Boltzmann Factor

Macroscopic system (Avogadro number of particles)

Number of particles, N; Volume V

S.E. for this N-body system is

$$\hat{H}\psi_j = E_j\psi_j \quad j = 1,2,3 \dots$$

Energy dependence $E_j(N,V)$: note below the dependence on N terms and $a = V^{1\backslash 3}$ term

Ideal gas (non-interacting particles):

$$E_j(N,V) = \epsilon_1 + \epsilon_2 + \cdots + \epsilon_N$$

Monatomic ideal gas in cubic container of length a. If we worry about translational motion only (ignoring electronic energy – a valid assumption mostly), $\epsilon's$ are just the translational energies – the energies of the P-I-B. Though no longer quantized as the length of the box is too large.

$$\epsilon_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$

What is the probability that the particle be in state j with energy $E_j(N,V)$?

Ensemble: Consider a large collection of such systems in thermal contact with an infinite heat reservoir at temperature T. No matter what we do the temperature remains T. Each system has the same values of N, V, T but the quantum states are likely to be different in each. Such a collection of systems is called an ensemble.

$$a_j = \text{\# of systems with energy } E_j(N,V)$$

$$\mathcal{A} = \text{total \# of systems in the ensemble}$$
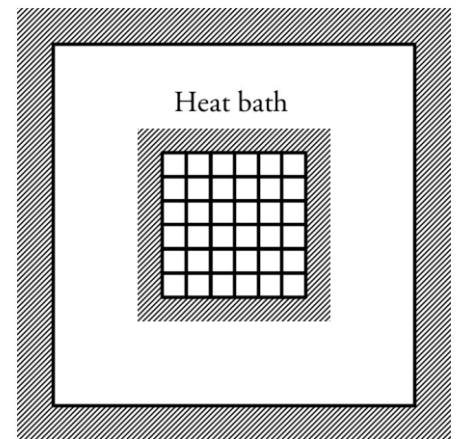
Now, $a_2/a_1 = f(E_1, E_2) = f(E_1 - E_2)$ ∵ this is the way to cancel the zero of energy from both the terms.

$$\frac{a_3}{a_1} = \frac{a_2}{a_1}.\frac{a_3}{a_2} \Rightarrow f(E_1 - E_3) = f(E_1 - E_2).f(E_2 - E_3)$$

This form of the function suggests an exponential, $e^{x+y} = e^x e^y \quad \Rightarrow \quad f(E) = e^{\beta E}$

$$\frac{a_n}{a_m} = e^{\beta(E_m - E_n)}$$

Or in general, $a_j = Ce^{\beta E_j}$

Partition Function $Q(N, V, T)$

$$\mathcal{A} = \sum_j a_j = C \sum_j e^{-\beta E_j} = CQ(N, V, \beta)$$

Use $\boxed{\beta = 1/k_B T}$ (worry later). So, $Q(N, V, T)$ can be written.

Q is essentially the ratio of the total number of particles to the number of particles in the lowest energy state (actually in state with zero energy, but then we define the reference of energy).

$$\frac{a_j}{\mathcal{A}} = p_j = \frac{e^{-\beta E_j}}{\sum_j e^{-\beta E_j}} = \frac{e^{-\beta E_j}}{Q} = \frac{e^{-E_j/k_B T}}{Q}$$

All macroscopic properties can be expressed in terms of $Q(N, V, \beta)$ or $Q(N, V, T)$. This is termed the *partition function*.

$$\boxed{Q(N, V, T) = \sum_j e^{-\beta E_j(N,V)}}$$

Average Ensemble Energy, $\boxed{\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}}$

$$\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = \frac{1}{Q}\left(\frac{\partial \sum e^{-\beta E_j}}{\partial \beta}\right)_{N,V} = \frac{1}{Q}\sum -E_j e^{-\beta E_j} = -\sum \frac{E_j e^{-\beta E_j}}{Q} = \sum -E_j p_j = -\langle E \rangle$$

$$\frac{\partial f}{\partial T} = \frac{\partial f}{\partial \beta}\cdot\frac{\partial \beta}{\partial T} = \frac{\partial f}{\partial \beta}\cdot\frac{d(1/k_B T)}{dT} = -\frac{1}{k_B T^2}\frac{\partial f}{\partial \beta}$$

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = k_B T^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

Monatomic Ideal Gas

$$Q(N, V, \beta) = \frac{[q(V,\beta)]^N}{N!} \quad \text{where} \quad q(V, \beta) = \left(\frac{2\pi m}{h^2 \beta}\right)^{3/2} V$$

$$\ln Q = N \ln q - \ln N! = -\frac{3N}{2}\ln\beta + \frac{3N}{2}\ln\left(\frac{2\pi m}{h^2}\right) + N\ln V - \ln N!$$

$$= -\frac{3N}{2}\ln\beta + \text{terms not involving } T$$

$$\langle E \rangle = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = \frac{3N}{2}\frac{d\ln\beta}{d\beta} = \frac{3N}{2\beta} = \frac{3}{2}N k_B T = \frac{3}{2}nRT$$

This is the result one gets from kinetic theory of gases too!.

So, **the ensemble average of a quantity equals the experimentally observed value of the quantity**. This is a fundamental principle of nature.

$$\bar{U} = \langle\bar{E}\rangle = \frac{3}{2}RT$$

Bar on top denotes molar quantities.

Heat Capacity: Monatomic Ideal Gas

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_{N,V} = \frac{3}{2}nR \quad \bar{C_V} = \frac{3}{2}R$$

Diatomic Ideal Gas

$$Q(N,V,\beta) = \frac{[q(V,\beta)]^N}{N!} \quad \text{where} \quad q(V,\beta) = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V\left(\frac{8\pi^2 I}{h^2\beta}\right)\frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}$$

$$\bar{U} = \frac{3}{2}RT + RT + \frac{N_A h\nu}{2} + \frac{N_A h\nu e^{-\beta h\nu}}{1 - e^{-\beta h\nu}}$$

$$\bar{C_V} = \frac{5}{2}R + R\left(\frac{h\nu}{k_B T}\right)^2\frac{e^{-h\nu/k_B T}}{(1 - e^{-h\nu/k_B T})^2}$$

Pressure, $\boxed{\langle P\rangle = \frac{1}{\beta}\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}}$

Pressure of a macroscopic system, $P_j(N,V) = -(\partial E_j/\partial V)_N$ (worry later)

$$\langle P\rangle = \sum_j p_j P_j = \sum_j -\left(\frac{\partial E}{\partial V}\right)_N\frac{e^{-\beta E_j}}{Q} = \frac{k_B T}{Q}\left(\frac{\partial Q}{\partial V}\right)_{N,\beta} = k_B T\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

Here we used, $Q = \sum_j e^{-\beta E_j(N,V)}$ to get $\left(\frac{\partial Q}{\partial V}\right)_{N,\beta} = -\beta\sum_j\left(\frac{\partial E}{\partial V}\right)_N e^{-\beta E_j}$

Monatomic ideal gas

$$Q(N,V,\beta) = \frac{[q(V,\beta)]^N}{N!} \quad \text{where} \quad q(V,\beta) = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V$$

$$\ln Q = N\ln q - \ln N! = -\frac{3N}{2}\ln\beta + \frac{3N}{2}\ln\left(\frac{2\pi m}{h^2}\right) + N\ln V - \ln N!$$
$$= N\ln V + \text{terms only in N and }\beta$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = \frac{N}{V} \quad or \quad P = \frac{Nk_B T}{V} = \frac{nRT}{V}$$

Same result for diatomic ideal gas too ($N\ln V$ is the only term in V in this case too).