Thermodynamics: Classical to Statistical

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Lecture - 19

Vibrational partition function; Introduction to grand canonical ensemble

Now, we discuss Vibrational partition function which we define as q_{vib}. For this, we consider again the simplest model like harmonic oscillator model. So q_{vib} can be written

$$q_{vib} = \sum_{v=0}^{\infty} e^{-\beta\epsilon_{vib}}$$

$$\text{Where, } \epsilon_{vib} = (v + \tfrac{1}{2})h\nu$$

v goes from 0, 1,2 etc, h is Planck's constant.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

where k is the bond force constant and μ is the reduced mass of the molecule.

So if we substitute the expression for vibrational energy into the partition function expression,

we get $$q_{vib} = \sum_{v=0}^{\infty} e^{-\beta\left(v+\frac{1}{2}\right)h\nu}$$

$$\Rightarrow \quad q_{vib} = e^{-\frac{\beta h\nu}{2}} \sum_{v=0}^{\infty} e^{-\beta v h\nu}$$

$$\Rightarrow \quad q_{vib} = e^{-\frac{\beta h\nu}{2}}(1 + e^{-\beta h\nu} + e^{-2\beta h\nu} + \cdots)$$

Consider $e^{-\beta h\nu} = x$

Then $1+e^{-\beta h\nu}+e^{-2\beta h\nu}+\cdots = 1+x+x^2\ldots\ldots = \frac{1}{1-x}$

if $x \ll 1$

So we can write $q_{vib} = \frac{e^{-\frac{\beta h\nu}{2}}}{1-e^{-\beta h\nu}}$

Consider $\theta_{vib} = \frac{h\nu}{k_B}$, θ_{vib} = vibrational temperature

Then $q_{vib} = \frac{e^{-\frac{\theta_{vib}}{2T}}}{1-e^{-\frac{\theta_{vib}}{T}}}$

Now, we have got the partition function or vibrational partition function, so we can calculate the average vibrational energy of a single harmonic oscillator.

$$<\epsilon_{vib}> = k_B T^2 \left(\frac{\partial \ln q_{vib}}{\partial T}\right)_V = -\left(\frac{\partial \ln q_{vib}}{\partial \beta}\right)_V$$

$$q_{vib} = \frac{e^{-\frac{\theta_{vib}}{2T}}}{1-e^{-\frac{\theta_{vib}}{T}}}$$

$$\Rightarrow \quad \ln q_{vib} = -\frac{\theta_{vib}}{T} - \ln\left(1-e^{-\frac{\theta_{vib}}{T}}\right)$$

$$\Rightarrow \quad \left(\frac{\partial \ln q_{vib}}{\partial T}\right)_V = \frac{\theta_{vib}}{T^2} - \frac{1}{1-e^{-\frac{\theta_{vib}}{T}}} \times \left(-e^{-\frac{\theta_{vib}}{T}}\right) \times \frac{\theta_{vib}}{T^2}$$

So $$<\epsilon_{vib}> = k_B\left(\frac{\theta_{Vib}}{2} + \frac{\theta_{vib}}{e^{\frac{\theta_{vib}}{T}}-1}\right)$$

If we have ‘N’ number of harmonic oscillators, then

$$<\epsilon_{vib}> = Nk_B\left(\frac{\theta_{Vib}}{2} + \frac{\theta_{vib}}{e^{\frac{\theta_{vib}}{T}}-1}\right)$$

Where $N = nN_A$

$$<\epsilon_{vib}> = nR\left(\frac{\theta_{Vib}}{2} + \frac{\theta_{vib}}{e^{\frac{\theta_{vib}}{T}} - 1}\right)$$

$$(C_V)_{vib} = \left(\frac{\partial <E>}{\partial T}\right)_V = R(\frac{\theta_{vib}}{T})^2 \frac{e^{-\frac{\theta_{vib}}{T}}}{(1 - e^{-\frac{\theta_{vib}}{T}})^2}$$

Next, we calculate the fraction of molecules in the v-th vibrational energy level and that is f_v

$$f_v = \frac{e^{-\beta h\nu\left(v + \frac{1}{2}\right)}}{q_{vib}}$$

$$\Rightarrow \quad f_v = (1 - e^{-\frac{\theta_{vib}}{T}})\, e^{-\frac{v\,\theta_{vib}}{T}}$$

So this is the expression for fractional molecules in the v-th vibrational energy level.

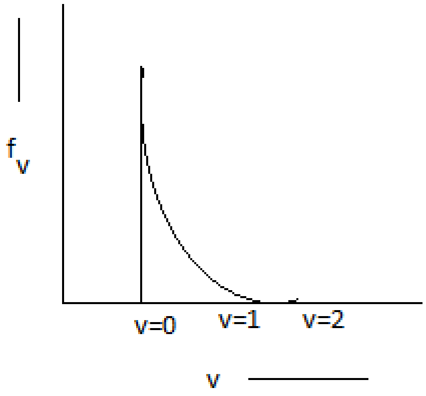
Next, we will consider one numerical example to see what is the fractional molecules in a particular vibrational energy level. One example is, calculate the fraction of N_2 gas molecules in the v = 0 and v =1 vibrational states at 300 K temperature. Consider, $\theta_{vib} = 3374$ K for N_2 gas.

Ans. $$e^{-\frac{\theta_{vib}}{T}} = e^{\frac{3374K}{300K}} = 1.31\times 10^{-5}$$

For v = 0 state, $f_0 = (1 - e^{-\frac{\theta_{vib}}{T}}) = 1 - 1.31\times 10^{-5} \approx 1$

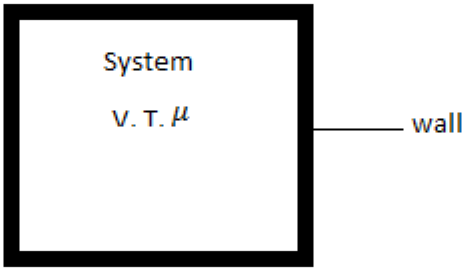
For v = 1 state, $f_1 = (1 - e^{-\frac{\theta_{vib}}{T}})\, e^{-\frac{\theta_{vib}}{T}} \approx 1.31\times 10^{-5}$

So if you plot f_v versus v , we get exponentially decay curve.



So far we have considered canonical ensemble. For canonical ensemble we know number of particle, volume of the system and temperature, these three quantities are fixed.

Now we consider another ensemble which is known as grand canonical ensemble. For grand canonical ensemble volume (V), temperature (T) and chemical potential (μ) is fixed, so number of molecules can vary from one state to another state.



So this is the thermal insulation and this is the system. These walls are both heat conducting and permeable to the passage of molecules. The grand canonical ensemble is applicable for open kind of system and the whole thing is isolated from surroundings.

Now in grand canonical ensemble μ, V, T is fixed. If there is more than one component in the system, then the chemical potential, μ of each component is the same from system to system like we did for canonical ensemble. Here we define one quantity a_{N_j}

Let a_{N_j} = the number of systems in the ensemble that contains 'N' molecules in the state 'j' in which energy is $E_{N_j}(V)$. It is a function of number of molecules 'N' as 'N' is permissible

So, you can write $\sum_N \sum_j a_{Nj} = A$ ………..(1)

A = Total number of systems in the ensemble

$$\sum_N \sum_j a_{Nj} E_{Nj} = E \text{ ………..(2)}$$

E = total energy of ensemble

$$\sum_N \sum_j a_{Nj} N_j = N \text{ …………(3)}$$

N = total number of particles or total number of molecules in the ensemble

So for any possible distribution like we did for canonical ensemble, the number of states is given by,

$$W(\{a_{Nj}\}) = \frac{A!}{\prod_N \prod_J a_{Nj}!} \text{ …………(4)}$$

So as we did for canonical ensemble, the distribution that maximizes 'W' subject to the condition or subject to the appropriate constants, we have three constants here. So if we maximize W of equation 4 under the constants mentioned above, we get

$$a_{Nj}{}^{*} = e^{-\alpha} e^{-\beta \epsilon_{Nj}} e^{-\gamma N}$$

If you go back and check, for canonical ensemble we had α and β two Lagrange's multiplier because we had two constants there. Here we are having three constants α, β and γ, these three terms.

$$\sum_N \sum_j a_{Nj}{}^{*} = A = e^{-\alpha} \sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}$$

$$\Rightarrow \quad e^{-\alpha} = \frac{A}{\sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}}$$

$$a_{Nj}{}^{*} = \frac{A}{\sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}} \times e^{-\beta E_{Nj}(V)}\, e^{-\gamma N}$$

$$\Rightarrow \quad p_{Nj}(V, T, \gamma) = \frac{a_{Nj}{}^{*}}{A} = \frac{e^{-\beta E_{Nj}(V)}\, e^{-\gamma N}}{\sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}}$$

$$\Rightarrow \quad p_{Nj} = \frac{e^{-\beta E_{Nj}(V)}\, e^{-\gamma N}}{\Theta\,(V,T,\gamma)}$$

This Θ is known as grand canonical partition function.