

# 2019 FYS4130 Statistical Physics

## Course Plan

[https://www.uio.no/studier/emner/matnat/fys/FYS4130/v19/lecture\\_plan.html](https://www.uio.no/studier/emner/matnat/fys/FYS4130/v19/lecture_plan.html)

## Important dates

**02.04 Deadline Oblig1 (received 19.03)**

**01.05 Deadline Oblig2 (received 10.04)**

**04.06 Final exam (written)**

**No lectures: 26.03 and 27.03**

# Module I: Thermodynamics (review) and the statistical ensembles

ti. 15. jan.	Thermodynamics laws, entropy
on. 16. jan.	Thermodynamic potentials, response functions and Maxwell's relations, thermodynamic stability
ti. 22. jan.	Phase space, Liouville's theorem, statistical ensembles
on. 23. jan.	Free particles in microcanonical ensemble
ti. 29. jan.	Canonical, grand canonical, isobaric ensemble
on. 30. jan.	Summary and questions

## Module II: Non-interacting particles, multiplicity function, partition function

## Module III: Weakly-interacting particles and Van der Waals fluid

## Module IV: Quantum gases

## Module V: Statistical description of magnetism

## Module V: Non-equilibrium statistical processes

# Lecture 1

Thermodynamics laws

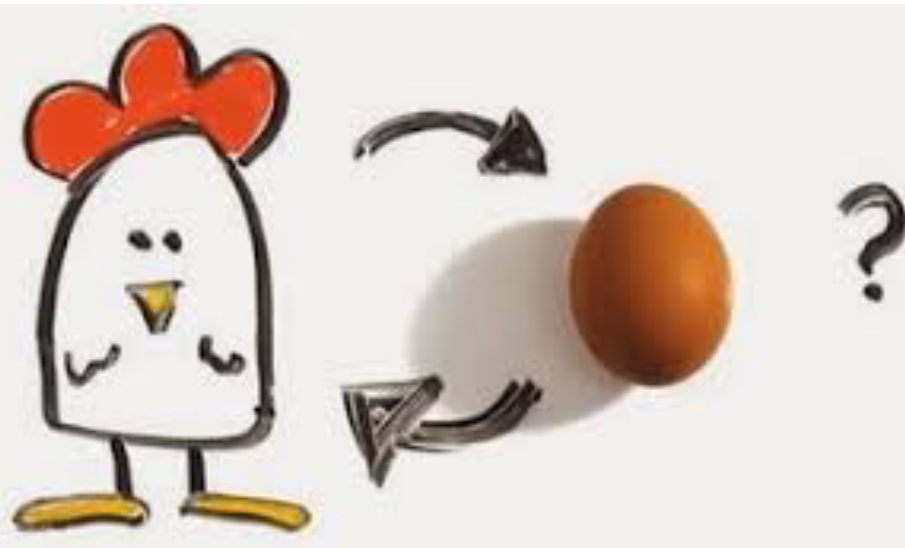
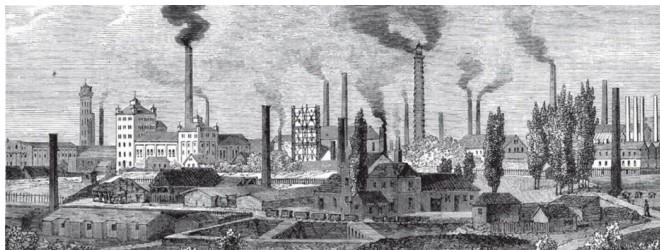
Entropy

15.01.2019

# Thermodynamics—Theory of principle

Physics of heat  $Q$  and work  $W$  and properties of matter that relate to  $Q$  and  $W$

- *invention* and *trigger* of the Industrial Revolution (1800→..)



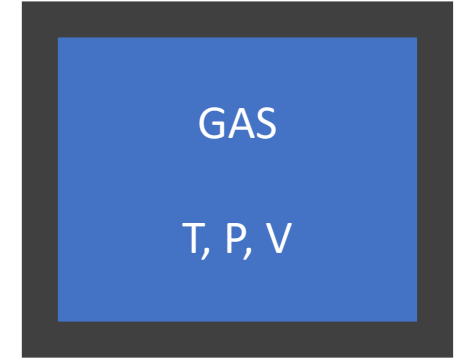
# Thermodynamics—Theory of principle

- Based on few empirically observed general properties elevated as thermodynamic principles
  - ❖ 1<sup>th</sup> law → conservation of energy
  - ❖ 2<sup>th</sup> law → defines **ENTROPY** (S) and entropy changes in relation to heat and work exchanges
- These laws are **UNIVERSALLY VALID**

## Thermodynamics: Definitions

### Thermodynamic system:

- Systems: *part of the Universe that we choose to study*
- Surrounding/environment/reservoir: *the rest of the Universe and much larger than the system*
- Boundary: *the surface separating the System from the Surrounding*



### How do we describe the system:

- A few macroscopic properties:  
pressure, temperature, volume, molar volume, ...
- Homogeneous or Heterogeneous
- State of the system:  
equilibrium or non-equilibrium
- Number of components:  
pure system or composite system

**For a one-component (pure) system**, all that is required is  $N$  (number of particles) and two other thermodynamic variables. All other properties then follow the **equation of state**.

$$P = f(N, V, T)$$

# Equation of state

$$P = P(V, T, N)$$

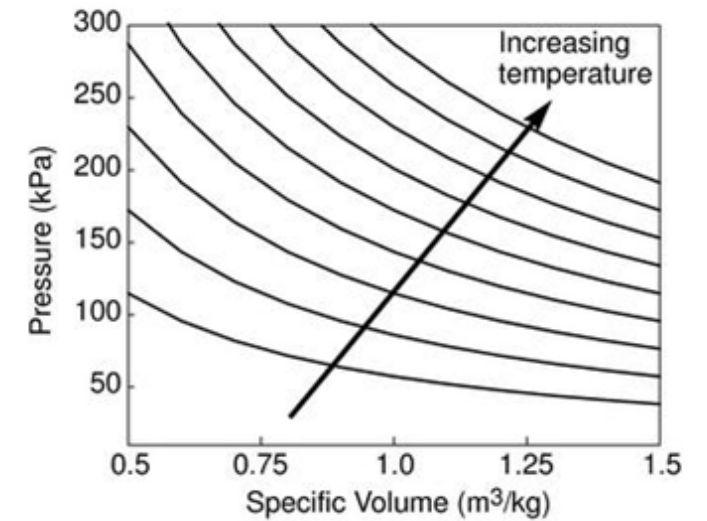
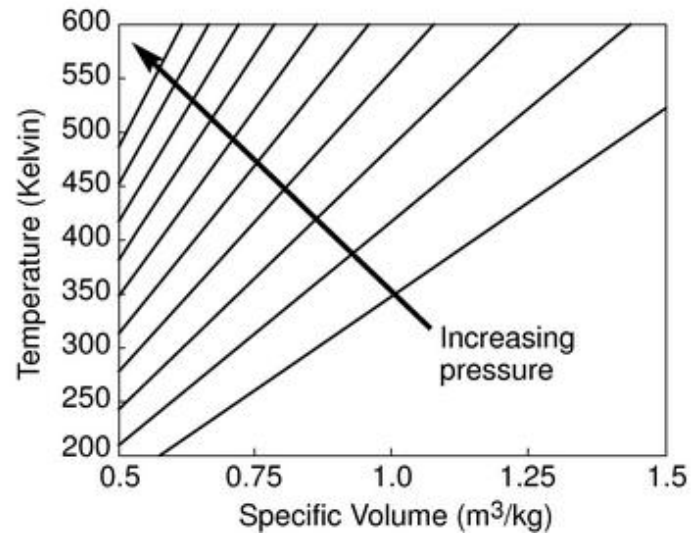
Ideal gas:

$$PV = NkT$$

Where  $k = 1.381 \times 10^{-23} \text{ J K}^{-1}$  is the Boltzmann's constant

$$P = kT\rho$$

Phase diagrams:



# Equation of state

$$P = P(V, T)$$

van der Waals equation of state for real fluids:

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}$$

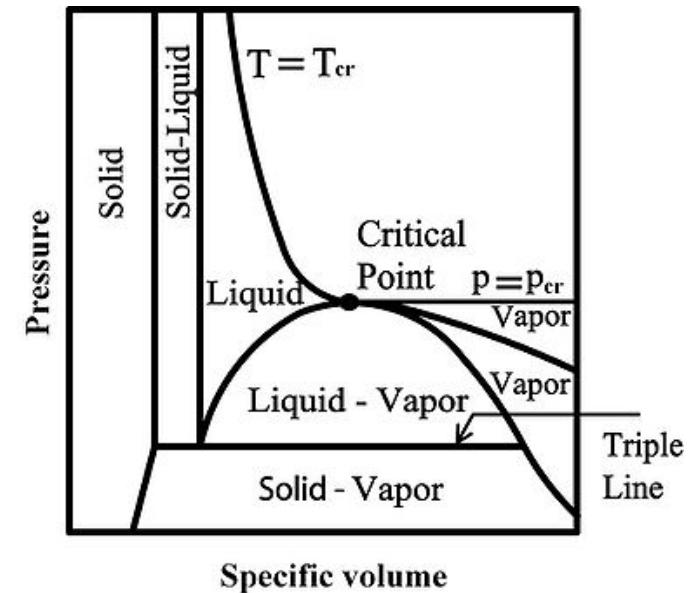
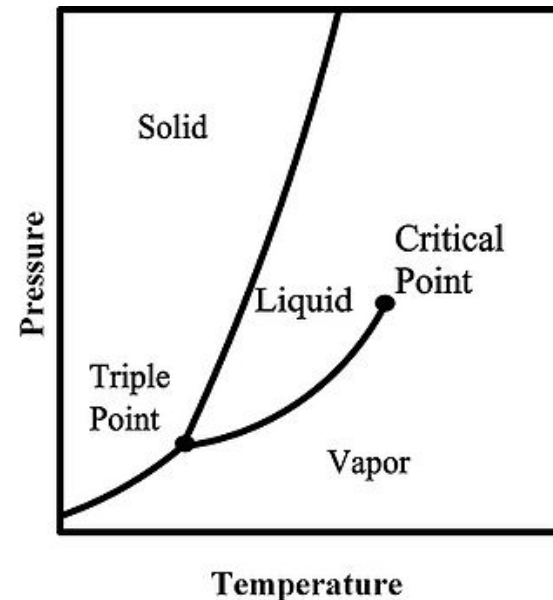
Where  $a$  is the strength of attractive forces between particles and  $b$  is the exclusion volume of each particle

Virial expansion (low density):

$$P = kT \sum_n \rho^n B_n(T)$$

With  $B_n(T)$  the virial coefficients, and  $B_1(T) = 1$

Phase diagrams:





# Statistical mechanics – Constructive theory

Invented to *explain* the principles of thermodynamics based on the **atomistic** description of matter – kinetic theory of gases (1870→)

## Thermodynamics:

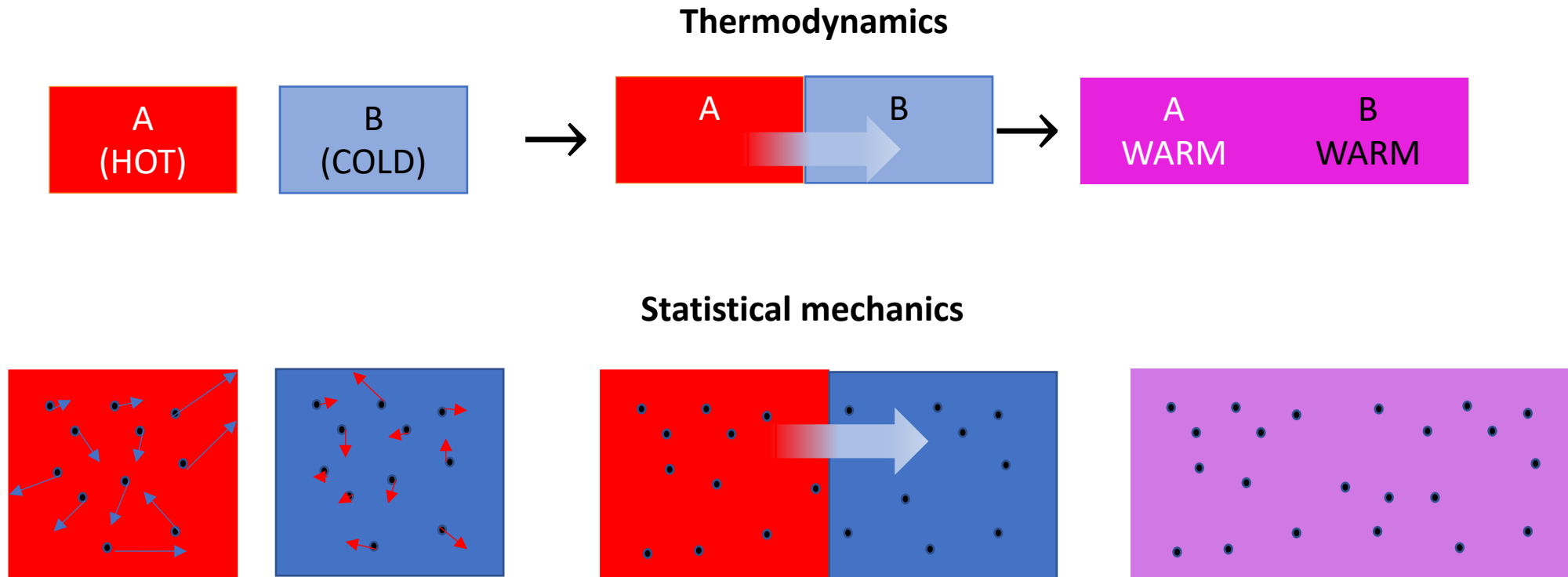
By virtue of the 2nd law of thermodynamics, heat *always* flows ***spontaneously*** from **hot** to **cold** until the same ***temperature*** is reached

## Statistical mechanics:

**Most likely**, heat flows spontaneously from hot to cold because the atoms of the **hot** system have more kinetic energy. Therefore there is a natural tendency that, by mutual collisions, **«hot»** atoms lose some of their energy while **«cold»** atoms gain some kinetic energy until everyone has *the same kinetic energy*, **on average**

# Statistical mechanics – Constructive theory

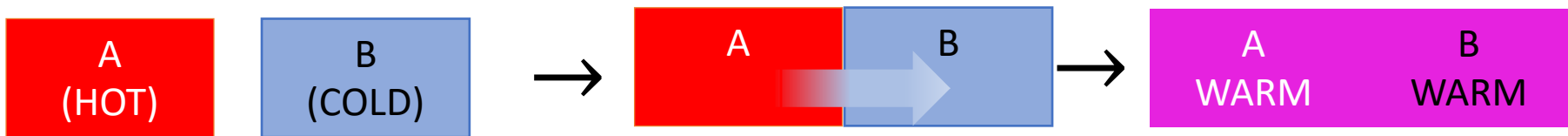
Invented to *explain* the principles of thermodynamics based on the atomistic description of matter



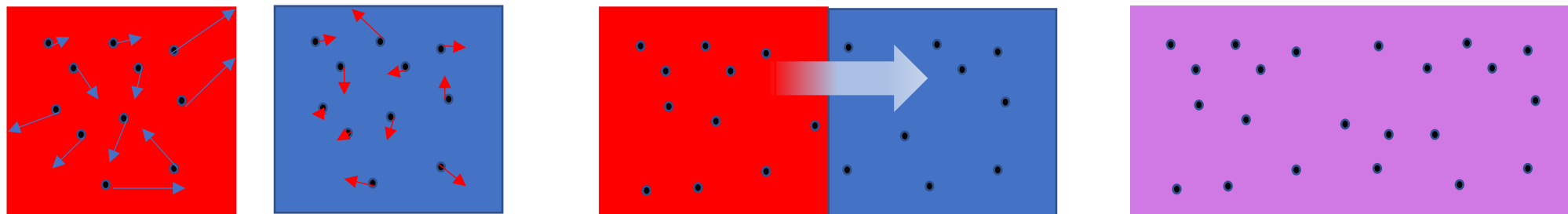
# Statistical mechanics – Constructive theory

Invented to *explain* the principles of thermodynamics based on the atomistic description of matter

**Thermodynamic process:** Spontaneous relaxation to **thermal equilibrium**



Spontaneous **heat diffusion** until the **equipartition of energy** is reached



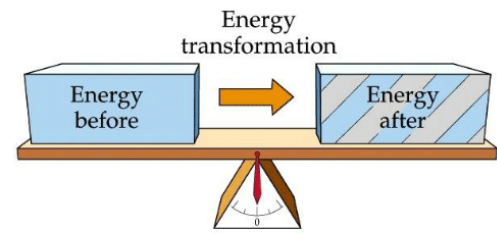
# Thermodynamics--Statistical mechanics: Correspondence

- «Atoms» := microscopic particles, neutral atoms, electrons, photons, phonons, ...

Thermodynamic system (T,P,V,N..)	Ensemble of particle configurations at (T,P,V,N...)
Equilibrium states and free energies	Partition functions and statistical ensembles
$F(T, V, N)$	$Z(T, V, N) = \sum_{\{i-\text{config}\}} e^{-\frac{H_i}{kT}}$

**Correspondence:  $F(T, V, N) = -kT \ln Z(T, V, N)$**

# First law of thermodynamics



# First law of thermodynamics: Conservation of energy

Energy cannot be destroyed or created but only transformed. A system can exchange energy with its environment in the form of heat and work exchanges.

**Energy of the Universe is conserved**

$$dU_{system} = \delta Q - \delta W, \quad dU_{surrounding} = -\delta Q + \delta W \Rightarrow dU_{universe} = dU_{system} + dU_{surrounding} = 0$$

**Heat and Work:** process variable, path-dependent, “energies in transit” (cannot be stored, only exchanged)

**Internal energy:** state variable, depends only on the state and not how it gets there (can be stored)

**Sign convention:**  $\delta W = PdV > 0$  when the volume of the system increases (*Work done by the system to the surroundings*)

# Second Law of thermodynamics

# Second law of thermodynamics

Clausius inequality:

$$dS \geq \frac{\delta Q}{T}$$

Clausius inequality: *Entropy change* must be larger or equal than the infinitesimal amount of heat exchanged at a given temperature  $T$  divided by that temperature

$$dS \geq \frac{\delta Q}{T}$$
$$[S] = \frac{\text{Joule}}{\text{Kelvin}}$$

$$dS = \frac{\delta Q_{rev}}{T} \text{ for a } \textit{reversible process}$$

$$\text{Cyclic process: } \oint \frac{\delta Q}{T} \leq 0$$



# Second law of thermodynamics

Clausius inequality for an isolated system

**Entropy tends to increase as the system spontaneously finds its equilibrium state**

$$dS \geq 0$$

Boltzmann's formula  $S = k \ln \Omega$ ,  $\Omega$  = multiplicity of a macrostate

***An isolated system will spontaneously evolve towards the most likely equilibrium state, i.e. The macrostate with maximum multiplicity  $\Omega$***

Clausius inequality:

$$dS \geq \frac{\delta Q}{T}$$

Entropy of the Universe:

$$dS \geq 0$$

System is drawn towards the state with highest probability

$$\Omega_{final} \geq \Omega_{initial}$$

# Second law of thermodynamics: refrigerators

Cyclic process:  $\oint \frac{\delta Q}{T} \leq 0$

**Clausius:** It is impossible for any system to operate in a cycle that takes heat from a cold reservoir and transfer it to a hot reservoir without any work

2nd law:  $\Delta S_{sys} + \Delta S_{res} \geq 0 \rightarrow \Delta S_{res} \geq 0$  ( $\Delta S_{sys} = 0$  for a cycle)

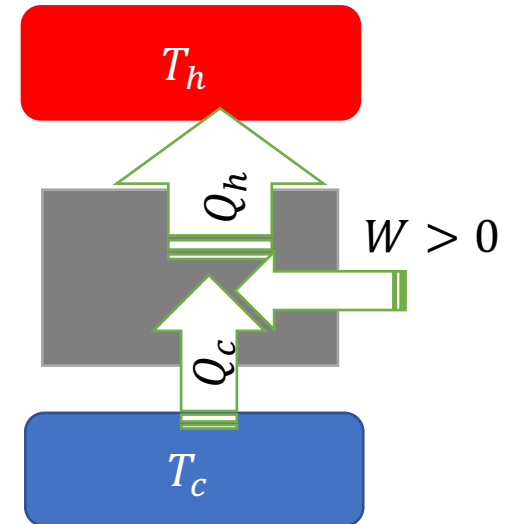
$$\frac{Q_h}{T_h} - \frac{Q_c}{T_c} \geq 0 \rightarrow \frac{Q_h}{Q_c} \geq \frac{T_h}{T_c} \rightarrow Q_h > Q_c$$

1st law:  $\Delta U = -Q_h + Q_c + W = 0$

$$Q_h = Q_c + W$$

Clausius inequality:

$$\oint \frac{\delta Q}{T} \leq 0$$



# Second law of thermodynamics: heat engines

Cyclic process:  $\oint \frac{\delta Q}{T} \leq 0$

**Kelvin:** It is impossible for any system to operate in a cycle that uses heat from a hot reservoir as work without also releasing some heat into a cold reservoir

2nd law:  $\Delta S_{sys} + \Delta S_{res} \geq 0 \rightarrow \Delta S_{res} \geq 0$

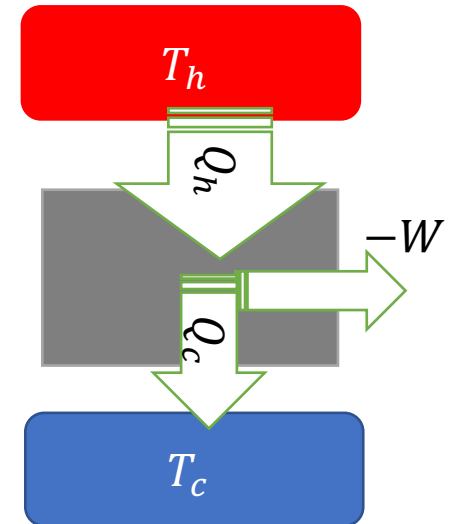
$$-\frac{Q_h}{T_h} + \frac{Q_c}{T_c} \geq 0 \rightarrow \frac{Q_c}{Q_h} \geq \frac{T_c}{T_h}$$

1st law:  $\Delta U = Q_h - Q_c - W = 0$

$$Q_h = Q_c + W$$

Clausius inequality:

$$\oint \frac{\delta Q}{T} \leq 0$$



## Thermodynamic inequality

$$TdS \geq \delta Q \rightarrow TdS \geq (dU + \delta W) \rightarrow$$

Principle of maximum work:

$$\delta W \leq -(dU - TdS)$$

*Work done by the system is maximum for a reversible process*

Reversible process: **Thermodynamic identity**

$$dU = TdS - PdV \rightarrow \delta W_{\max} = PdV$$

**Thermodynamic inequality**

$$dU \leq TdS - PdV$$

# Entropy

- Thermodynamic identity can only determine entropy change
- Entropy of a state can be evaluate up to the entropy constant

$$dS = \frac{1}{T} dU + \frac{P}{T} dV$$

Example: **Ideal gas entropy**

Equipartition of energy (3D)  $U = \frac{3}{2} NkT \rightarrow dU = \frac{3}{2} NkdT$

Equation of state:  $PV = NkT \rightarrow P(V) = \frac{NkT}{V}$

$$dS = \frac{3}{2} Nk \frac{dT}{T} + Nk \frac{dV}{V}$$

$$S - S_0 = \frac{3}{2} Nk \ln \left( \frac{T}{T_0} \right) + Nk \ln \left( \frac{V}{V_0} \right)$$

$S = Nk \left[ \frac{3}{2} \ln T + \ln V + \sigma_0 \right]$ ,  $\sigma_0(h, m, k)$  determined only from **statistical mechanics**

# Entropy

- Serious problem with the entropy obtained by integrating the thermodynamic identity is that it is **NOT EXTENSIVE**

$$S(U, V, N) = N k \left[ \frac{3}{2} \ln \left( \frac{U}{N} \right) + \ln V + \sigma_0 \right] \quad (1)$$

$$\text{Using } U = \frac{3}{2} N k T$$

- *Extensivity condition: homogeneous function (scale invariance)*

$$\tilde{U} = \frac{U}{N}, \tilde{V} = \frac{V}{N} \rightarrow S(U, V, N) = N \tilde{S}(\tilde{U}, \tilde{V}, 1)$$

Entropy is an additive quantity just like energy and volume: *the entropy of  $N$  particles is the sum of the entropy of each particle*

**But eq. (1) does not fulfill this condition!**

# Entropy of mixing and Gibbs paradox: $\Delta S$

$$U_{initial} = U_A + U_B = 2U$$

$$V_{initial} = V_A + V_B = 2V$$

$$N_{initial} = N_A + N_B = 2N$$

- If the gas is **the same** on both sides of the wall

$$S_A + S_B = 2S_{initial}(U, V, N)$$

$$\Delta S = S_{final}(U, V, N) - 2S_{initial}(U, V, U)$$

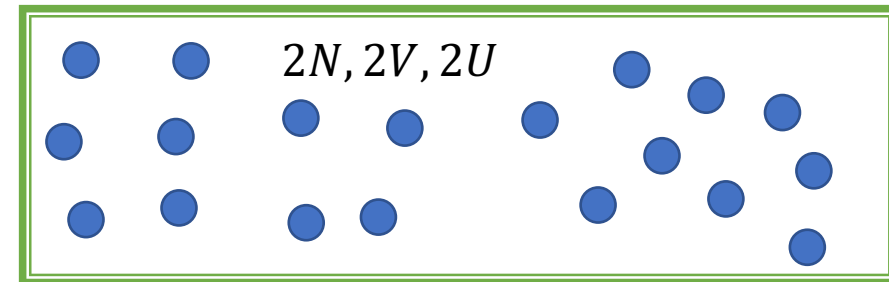
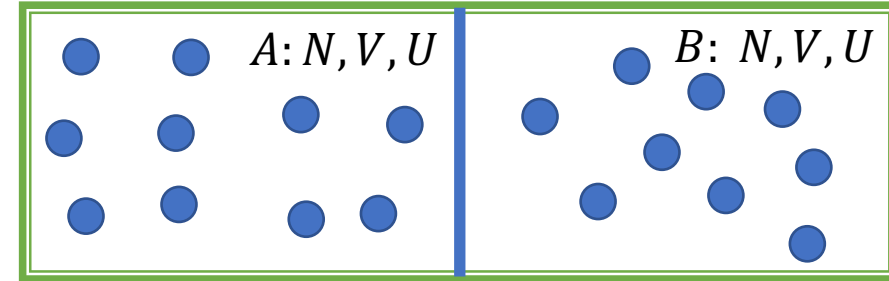
- Using Eq. (1)

$$\Delta S = 2kN \left[ \ln(2V) + \frac{3}{2} \ln\left(\frac{2U}{2N}\right) + \sigma_0 \right] - 2kN \left[ \ln V + \frac{3}{2} \ln\left(\frac{U}{N}\right) + \sigma_0 \right]$$

$$\Delta S = 2kN \ln 2 \neq 0!$$

(violate 2nd law of thermodynamics— the total system hasn't changed its equilibrium state -- and the extensivity property)

**FIXED:** Divide by  $k \ln N!$  in Eq. (1), and its explanation lies in statistical mechanics!



$$U_{final} = 2U$$

$$V_{final} = 2V$$

$$N_{final} = 2N$$

# Entropy of mixing: $\Delta S$

- If the gas is **different (distinguishable)** on both sides of the wall

$$\Delta S_t = \Delta S_A + \Delta S_B$$

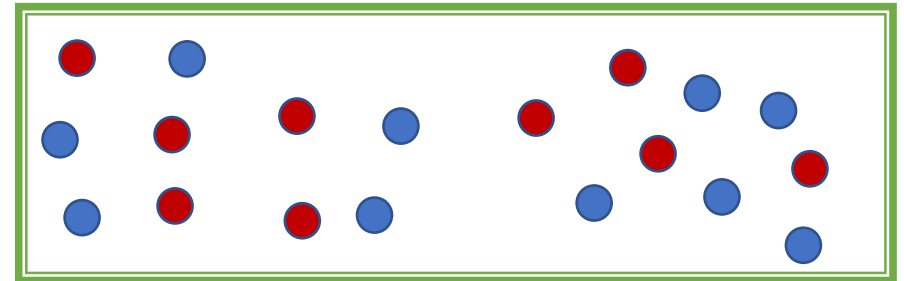
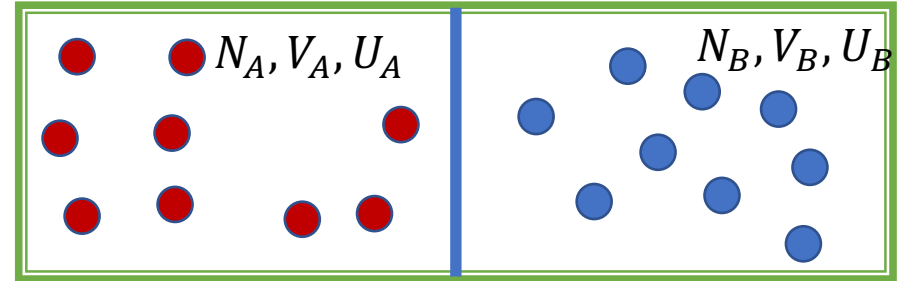
Using Eq. (1) (suppose  $U_A = U_B$ )

$$\Delta S_t = kN \ln \frac{V_{A,final}}{V_{A,initial}} + kN \ln \frac{V_{B,final}}{V_{B,initial}}$$

$$\Delta S_t = 2kN \ln 2$$

- Entropy increases when we mix **distinguishable** gases

- Effectively, the available volume increases upon mixing hence the number of configurations increases



$$N_A + N_B, V_A + V_B, U_A + U_B$$