2.6 Entropy

2nd Law of Thermodynamics - Any large system will be found in in macrostate with maximum multiplicity (aside from unmeasurably small fluctuations).

$\Rightarrow$ Multiplicity increases (aside from fluctuations)

If you start in a macrostate away from Ω_{max}, the system evolves until Ω_{max} achieved.

Entropy $\boxed{S \equiv k_B \ln \Omega}$

Multiplicity increase $\longrightarrow$ Entropy increase

Examples

Einstein Solid $\Omega(N,q) = \frac{1}{\sqrt{2\pi(q+N)q/N}} \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N$

q = total # of quanta

To see how behaves define $\bar{q}_1 = q/N$ (the average # of quanta in 1 oscillator

$$\Omega(N,q) = \frac{1}{\sqrt{2\pi \bar{q}_1(\bar{q}_1+1)N}} \left(\frac{\bar{q}_1+1}{\bar{q}_1}\right)^{\bar{q}_1 N} \left(\bar{q}_1+1\right)^N = \frac{1}{\sqrt{2\pi \bar{q}_1(\bar{q}_1+1)N}} \left[\frac{(\bar{q}_1+1)^{(\bar{q}_1+1)}}{\bar{q}_1^{\bar{q}_1}}\right]^N$$

$$S = k_B\left[\underbrace{N \ln\left[(\bar{q}_1+1)\left(1+\frac{1}{\bar{q}_1}\right)^{\bar{q}_1}\right]}_{\text{large}} + \underbrace{\frac{1}{2}\ln\left(2\pi \bar{q}_1(\bar{q}_1+1)N\right)}_{\text{regular}}\right]$$

If $\bar{q}_1$ is large $\left(1+\frac{1}{\bar{q}_1}\right)^{\bar{q}_1} \cong e$ and $\bar{q}_1 + 1 \cong \bar{q}_1$

$$S \cong N k_B\left[\ln(\bar{q}_1) + \ln e\right] = N k_B\left[\ln(\bar{q}_1) + 1\right]$$

Important: S is proportional to N in the thermodynamic limit

$S/N \longrightarrow$ constant as $N \to \infty$

Note S increases as $\bar{q}_1$ increases ($\bar{q}_1$ will increase with temperature) but not quickly!

What about small $\bar{q}_1$? $\quad \bar{q}_1 \ll 1$

$$S/N = k_B \left[\ln(1+\bar{q}_1) + \bar{q}_1 \ln\left(1+\frac{1}{\bar{q}_1}\right) \right] \approx k_B \left[\bar{q}_1 \left\{ 1 - \ln(\bar{q}_1) \right\} \right]$$

For example $N = N_A \quad \bar{q}_1 = 100$,

$$S = 6\times10^{23} \times 1.38\times10^{-23}\ \text{J/K}\ [\ln 100 + 1] = 46\ \text{J/K}$$

$N = N_A \quad \bar{q}_1 = 0.01 \qquad S = 6\times10^{23} \times 1.38\times10^{-23}\ [0.01\ [1 - \ln 0.01]]$

$$= 0.46\ \text{J/K}$$

Suppose you have a composite system made up of A & B

$$\Omega_{TOT} = \Omega(A)\,\Omega(B)$$

$$\Rightarrow \quad S_{TOT} = k_B \ln \Omega_{TOT} = k_B \ln[\Omega(A)\Omega(B)] = k_B \ln \Omega(A) + k_B \ln \Omega_B$$

$$= S_A + S_B$$

Careful look at two Einstein solids in equilibrium

$N = N_A + N_B \qquad \bar{q}_1 = q/N$

$$S = k_B \left\{ N \ln\left[\bar{q}_1 \left(1+\frac{1}{\bar{q}_1}\right)^{\bar{q}_1} \right] + \frac{1}{2} \ln\left[2\pi \bar{q}_1 (\bar{q}_1+1) N \right] \right\}$$

$$S - S_A - S_B = k_B \frac{1}{2} \ln\left[\frac{N}{2\pi \bar{q}_1 (\bar{q}_1+1) N_A N_B} \right] \qquad S \neq S_A + S_B$$

How big is the error? From above $N = N_A \quad \bar{q}_1 = 100 \quad S = 46\ \frac{\text{J}}{\text{K}}$

Take $N_A = \frac{1}{2} 6\times10^{23} \qquad N_B = \frac{1}{2} 6\times10^{23} \qquad \bar{q}_1 = 100$

$S - S_A - S_B = -32\, k_B = -4.4\times10^{-22}\ \text{J/K}$ due to approx in calcs

Now let's look at the entropy of an ideal gas

$$\Omega = \frac{1}{N!}\left[\left(\frac{4m\pi}{3}\right)^{3/2}\frac{\bar{E}_1^{3/2}\bar{V}_1 e^{5/2}}{h^3}\right]^N \qquad \bar{E}_1 = U/N \qquad V_1 = V/N$$

$$\Rightarrow \quad S = N k_B\left\{\ln\left[\left(\frac{4m\pi}{3}\right)^{3/2}\frac{\bar{E}_1^{3/2}\bar{V}_1}{h^3}\right] + 5/2 + \cancel{\frac{1}{N}\ln N}\right\} \quad \text{drop}$$

This is known as the Sackur-Tetrode Equation (discovered 1912 independently by Sackur & Tetrode)

* Note that I used $E_1 = U/N$ this is only correct for a monatomic gas where $\underline{\underline{f=3}}$

The actual expression should contain an extra $\frac{3}{2}\ln(3/f)$ inside of $\{\}$

Example: 1 mole of He at 300K

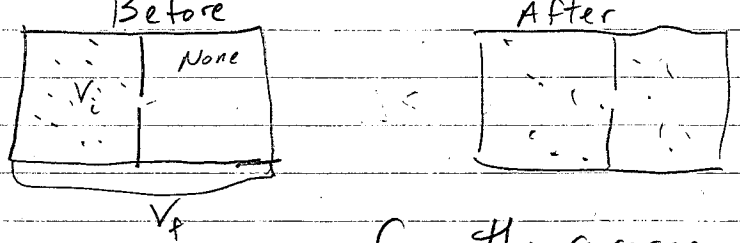
$$\bar{E}_1 = \tfrac{3}{2}k_B T = 6.21\times10^{-21}\,J$$
$$m = 4\cdot 1.67\times10^{-27}\,kg = 6.68\times10^{-27}\,kg$$
$$\bar{V}_1 = 0.025\,m^3/6.02\times10^{23} = 4.15\times10^{-26}\,m^3$$

$$S = 6.02\times10^{23}\;1.38\times10^{-23}\,J/K \times\left\{\ln\left[\left(4\times6.68\times10^{-27}\,kg\,\pi/3\right)^{3/2}\frac{(6.21\times10^{-21}J)^{3/2}\,4.15\times10^{-26}m^3}{(6.626\times10^{-34}J\,s)^3}\right] + 5/2\right\}$$
$$= 8.31\,J/K\left\{\ln(3.27\times10^5) + 2.5\right\}$$
$$= 8.31\,J/K\left\{12.7 + 2.5\right\} = \underline{126\,J/K}$$

Suppose you keep U, N fixed but V varies

$$S(N,U,V_f) - S(N,U,V_i) = Nk_B\{\ln(\text{constant}) + \ln(V_f) - \ln(\text{constant}) - \ln(V_i)\}$$
$$= Nk_B\ln(V_f/V_i)$$

(same)



$\Delta S > 0$

Can the reverse happen?

1.24 Quasistatic isothermal expansion

Chap 1 pg 24 $Q = N k_B T \ln(V_f/V_i)$

Note $Q/T = \Delta S$! $\Rightarrow \frac{1}{T} = \frac{\Delta S}{Q}$

Now let's look at $\left(\frac{\partial S}{\partial U}\right)_{N,V}$

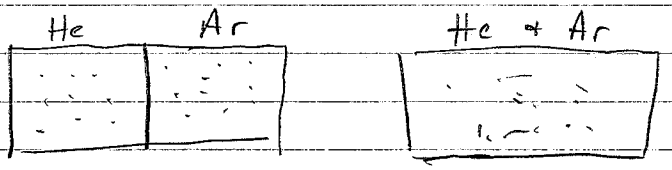
$S = N k_B \{ \frac{3}{2} \ln(U) + \text{constants} \}$

$\Rightarrow \left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{3}{2} \frac{N k_B}{U}$ but remember $U = \frac{3}{2} N k_B T$

$\Rightarrow \left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T}$!!!! A definition of temperature!!!!

Does this hold for a system not ideal gas??

Entropy of mixing:

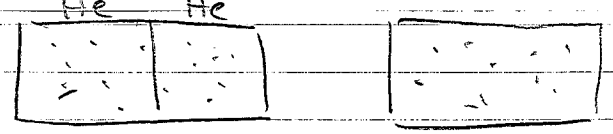


The change in entropy is just $\Delta S = N_{He} k_B \ln\left(\frac{V}{V_i(He)}\right) + N_{Ar} k_B \ln\left(\frac{V}{V_i(Ar)}\right)$

Suppose $V_i(He) = V_i(Ar) = V/2 \Rightarrow \Delta S = (N_{He} + N_{Ar}) k_B \ln(2)$

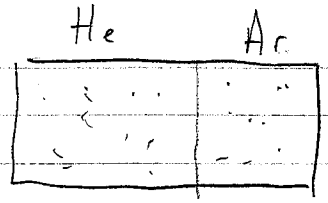
When the original derivation was made for ideal gas, the $1/N!$ was <u>not</u> included in the derivation because every atom/molecule was thought to be distinguishable.

Gibbs noticed this problem (Gibbs paradox) and noted how to fix



$\Delta S = 0$ because only depends on V/N

Prob 2.37



$N_{Ar} = x N$ $\quad N_{He} = (1-x) N$

$V_i(Ar) = x V$ $\quad V_i(He) = (1-x) V$

(must have $\frac{V}{N}$ same for both otherwise P or T is different)

$$\Delta S = N_{He} k_B \ln\left(\frac{V}{V_i(He)}\right) + N_{Ar} k_B \ln\left(\frac{V}{V_i(Ar)}\right) =$$

$$= N k_B \left[(1-x) \ln\left[\frac{1}{1-x}\right] + x \ln\left(\frac{1}{x}\right)\right] = -N k_B \left[(1-x)\ln(1-x) + x \ln x\right]$$

Reversible/ irreversible

Suppose you do a process where $\Delta S > 0$. Can you exactly undo the process? No because that would give $\Delta S < 0$

If you did a process where $\Delta S = 0$, then you can reverse the process.

In the real world, no process has $\Delta S = 0$.

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Example: Adiabatic expansion/compression of monatomic gas $VT^{3/2} = \text{constant}$

$$S = N k_B \left\{ \ln(\text{constants}) + \ln(V U^{3/2}) \right\}$$

$$= N k_B \left\{ \ln(\text{constants}) + \ln(V T^{3/2}) \right\} \Rightarrow \Delta S = 0 !$$

↳ constant!

Example: Heat flow - remember that flow of heat from hot object to cold object increases multiplicity
$\Rightarrow$ Heat flow always $\Delta S > 0 \Rightarrow$ Not reversible

ΔS is always increasing... why did the universe start with low S?