

Microscopic Interpretation of Entropy

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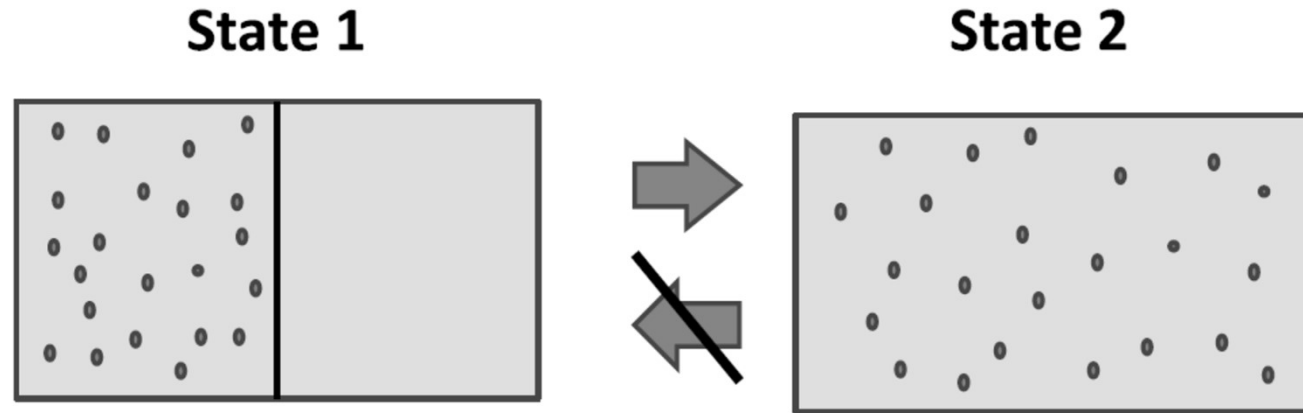
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Where do we stand on Entropy?

- Entropy-A state function that emerges from analysis of Carnot cycle (Emphasis: Reversible processes)
- $\Delta S = \left(\frac{Q}{T}\right)_{rev}$
- Irreversible processes generate entropy & Entropy is not a conserved quantity; $(\Delta S)_{isolated} \geq 0$
- Agenda: “What is entropy?”
- Scope of the answer: State function internal energy (U) was interpreted in terms of “thermal energy” stored in the molecular degrees of freedom; Each excitable DOF=0.5 * kT; U assisted in moving beyond mechanics to TD; Likewise, can we interpret entropy with internal mechanics of matter?

Gas Chamber & Disorder



- Isolated Gas Chamber: Partition removed \rightarrow At “equilibrium”, Gas spreads uniformly to occupy the entire chamber
- As $Q=0$, Is “ $\Delta S = \frac{Q}{T} = 0$ ”?; Wrong! Note: $\Delta S = \left(\frac{Q}{T}\right)_{rev}$
- Free expansion of ideal gas; $U_2=U_1$ & $T_2=T_1$

What is an “equivalent” reversible path?

- Equivalent reversible path connects the 2 relevant states
- Free expansion of ideal gas in isolation; $\therefore U_2=U_1$ & $T_2=T_1$; $V_2=2V_1$
- $\Delta U=0$; $\therefore q=0$ (1st TD law)
- $\Delta S = S_2 - S_1 = \int_1^2 \frac{PdV}{T} = \int_1^2 \frac{nRdV}{V} = n * R * \ln 2 = K * \ln 2^N$ (as $R = N_{Ava} * k$)
- $\Delta S = NK * \ln 2$; Result of macroscopic TD

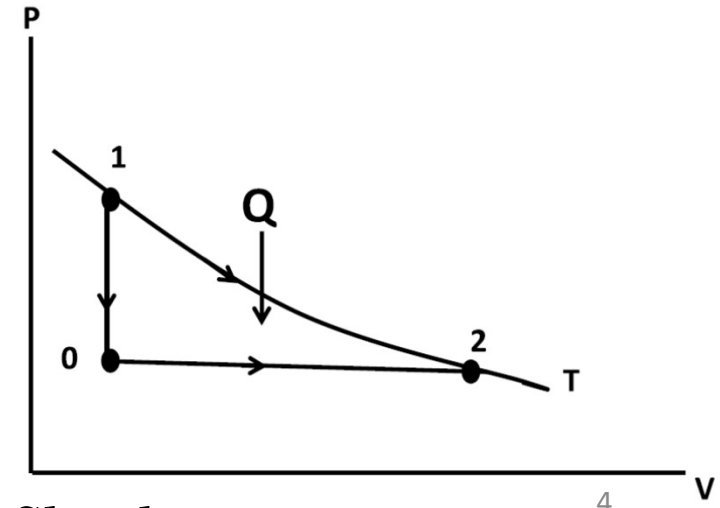


Fig: Fundamentals of Physics-1; R. Shankar

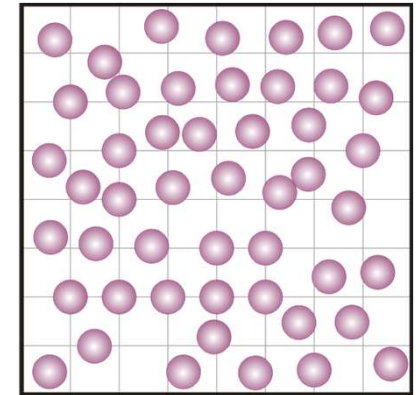
Microscopic TD: Boltzmann Equation



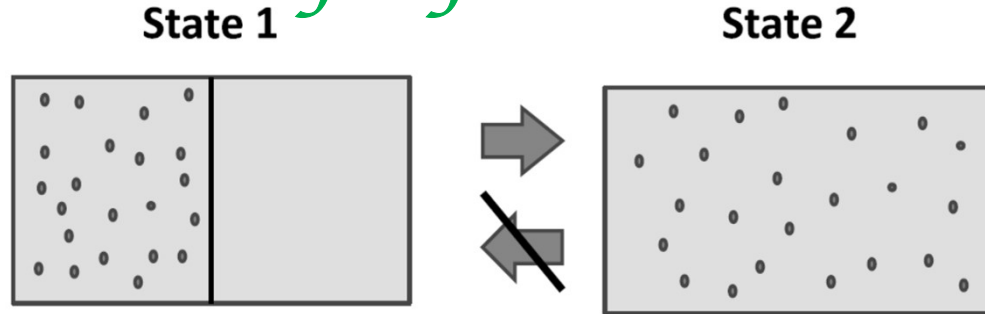
- $S(U,V,N) = K \cdot \ln \Omega(U,V,N)$
- $\Omega(U,V,N)$ = # of different microscopic states compatible with its macroscopic properties (i.e. U , V & N)
- Microscopic TD is also referred to as Statistical TD or Statistical Mechanics

Computing with a “Lattice model”

- Each lattice has volume $\sim r^3$; ($r \sim$ atomic radius)
- # of lattice points: $L_1 = (V_1/r^3)$; $L_1 \gg N$; $L_2 = 2L_1$
- $\Omega_1 = (L_1)^N$; $\Omega_2 = (2L_1)^N = 2^N * (L_1)^N$
- $\Delta S = S_2 - S_1 = K \ln \Omega_2(U, V, N) - K \ln \Omega_1(U, V, N) = K * \ln 2^N$
- $\Delta S = NK * \ln 2$; Result of microscopic TD
- Caveat of the model: We have not considered distribution in momentum states but this does not matter for free expansion (remember internal energy does not change)



Why “Spontaneous”?



- What entropy increases?: The number of ways of distributing atoms increased after removal of partition(only left \rightarrow either left or right)
- Many (in fact many many many many!) ways of distributing gas atoms more or less uniformly across the entire box compared to distributing all gas atoms into one-half of a box without partition
- What is spontaneous is what occurs “naturally” i.e. more ways of occurring...
- Other spontaneous processes like mixing, heat dissipation can also be rationalized in a similar manner

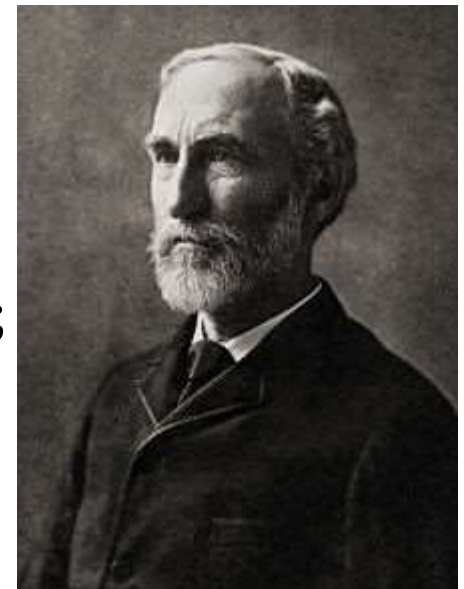
Fig: Fundamentals of Physics-1; R. Shankar

Is $S(U,V,N)=K \ln \Omega(U,V,N)$ intuitive?

- S is extensive: $S=S_2 + S_1$; 1 & 2 are subsystems
- $\Omega = \Omega_1 * \Omega_2$
- $S=K \ln(\Omega_1 * \Omega_2)= K \ln(\Omega_1)+ K \ln(\Omega_2)= S_2 + S_1$

Microscopic TD should reflect macroscopically doable experiments

- Boltzmann equation addresses Macroscopic experiment conducted at controlled (U, V, N); $S(U, V, N) = K \ln \Omega(U, V, N)$
- Gibbs formalism addresses Macroscopic experiment conducted at controlled (T, V, N); $F(T, V, N) = -KT \ln Z(T, V, N)$
- $P(i) = \frac{e^{\frac{-\epsilon_i}{KT}}}{Z(T, V, N)}$; $Z(T, V, N) = \sum_i e^{\frac{-\epsilon_i}{KT}}$
- $Z(T, V, N) \rightarrow$ “Canonical” (typical) partition function;
 $\Omega(U, V, N) \rightarrow$ MicroCanonical partition function



Shannon's Measure of Information (SMI) & Entropy

- $H = -K \sum_{i=1}^n p_i \log p_i$
- H can be associated with S and K with Boltzmann's constant if p_i correlated to “phase-space” of a thermodynamical system

Closure on “classical” physics (~pre-1900)

Table 18-1 Classical Physics

Maxwell's equations

I. $\nabla \cdot \mathbf{E} = \frac{\rho}{\epsilon_0}$ (Flux of \mathbf{E} through a closed surface) = (Charge inside)/ ϵ_0

II. $\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$ (Line integral of \mathbf{E} around a loop) = $-\frac{d}{dt}$ (Flux of \mathbf{B} through the loop)

III. $\nabla \cdot \mathbf{B} = 0$ (Flux of \mathbf{B} through a closed surface) = 0

IV. $c^2 \nabla \times \mathbf{B} = \frac{\mathbf{j}}{\epsilon_0} + \frac{\partial \mathbf{E}}{\partial t}$ c^2 (Integral of \mathbf{B} around a loop) = (Current through the loop)/ ϵ_0
 $+ \frac{\partial}{\partial t}$ (Flux of \mathbf{E} through the loop)

[Conservation of charge
 $\nabla \cdot \mathbf{j} = -\frac{\partial \rho}{\partial t}$ (Flux of current through a closed surface) = $-\frac{\partial}{\partial t}$ (Charge inside)]

Force law

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

Law of motion

$$\frac{d}{dt}(\mathbf{p}) = \mathbf{F}, \quad \text{where} \quad \mathbf{p} = \frac{m\mathbf{v}}{\sqrt{1 - v^2/c^2}} \quad (\text{Newton's law, with Einstein's modification})$$

Gravitation

$$\mathbf{F} = -G \frac{m_1 m_2}{r^2} \mathbf{e}_r$$

$$S(\mathbf{U}, \mathbf{V}, \mathbf{N}) = K \ln \Omega(\mathbf{U}, \mathbf{V}, \mathbf{N})$$

$$F(\mathbf{T}, \mathbf{V}, \mathbf{N}) = -KT \ln Z(\mathbf{T}, \mathbf{V}, \mathbf{N})$$