TOPIC
DR. R. K. Hadda
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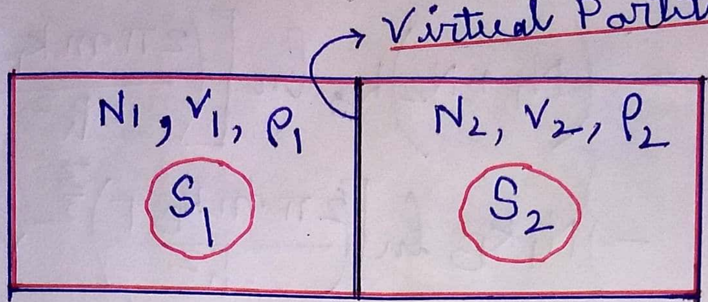
GIBB'S PARADOX and Indistinguishability From Classical Thermodynamics

Entropy (S) is an Extensive property



• Mark Tuckerman (.pdf file)
• Statistical Mechanics by Kerson Huang

After removing Partition and allowing free mixing, $\Rightarrow$ $V = V_1 + V_2$

$N = N_1 + N_2$

Before mixing total entropy, $S_b = S_1 + S_2$

Assuming total entropy, S_a (After mixing)

Now, let us define entropy as function of N & V

Case − I : Particles of system are distinguishable

$$\Rightarrow \quad Z(N, V, T) = (q_{trans}\, q_{elec}\, q_{rot})^N$$

For omitting (N!) from denominator

$$\Rightarrow \quad \ln(Z(N, V, T)) = N \ln(q_{trans}\, q_e\, q_r)$$

Missing factor $\Rightarrow \ln(N!) \Rightarrow N\ln(N) - N$

(In comparison to indistinguishable Particles)

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Entropy, $S = Nk_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} V e^{3/2}\right]$

$+ S_{elec}$

$$\Rightarrow S_a - S_b = (N_1+N_2)k_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} V e^{3/2}\right]$$
$$- \left\{N_1 k_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} V_1 e^{3/2}\right] + N_2 k_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}} V_2 e^{3/2}\right]\right\}$$
$$+ \left(S_e(\text{after}) - S_e(\text{before})\right)$$

$$\Rightarrow \Delta S = (S_a - S_b) = (N_1+N_2)k_B \ln(V_1+V_2) - N_1 k_B \ln(V_1) - N_2 k_B \ln(V_2)$$

$\because$ Neglecting electronic contribution as it's very less

$$= N_1 \ln\left(\frac{V_1+V_2}{V_1}\right) + N_2 \ln\left(\frac{V_1+V_2}{V_2}\right)$$
$$= N_1 \ln\left(1+\frac{V_2}{V_1}\right) + N_2 \ln\left(1+\frac{V_1}{V_2}\right) > 0$$

$$\Rightarrow S_a - S_b > 0 \Rightarrow S_a > S_b$$

Now, if we think densities are same for sake of simplicity, i.e.,

$$\frac{N_1}{V_1} = \frac{N_2}{V_2}$$

$$\Rightarrow \left(\frac{N_1}{V_1}\right) = \left(\frac{N_2}{V_2}\right) = \left(\frac{N_1+N_2}{V_1+V}\right)$$

However, $S_a > S_b$ thus implies that Entropy is not an Extensive Property while virtual mixing or virtual walls are... continued

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Thus distinguishable particles of ideal gases violates extensive property of Entropy, i.e., Gibb's Paradox.

Case-II : Indistinguishability of Particles and Solution to Gibb's Paradox

$$Z(N,V,T) = (q_{trans}\, q_e\, q_n)^N / N!$$

leads to Sackur-Tetrode Equation

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

$$\Rightarrow \Delta S = S_a - S_b$$

$$= (N_1+N_2)k_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\left(\frac{V e^{5/2}}{N_1+N_2}\right)\right] + S_e(\text{after})$$

$$- N_1 k_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\left(\frac{V_1 e^{5/2}}{N_1}\right)\right]$$

$$- N_2 k_B \ln\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{\frac{3}{2}}\left(\frac{V_2 e^{5/2}}{N_2}\right)\right]$$

$$- S_e(\text{before})$$

$$= (N_1+N_2)k_B \ln\left(\frac{V_1+V_2}{N_1+N_2}\right) - N_1 k_B \ln\left(\frac{V_1}{N_1}\right) - N_2 k_B \ln\left(\frac{V_2}{N_2}\right)$$

Ignoring electronic contribution of S_e

$$\Rightarrow \Delta S = S_a - S_b$$

$$= N_1 k_B \ln\left(\frac{(V_1+V_2)}{(N_1+N_2)}\left(\frac{N_1}{V_1}\right)\right)$$

$$+ N_2 k_B \ln\left(\frac{(V_1+V_2)}{(N_1+N_2)}\left(\frac{N_2}{V_2}\right)\right)$$

Similarly, consideration of same densities in two different compartments gives virtual mixing through virtual walls.

i.e., $\left(\frac{N_1}{V_1}\right) = \left(\frac{N_2}{V_2}\right) = \left(\frac{N_1+N_2}{V_1+V_2}\right) = \rho$

$$\Rightarrow S_a - S_b = N_1 k_B \ln\left(\left(\frac{1}{\rho}\right)\cdot\rho\right) + N_2 k_B \ln\left(\frac{1}{\rho}\cdot\rho\right)$$

$$= 0$$

$\Rightarrow$ Total Entropy in presence and absence of virtual walls remains same!!

$\Rightarrow$ Entropy is extensive property while particles of systems are indistinguishable.