

Lecture 8

Thermodynamic equilibrium: temperature, pressure

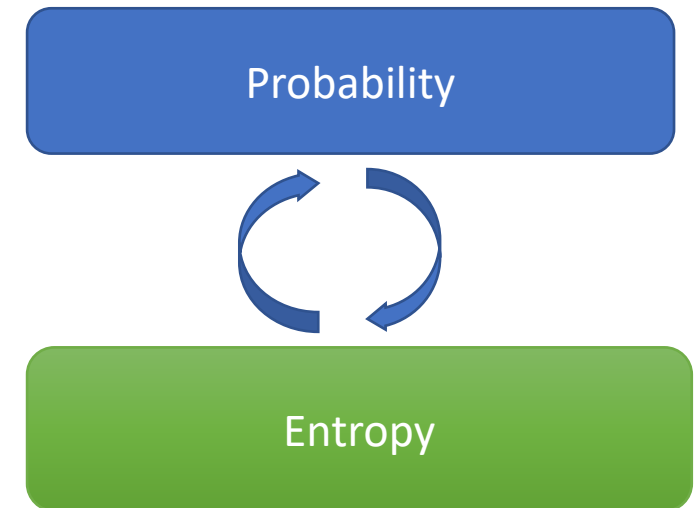
12.09.2018

Boltzmann's Entropy

Relate the number of **microstates** (multiplicity) with the thermodynamic (**macroscopic**) state of the system

$$S = k \ln \Omega, \quad k = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

Relate the thermodynamic state of the system with the **probability** to be in a given macrostate



Second law of thermodynamics

probabilistic law and isolated systems



Things that are more
probability, tend to occur
more often

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

Entropy increases
 $\Delta S \geq 0$

Time flows in **one way**
Arrow of Time

$$\Delta S = k \ln \frac{\Omega_{final}}{\Omega_{initial}}$$

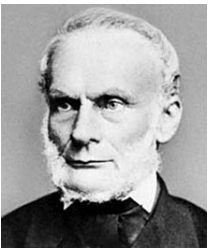
For an isolated system, the entropy can never decrease

$$\Delta S \geq 0$$

$\Delta S > 0$ for irreversible
 $\Delta S = 0$ for reversible

Second law of thermodynamics

heat flow and principle of maximum work



Clausius inequality

Entropy cannot be less than the heat exchange over temperature

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

For a **reversible** process, the entropy change is directly proportional to heat
Clausius relation

$$TdS = \delta Q_{rev}$$

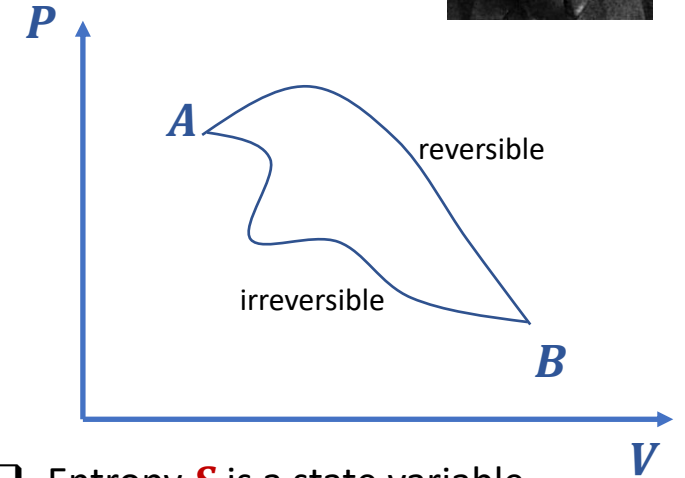
$$\frac{\delta Q_{rev}}{T} > \frac{\delta Q_{irrev}}{T}$$

Principle of maximum work

Using the 1st law of thermodynamics, $dU = \delta Q + \delta W$

$$TdS \geq dU - \delta W \rightarrow \delta W \geq dU - TdS \rightarrow \delta W \geq -PdV = \delta W_{rev}$$

Delivered work $-\delta W$ is maximum in a reversible process



- ☐ Entropy **S** is a state variable
- ☐ Entropy change ΔS depends only on the initial and final states, *independent on the path*
- ☐ *We compute ΔS from the reversible path*
- ☐ $PdV \geq -\delta W$, the work extracted from the system is maximum in a reversible path

Ideal gas: entropy S

Multiplicity of a macrostate of an ideal gas with N particles in a fixed volume V and energy U

$$\Omega(U, V, N) = \frac{1}{N! \left(\frac{3N}{2}\right)!} V^N \left(\frac{2\pi m U}{h^2}\right)^{\frac{3N}{2}} = f(N) V^N U^{\frac{3N}{2}}$$

$$\begin{aligned} \ln \left(N! \left(\frac{3N}{2}\right)! \right) &= N \ln N - N + \frac{3N}{2} \ln \frac{3N}{2} - \frac{3N}{2} \\ &= \frac{5N}{2} \ln N - \frac{5N}{2} + \frac{3N}{2} \ln \frac{3}{2} \end{aligned}$$

- Sackur-Tetrode Entropy:

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

$$S(U, V, N) = kN \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right]$$

Entropy is extensive (additive):

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

Entropy of mixing: ΔS

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

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

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

- Using Sackur-Tetrode formula

$$\Delta S_t = 2kN \left[\ln \left(\frac{2V}{2N} \left(\frac{4\pi m 2U}{3h^2} \frac{2N}{2N} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right] - 2kN \left[\ln \left(\frac{V}{N} \left(\frac{4\pi m U}{3h^2} \frac{N}{N} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right]$$

$$\Delta S_t = 0$$

Nothing changes, when we remove the wall! (that's good)

Gibbs paradox: if we didn't use that particles were indistinguishable (divide by $N!$), then

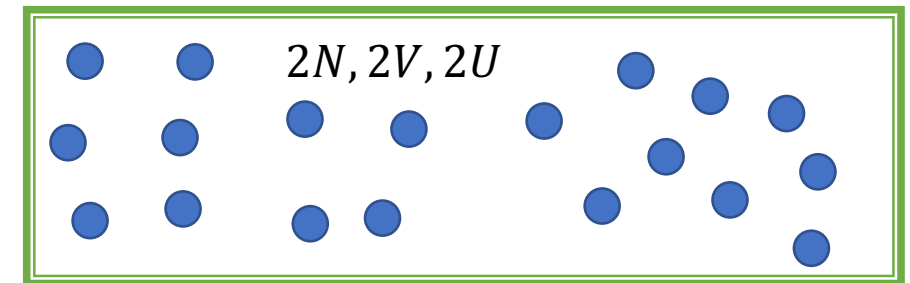
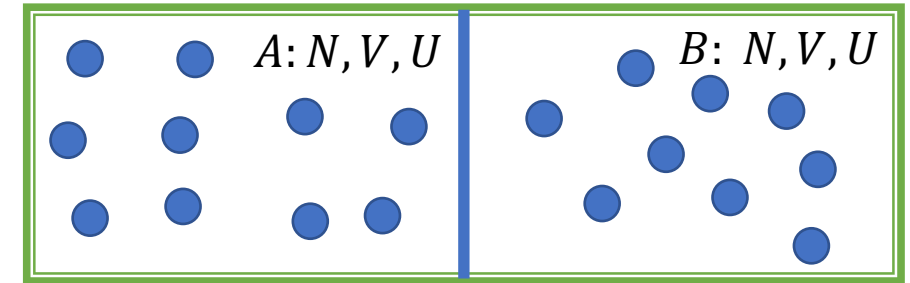
$$\Delta S_t = 2kN \ln(2V) - 2kN \ln V = 2kN \ln 2 > 0$$

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

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

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

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



$$U_{final} = 2U$$

$$V_{final} = 2V$$

$$N_{final} = 2N$$

Entropy of mixing: ΔS

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

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

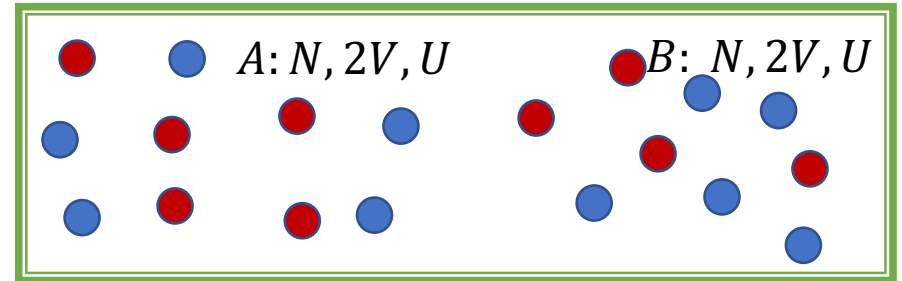
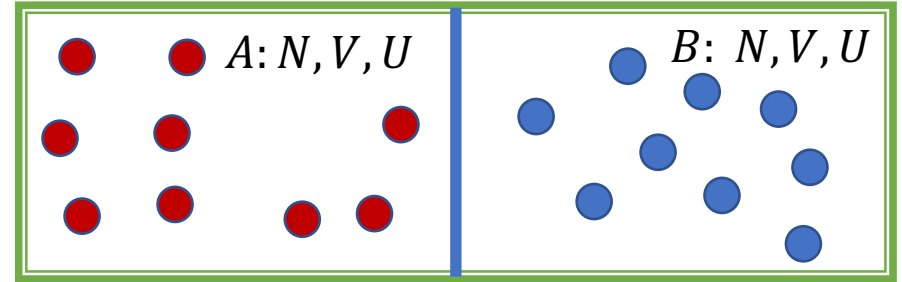
Using Sackur-Tetrode formula

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

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

❑ Entropy increases when we mix *different* gases

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



Thermal equilibrium

At equilibrium, the multiplicity is maximized. This means that the **equilibrium state** has **maximum entropy**

(Equilibrium is *relative* to the environment, another system with which it interacts with, or itself when isolated)

Thermal equilibrium of two interacting systems through **energy** exchange. $\Omega_{\text{total}} = \Omega_A(U_A, V_A) \cdot \Omega_B(U_B, V_B)$

$$\frac{\partial \Omega_{\text{total}}}{\partial U_A} = 0 \rightarrow \frac{\partial S_{\text{total}}}{\partial U_A} = 0$$
$$\frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0 \rightarrow \frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_B} \frac{dU_B}{dU_A} = 0 \rightarrow \frac{\partial S_A}{\partial U_A} - \frac{\partial S_B}{\partial U_B} = 0$$

System A and system B have the same temperature $\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \equiv \frac{1}{T}$

$$T = \left(\frac{\partial S}{\partial U} \right)_{V,N}^{-1}$$

Temperature is a measure of system's ability to exchange energy

- ☐ The system with higher $\frac{\partial S}{\partial U}$ (smaller T) will absorb energy
- ☐ The system with **higher T** will **give energy** to the system with *lower T*

Example: *Paramagnets: S and T*

Number of spin configurations with N_{\uparrow} out of N spins

$$\Omega(N, N_{\uparrow}) = \frac{N!}{N_{\uparrow}! (N - N_{\uparrow})!} \approx_{N \gg 1} \frac{N^N}{N_{\uparrow}^{N_{\uparrow}} (N - N_{\uparrow})^{N - N_{\uparrow}}}$$

Entropy of a macrostate with N_{\uparrow}

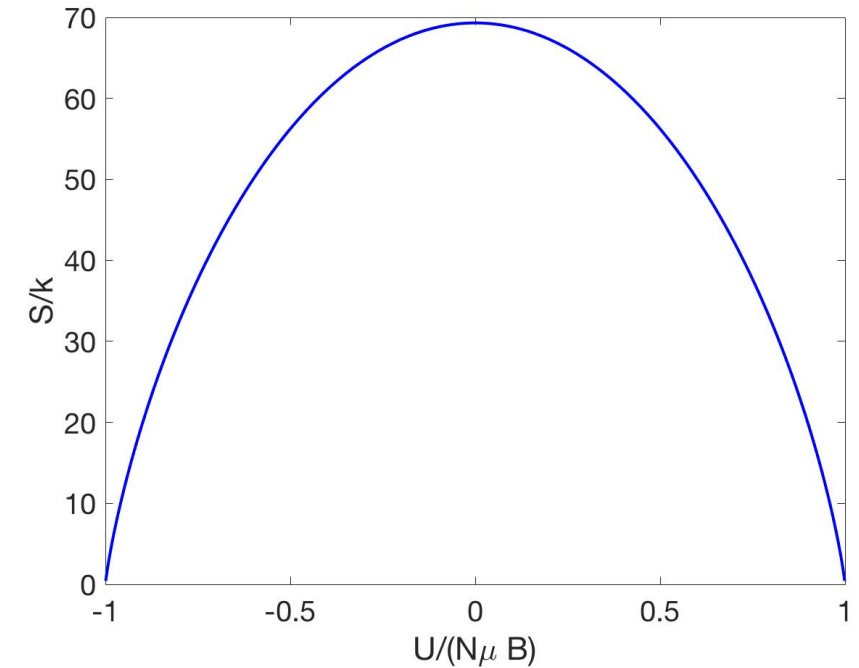
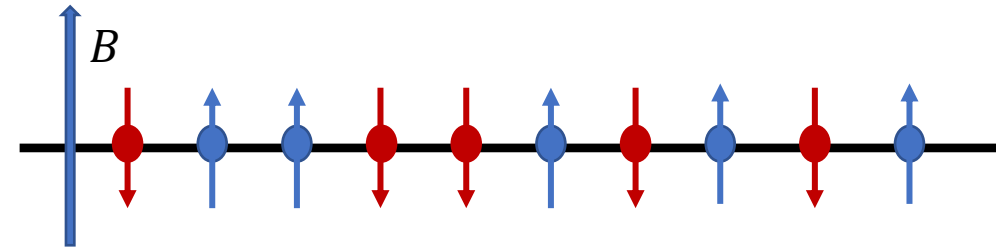
$$S(N_{\uparrow}) = k[N \ln N - N_{\uparrow} \ln N_{\uparrow} - (N - N_{\uparrow}) \ln(N - N_{\uparrow})]$$

Total energy of a macrostate with N_{\uparrow}

$$U(N_{\uparrow}) = -\mu B(N_{\uparrow} - N_{\downarrow}) = -\mu B(2N_{\uparrow} - N) \rightarrow N_{\uparrow} = \frac{N}{2} - \frac{U}{2\mu B}$$

Net magnetization of a macrostate with N_{\uparrow}

$$M(N_{\uparrow}) = \mu(N_{\uparrow} - N_{\downarrow}) = -\frac{U}{B}$$



Entropy of a macrostate with N_{\uparrow}

$$S(N_{\uparrow}) = k[N \ln N - N_{\uparrow} \ln N_{\uparrow} - (N - N_{\uparrow}) \ln(N - N_{\uparrow})]$$

Temperature of a macrostate with N_{\uparrow}

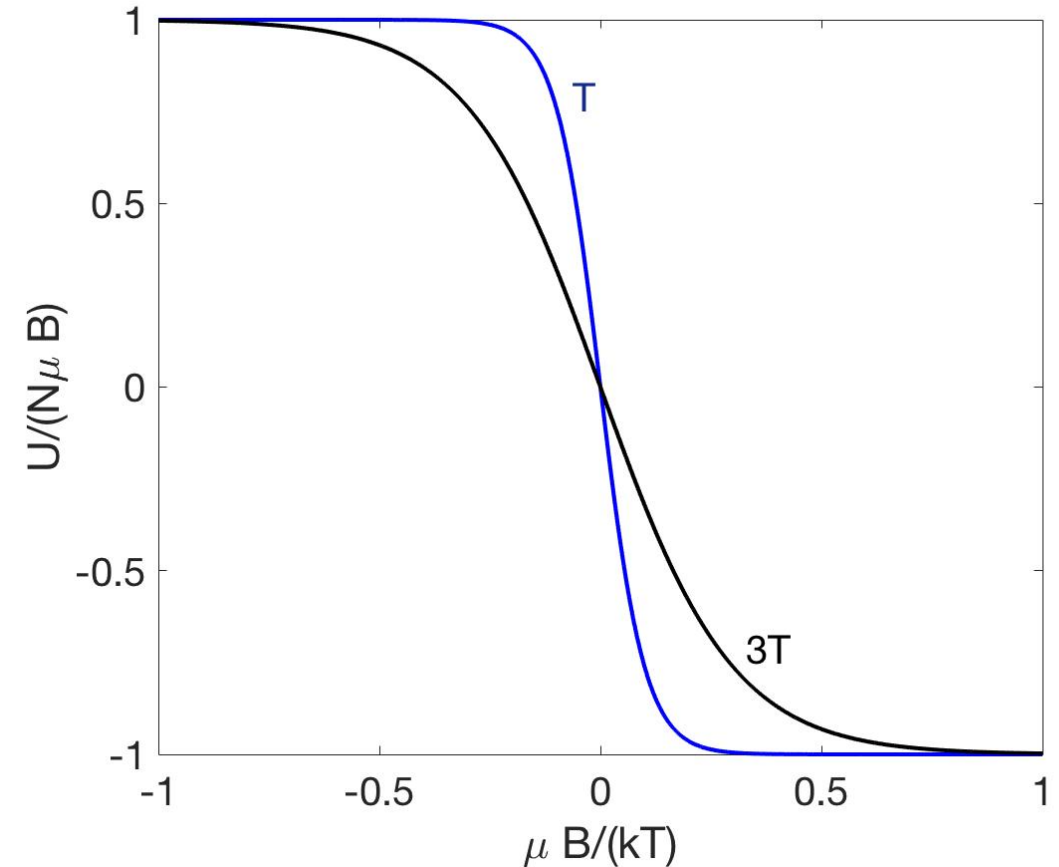
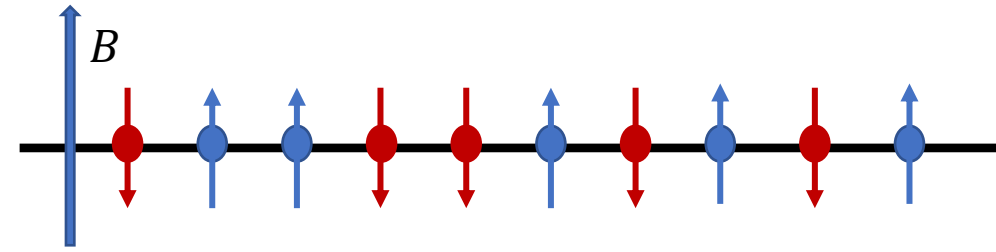
$$\frac{1}{T} = \frac{\partial S}{\partial N_{\uparrow}} \frac{\partial N_{\uparrow}}{\partial U} = k(-\ln N_{\uparrow} - 1 + \ln(N - N_{\uparrow}) + 1) \frac{1}{-2\mu B}$$

$$T = \frac{2\mu B}{k} \left[\ln \frac{N_{\uparrow}}{N - N_{\uparrow}} \right]^{-1} \rightarrow \frac{1}{T} = \frac{k}{2\mu B} \ln \frac{\frac{N}{2} - \frac{U}{2\mu B}}{\frac{N}{2} + \frac{U}{2\mu B}}$$

Total energy of a macrostate at a give temperature T

$$\frac{\frac{N}{2} - \frac{U}{2\mu B}}{\frac{N}{2} + \frac{U}{2\mu B}} = \exp\left(\frac{2\mu B}{kT}\right) \rightarrow \frac{N}{2} - \frac{U}{2\mu B} = \left(\frac{N}{2} + \frac{U}{2\mu B}\right) \exp\left(\frac{2\mu B}{kT}\right)$$

$$U = N\mu B \frac{1 - \exp\left(\frac{2\mu B}{kT}\right)}{1 + \exp\left(\frac{2\mu B}{kT}\right)} \rightarrow U = -N\mu B \tanh\left(\frac{\mu B}{kT}\right)$$

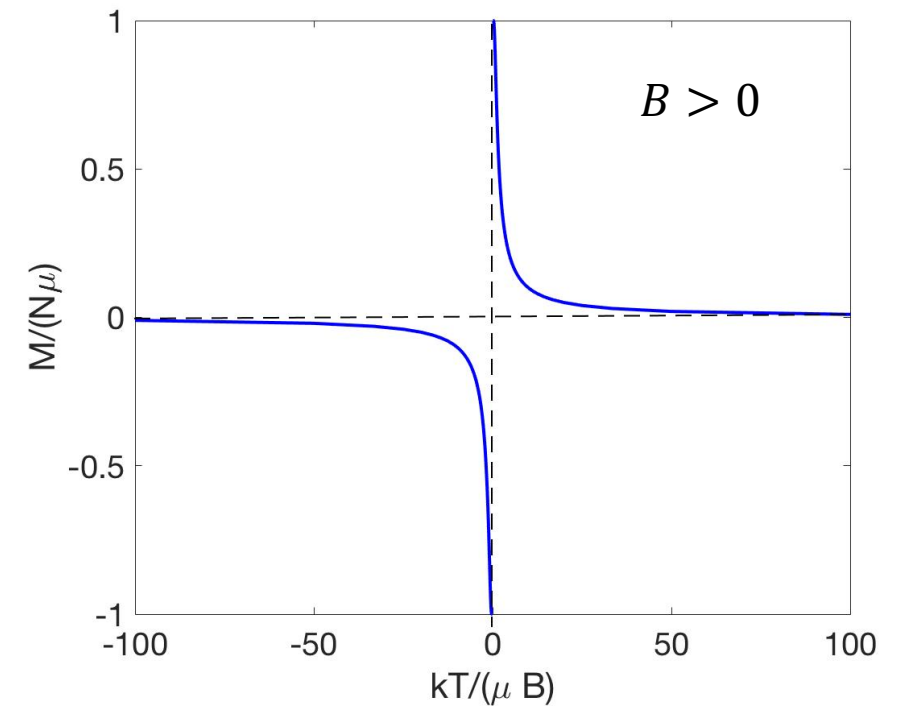
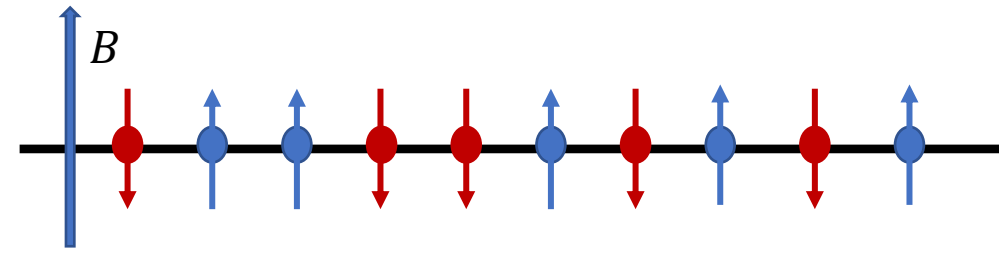
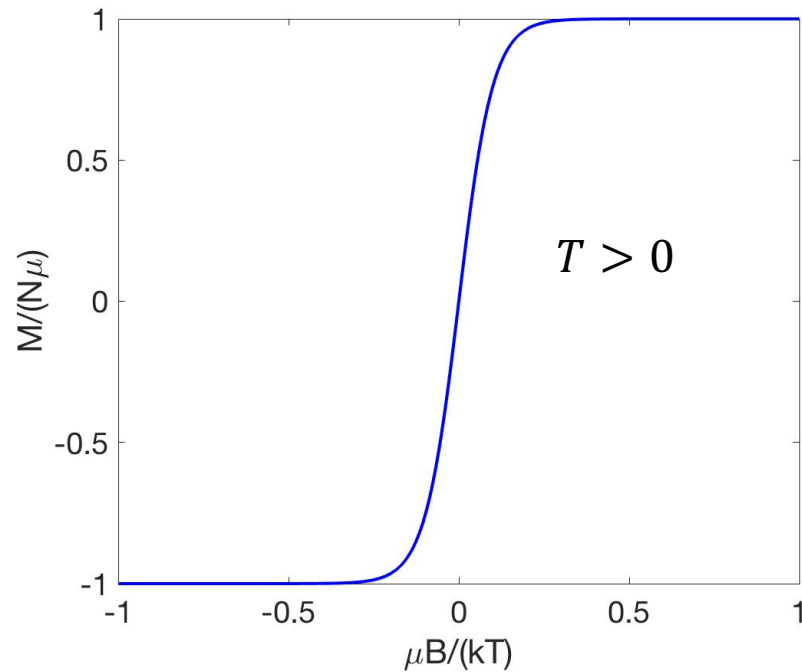


Net magnetization of a macrostate with N_{\uparrow}

$$M(T) = N\mu \tanh\left(\frac{\mu B}{kT}\right)$$

$T \rightarrow \infty, \quad M \rightarrow 0$ (*max randomness*)

$T < 0, \quad M$ is in the opposite with B



Ideal gas: S and T

- Entropy:

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

- Temperature:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U} \right)_{V, N} = \frac{3Nk}{2} \frac{d}{dU} \ln U = \frac{3Nk}{2} \frac{1}{U} \rightarrow U(T) = \frac{3NkT}{2}$$

Equipartition of energy: $\frac{3kT}{2}$ for the kinetic energy per particle in 3D

- Heat capacity C_V :

$$C_V = \frac{dU}{dT} \rightarrow C_V = \frac{3Nk}{2}$$

Mechanical equilibrium: What stays the same?

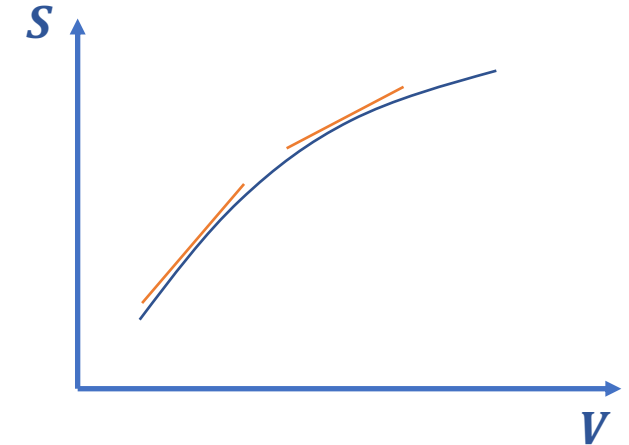
Mechanical and thermal equilibrium of two interacting systems through *energy* and *volume* exchange

$$\frac{\partial S_{total}(U_A, V_A)}{\partial U_A} = 0 \quad \text{and} \quad \frac{\partial S_{total}(U_A, V_A)}{\partial V_A} = 0$$
$$\frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = 0 \rightarrow \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_B} \frac{dV_B}{dV_A} = 0 \rightarrow \frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B} = 0$$

System A and system B have the same pressure: $T_A \frac{\partial S_A}{\partial V_A} = T_B \frac{\partial S_B}{\partial V_B} \equiv P$

$$P = T \left(\frac{\partial S}{\partial V} \right)_{U, N}$$

Pressure is a measure of system's ability to exchange volume



- ❑ The system with higher $\frac{\partial S}{\partial V}$ (higher P) will tend to expand
- ❑ The system with **higher P** will **expand** at the expense of the *compression* of the one with *lower P*

Pressure P in the ideal gas:

- Entropy:

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

- Equation of state:

$$P = T \left(\frac{\partial S}{\partial V} \right)_{U, N} = NkT \frac{d}{dV} \ln V = \frac{NkT}{V} \rightarrow \mathbf{PV = NkT}$$

This is now derived from counting the number of microstates for the gas particles!

- Heat capacity C_P :

$$C_P = C_V + P \left(\frac{\partial V}{\partial T} \right)_P \rightarrow C_P = \frac{3Nk}{2} + Nk = \frac{5Nk}{2}$$

Thermodynamic identity

- Entropy computed from the multiplicity of a macrostate at fixed U , V , and N

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

- Change in entropy due to *energy change* or *volume change* has a differential form

$$dS = \left(\frac{\partial S}{\partial U} \right)_{V,N} dU + \left(\frac{\partial S}{\partial V} \right)_{U,N} dV$$

- Using the definitions for T and P

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

- Thermodynamic identity for $U(S, V)$

$$dU = TdS - PdV$$

We have derived the first law of thermodynamics for a reversible change (system goes through equilibrium states)!

Gas expansion: ΔS

- Entropy:

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

- Isolated system ($\Delta U = 0$, $\Delta N = 0$) only V changes during expansion

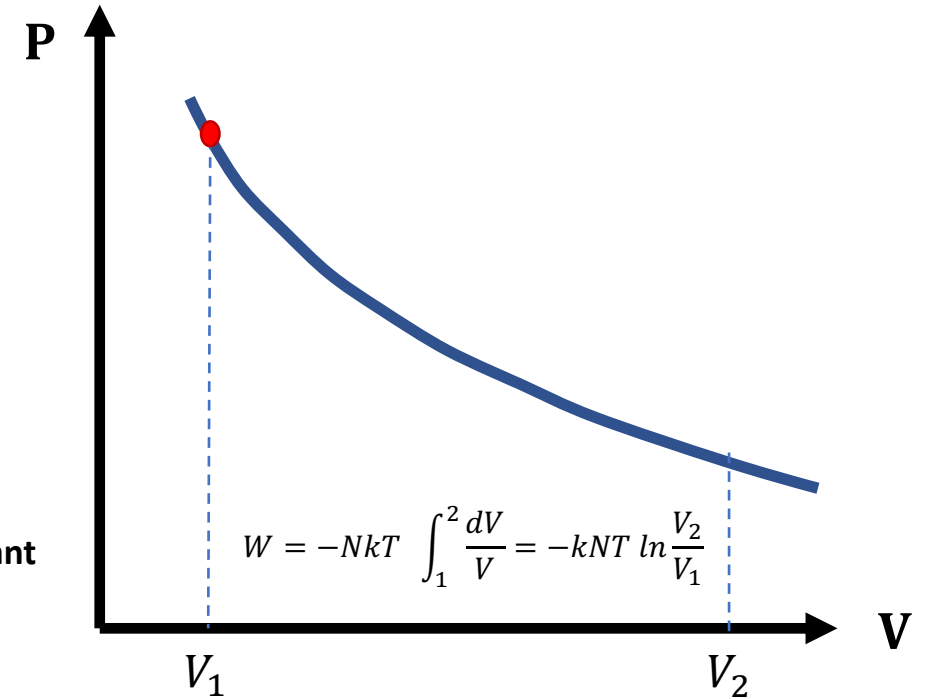
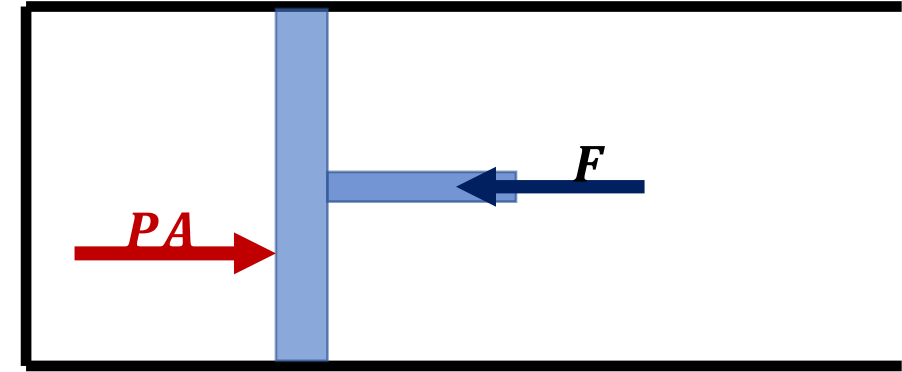
From Boltzmann's formula of S :

$$\Delta S = S_2 - S_1 = kN \ln \frac{V_2}{V_1}$$

From 1st & 2nd laws of thermodynamics: (along the isothermal path)

$$T\Delta S = Q_{\text{rev}} = -W_{\text{rev}} = kNT \ln \frac{V_2}{V_1}$$

- ❑ ΔS is related to heat during the quasistatic isothermal expansion
- ❑ $\Delta S > 0$ because of the heat absorbed by the expanding gas to keep its internal energy constant



ΔS is path-independent

- What if we choose the path A-B (isochoric+isobaric) instead of the isothermal path?
- What will happen then?

Use the definition of entropy from heat $dS = \frac{\delta Q_{rev}}{T}$

The entropy change $\Delta S = S_2 - S_1$ is then $\Delta S = \int_{A \rightarrow B \text{ path}} \frac{\delta Q_{rev}}{T}$

$$\Delta S = \int_{\text{path}_{\text{isochoric}}} \frac{\delta Q_{rev}}{T} + \int_{\text{path}_{\text{isobaric}}} \frac{\delta Q_{rev}}{T} = \int_{\text{path}_{\text{isochoric}}} \frac{dU}{T} + \int_{\text{path}_{\text{isobaric}}} \frac{dU + PdV}{T}$$

$$\Delta S = C_V \int_a^b \frac{dT}{T} + C_P \int_b^c \frac{dT}{T} = C_V \int_a^b \frac{dT}{T} + C_P \int_b^c \frac{dT}{T}$$

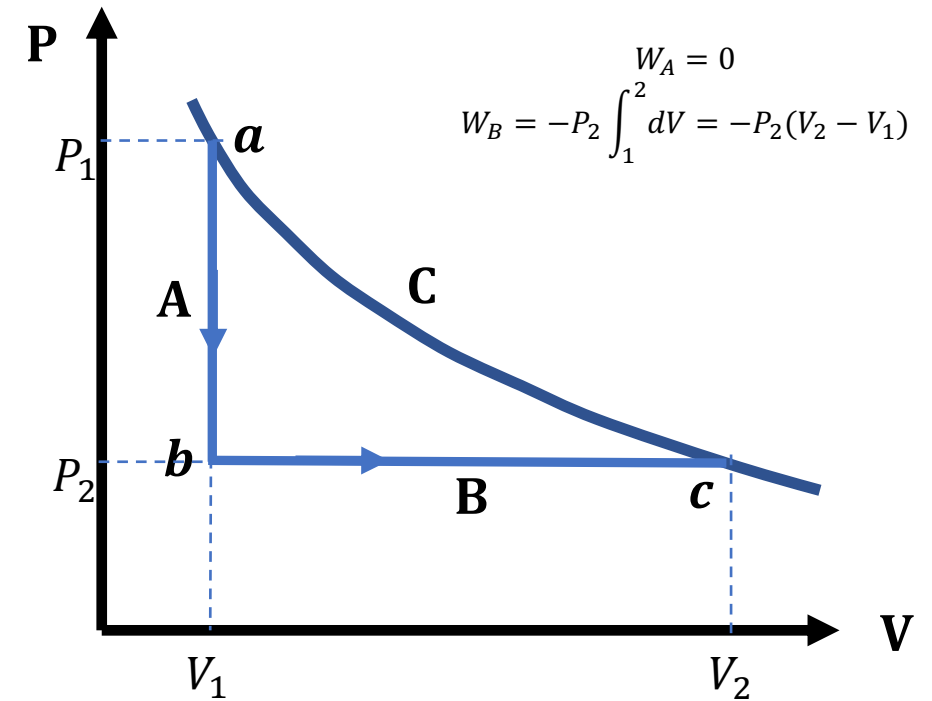
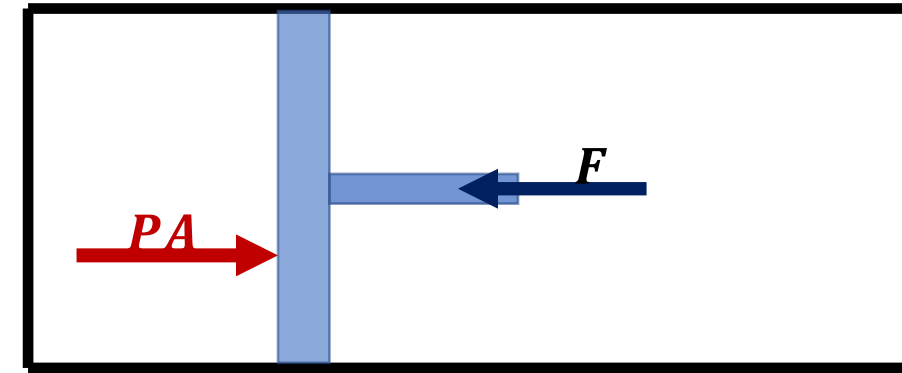
$$\Delta S = C_V \ln \frac{T_b}{T_a} + C_P \ln \frac{T_c}{T_b} = C_V \ln \frac{P_2 V_1}{P_1 V_1} + C_P \ln \frac{P_2 V_2}{P_2 V_1}$$

$$\Delta S = C_V \ln \frac{P_2}{P_1} + C_P \ln \frac{V_2}{V_1} = C_V \ln \frac{T_2/V_2}{T_1/V_1} + C_P \ln \frac{V_2}{V_1}$$

$$\Delta S =_{(T_1=T_2)} C_V \ln \frac{V_1}{V_2} + (C_V + Nk) \ln \frac{V_2}{V_1} = Nk \ln \frac{V_2}{V_1}$$

□ Entropy change is the same as on the isothermal path

□ Moral: Choose the simplest path between the states to compute ΔS



Free gas expansion: ΔS

- Irreversible expansion with no heat, no work

$$\Delta U = Q + W = 0 + 0 = 0$$

- As the gas expands freely into the vacuum, **its entropy changes because of volume change**
- **The multiplicity of a state with higher volume is larger, hence the entropy increases**

$$\Delta S = kN \ln \frac{V_{final}}{V_{initial}} > 0 \rightarrow V_{final} > V_{initial}$$

So this irreversible process must only be an expansion according to the 2nd law of thermodynamics

