Review

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Contents

1 The Second Law

1.1 Two State System

$$\Omega(N, n) = \frac{N!}{n! \cdot (N - n)!} \equiv \binom{N}{n} \tag{1}$$

$$\Omega(N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow! N_\downarrow!} \tag{2}$$

1.2 Einstein Model of a Solid

$$\Omega(N, q) = \binom{q + N - 1}{q} = \frac{(q + N - 1)!}{q!(N - 1)!} \tag{3}$$

1.3 Interacting Systems

The spontaneous flow of energy stops when a system is at, or very near, its most likely macro state, that is, the macro state with the greatest multiplicity. This "low of increase of multiplicity" is one version of the famous **second law of thermodynamics**.

1.4 Large Systems

Stirling's Approximation

$$N! \approx N^N e^{-N} \sqrt{2\pi N} \tag{4}$$

Often the $\sqrt{2\pi N}$ can be omitted.

Multiplicity of a Large Einstein Solid

$$\Omega(N, q) = e^{N \log\left(\frac{q}{N}\right)} e^N = \left(\frac{eq}{N}\right)^N \quad \text{when } q \gg N \tag{5}$$

Sharpness of the Multiplicity Function   The Gaussian curve has a peak at $x = 0$ and a sharp fall-off on either side. The multiplicity falls of to $\frac{1}{e}$ of its maximum value when

$$N \left(\frac{2x}{q} \right)^2 = 1 \quad \text{or} \quad x = \frac{q}{2\sqrt{N}} \tag{6}$$

This is a very large number, but comparatively to the full scale it is very small. The width of the Gaussian is given by

$$\text{Width} = \frac{q}{\sqrt{N}} \tag{7}$$

1.5   The Ideal Gas

Multiplicity of a Monatomic Ideal Gas

$$\Omega_N \approx \frac{1}{N!} \frac{V^N}{h^{3N}} \frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2} \right)!} \left(\sqrt{2mU} \right)^{3N} \tag{8}$$

$$\Omega(U, V, N) = f(N) V^N U^{\frac{3N}{2}} \tag{9}$$

1.6   Entropy

$$S \equiv k \log \Omega \tag{10}$$

Entropy of an Ideal Gas

$$S = Nk \left[\log \left(\frac{V}{N} \left(\frac{4\pi mU}{3Nh^2} \right)^{\frac{3}{2}} \right) + \frac{5}{2} \right] \tag{11}$$

If volume changes then

$$\Delta S = Nk \log \frac{V_f}{V_i} \quad \text{U,N fixed} \tag{12}$$

Entropy of Mixing

$$\Delta S_{total} = \Delta S_A + \Delta S_B \tag{13}$$

2 Interactions and Implications

2.1 Temperature

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \quad \text{at equilibrium} \tag{14}$$

$$T \equiv \left(\frac{\partial S}{\partial U}\right)^{-1} \tag{15}$$

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{N,V} \tag{16}$$

2.2 Entropy and Heat

Predicting Heat Capacities

$$C_V \equiv \left(\frac{\partial U}{\partial T}\right)_{N,V} \tag{17}$$

$$\tag{18}$$

For an Einstein solid with $q \gg N$

$$C_V = \frac{\partial}{\partial T}\left(NkT\right) = Nk \tag{19}$$

For a monatomic ideal gas

$$C_V = \frac{\partial}{\partial T}\left(\frac{3}{2}NkT\right) = \frac{3}{2}Nk \tag{20}$$

Measuring Entropies

$$dS = \frac{dU}{T} = \frac{Q}{T} \tag{21}$$

$$dS = \frac{C_V dT}{T} \tag{22}$$

$$\Delta S = S_f - S_i = \int_{T_i}^{T_f} \frac{C_V}{T}dT \tag{23}$$

$$C_V \to 0 \quad \text{as} \quad T \to 0 \tag{24}$$

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2.3   Paramagnetism

Weird, and can have negative temperature, as the state with greatest entropy is when half are up, and half are down, event though more energy is present with more down spins, it wants to move back to half way, thus it has negative temperature, but is hotter than high temperature.