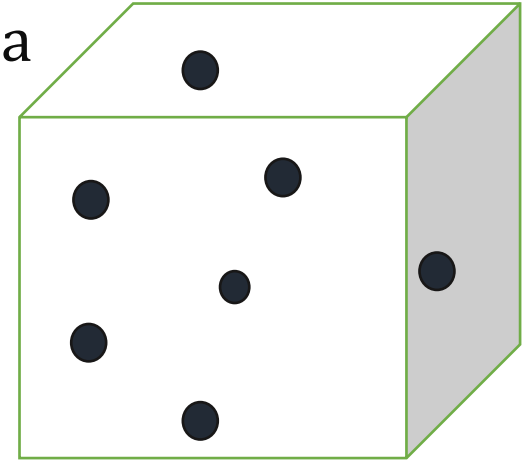# Lecture 7

Entropy, 2nd law of thermodynamics

10.09.2018

Multiplicity function for N particles in 3D

Number of way of arranging N identical, independent, free particles in a 3D box of fixed volume V and fixed total energy U

$$\Omega_N^{3D}(U,V) = \frac{1}{N!\left(\frac{3N}{2}\right)!}\,V^N\left(\frac{2\pi mU}{h^2}\right)^{\frac{3N}{2}}$$

Generic expression when we consider only the U and V dependence

$$\Omega_N^{3D}(U,V) = f(N)V^N U^{\frac{3N}{2}}$$

Two weakly interacting ideal gases

- $\Omega_N = f(N) V^N U^{\frac{3N}{2}}$ for each gas A and B

- Total multiplicity: $\Omega_{total} = \Omega_N^A \cdot \Omega_N^B = f(N)^2 (V_A V_B)^N (U_A U_B)^{\frac{3N}{2}}$

$$\Omega_{total}(U_A, V_A) = f(N)^2 [V_A(V - V_A)]^N [U_A(U - U_A)]^{\frac{3N}{2}}$$
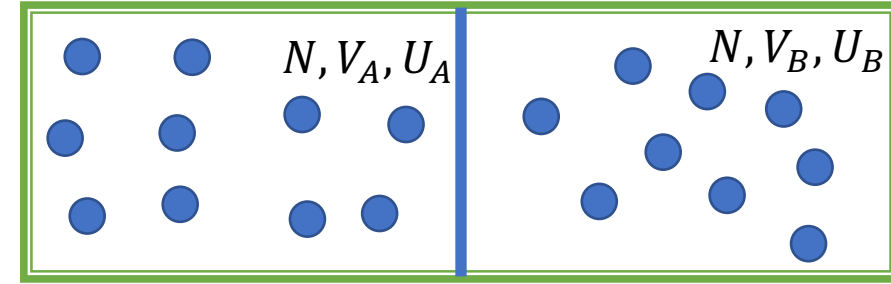
- Macrostate with the maximum multiplicity:

$$\frac{\partial \Omega_{total}}{\partial U_A} = 0, \qquad \frac{\partial \Omega_{total}}{\partial V_A} = 0$$

$U_A = U_B = \frac{U}{2}$ and $V_A = V_B = \frac{V}{2}$

$\Omega_{total}^{max} = f(N)^2 \left(\frac{V}{2}\right)^{2N} \left(\frac{U}{2}\right)^{3N}$ is the multiplicity of the system at **equilibrium**

What is the shape of the multiplicity for states near the most likely state?

$$U = U_A + U_B$$
$$V = V_A + V_B$$
$$N = N_A = N_B$$

Two weakly interacting ideal gases

- Total multiplicity: $\Omega_{total} = f(N)^2 (V_A V_B)^N (U_A U_B)^{\frac{3N}{2}}$

- States near the most likely state by varying U

$U_A = \frac{U}{2} + x, U_B = \frac{U}{2} - x$ with $x \ll U/2$, while $V_A = V_B = \frac{V}{2}$

<div align="right">

$$N, V_A, U_A \qquad N, V_B, U_B$$

$$U = U_A + U_B$$
$$V = V_A + V_B$$

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$$\Omega_{total} = f(N)^2 \left(\frac{V}{2}\right)^{2N} \left[\left(\frac{U}{2}\right)^2 - x^2\right]^{\frac{3N}{2}}$$

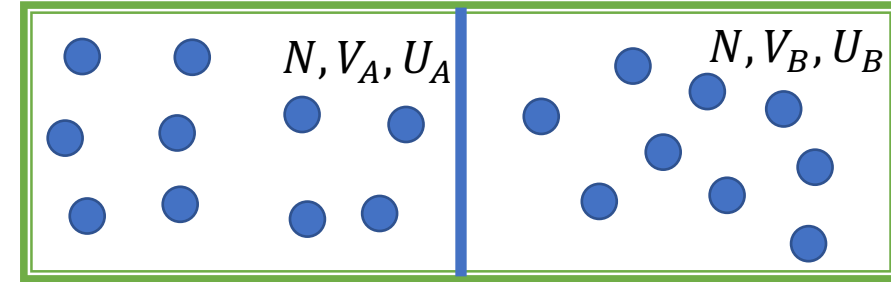Taking the logarithm and looking only at the U-dependence

$$\ln \Omega_{total} \sim \frac{3N}{2} \ln\left[\left(\frac{U}{2}\right)^2 - x^2\right] = 3N \ln\left(\frac{U}{2}\right) + \frac{3N}{2} \ln\left[1 - \left(\frac{2x}{U}\right)^2\right]$$

$$\ln \Omega_{total} \sim 3N \ln\left(\frac{U}{2}\right) - \frac{3N}{2}\left(\frac{2x}{U}\right)^2$$

$$\Omega_{total}\left(x = U_A - \frac{U}{2}\right) = f(N)^2 \left(\frac{V}{2}\right)^{2N} \left(\frac{U}{2}\right)^{3N} \cdot \exp\left(-\frac{3N}{2}\left(\frac{2x}{U}\right)^2\right)$$
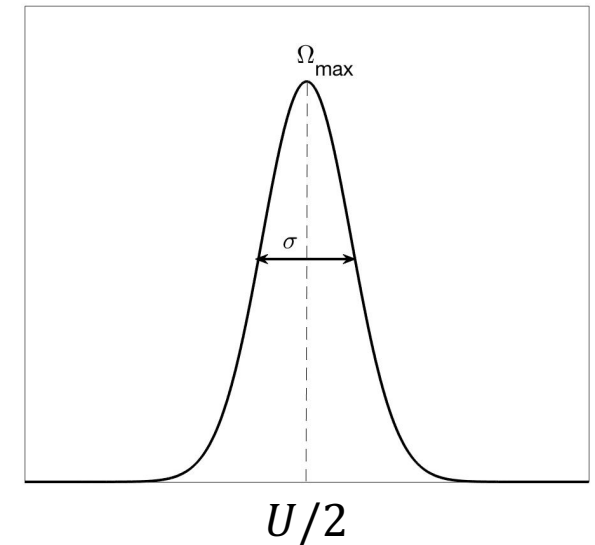
$$\Omega_{total}(U_A) = \Omega_{total}^{max} \cdot \exp\left(-\frac{3N}{2}\left(\frac{2}{U}\right)^2 \left(U_A - \frac{U}{2}\right)^2\right)$$

The width scales as $\boldsymbol{\sigma_U = 2 \cdot \frac{U}{2}\sqrt{\frac{2}{3N}} = \frac{U}{\sqrt{\frac{3N}{2}}} \to 0 \quad as \quad N \to \infty}$

<div align="right">

$$\Omega_{max}$$

$$\sigma$$

$$U/2$$

</div>

Two weakly interacting ideal gases

- Total multiplicity: $\Omega_{total} = f(N)^2 (V_A V_B)^N (U_A U_B)^{\frac{3N}{2}}$

- States near the most likely state by varying V

$V_A = \frac{V}{2} + y, V_B = \frac{V}{2} - y \; with \; y \ll V/2$, while $U_A = U_B = \frac{U}{2}$

$$\Omega_{total} = f(N)^2 \left(\frac{U}{2}\right)^{3N} \left[\left(\frac{V}{2}\right)^2 - y^2\right]^N$$

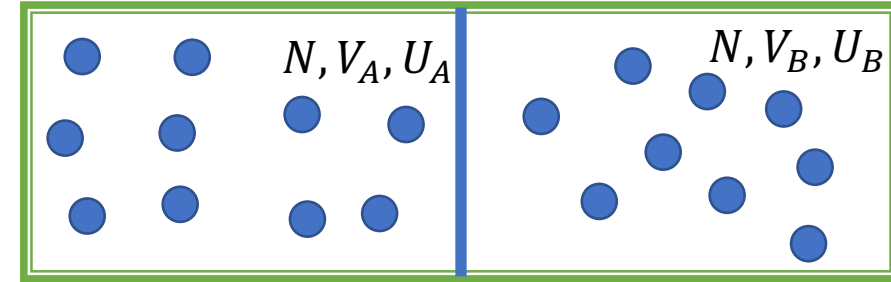Taking the logarithm and looking only at the V-dependence

$$\ln \Omega_{total} \sim N \ln \left[\left(\frac{V}{2}\right)^2 - y^2\right] = N \ln \left(\frac{V}{2}\right) + N \ln \left[1 - \left(\frac{2y}{V}\right)^2\right]$$

$$\ln \Omega_{total} \sim N \ln \left(\frac{V}{2}\right) - N \left(\frac{2y}{V}\right)^2$$

$$\Omega_{total} \left(y = V_A - \frac{V}{2}\right) = f(N)^2 \left(\frac{V}{2}\right)^{2N} \left(\frac{U}{2}\right)^{3N} \cdot \exp\left(-N \left(\frac{2y}{V}\right)^2\right)$$
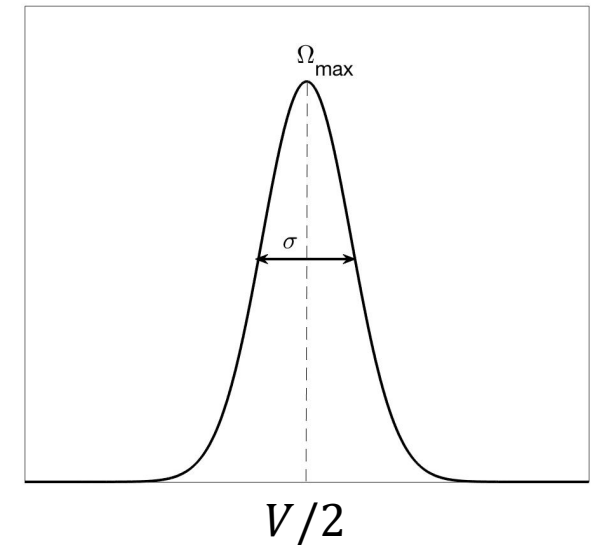
$$\Omega_{total}(V_A) = \Omega_{total}^{max} \cdot \exp\left(-N \left(\frac{2}{V}\right)^2 \left(V_A - \frac{V}{2}\right)^2\right)$$

The width scales as $\boldsymbol{\sigma_V = 2 \cdot \frac{V}{2}\sqrt{\frac{1}{N}} = \frac{V}{\sqrt{N}} \to 0 \quad as \quad N \to \infty}$

N, V_A, U_A $\qquad$ N, V_B, U_B

$U = U_A + U_B$
$V = V_A + V_B$

Ω_{max}

σ

$V/2$

Two weekly interacting ideal gases

$$U = U_A + U_B$$
$$V = V_A + V_B$$
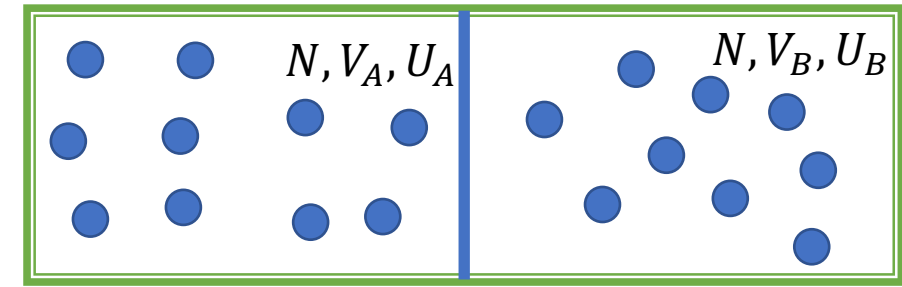
- Macrostates near the most likely state

$$\Omega_{total}(V_A, U_A) = \Omega_{total}^{max} \cdot \exp\left(-N\left(\frac{2}{V}\right)^2 \left(V_A - \frac{V}{2}\right)^2\right) \cdot \exp\left(-\frac{3N}{2}\left(\frac{2}{U}\right)^2 \left(U_A - \frac{U}{2}\right)^2\right)$$
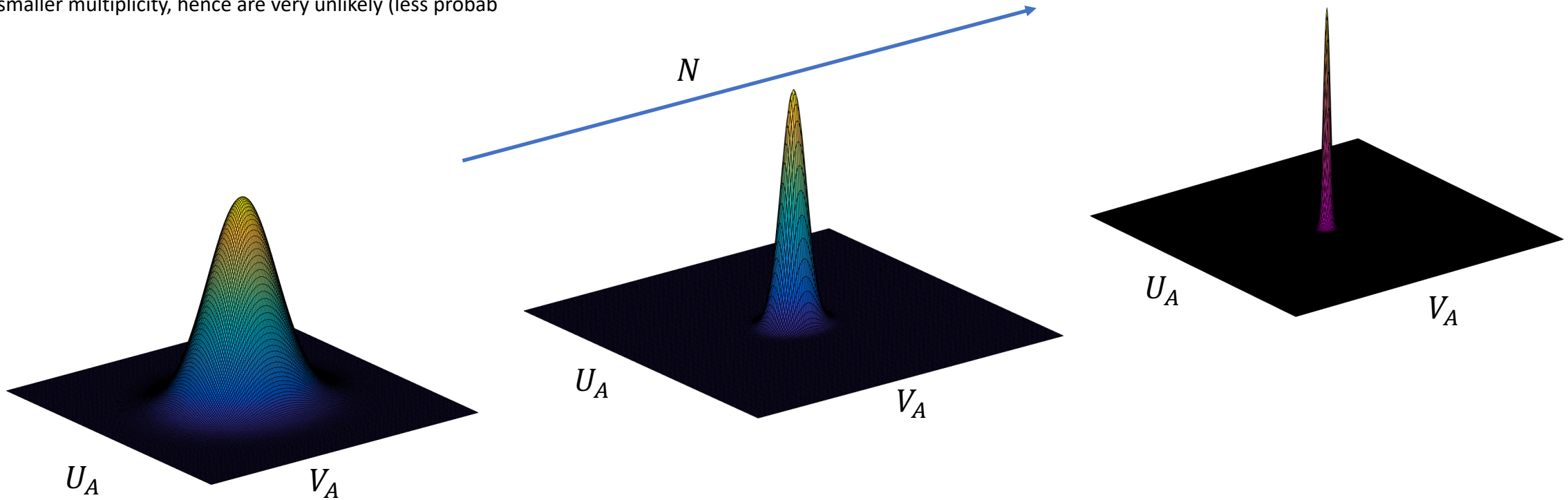
$$\Omega_{total}(V_A, U_A) \to_{N \gg 1} \Omega_{total}^{max} \, \delta\left(V_A - \frac{V}{2}\right) \delta\left(U_A - \frac{U}{2}\right)$$

The number of particle configurations away from the equilibrium macrostate correspond to a much

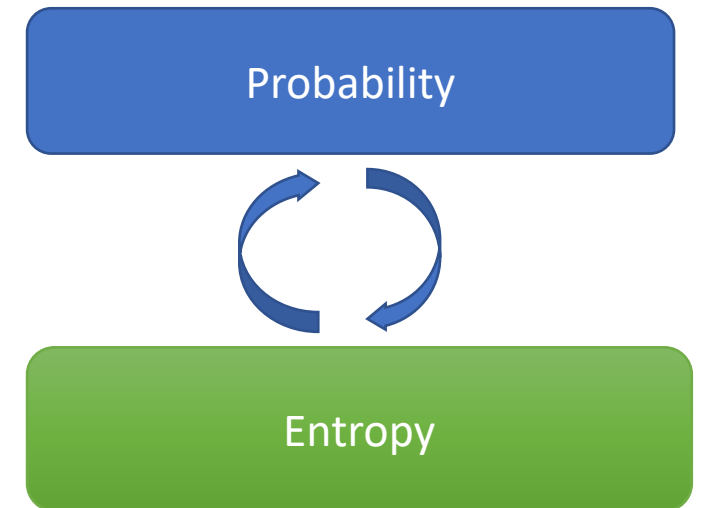smaller multiplicity, hence are very unlikely (less probab

Boltzmann's Entropy

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

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

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

Probability

Entropy

Second law of thermodynamics
probabilistic law

Change in entropy between two thermodynamic states is given in terms of the corresponding multiplicities

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

For an isolated system, the entropy can never decrease

$$\Delta S \geq 0$$

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

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

Boltzmann's Entropy and 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)

Example:

Thermal equilibrium of two interacting ideal gases through energy exchange

$$\frac{\partial \Omega_{total}}{\partial U_A} = 0 \rightarrow \frac{\partial S_{total}}{\partial U_A} = 0$$

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

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

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

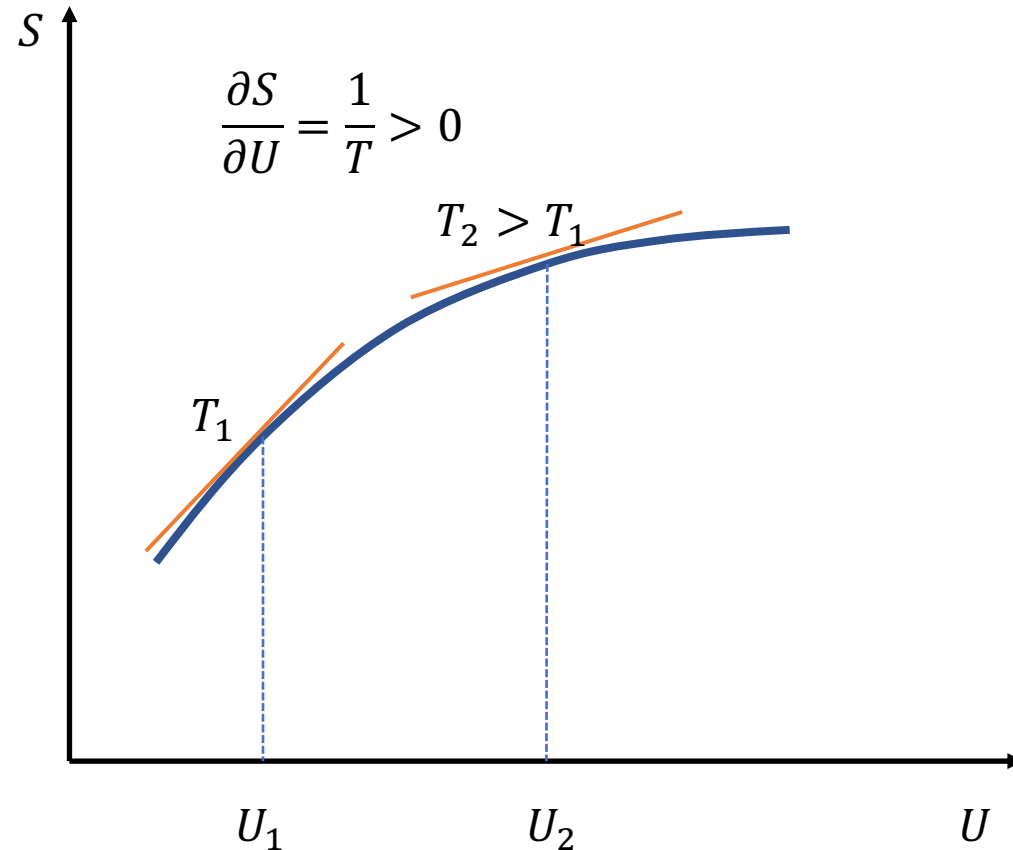*Temperature is the measure of system's ability to exchange energy*

Most likely macrostate

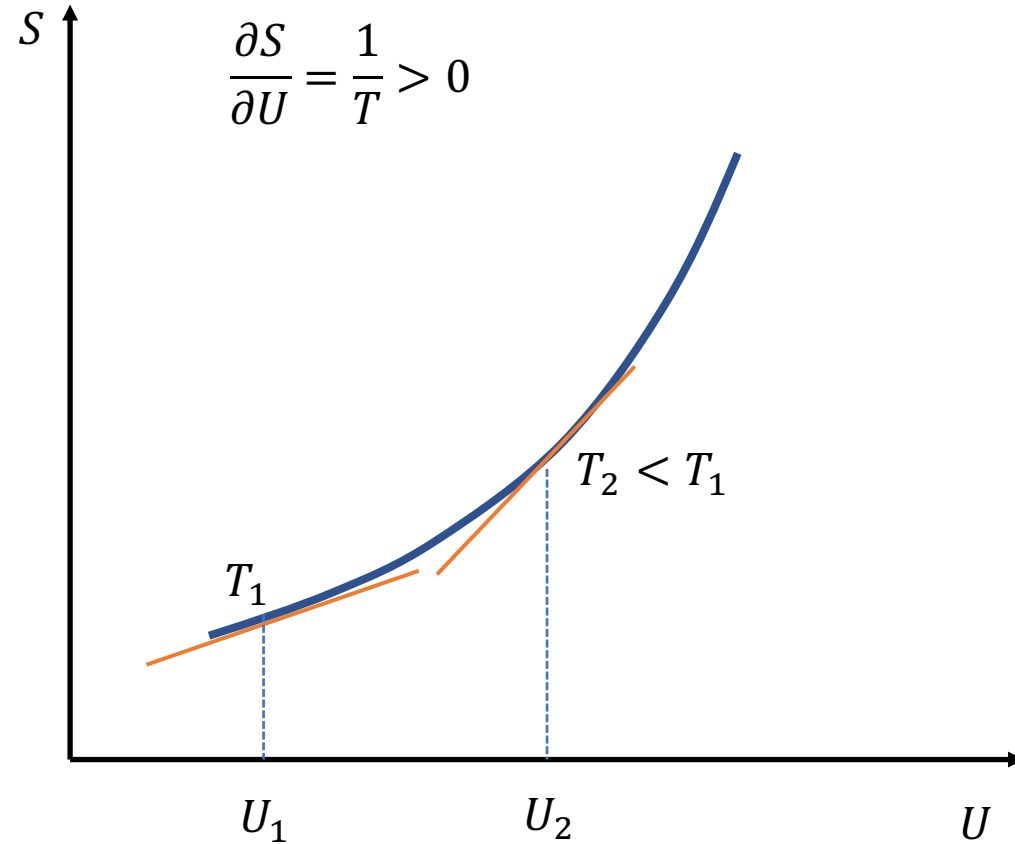Maximum total Entropy
Thermodynamic equilibrium

Interacting systems have the
temperature at equilibrium

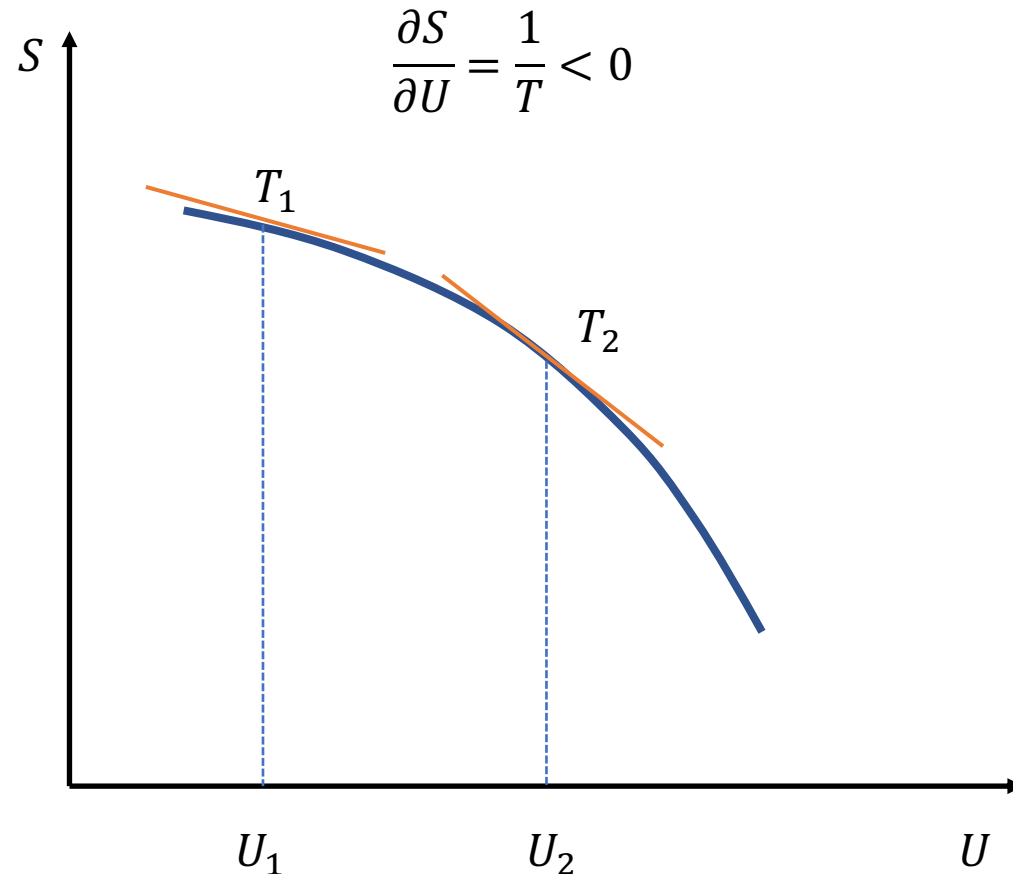# $S(U)$ for isolated systems

$$\frac{\partial S}{\partial U} = \frac{1}{T} > 0$$

$T_2 > T_1$

T_1

S

U_1 U_2 U

- ❑ T increases as U increases

- ❑ To increase its entropy, the system receives energy and increases its temperature

$S(U)$ for isolated systems

$$\frac{\partial S}{\partial U} = \frac{1}{T} > 0$$

$T_2 < T_1$

T_1

U_1 U_2 U

- ❑ T decreases as U increases

- ❑ Added energy goes into potential energy

- ❑ *eg: Stars and clusters held by gravitational pull*

$S(U)$ for isolated systems

$$\frac{\partial S}{\partial U} = \frac{1}{T} < 0$$

- ❑ Negative temperature

- ❑ Entropy decreases with increasing energy

- ❑ Energy is bound, so that the system becomes more «ordered» towards reaching its maximum energy (saturation)

- ❑ *Eg: nuclear paramagnetism*

(Maximum energy is when all spins are anti-parallel wrt to the external magnetic field)

Boltzmann's Entropy for an isolated system

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

- $\frac{\partial S}{\partial U} > 0 \rightarrow T > 0$

  ❑ Entropy increases with increasing energy

  ❑ System in a low-energy state has a higher tendency to increase its entropy by energy gain (*higher steepness, low T*) then system in a higher energy-state (*lower steepness, high T*)

  ❑ Temperature increases with added energy

  ❑ Absorbs energy

- $\frac{\partial S}{\partial U} = 0 \rightarrow T = \infty$

  ❑ Entropy is at maximum

  ❑ Temperature is infinite, meaning that the system will give away energy to anything that comes into contact with

- $\frac{\partial S}{\partial U} < 0 \rightarrow T < 0 \ (T > -\infty)$

  ❑ Entropy decreases with increasing energy

  ❑ Temperature is negative but actually this means higher than infinity. This meaning that the system will give away energy to anything that comes into contact with

  ❑ Radiate energy
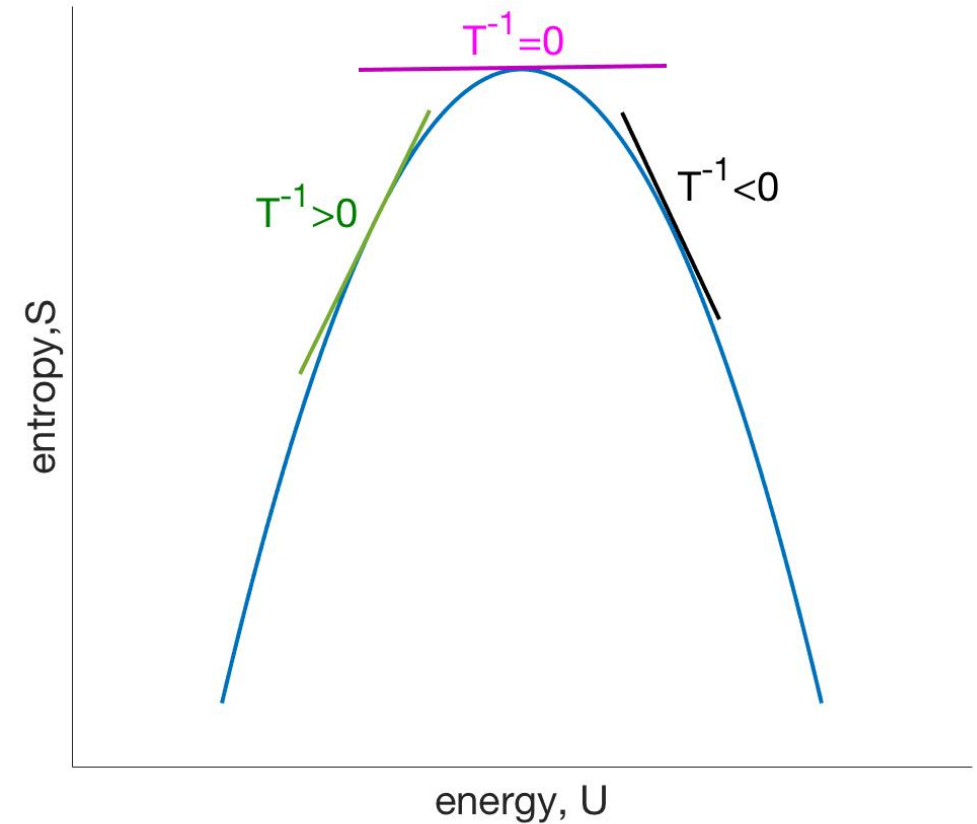
Second law of thermodynamics
heat flow law

The thing that increases by an infinitesimally added heat δQ at a given temperature T in a reversible way

$$dS = \frac{\delta Q_{rev}}{T}$$

The heat transfer in an irreversible change is smaller than the reversible heat at a given T
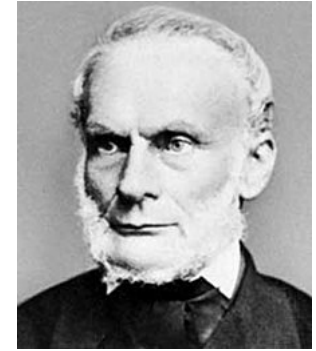
$$\frac{\delta Q_{irrev}}{T} < \frac{Q_{rev}}{T}$$

Clausius inequality

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

Using the 1st law of thermodynamics,

$$dU = \delta Q + \delta W,$$

$$for\ a\ reversible\ path:\ dU = \delta Q_{rev} - PdV \rightarrow \quad \mathbf{TdS = dU + PdV}$$
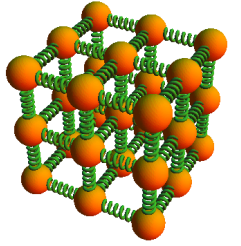
Clausius inequality:
For a cyclic process
$$\oint \frac{\delta Q}{T} \leq 0$$

It is impossible to construct a machine that transfers heat from a cool to a hot reservoir without work

Heat flows sponteneously one way

Einstein crystal: S and T

Multiplicity of a macrostate with q units of energy distributed among N identical oscillators

$$\Omega(q, N) = \frac{(N-1+q)!}{q!\,(N-1)!} \approx_{q \gg N \gg 1} \left(\frac{eq}{N}\right)^N$$

- Entropy:

$$S(q, N) = kN\left[\ln\left(\frac{q}{N}\right) + 1\right], \qquad q \equiv \frac{U}{\hbar\omega}$$

- Temperature:

$$T = \left(\frac{\partial S}{\partial U}\right)^{-1} = \left(kN\frac{d}{dU}\ln U\right)^{-1} \rightarrow U = NkT$$

Equipartition of energy: $\frac{kT}{2}$ for the kinetic energy and $\frac{kT}{2}$ for the potential energy per oscillator

- $S(U, N) = kN\left[\ln\left(\frac{U}{N\hbar\omega}\right) + 1\right] \rightarrow S(T, N) = kN\left[\ln\left(\frac{kT}{\hbar\omega}\right) + 1\right]$

- Heat capacity C_V:

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

Ideal gas: entropy S

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

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

$$ln\left(N!\left(\frac{3N}{2}\right)!\right) = N \, ln \, N - N + \frac{3N}{2} ln \frac{3N}{2} - \frac{3N}{2}$$

$$= \frac{5N}{2} ln \, N - \frac{5N}{2} + \frac{3N}{2} ln \frac{3}{2}$$

- Sackur-Tetrode Entropy:

$$S(U, V, N) = k \, ln \, \Omega(U, V, N)$$

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

Entropy is extensive:

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

Ideal gas: entropy S and temperature T

- Sackur-Tetrode Entropy:

$$S(U, V, N) = k \, ln \, \Omega(U, V, N)$$

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

- Temperature:

$$T = \left(\frac{\partial S}{\partial U} \right)^{-1} = \left(kN \frac{d}{dU} \, ln \, U^{\frac{3}{2}} \right)^{-1} = \left(\frac{3kN}{2} \frac{1}{U} \right)^{-1} \rightarrow U = \frac{3NkT}{2}$$

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

- Heat capacity C_V:

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