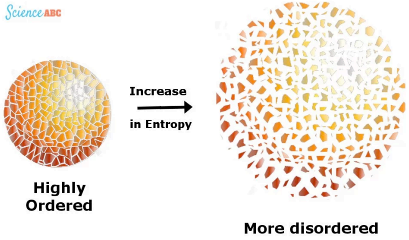
General Physics II: Thermodynamics

Prof. M. Hirschmann

Spring semester 2024



Recap… Lecture 5, First law of TD

- What is the first law of Thermodynamics of a closed system?

- How is first law modified for different thermodynamic systems (other than closed)?

- Which thermal processes for gas (to change its state) do you know?

Recap… Lecture 5, The first law in different thermal processes

- How can we compute the internal energy for isochoric/isovolumetric $\Delta V = 0$ processes?

- How for isobaric $\Delta P = 0$ processes?

- How for isothermal $\Delta T = 0$ processes?

- How for adiabatic $Q = 0$ processes?

Content of this course — today's lecture

Lecture 1: —Chapter 1. Introduction
—Chapter 2. Temperature and zeroth law of thermodynamics

Lecture 2: —Chapter 3. Gas laws

Lecture 3: —Chapter 4. Statistical thermodynamics I: Kinetic theory of gas (slides in previous file)
—Mathematical Excursion — Preparation for Chapter 5.

Lecture 4: —Chapter 5. Statistical thermodynamics II (Boltzmann factor, Maxwell-Boltzmann distribution)

Lecture 5: —Chapter 6. Energy, heat and heat capacity

Lecture 6: —Chapter 7. First law of thermodynamics and thermal processes

Lecture 7: — Mock exam I *with Dr. Tress*

Lecture 8: —Chapter 8. Entropy and the second and third law of thermodynamics

Lecture 9/10: —Chapter 9. Thermal machines

Lecture 11: —Chapter 10. Thermodynamic potentials and equilibria

Lecture 12: —Mock Exam II *with Dr. Tress*
Lecture 13: —Chapter 11. Heat transfer (Conduction, Convection, Radiation)

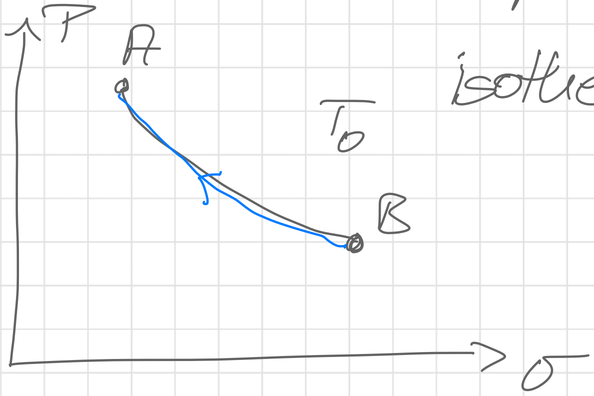
Lecture 14: —Final review and open questions

8. Entropy and the second and third law of thermodynamics

- 8.1 Reversible and irreversible processes
- 8.2 Entropy
- 8.3 The second law of TD
- 8.4 The third law of TD
- 8.5 Entropy and the first law of TD
- 8.6 Statistical interpretation of entropy

8.1 Reversible and irreversible processes

So far: all thermal processes from Chap. 6/7 are reversible.



isothermal expansion

$$W_{A\to B} = \int_A^B P\,dV =$$

$$= \int_{V_A}^{V_B} \frac{nRT_0}{V}\,dV = nRT_0 \log\frac{V_B}{V_A} > 0$$

W done <u>by</u> gas on environment

since T_0 = const → $\Delta E_{int} = 0$

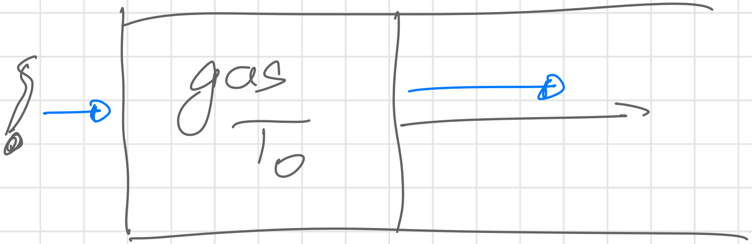
↳ $Q_{A\to B} = W_{A\to B}$

(system is taking in heat)

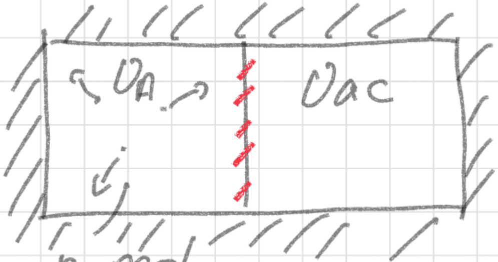
Once system is at B, it can do the same path back to A (isothermal compression)

$$W_{B\to A} = -W_{A\to B} \; ; \quad Q_{B\to A} = -Q_{A\to B}$$

Any process that can be reversed by changing signs of Q & W is reversible



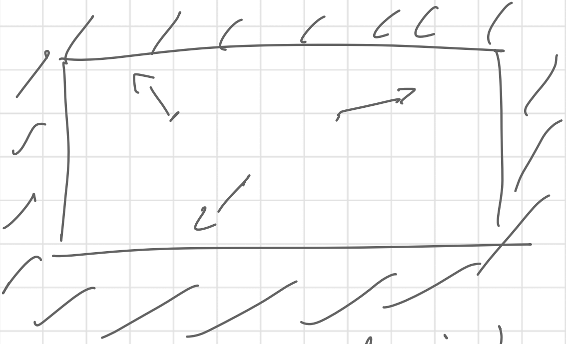
Now: Thermally isolated container with V_B



n-mol ideal gas

V_A, P_A & T_0

remove wall $\longrightarrow$



gas expands into entire volume

V_B, P_B, T_0

Thermal isolation: $Q = 0$

No work : $W = 0$

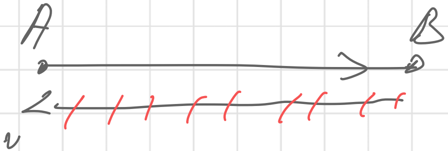
$\hookrightarrow \Delta E_{int} = 0 \longrightarrow T = const$

Because Q & W are zero, this process cannot be reversed by changing the si

→ Any process that cannot be reversed by changing the sign of Q & W is called irreversible

Impossible to go back to the initial state

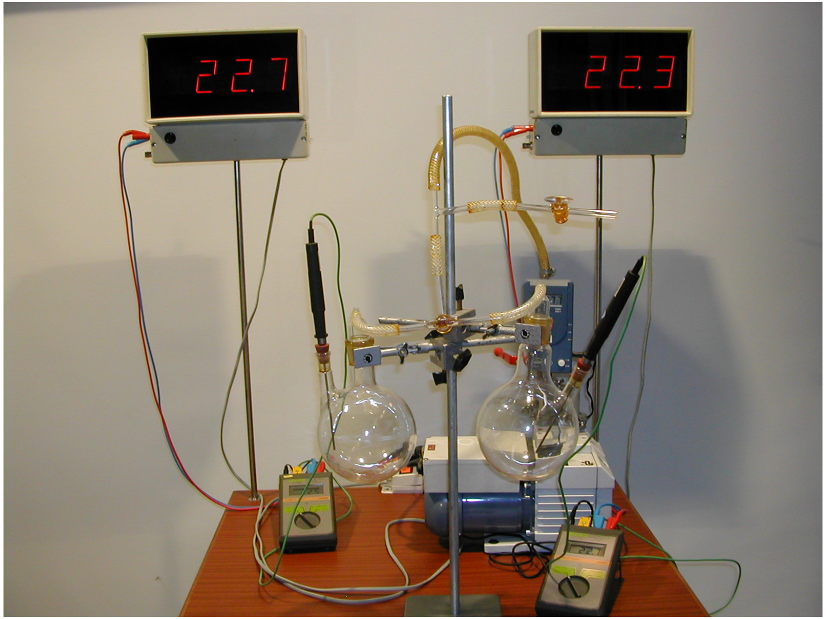
"Arrow of time" comes in:



"Special" as for most physics laws, reversibility in time is given.

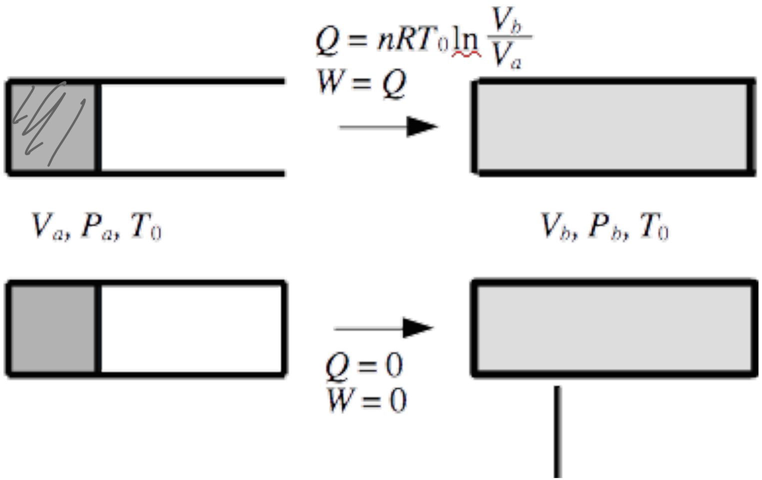
Experiment 339: Joule free expansion

- Initially, both balloons are filled with air. Then, the air is evacuated from balloon 1, after which valve 1 is closed, and the vacuum pump is stopped.
- Wait for the temperatures to balance between the two balloons. (This equilibrium can be accelerated by heating balloon 1 with hands.)
- The identical temperature of the two balloons is the reference temperature.
- **Connect the two balloons using valve 2 at temperature (T)**: For an ideal gas, we expect no T change because W and Q equal to zero
- In reality: In balloon 1, an increase in temperature of +T is observed. In balloon 2, a decrease in temperature of -T is observed, because gases are not ideal.



Summary 8.1 Reversible & Irreversible thermodynamic processes

- Any process, that can be reversed by changing signs of Q and W, is reversible.
- Any process, that cannot be reversed by changing signs of Q and W is irreversible. “Arrow of time comes in”



8.2 Entropy

New quantity for describing reversible & irreversible processes :

Entropy S $[J/K]$

Reversible processes from state $A \to B$, Q, T

$$\boxed{\Delta S := \frac{Q}{T}}$$

In differential form:

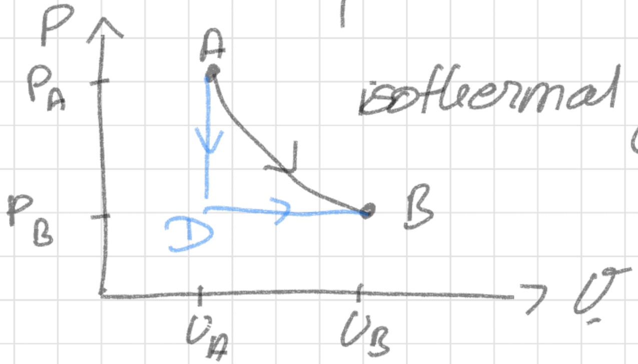
$$\boxed{dS = \frac{dQ}{T}}$$

$$\hookrightarrow \Delta S = \int_A^B \frac{dQ}{T}$$

Note : Entropy S is a state variable.

Demonstration that S is a state variable:

Previous example:



isothermal gas expansion at T_0

$A \to B$:
$$\Delta S = \int_A^B \frac{dQ}{T_0} = \frac{Q_{A\to B}}{T_0} \underset{\substack{\uparrow \\ \Delta E_{int}=0}}{=} \frac{W_{A\to B}}{T_0} =$$

$$= \frac{nR\cancel{T_0}\log\frac{V_B}{V_A}}{\cancel{T_0}} = nR\log\frac{V_B}{V_A}$$

$A \to D \to B$:

$A \to D$: $\Delta V = 0$; $Q = nC_V\Delta T$ isochoric

$$\Delta S = \int_A^D \frac{dQ}{T} = \int_A^D \frac{nC_v\,dT}{T} = nC_v \int_A^D \frac{dT}{T}$$

$$= nC_v \log\frac{T_D}{T_A} = nC_v \log\frac{T_D}{T_0}$$

$D \to B$: $\Delta P = 0$ isobaric

$$\Delta S = \int_D^B \frac{dQ}{T} = \int_D^B \frac{nC_p\,dT}{T} = n\underset{\substack{\| \\ C_v + R\ (\text{ideal gas})}}{C_p} \log\frac{T_B}{T_D}$$

$$= n\,(C_v + R)\log\frac{T_0}{T_D}$$

$A \to D \to B$

$$\Delta S = nC_v \log\frac{T_D}{T_0} + n\,(C_v + R)\log\frac{T_0}{T_D} =$$

$$= \cancel{nC_V \log\frac{T_D}{T_0}} + \cancel{nC_V \log\frac{T_0}{T_D}} + nR\log\frac{T_0}{T_D}$$

because $\log(x) = -\log\left(\frac{1}{x}\right)$

$$\Delta S = nR\log\frac{T_0}{T_D}$$

Ideal gas law:

$nRT_0 = P_A V_A = P_B V_B$ (at A, B)

$nRT_D = P_B \cdot V_A$ (at D)

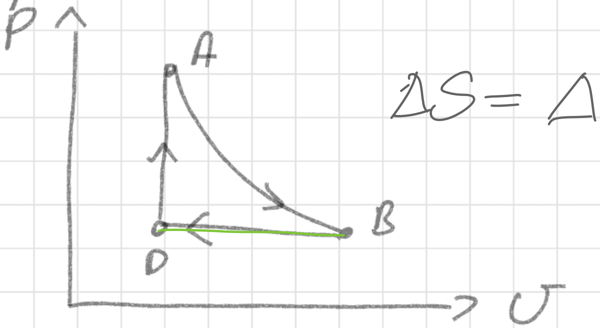
$$\Rightarrow \Delta S = nR\log\frac{\cancel{P_B} V_B / \cancel{nR}}{\cancel{P_B} V_A / \cancel{nR}} = nR\log\frac{V_B}{V_A}$$

$$\Rightarrow \Delta S_{A\to B} = \Delta S_{A\to D\to B}$$

✓ S is a state variable

circle

Implication: if paths can be reversed → loop process



$$\Delta S = \Delta S_{A\to B} + \underbrace{\Delta S_{B\to D} + \Delta S_{D\to A}}_{= -\Delta S_{A\to D\to B}}$$

$= 0$

Common way to write that:

$$\boxed{\oint dS = \oint \frac{dQ}{T} = 0}$$

integral around a circle/loop process
initial = final state

At a reversible circle process, S stays const ($\Delta S = 0$)

So far: Entropy in reversible processes ($\Delta S > 0$ if $V_B > V_A$)

$$dS_{env} = \frac{dQ}{T}$$

ΔS due to heat exchange with environment

Now: Complete definition of entropy, to also describe irreversible processes

$$\boxed{dS_{system} = dS_{env} + \underbrace{dS_{Prod}}_{\text{Entropy production}}}$$

entropy balance equation

total entropy change in our system

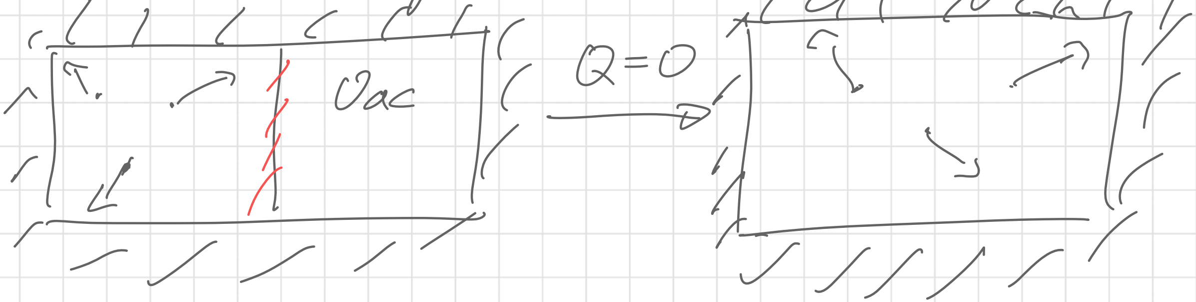
Entropy production

e.g. friction, viscous forces

quantifies irreversibility of pr.

For irreversible processes:

Joule-free expansion of gas



$$dS_{env} = 0$$

$$\boxed{dS_{prod} > 0}$$

For reversible processes:

$$\boxed{dS_{prod} = 0}$$

$$\Longrightarrow \boxed{dS_{system} = dS_{env} = \frac{dQ}{T}}$$

In general:

$$\boxed{\begin{aligned} dS_{system} &\geq dS_{env} \\ &\geq \frac{dQ}{T} \end{aligned}}$$

with equality only for reversible processes.

Note on S_{env} in reversible & irreversible processes:

Reversible processes:

$$\Delta S_{syst} = \int \frac{dQ_{rev}}{T}$$

$$= \Delta S_{env}$$

Irreversible processes:

$$\Delta S_{syst} > \int \frac{dQ_{irr}}{T} = \Delta S_{env}$$

because of internal S production

For the same initial & final states, for the same ΔS:

$$\boxed{\int \frac{dQ_{rev}}{T} \geq \int \frac{dQ_{irr}}{T}}$$

ΔS_{env} is the largest for a reversible process;

For a irreversible process: ΔS_{env} is smaller because of entropy prod.

Example:

Process with friction

irreversible process

S is internally produced

This means that for the same total change in S, less entropy needs to be transferred via heat exchange with environment

→ $\int \frac{dQ_{irr}}{T}$ smaller than in a reversible

Summary 8.2 Entropy

- Entropy S is a state variable (independent of the path of the process), important for distinguishing between reversible and irreversible processes
- $dS_{system} = \boxed{dS_{env}} + dS_{prod}$; with $dS_{env} = \frac{dQ}{T}$
  - dS_{env}: change of entropy due to heat exchange with environment
  - dS_{prod}: entropy production due to dissipation within the system, “measure for disorder”
- Entropy only due to heat exchange with environment (reversible processes)

$$\Delta S = \int_A^B \mathrm{d}S = \int_A^B \frac{\tilde{\mathrm{d}}Q}{T}$$

adiabatic process: $dS_{env} = 0$ (as $dQ = 0$)

  - dS_{env} in isothermal processes

$$\Delta S_{ab} = \frac{Q}{T_0} = nR\ln\frac{V_b}{V_a}$$

  - dS_{env} in isochoric processes

$$\Delta S_{ad} = nC_V\int_{T_0}^{T_d}\frac{dT}{T} = nC_V\ln\frac{T_d}{T_0}$$

  - dS_{env} in isobaric processes

$$\Delta S_{db} = nC_P\int_{T_d}^{T_0}\frac{dT}{T} = n\left(C_V + R\right)\ln\frac{T_0}{T_d}$$

Summary 8.2 Entropy

- Entropy due to heat exchange with environment
  - Reversible: $dS_{env} > (\text{or} <)\ 0$
  - Irreversible (e.g free expansion process: $dS_{env} = 0$)

$$\Delta S_{env} = \int_A^B \frac{\tilde{\mathrm{d}}Q_{\text{reversible}}}{T} > \int_A^B \frac{\tilde{\mathrm{d}}Q_{\text{irreversible}}}{T}$$

heat exchange with env. in reversible process larger than in irreversible one

- Entropy production due to dissipation within a system
  - Reversible: $dS_{prod} = 0$
  - Irreversible: $dS_{prod} > 0$ (e.g. free expansion of gas at T=const and Q=0, but S_{system} not necessarily zero)

8.3 The second law of thermodynamics

Each TD system has an extensive state variable S, called entropy.

The entropy S of a thermally isolated system (no heat exchange) and/or adiabatic system $(Q=0)$ cannot be decreased over time:

$$\boxed{\Delta S_{system} \geq 0}$$

equality only for reversible process

$Q=0$

$dS_{env}=0$

$\Delta S_{syst} = \Delta S_{Prod}$

Alternative formulation: heat flows spontaneously only from a hoter to a cooler body/syst.

8.4 The third law of thermodynamics , also Nernst theorem (1904)

Is a TD system at absolute zero ($T = 0K$) in thermodynamic equilibrium, then its entropy has a fixed value S_0 independent of V, P, material etc.

$$\boxed{\lim_{T \to 0K} S = S_0}$$

In classic TD: S_0 is just a const

Statistical TD: $S_0 = 0 \, J/K$

8.5 Entropy and the first law of thermodynamics

With entropy, we can re-write the first law of TD:

$$\rightarrow \boxed{\begin{aligned} dE_{int} &= dQ - dW \\ dE_{int} &= TdS - PdV \end{aligned}} \quad dS = \frac{dQ}{T}$$

always valid (irreversible + reversible processes)

But: $$\left.\begin{aligned} dW &= PdV \\ dQ &= TdS \end{aligned}\right\}$$ only true for reversible processes

Recall: $dS = dS_{prod} + dS_{env}$ (dS can have an irrev. comp.)

if $dS_{prod} > 0$ (irrev. process)

$dQ \neq TdS$

$dW \neq PdV$

Interpretation:

In a irreversible process, portion of energy added to a system (in form of work or heat) is irreversibly converted into internal energy, manifesting as internal entropy production

↳ Process is dissipating energy, with less work output & more heat being added.

Note: $d E_{int} = T dS - P dV$

looks like a total differential of $E_{int}(S, V)$

$$\boxed{d E_{int} = \frac{\partial E_{int}}{\partial S} dS + \frac{\partial E_{int}}{\partial V} dV}$$

Comparing both equations:

$$T = \frac{\partial E_{int}}{\partial S} \quad ; \quad P = -\frac{\partial E_{int}}{\partial V}$$

Intensive variables (T, P) are conjugates of extensive variable (S, V)

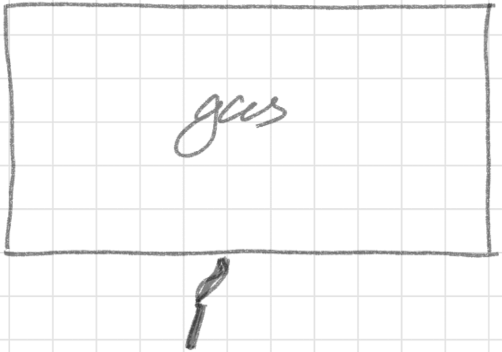
Entropy & first law in simple TD systems:

A homogeneous system, where the state is determined by a single state variable, entropy S, is called a simple system.

Entropy is defined globally

Homogeneous: same intensive quantities (T, P) everywhe

I. Closed & rigid system filled with gas, heat added



ridig: $dV = 0$, no work

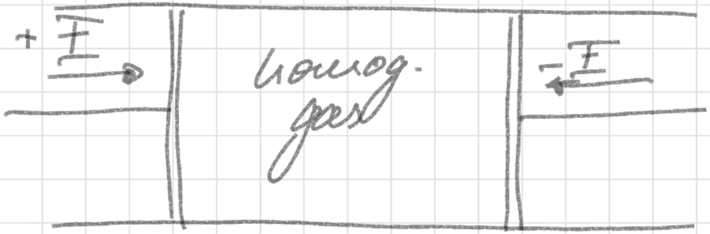
$\to dE_{int} = TdS = dQ$ $\quad = dS_{env} + dS_{prod}$

$\to dS_{Prod} = 0$ (entropy balance equ.)

Heat transfer between simple system & environment: reversible process

Total heat exchange: $Q = \int_i^f dQ = \int_{S_i}^{S_f} TdS$

II. Closed, adiabatic system, subjected to mechanical action



consider reversible displacement of the pistons (no S production)

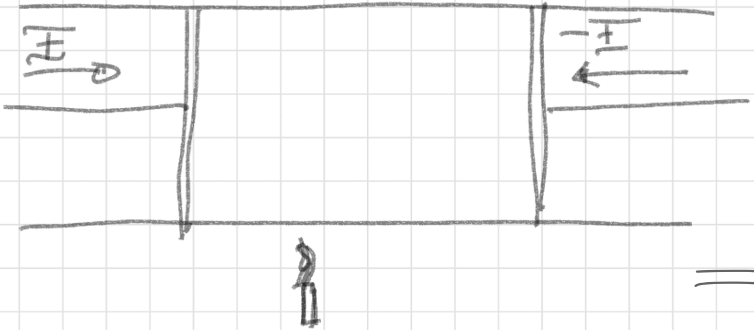
adiabatic: $dQ = 0$

$\hookrightarrow dS = 0$

$\Rightarrow dE_{int} = -PdV = -dW$ (reversible adiabatic pr.)

$$W = \int PdV$$

III. Closed simple system, subjected to mechanical action & heat transfer



$$dE_{int} = TdS - PdV = dQ - dW$$

$$\Longrightarrow \cancel{TdS_{env}} + TdS_{Prod} - PdV = \cancel{dQ} - dW$$

Reversible displacement of pistons: $dS_{Prod} = 0$

Then $dW = PdV$; $dQ = TdS$

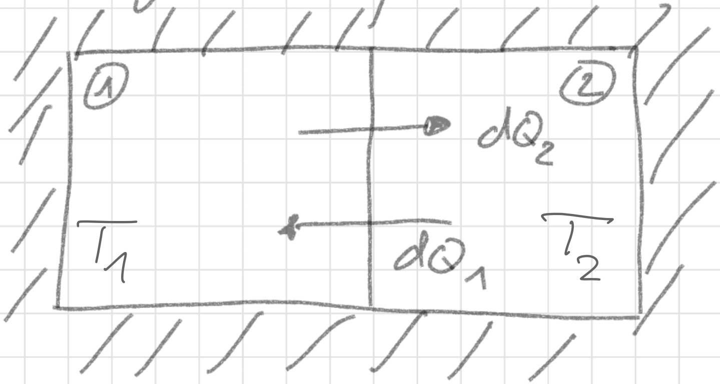
$$Q = \int dQ = \int TdS$$

$$W = \int PdV$$

Entropy & first law in subsystems (inhomogeneous systems)

Analysis of evolution of an isolated system composed of two homogeneous subsystems, separated by different types of walls (rigid ⟷ moving, diathermal, impermeable)
↳ equilibrium considerations & entropy production

I. Rigid & impermeable, diathermal wall



Question: What is the entropy in thermal equilibrium?

$S = S_1 + S_2$ (extensive quantity)

$E_{int} = E_{int,1} + E_{int,2}$

Also: $dS = dS_1 + dS_2$ (0) ; $dE_{int} = dE_{int,1} + dE_{int,2}$

Since system is isolated: $dE_{int} = 0 \longrightarrow dE_{int,1} = -dE_{int,2}$ (1)

No work done (rigid): $dW = 0$; $dW_1 = 0$; $dW_2 = 0$

First law: $dE_{int,1} = dQ_1$; $dE_{int,2} = dQ_2$ (2)

$$\xrightarrow{(1)} dQ_1 = -dQ_2$$

Each subsystem is a rigid, simple system: no S_{Prod}

$$\hookrightarrow dS_1 = \frac{dQ_1}{T_1} \quad \& \quad dS_2 = \frac{dQ_2}{T_2}$$

$$\hookrightarrow dS_1 = \frac{dE_{int,1}}{T_1} \quad \& \quad dS_2 = \frac{dE_{int,2}}{T_2}$$

From (0): $$dS = \frac{dE_{int,1}}{T_1} + \frac{\overbrace{dE_{int,2}}^{= -dE_{int,1}}}{T_2} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_{int,1} \quad (3) \quad \Big| : dE_{int,1}$$

$$\frac{dS}{dE_{int,1}} = \frac{1}{T_1} - \frac{1}{T_2}$$

In thermal equilibrium:

$$T_1 = T_2$$

$$\Longrightarrow \boxed{\frac{dS}{dE_{int,1}} = 0}$$

thermal equi. condition for S in classic TD

↪ S of an isolated system is maximum at thermal equilibrium

(re-call: statistical TD: maximisation of microstates in thermal equil.)

Question 2: What is the entropy production?

System isolated: $dS \geq 0$ (2nd law)

$$dS_{env} = 0$$

From (3) follows: $$\boxed{dS = dS_{prod} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dQ_1 \geq 0} \quad (4)$$

Note: if $T_1 \neq T_2$ $\quad dS_{prod} \neq 0 \quad$ even if $dS_{prod,1} = 0$

$$dS_{prod,2} = 0$$

↳ $dS_{prod} \neq dS_{prod,1} + dS_{prod,2}$

⟹ Entropy production is not an extensive quantity.

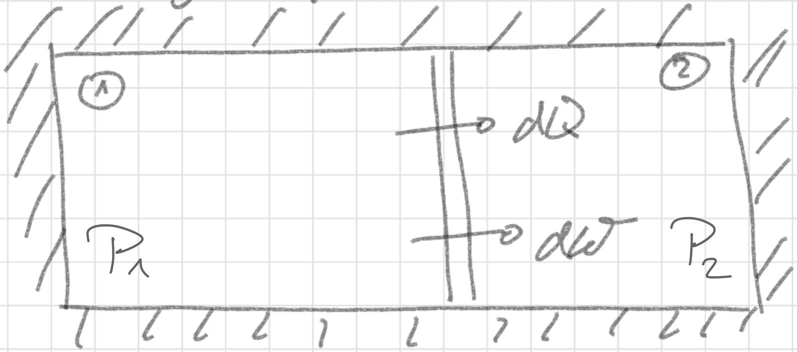
Implication from (4):

To fullfill 2nd law ("≥ 0"): $T_2 > T_1$ and $dQ_1 > 0$ (or vice versa)

Equivalent formulation of 2nd law:

Heat transfer must go from hot to cold in an isolated system.

II. Moving impermeable & diathermal wall



① & ② are in thermal eq.

Question 1: What is S at mechanical equilibrium ($P_1 = P_2$)?

$U = U_1 + U$ (extensive qu.)

Since $U = const$; $dU = 0 \Longrightarrow dU_1 = -dU_2$

E_{int} : $E_{int} = E_{int,1} + E_{int,2}$ & $dE_{int,2} = -dE_{int,1}$

since $dE_{int} = 0$

1st law: $dE_{int,1} = dQ_1 - dW_1$; $dE_{int,2} = dQ_2 - dW_2$

Because $T_1 = T_2 = T$

$$dE_{int,1} = T\,dS_1 - P_1\,dV_1 \;;\quad dE_{int,2} = T\,dS_2 - P_2\,dV_2$$

$$\hookrightarrow \; dS_1 = \frac{1}{T}\left(dE_{int,1} + P_1\,dV_1\right) \;;\quad dS_2 = \frac{1}{T}\left(\underset{-dE_{int,1}}{\underset{\parallel}{dE_{int,2}}} + P_2\,\underset{-dV_1}{\underset{\parallel}{dV_2}}\right)$$

Total $dS = dS_1 + dS_2$:

$$dS = \frac{1}{T}\left(\cancel{dE_{int,1}} + P_1\,dV_1 - \cancel{dE_{int,1}} - P_2\,dV_1\right)$$

$$dS = \frac{1}{T}\left(P_1 - P_2\right)dV_1 \quad (5) \quad \Big|\, dV_1$$

$$\Longrightarrow \boxed{\frac{dS}{dV_1} = \frac{1}{T}\left(P_1 - P_2\right)}$$ in mechanical equi.: $P_1 = P_2$

$$\boxed{\frac{dS}{dV_1} = 0}$$ mech. equilibrium condition for S

S in an isolated system is maximum at mechanical equil.

Question 2: What is the S production?

Isolation & 2nd law: $dS_{exch} = 0$; $dS \geq 0$

From (5):

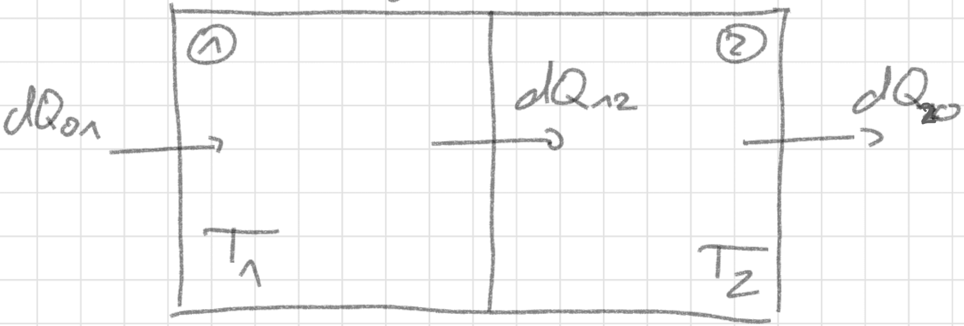
$$dS = dS_{Prod} = \frac{1}{T}(P_1 - P_2)\, dV_1 \geq 0$$

To fulfil 2nd law: $P_1 > P_2$ & $dV_1 > 0$ (or vice versa)

2 Examples show: Entropy is produced whenever a transport of heat & work occurs within an inhomog., isolated system with a T or P gradient.

Example: Stationary heat transfer between two blocks

Consider a system consisting of 2 simple systems that are rigid blocks in thermal contact with $T_1 > T_2$



Stationary process:

State variables do not change with time

$\Longrightarrow T_{1/2}$ & $S_{1/2}$ const !

Question: for a stationary process, show that

$$dQ = dQ_{01} = dQ_{12} = dQ_{20}$$

In stationary case: $dS_1 = 0$, $dS_2 = 0$

The blocks are simple, rigid systems: $dS_{prod,1} = 0$

$dS_{prod,2} = 0$

$$\Longrightarrow \quad dS_1 = \frac{dQ_{01} - dQ_{12}}{T_1} = 0 \quad \Longrightarrow \quad dQ_{01} = dQ_{12}$$

$$dS_2 = \frac{dQ_{12} - dQ_{20}}{T_2} = 0 \quad \Longrightarrow \quad dQ_{12} = dQ_{20}$$

$$\Longrightarrow \quad dQ_{01} = dQ_{12} = dQ_{20}$$

Summary 8.3-8.5 Entropy & the three laws of Thermodynamics

- Entropy and the first law of TD: $dE_{int} = dQ - dW = TdS - PdV$
  - Only for reversible processes: $dQ = TdS$ & $dW = PdV$

    For irrev. processes: $S_{Prod} \neq 0$
- Second law of Thermodynamics: each thermodynamic system has a state variable called entropy S. The total entropy of thermally isolated/adiabatic system (Q=0) cannot decrease over time: $\Delta S \geq 0$
  - —> Entropy is not conserved but increases for most natural processes (unless they are fully reversible)
- Third law of Thermodynamics: The entropy of a system converges to a constant value $S_0 = 0$ for $T \rightarrow 0$, independent of all the other properties for the particular system.

8.6 Statistical interpretation of Entropy

Recall from Chapter 5: $\frac{d \log \Omega}{dE} = \frac{1}{k_B T}$ (1)

Chapter 8.5: $dE_{int} = TdS - PdV$

$$T = \frac{\partial E_{int}}{\partial S} \longrightarrow \frac{1}{T} = \frac{\partial S}{\partial E_{int}} \quad (2)$$

Put (2) into (1):

$$k_B \cdot \frac{d \log \Omega}{dE} = \frac{\partial S}{\partial E} \quad \Big| \int dE$$

$$\boxed{S = k_B \log \Omega}$$

Statistical interpretation of the second law:

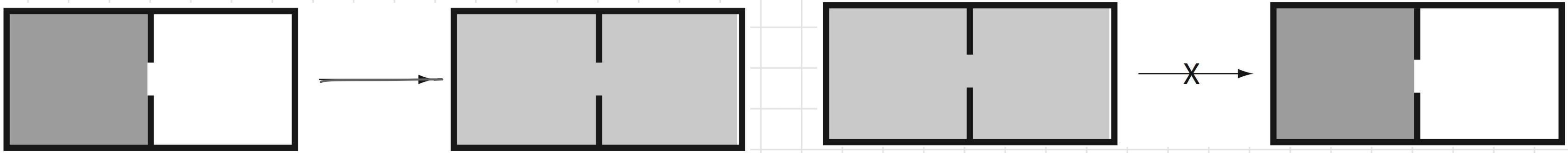
In a thermally isolated system. $\Delta S \geq 0$

→ entropy must increase (S_{Prod}) with time (or stay const)

→ from more order (fewer Ω) to less order (more Ω)

→ with time, a thermally isolated system can only keep the same amount or less order

→ because higher # of microstates implies a larger P of a macroscopic state → S must increase



Statistical interpretation of the third law:

$$\lim_{T \to 0K} S = 0$$

Since $S = k_B \log \Omega$

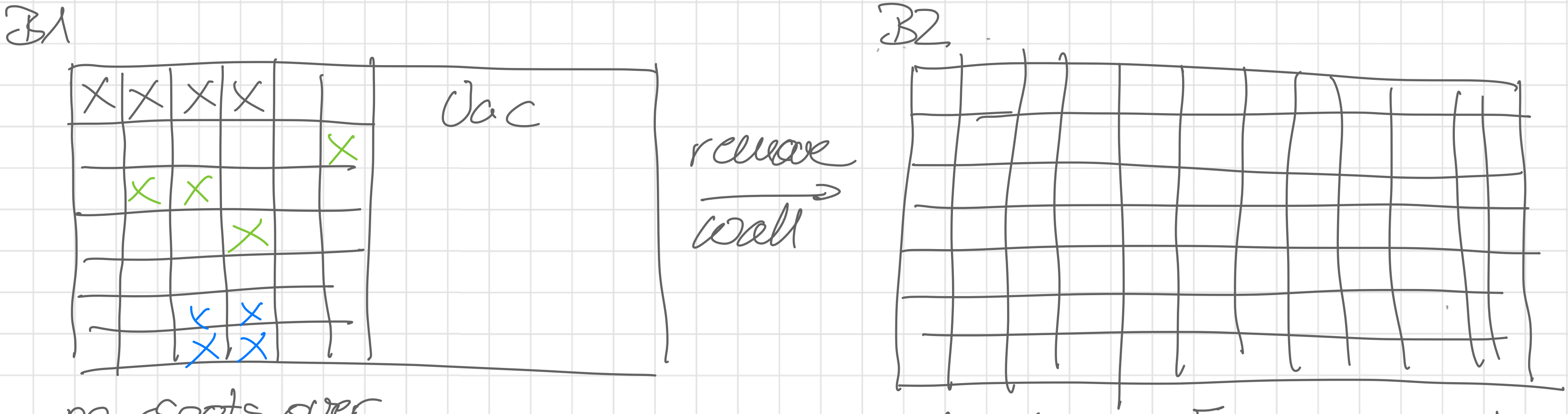
$\hookrightarrow \Omega \to 1$

State of "perfect" order with only one possible microstate.

Statistical view of the free expansion process (irrev.)

$$Q=0 \rightarrow \Delta S_{env}=0 \text{ but } \Delta S_{Prod}>0$$

Question: How much entropy is produced?



m spots over which N gas particles can be distr.

doubling V: 2m spots over which N gas particles can be distrib

Analyse: how many possibilities for distributing N particles?

B1: $S = k_B \log \Omega$

From combinatorics:

$$\Omega = \binom{m}{N} = \frac{m!}{(m-N)!\,N!}$$

Stirling's formula:

$\ln(x!) \approx x \ln x - x$

# of combinations if N particles are distributed over m spots

$$\Rightarrow S = k_B \ln \frac{m!}{(m-N)!\,N!} = k_B\left(\ln m! - \ln(m-N)! - \ln N!\right)$$

$$\approx k_B\left[m \ln m - \cancel{m} - (m-N)\ln(m-N) + \cancel{(m-N)} - N \ln N + \cancel{N}\right] =$$

$$\Rightarrow S = k_B\left[m \ln m - (m-N)\ln(m-N) - N\ln N\right]$$

$$= k_B\left[\underline{m\ln m} - \underline{m\ln(m-N)} + \underline{N\ln(m-N)} - \underline{N\ln N}\right]$$

$$= k_B\left[-m\ln\frac{m-N}{m} + N\ln\frac{m-N}{N}\right]$$

$$= k_B\left[-m\ln\left(1-\underset{\to 0}{\frac{N}{m}}\right) + N\ln\left(\underbrace{\frac{m}{N}}_{\to\infty} - \underset{\text{negligib}}{1}\right)\right]$$

atoms are infinitesimally small

$m \to \infty$

Taylor approximation: $\ln(1-x) \boxed{= -x} - \frac{x^2}{2} - \dots$

if $x \approx 0$

$$S \approx k_B\left[-\cancel{m}\left(-\frac{N}{\cancel{m}}\right) + N\ln\left(\frac{m}{N}\right)\right]$$

$$\Rightarrow \quad S = k_B \left[N + N \ln\left(\frac{m}{N}\right) \right]$$

$$m \to \infty \Rightarrow S \to \infty$$

But: ΔS between B1 (m) & B2 $(2m)$

$$\Rightarrow \Delta S = S(2m) - S(m) = k_B \left(\cancel{N} + N \ln \frac{2m}{N} - \cancel{N} - N \ln \frac{m}{N} \right)$$

$$= k_B N \left(\ln 2m - \cancel{\ln N} - \ln m + \cancel{\ln N} \right)$$

$$= k_B N \ln \frac{2m}{m} = k_B N \ln 2$$

$$\boxed{= k_B N \ln \frac{V_2}{V_1}} \quad \text{as} \quad V_2 = 2 V_1$$

same as for an isothe
expansion proc.

S change in a reversible, isothermal expansion is a valid approximation for an irreversible free expansion process, because S is a state fct, & conditions are „similar"

Summary 8.6, Statistical interpretation of entropy

- The entropy S of a particular macro state of a TD system is related to the number of microstates on a particle level:

$$\boxed{S = k\ln\Omega}$$

- Implications of the second law of TD: An increasing entropy ΔS ≥ 0 of an adiabatic system (Q=0) implies that a system evolves from more order (lower Omega) to equal or less order (equal or higher Omega) with time (equality for reversible process only).
  - entropy increase is purely driven by higher probabilities of certain combinations of microstates
  - heat flow from hot to cold object: much more microstates, thus higher probability, for this scenario then for the reverse process
- Implications for the third law of TD: for T—>0 also S—>0, this would imply log Omega=0, only one micro state, meaning a system would be maximum order
- Entropy change for free expansion in an thermally isolated system: approximated by a reversible, isothermal process

$$\Delta S \approx nR\ln\frac{V_b}{V_a}$$

WHAT IS ENTROPY?

TEDEd

(AND WHY IS IT USEFUL?)

Conceptual Questions:

- Why is the first law of TD not sufficient to describe TD systems?
- What is entropy in classic TD and in statistical view?
- How to calculate entropy, if changes of state are irreversible? — replacement by an reversible process
- A gas is allowed to expand (a) adiabatically and (b) isothermally. In each process, does the entropy increase, decrease of stay the same?
- Give three examples of naturally occurring processes in which order goes to disorder.
- Which statement is true regarding gut entropy change of an ice cube that melts? (a) Since melting occurs at the melting point temperature, there is not temperature change so there is no entropy change; (b) Entropy increases. (c) Entropy decreases.
- Describe a reversible and irreversible possibility to expand gas isothermally.
- Which do you think has the greater entropy, 1kg of solid iron or 1kg of liquid iron?
- Living organisms, as they grow, convert relatively simple food molecules into a complex structure. Is this a violation of the 2nd law of TD?
- Think of your questions!

Up next:

Lecture 1: —Chapter 1. Introduction
—Chapter 2. Temperature and zeroth law of thermodynamics

Lecture 2: —Chapter 3. Gas laws

Lecture 3: —Chapter 4. Statistical thermodynamics I: Kinetic theory of gas (slides in previous file)
—Mathematical Excursion — Preparation for Chapter 5.

Lecture 4: —Chapter 5. Statistical thermodynamics II (Boltzmann factor, Maxwell-Boltzmann distribution)

Lecture 5: —Chapter 6. Energy, heat and heat capacity

Lecture 6: —Chapter 7. First law of thermodynamics and thermal processes

Lecture 7: — Mock exam I *with Dr. Tress*

Lecture 8: —Chapter 8. Entropy and the second and third law of thermodynamics

Lecture 9/10: —Chapter 9. Thermal machines

Lecture 11: —Chapter 10. Thermodynamic potentials and equilibria

Lecture 12: —Mock Exam II *with Dr. Tress*
Lecture 13: —Chapter 11. Heat transfer (Conduction, Convection, Radiation)

Lecture 14: —Final review and open questions