# Lecture 6. Entropy of an Ideal Gas (Ch. 3)

Today we will achieve an important goal: we'll derive the equation(s) of state for an ideal gas from the principles of statistical mechanics. We will follow the path outlined in the previous lecture:

- Find $\Omega\,(U, V, N,...)$ – the most challenging step

- **$S\,(U, V, N,...) = k_B \ln \Omega\,(U, V, N,...)$**

- $T \equiv \left(\dfrac{\partial S(U, V, N,...)}{\partial U} \right)^{-1}$

- Solve for **$U = f\,(T, V, N,...)$**

So far we have treated quantum systems whose states in the configuration (phase) space may be enumerated. When dealing with classical systems with translational degrees of freedom, we need to learn how to calculate the multiplicity.
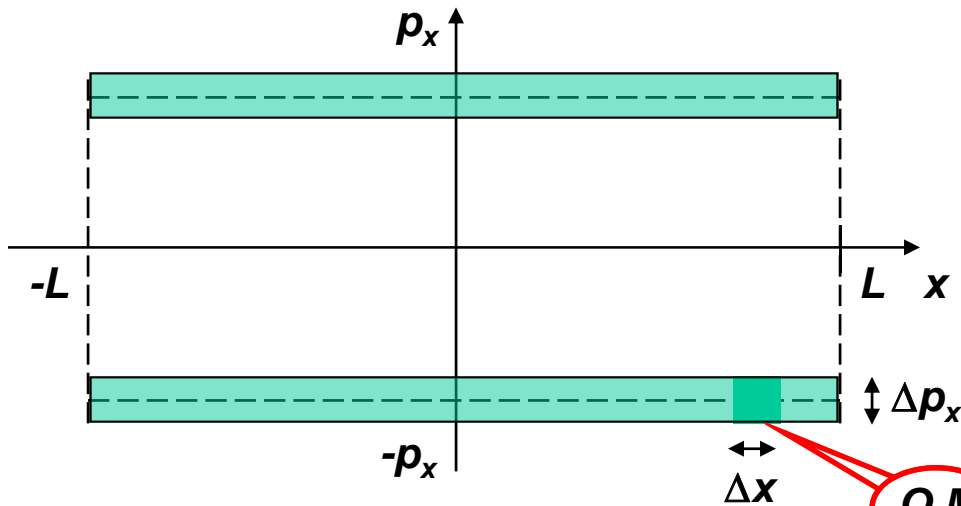
- is more complicated than that for an Einstein solid, because it depends on *three* rather than *two* macro parameters (e.g., **N**, **U**, **V**).
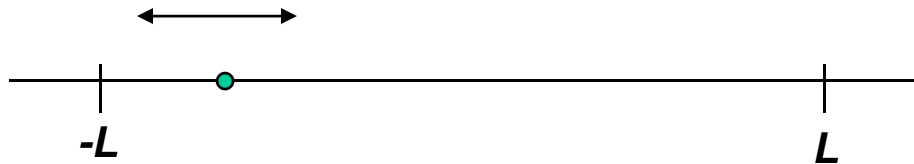
Example: particle in a one-dimensional "box"

-L   **L**

The total number of ways of filling up the cells in phase space is the product of the number of ways the "space" cells can be filled times the number of ways the "momentum" cells can be filled
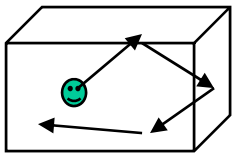
$$\Omega = \Omega_{space}\Omega_{p}$$

Quantum mechanics (the uncertainty principle) helps us to numerate all different states in the configuration (phase) space:

$$\Delta x \cdot \Delta p_x \geq h$$

The number of microstates: $\propto \dfrac{L \; \Delta p_x}{\Delta x \cdot \Delta p_x} = \dfrac{2L \cdot \Delta p_x}{h}$

For a molecule in a three-dimensional box: the state of the molecule is a point in the **6D** space - its position (x,y,z) and its momentum (p_x, p_y, p_z). The number of "space" microstates is:

$$\Omega_{space} = \frac{V}{\Delta x \cdot \Delta y \cdot \Delta z} = \frac{V}{\Delta x^3}$$

For **N** molecules:

$$\Omega_{space} = \left(\frac{V}{\Delta x^3} \right)^N$$

There is some momentum distribution of molecules in an ideal gas (Maxwell), with a long "tail" that goes all the way up to $p = (2mU)^{1/2}$ (**U** is the **total** energy of the gas). However, the momentum vector of an "average" molecule is confined within a sphere of radius $p \sim (2mU/N)^{1/2}$ (**U/N** is the **average** energy per molecule). Thus, for a single "average" molecule:

$$\Omega_p \propto \frac{\frac{4}{3} \pi \bar{p}^3}{\Delta p_x \cdot \Delta p_y \cdot \Delta p_z}$$
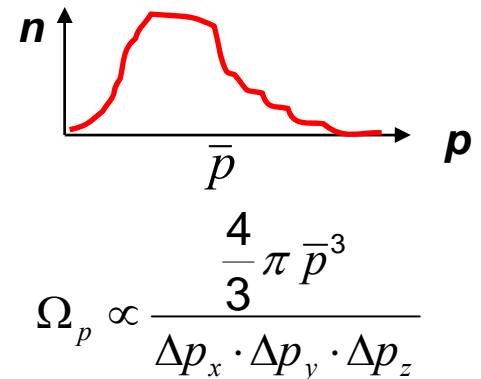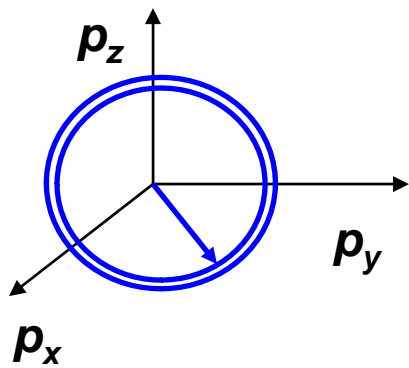
The total number of microstates for **N** molecules:

$$\Omega = \Omega_{space} \Omega_p \approx \left(\frac{V \times \bar{p}^3}{\Delta x^3 \cdot \Delta p_x{}^3} \right)^N = \left(\frac{V \times V_p}{h^3} \right)^N$$

However, we have over-counted the multiplicity, because we have assumed that the atoms are distinguishable. For **indistinguishable** quantum particles, the result should be divided by **N!** (the number of ways of arranging N identical atoms in a given set of "boxes"):

$$\Omega_{indistinguishable} \approx \frac{1}{N!} \left(\frac{V \times V_p}{h^3} \right)^N$$

More Accurate Calculation of Ω_N (I)

Momentum constraints:

1 particle -
$$p_x^2 + p_y^2 + p_z^2 = 2mU$$

2 particles -
$$p_{1x}^2 + p_{1y}^2 + p_{1z}^2 + p_{2x}^2 + p_{2y}^2 + p_{2z}^2 = 2mU$$

The accessible momentum volume for **N** particles = the "area" of a 3*N*-dimensional hyper-sphere $\times\Delta p$

$$\text{"area"} = \frac{2\pi^{3N/2}}{\left(\frac{3N}{2}-1\right)!}r^{3N-1}$$

$N=1$

$$\frac{2\pi^{3/2}}{(1/2)!}r^2 = \left[(1/2)! = \sqrt{\pi}/2\right] = 4\pi r^2$$

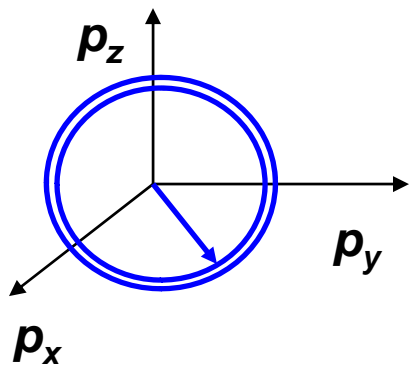$$\Omega_N \approx \frac{1}{N!}\frac{V^N}{(3N/2)!}\left(\frac{2\pi mU}{h^2}\right)^{3N/2}2\Delta p$$

The reason why **m** matters: for a given **U**, a molecule with a larger mass has a larger momentum, thus a larger "volume" accessible in the momentum space.

Monatomic ideal gas: (3*N* degrees of freedom)

$$\Omega_{indistinguishable}(U,V,N) = \left[\frac{e^{5/2}}{h^3}\frac{V}{N}\left(\frac{4\pi mU}{3N}\right)^{3/2}\right]^N 2\Delta p$$

$$\Omega(U) \propto U^{fN/2}$$

f N- the total # of "quadratic" degrees of freedom

For a particle in a box $(L)^3$: (Appendix A)

$$E\left(n_x, n_y, n_z\right) = \frac{p_x^2 + p_y^2 + p_z^2}{2m} = \frac{h^2}{8mL^2}\left(n_x^2 + n_y^2 + n_z^2\right) \qquad \Delta p_x = \frac{h}{2L}$$

If p>>Δp, the total degeneracy (multiplicity) of *1* particle with energy U is:

$n_x, n_y, n_z > 0$

$$\Omega_1\left(U\right) = \frac{1}{2^3}\frac{S_3^p \Delta p}{\left(\Delta p\right)^3} = \frac{1}{2^3}\frac{\left(2L\right)^3}{h^3}\left(S_3^p \Delta p\right) = \frac{V}{h^3}\left(S_3^p \Delta p\right)$$

If p>>Δp, the total degeneracy (multiplicity) of *N* indistinguishable particle with energy U is:

$$\Omega_N\left(U\right) = \frac{1}{N!}\frac{V^N}{h^{3N}}\left(S_{3N}^p \Delta p\right)$$

Plug in the "area" of the hyper-sphere:

$$\Omega_{indistinguishable}\left(U, V, N\right) = \left[\frac{e^{5/2}}{h^3}\frac{V}{N}\left(\frac{4\pi mU}{3N}\right)^{3/2}\right]^N \cdot \left(2\Delta p\right)$$

Entropy of an Ideal Gas

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

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

The Sackur-Tetrode equation: *(Monatomic ideal gas)*

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

$$= Nk_B \ln \left[\frac{V}{N} \left(\frac{U}{N} \right)^{3/2} \right] + \frac{3}{2} Nk_B \left[\frac{5}{3} + \ln \left(\frac{4\pi m}{3h^2} \right) \right] = Nk_B \ln \frac{V}{N} + \frac{3}{2} Nk_B \ln \frac{U}{N} + \varphi(N,m)$$
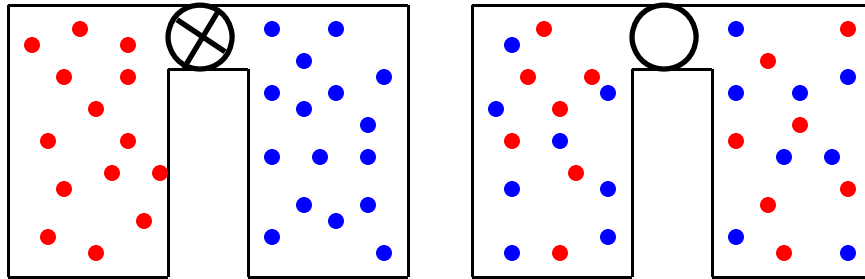
an average volume   an average energy
per molecule   per molecule

In general, for a gas of
polyatomic molecules:

$$S(N,V,T) = N k_B \ln \frac{V}{N} + \frac{f}{2} N k_B \ln T + \varphi(N,m)$$

$f \Rightarrow$ 3 (monatomic), 5 (diatomic), 6 (polyatomic)

Problem

Two cylinders (V = 1 liter each) are connected by a valve. In one of the cylinders – Hydrogen (H_2) at $P = 10^5$ Pa, $T = 20^0C$, in another one – Helium (He) at $P = 3 \cdot 10^5$ Pa, $T = 100^0C$. Find the entropy change after mixing and equilibrating.

For each gas:
$$\Delta S(N,V,T) = N k_B \ln\frac{V_f}{V_i} + \frac{f}{2} N k_B \ln\frac{T_f}{T_i}$$

The temperature after mixing:
$$U_1(T_1) + U_2(T_2) = U_{total}(T_f) \qquad \frac{5}{2} N_1 k_B T_1 + \frac{3}{2} N_2 k_B T_2 = \left(\frac{5}{2} N_1 k_B + \frac{3}{2} N_2 k_B\right) T_f$$
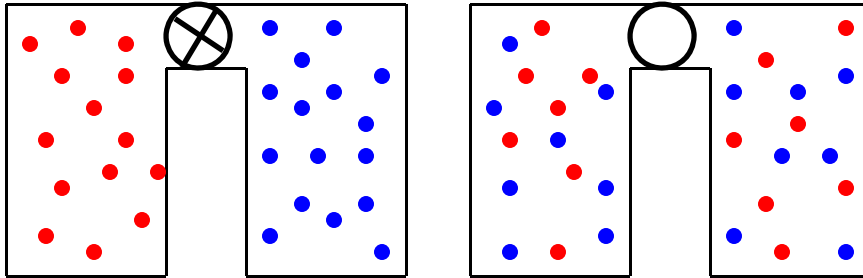
$$T_f = \frac{\frac{5}{2} N_1 k_B T_1 + \frac{3}{2} N_2 k_B T_2}{\frac{5}{2} N_1 k_B + \frac{3}{2} N_2 k_B} = \frac{5 P_1 + 3 P_2}{5\frac{P_1}{T_1} + 3\frac{P_2}{T_2}}$$

H_2 : $\quad \Delta S_{H_2} = N k_B \ln 2 + \frac{5}{2} N k_B \ln\frac{T_f}{T_1}$
He : $\quad \Delta S_{He} = N_2 k_B \ln 2 + \frac{3}{2} N_2 k_B \ln\frac{T_f}{T_2}$

$$\Delta S_{total} = \Delta S_{H_2} + \Delta S_{He} = (N_1 + N_2) k_B \ln 2 + \frac{k_B}{2}\left[5 N_1 \ln\frac{T_f}{T_1} + 3 N_2 \ln\frac{T_f}{T_2}\right] \qquad \Delta S_{total} = 0.67 \text{ J/K}$$

Entropy of Mixing

Consider two different ideal gases (N_1, N_2) kept in two separate volumes (V_1, V_2) at the same temperature. To calculate the increase of entropy in the mixing process, we can treat each gas as a separate system. In the mixing process, **U/N** remains the same (**T** will be the same after mixing). The parameter that changes is **V/N:**
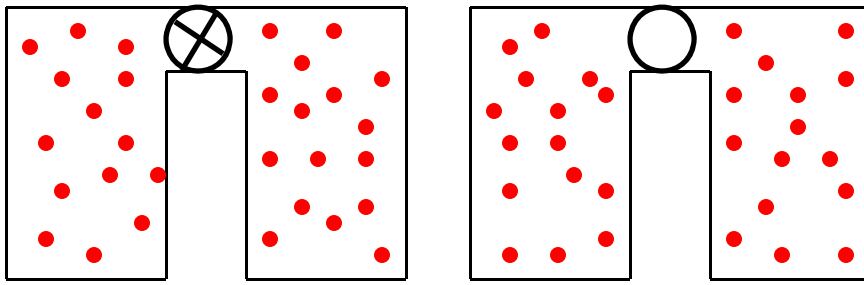
$$S(N,V,U) = N k_B \left\{ \ln\left[\frac{V}{N} \left(\frac{4\pi m}{3h^2} \frac{U}{N} \right)^{3/2} \right] + \frac{5}{2} \right\}$$

$$\frac{\Delta S_{total}}{k_B} = \frac{\Delta S_A + \Delta S_B}{k_B} = N_1 \ln\left(\frac{V}{V_1} \right) + N_2 \ln\left(\frac{V}{V_2} \right)$$

if **$N_1 = N_2 = 1/2 N$** , **$V_1 = V_2 = 1/2 V$**

$$\frac{\Delta S_{total}}{k_B} = \frac{N}{2} \ln\left(\frac{V}{V/2} \right) + \frac{N}{2} \ln\left(\frac{V}{V/2} \right) = \boxed{N \ln 2}$$

The total entropy of the system is greater after mixing – thus, **mixing is irreversible**.

$$\frac{\Delta S_{\text{total}}}{k_B} = \frac{\Delta S_A + \Delta S_B}{k_B} = N_1 \ln\left(\frac{V}{V_1}\right) + N_2 \ln\left(\frac{V}{V_2}\right)$$

- applies only if two gases are **different**!

If two mixing gases are of the same kind (**indistinguishable** molecules):

$$\Delta S_{\text{total}}/k_B = \left(S_{total} - S_A - S_B\right)/k_B = \left(N_1 + N_2\right)\ln\left(\frac{V_1 + V_2}{N_1 + N_2}\right) - N_1 \ln\left(\frac{V_1}{N_1}\right) - N_2 \ln\left(\frac{V_2}{N_2}\right)$$

$$= N_1 \ln\left(\frac{V}{N}\frac{N_1}{V_1}\right) + N_2 \ln\left(\frac{V}{N}\frac{N_2}{V_2}\right) = 0 \quad \text{if} \quad \frac{N_1}{V_1} = \frac{N_2}{V_2} = \frac{N}{V}$$

$\Delta S_{total} = 0$ because U/N and V/N available for each molecule remain the same after mixing.

$$S(N,V,U) = N k_B \ln\left[\frac{V}{N}\left(\frac{4\pi m}{3h^2}\frac{U}{N}\right)^{3/2}\right] + \frac{5}{2} N k_B \qquad \Omega_N = \frac{1}{N!}\frac{V^N}{h^{3N}}\frac{2\pi^{3N/2}}{\left(\frac{3N}{2}\right)!}\left(\sqrt{2mU}\right)^{3N}$$

Quantum-mechanical **indistinguishability** is important! (even though this equation applies only in the low density limit, which is "classical" in the sense that the distinction between fermions and bosons disappear.

Problem

Two identical perfect gases with the same pressure **P** and the same number of particles **N**, but with different temperatures T_1 and T_2, are confined in two vessels, of volume V_1 and V_2, which are then connected. find the change in entropy after the system has reached equilibrium.

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

$$S_i = S_1 + S_2 = N k_B \ln\left[\frac{V_1}{N}(\alpha T_1)^{3/2}\right] + \frac{5}{2}N k_B + N k_B \ln\left[\frac{V_2}{N}(\alpha T_2)^{3/2}\right] + \frac{5}{2}N k_B$$

$$S_f = 2Nk_B \ln\left[\frac{(V_1+V_2)}{2N}(\alpha T_f)^{3/2}\right] + \frac{5}{2}2Nk_B \qquad T_f = \frac{T_1 + T_2}{2} \quad \text{- prove it!}$$

$$\frac{\Delta S}{N k_B} = \ln\left[\left\{\frac{(V_1+V_2)}{2N}\right\}^2 \frac{N^2}{V_1 V_2}\right] + \ln\left[\frac{(\alpha T_f)^3}{(\alpha T_1)^{3/2}(\alpha T_2)^{3/2}}\right] = \ln\left[\frac{(V_1+V_2)^2}{4V_1 V_2}\right] + \frac{3}{2}\ln\left[\frac{(T_f)^2}{T_1 T_2}\right] =$$

$$\ln\left[\frac{(V_1+V_2)^2}{4V_1 V_2}\right] + \frac{3}{2}\ln\left[\frac{(T_1+T_2)^2}{4T_1 T_2}\right] = \left[P(V_1+V_2) = 2Nk_B\frac{T_1+T_2}{2}\right] = \frac{5}{2}\ln\left[\frac{(T_1+T_2)^2}{4T_1 T_2}\right]$$

at $T_1 = T_2$, $\Delta S = 0$, as it should be (Gibbs paradox)

An Ideal Gas: from $S(N,V,U)$ - to $U(N,V,T)$

Ideal gas:
(*fN* degrees of freedom)

$$\Omega\left(U,V,N\right)=f\left(N\right)V^{N}U^{fN/2}$$

$$S\left(U,V,N\right)=\frac{f}{2}Nk_{B}\ln\frac{U}{N}+Nk_{B}\ln\frac{V}{N}+\varphi\left(N,m\right)$$

$$\frac{1}{T}=\frac{\partial S}{\partial U}=\frac{f}{2}\frac{Nk_{B}}{U} \quad \Rightarrow \quad \boxed{U(N,V,T)=\frac{f}{2}Nk_{B}T}$$

- the "energy" equation of state

- in agreement with the equipartition theorem, the total energy should be ½$k_B$$T$ times the number of degrees of freedom.

The heat capacity for
a monatomic ideal gas:

$$C_{V}=\left(\frac{\partial U}{\partial T}\right)_{V,N}=\frac{f}{2}Nk_{B}$$

Partial Derivatives of the Entropy

We have been considering the entropy changes in the processes where two interacting systems exchanged the thermal energy but the volume and the number of particles in these systems were fixed. In general, however, we need more than just one parameter to specify a macrostate, e.g. for an ideal gas

$$S = S\left(U, V, N\right) = k_B \ln \Omega\left(U, V, N\right)$$

When all macroscopic quantities **S,V,N,U** are allowed to vary:

$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{N,U} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$
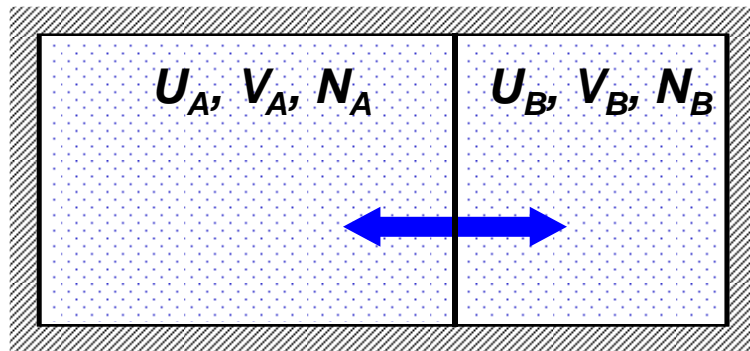
We are familiar with the physical meaning only one partial derivative of entropy:

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

Today we will explore what happens if we let the **V** vary, and analyze the physical meaning of the other two partial derivatives of the entropy:
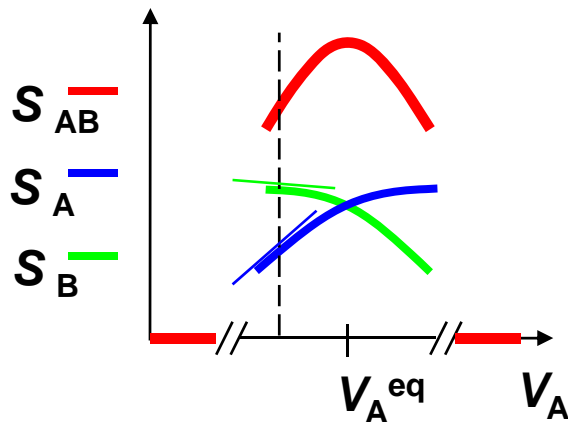
$$\left(\frac{\partial S}{\partial V}\right)_{U,N}$$

Mechanical Equilibrium and Pressure

U_A, V_A, N_A | U_B, V_B, N_B

Let's fix U_A, N_A and U_B, N_B, but allow V to vary (the membrane is insulating, impermeable for gas molecules, but its position is not fixed). Following the same logic, spontaneous "exchange of volume" between sub-systems will drive the system towards mechanical equilibrium (the membrane at rest). The equilibrium macropartition should have the largest (by far) multiplicity $\Omega\,(U,\ V)$ and entropy $S\,(U,\ V)$.

e.g. ideal gas
$$\left(\frac{\partial S}{\partial V}\right)_{U,N} = \frac{k_B N}{V} = \frac{P}{T}$$

In mechanical equilibrium:

$$\frac{\partial S_{AB}}{\partial V_A} = \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = \frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B} = 0$$

$$(\ \partial V_A = -\ \partial V_B\ ) \qquad \boxed{\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}}$$

- the volume-per-molecule should be the same for both sub-systems, or, if T is the same, P must be the same on both sides of the membrane.

S AB

S A

S B

$V_A{}^{eq}$ V_A

The stat. phys. definition of pressure:

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

The "Pressure" Equation of State for an Ideal Gas

The "energy" equation of state ($U \leftrightarrow T$):

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{f}{2} N k_B \frac{1}{U}$$

$$\boxed{U = \frac{f}{2} N k_B T}$$

Ideal gas:
(*fN* degrees of freedom)

$$S(N,V,T) = N k_B \ln\frac{V}{N} + \frac{f}{2} N k_B \ln T + \varphi(N,m)$$

The "pressure" equation of state ($P \leftrightarrow T$):

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

$$\boxed{PV = N k_B T}$$

- we have finally derived the equation of state of an ideal gas from first principles!

Thermodynamic identity I

Let's assume N is fixed,
$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{N,U} dV$$

thermal equilibrium:
$$\left(\frac{\partial S}{\partial U}\right)_{V,N} = \frac{1}{T}$$

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

$$\Rightarrow \quad dS = \frac{1}{T}dU + \frac{P}{T}dV \quad \text{i.e.} \quad \boxed{dU = TdS - PdV}$$

Quasi-Static Processes

$$dU = T\,dS - P\,dV$$

$$\longleftrightarrow$$

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

(*quasi-static* processes with fixed **N**)

(*all* processes)

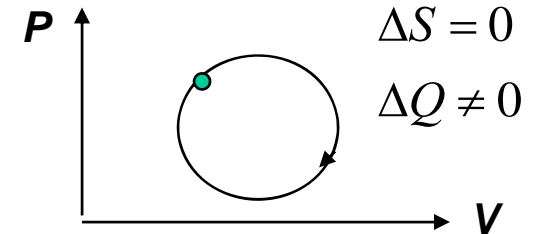Thus, for *quasi-static processes* :

$$\delta Q = T\,dS$$

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

Comment on State Functions :

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

- is an exact differential (**S** is a state function). Thus, the factor **1/T** converts δ**Q** into an exact differential for quasi-static processes.

P

$\Delta S = 0$

$\Delta Q \neq 0$

V

Quasistatic adiabatic (δ**Q = 0**) **processes**: $\boxed{dS = 0}$ $\Rightarrow$ **isentropic processes**

The quasi-static adiabatic process with an ideal gas :

$$PV^{\gamma} = const \qquad VT^{\gamma-1} = const$$

- we've derived these equations from the 1st Law and **PV=RT**

On the other hand, from the Sackur-Tetrode equation for an isentropic process :

$$\Delta S = 0 \quad \Rightarrow \quad VT^{f/2} = const \quad \longrightarrow \quad VT^{\frac{1}{\gamma-1}} = const$$

(a) Calculate the entropy increase of an ideal gas in an *isothermal* process.

(b) Calculate the entropy increase of an ideal gas in an *isochoric* process.

You should be able to do this using (a) Sackur-Tetrode eq. and (b) $d S = \dfrac{\delta Q}{T}$

$$\delta Q = dU + PdV = Nk_B\left(\frac{f}{2}dT + \frac{T}{V}dV\right)$$

$$dS = \frac{\delta Q}{T} = Nk_B\left(\frac{f}{2}\frac{dT}{T} + \frac{dV}{V}\right)$$

$$\Omega(U,V,N) = f(N)V^N U^{fN/2} \longrightarrow S = Nk_B \ln\left[g(N)VT^{f/2}\right]$$

$$\Delta S_{T=const} = Nk_B \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta S_{V=const} = \frac{f}{2}Nk_B \ln\left(\frac{T_f}{T_i}\right)$$

Let's verify that we get the same result with approaches **a)** and **b)** (e.g., for *T*=const):

Since $\Delta U = 0$, $\;\delta Q = -\delta W = \displaystyle\int_V^{V_f} \frac{N k_B T}{V}\, dV = N k_B T \ln\left(\frac{V_f}{V_i}\right)$ $\Rightarrow$ $\Delta S = \dfrac{\delta Q}{T}$

(*Pr.* 2.34)

Problem:

A bacterias of mass **M** with heat capacity (per unit mass) **C**, initially at temperature $T_0 + \Delta T$, is brought into thermal contact with a heat bath at temperature T_0.

(a) Show that if $\Delta T << T_0$, the increase ΔS in the entropy of the entire system (body+heat bath) when equilibrium is reached is proportional to $(\Delta T)^2$.

(b) Find ΔS if the body is a bacteria of mass 10^{-15}kg with **C**=4 kJ/(kg·K), T_0=300K, ΔT=0.03K.

(c) What is the probability of finding the bacteria at its initial $T_0 + \Delta T$ for Δt =10^{-12}s over the lifetime of the Universe (~10^{18}s).

(a)

$$\Delta S_{body} = \int_{T_0+\Delta T}^{T_0} \frac{\delta Q}{T'} = \int_{T_0+\Delta T}^{T_0} \frac{CdT'}{T'} = C\ln\left(\frac{T_0}{T_0+\Delta T}\right) < 0 \qquad \Delta S_{heat\,bath} = \frac{\delta Q}{T_0} = \frac{-\int_{T_0+\Delta T}^{T_0} CdT'}{T_0} = \frac{C\Delta T}{T_0} > 0$$

$$\Delta S_{total} = \Delta S_{body} + \Delta S_{heat\,bath} = C\frac{\Delta T}{T_0} - C\ln\left(\frac{T_0+\Delta T}{T_0}\right) \approx \left[\ln(1+\alpha) = \alpha - \frac{\alpha^2}{2} + \frac{\alpha^3}{3} - ...\right] = \frac{C}{2}\left(\frac{\Delta T}{T_0}\right)^2 > 0$$

(b)

$$\Delta S_{total} = \frac{C}{2}\left(\frac{\Delta T}{T_0}\right)^2 = \frac{4\cdot10^3 \times 1\cdot10^{-15}J/K}{2}\left(\frac{0.03}{300}\right)^2 = 2\cdot10^{-20}J/K$$

(b) Ω for the (non-equilibrium) state with $T_{bacteria}$ = 300.03K is greater than Ω in the equilibrium state with $T_{bacteria}$ = 300K by a factor of

$$\frac{\Omega_{T_0}}{\Omega_{T_0+\Delta T}} = \exp\left(\frac{\Delta S_{total}}{k_B}\right) = \exp\left(\frac{2 \cdot 10^{-20} J/K}{1.38 \cdot 10^{-23} J/K}\right) \approx e^{1450} \approx 10^{630}$$

The number of "1ps" trials over the lifetime of the Universe: $\quad \dfrac{10^{18}}{10^{-12}} = 10^{30}$

Thus, the probability of the event happening in 10^{30} trials:

$$(\# \text{ events})(\text{probability of occurrence of an event}) = 10^{30} \times 10^{-630} \rightarrow 0$$