frac{\partial S}{\partial N_i}\, dN_i$$

where

$$dS = \underbrace{\left.\frac{\partial S}{\partial U}\right|_{V,N}}_{=\frac{1}{T}} dU + \underbrace{\left.\frac{\partial S}{\partial V}\right|_{U,N}}_{\frac{p}{T}} dV + \sum_i \underbrace{\frac{\partial S}{\partial N_i}}_{-\frac{\mu_i}{T}} dN_i$$

$T \hat{=}$ Temperature

$p \hat{=}$ pressure

$\mu_i \hat{=}$ chemical potential

Equations of state take the form

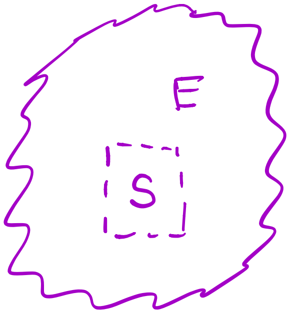
$$\frac{1}{T} = \left.\frac{\partial S}{\partial U}\right|_{V,N} \Rightarrow T(U,V,N)$$

1.2 Description of irreversible (out-of-equilibrium) processes

Generally out-of-equilibrium situations will arise in any real world system eg due to

external influence

-> system needs time to react to change of environment



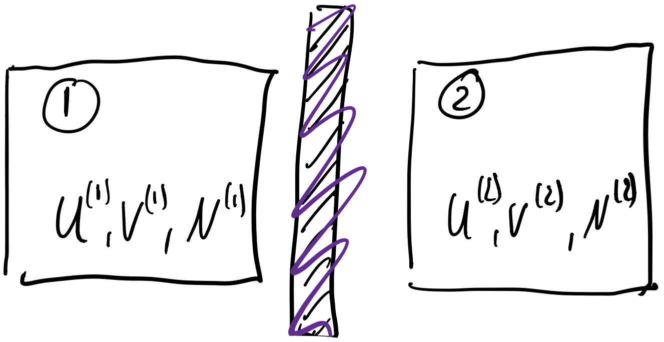
evolution

-> system has not had sufficient time to approach equilibrium

Challenge: How to describe such systems?

Discrete systems

Consider system made up of two sub-systems ① and ②, described in terms of the extensive variables $X_i^{(1)}, X_i^{(2)}$ for each sub-system



If the two sub-systems are isolated from each other, we can expect that on large time scales each sub-system will be in its own equilibrium state.

We will assume for simplicity that ① & ② are in equilibrium at initial time

Now if the isolation is removed,
e.g by lifting the wall, making it permeable
or making it moveable

→ sub-systems ①, ② can exchange
U, V, N

in general the system will be
out-of-equilibrium

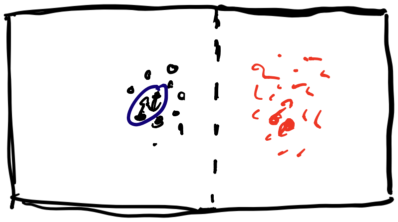
Now if we wait long enough,
system will again reach
equilibrium state

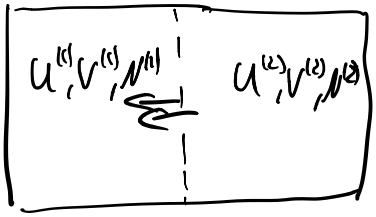
→ non-equilibrium states are of
transient nature

Ultimately everything is described
by
$$X_i^{(tot)} = X_i^{(1)} + X_i^{(2)}$$

Now the answer to the question what happens in between crucially depends on the time scale that we consider

Can identify at least two relevant time scales





τ_{Micro}

individual constituents (atoms, molecules, ...) interact

τ_{Macro}

changes of extensive macroscopic variables $X_i^{(1/2)}$ occur

Now to describe the system macroscopically one exploits the fact that typically there is a separation of scales

$$\tau_{micro} \ll \tau_{macro}$$

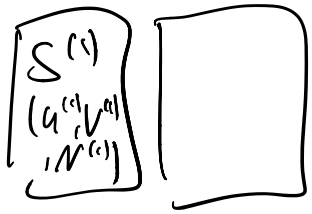
If $\tau_{Macro} \gg \tau_{Micro}$ the variables $X_i^{(1/2)}$ are referred to as slow variables and each sub-system has enough time to stay close to equilibrium throughout the non-equilibrium evolution of the system

Idea: parametrize the evolution on macroscopic time scales as sequence of equilibrium states of each sub-system (A)

$$\{X_i^{(A)}(t)\}$$

with which we can associate an entropy

$$S^{(A)}(\{X_i^{(A)}(t)\})$$



for each sub-system

Entropy production, Affinities & Fluxes

If the whole system ①+② is isolated the extensive macroscopic quantities X_i are globally conserved

$$X_i^{tot}(t) = X_i^{(1)}(t) + X_i^{(2)}(t) = \text{const}$$

So allowed variations for each subsystem are

$$dX_i^{(1)} + dX_i^{(2)} = 0 \Rightarrow dX_i^{(1)} = -dX_i^{(2)}$$

Since entropy is <u>additive</u>

$$S^{tot}(t) = S^{(1)}\left(X_i^{(1)}(t)\right) + S^{(2)}\left(X_i^{(2)}(t)\right)$$

and we can determine the final global equilibrium state based on the second postulate

$$\left.\frac{\partial S^{tot}(t)}{\partial X_i^{(1)}}\right|_{\{X_i^{tot}\}} = 0$$

Since variations of $X_i^{(1)}$ are not independent of variations of $X_i^{(2)}$ we get

$$\left.\frac{\partial S^{(tot)}}{\partial X_i^{(1)}}\right|_{\{X_i^{tot}\}} = -\left.\frac{\partial S^{(tot)}}{\partial X_i^{(2)}}\right|_{\{X_i^{tot}\}}$$

$$= \frac{\partial S^{(1)}}{\partial X_i^{(1)}} - \frac{\partial S^{(2)}}{\partial X_i^{(2)}}$$

$$= Y_i^{(1)} - Y_i^{(2)} \underset{\text{equilibrium}}{\overset{!}{=}} 0$$

So equilibrium state is characterized by same values of conjugate intensive variables $Y_i^{(1)} = Y_i^{(2)}$

e.g if energy can be exchanged between different subsystems, global equilibrium will have the same temperature for each subsystem

Generally $Y_i^{(1)} \neq Y_i^{(2)}$ for non-equilibrium system, and the quantity that characterizes the deviation

$$\boxed{\mathcal{F}_i = Y_i^{(1)} - Y_i^{(2)} = \frac{\partial S}{\partial X_i^{(1)}}\Bigg|_{\{X_i^{tot}\}}}$$

is called affinity or generalized force

where in equilibrium

$$\mathcal{F}_i^{eq} = 0$$

Systems out-of-equilibrium will generally change their state, which macroscopically is described by change in the extensive macroscopic quantities $\{X_i^{(A)}\}$ of each subsystem

Characterized by the flux

$$J_i = \frac{d}{dt} X_i^{(1)}$$

of e.g. energy, particle number, ...
which for the simple example of two containers corresponds to the amount of X_i transferred from to per unit time

Entropy production occurs due to non-vanishing flux

$$\frac{d}{dt} S^{tot} = \sum_i \underbrace{\frac{\partial S^{tot}}{\partial X_i^{(1)}}}_{= F_i} \underbrace{\frac{dX_i^{(1)}}{dt}}_{= J_i} = \sum_i F_i J_i$$

and assumes bilinear form in affinities and fluxes