

Lecture 10

Degrees of freedom:

Why is it easier to trap an ant? Why is it difficult to trap a mosquito? Why is it more difficult to trap a fly? The answer lies in degrees of freedom which commonly signifies the extent of freedom a system enjoys. For movement in a plane degrees of freedom is two and for movement in air degrees of freedom is three. This means we need to fix/define two and three coordinates respectively. So, more an object enjoys freedom, the greater will be the number of parameters needed to define an object.

Let us extend the situation for an atom/molecule.

An atom has translational motion only. So, to define motion of an atom we need three coordinates. Similarly, three quadratic term, i.e. $\frac{1}{2} \mu u^2$, $\frac{1}{2} m v^2$, $\frac{1}{2} m w^2$ are necessary to define K.E. of the molecule (u, v, w are component of velocity in x, y, z coordinates respectively). So, **degrees of freedom are three**.

For a diatomic molecule, there will be translational motion along three axes i.e. translational degrees of freedom = 3. There could be rotation around two axes perpendicular to inter-atom axis.

Thus rotational degrees of freedom = 2 $\left[\frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2 \right]$

There will be only one type of vibrational motion i.e. extension and compression. So, vibrational degrees of freedom = 1. $[K.E._{vib} = \frac{1}{2} \mu \left(\frac{dx}{dt} \right)^2]$

So, **total degrees of freedom for a diatomic molecule = 3+2+1 = 6**

Change in how many coordinates?

For an N atomic molecule the degrees of freedom = $3N$

For a linear molecule (example: CO_2)

Translational degrees of freedom = 3

Rotational degrees of freedom = 2 (it behaves like a diatomic molecule)

Vibrational degrees of freedom = $3N - (3+2) = 3N - 5$

For a non-linear molecule (example: H_2O)

Translational degrees of freedom = 3

Rotational degrees of freedom = 3

Vibrational degrees of freedom = $3N - (3+3) = 3N - 6$

So, the degrees of freedom may be defined as the number of independent quadratic terms necessary to define the total kinetic energy of a 'moving' molecule.

Equipartition principle:

Assumption: To calculate average kinetic energy per mode of translational motion, the translational energy levels are considered to be continuous rather than discrete. [classical]

Thus, $\langle \epsilon_x \rangle = \frac{1}{2} m \langle u^2 \rangle = \frac{1}{2} m \cdot \frac{1}{n} \int_{-\infty}^{+\infty} u^2 dn_u$ [u component varying from $(-) \infty$ to $(+) \infty$]

$$\Rightarrow \langle \epsilon_x \rangle = \frac{1}{2} m \cdot \int_{-\infty}^{+\infty} u^2 \cdot \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \cdot e^{-\frac{m u^2}{2kT}} \cdot du \quad [\text{in 1D} \quad \frac{dn_u}{n} = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \cdot e^{-\frac{m u^2}{2kT}} \cdot du]$$

$$= \frac{1}{2} m \cdot \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \cdot \int_{-\infty}^{+\infty} u^2 \cdot e^{-\frac{m u^2}{2kT}} \cdot du = \frac{1}{2} m \cdot \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \cdot \sqrt{2} \cdot \left(\frac{kT}{m}\right)^{\frac{3}{2}} \cdot \sqrt{\pi} \Rightarrow \boxed{\langle \epsilon_x \rangle = \frac{1}{2} k T}$$

$$\text{Let, } \frac{m u^2}{2kT} = x, \quad \text{so, } u \cdot du = \frac{kT}{m} \cdot dx$$

$$\int_{-\infty}^{+\infty} u^2 \cdot e^{-\frac{m u^2}{2kT}} \cdot du = 2 \cdot \int_0^{\infty} u^2 \cdot e^{-\frac{m u^2}{2kT}} \cdot du$$

$$= 2 \cdot \int_0^{\infty} \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \cdot x^{\frac{1}{2}} \cdot e^{-x} \cdot \frac{kT}{m} \cdot dx$$

$$= \left(\frac{2kT}{m}\right)^{\frac{3}{2}} \cdot \int_0^{\infty} x^{\frac{1}{2}} \cdot e^{-x} \cdot dx$$

$$= \left(\frac{2kT}{m}\right)^{\frac{3}{2}} \cdot \frac{1}{2} \sqrt{\pi}$$

$$= \sqrt{2} \cdot \left(\frac{kT}{m}\right)^{\frac{3}{2}} \cdot \sqrt{\pi}$$

The same is also valid for other modes of translational motions.

Therefore, kinetic energy of translational motion is equally distributed among modes of translational motions. This principle of equipartition of [kinetic energy](#) for translational energy levels was extended to rotational and vibrational levels by Boltzmann i.e. kinetic energy associated with each mode of rotational and vibrational motion is $(\frac{1}{2} k T)$.

Thus, equipartition principle of kinetic energy can be stated as “Total [kinetic energy](#) is equally distributed to all the [independent](#) quadratic terms needed to define the kinetic energy of the molecule in motion”.

Now, since each vibrational mode consists of potential and kinetic energy and the average of the two being same, it is considered that for each mode of vibrational motion, the potential energy is $(\frac{1}{2} k T)$ and the kinetic energy is $(\frac{1}{2} k T)$.

Let us take the example of CO₂

$$\begin{aligned}\epsilon_{\text{total}} &= \epsilon_{\text{tr}} + \epsilon_{\text{rot}} + \epsilon_{\text{vib}} \\ &= (3 \times \frac{1}{2} k T) + (2 \times \frac{1}{2} k T) + \underbrace{((3 \times 3 - 5) \times \frac{1}{2} k T)}_{\text{Kinetic}} + \underbrace{((3 \times 3 - 5) \times \frac{1}{2} k T)}_{\text{Potential}} \\ &= \frac{13}{2} k T\end{aligned}$$

To generalize,

For a linear n-atomic molecule

$$\epsilon_{\text{total}} = (3 \times \frac{1}{2} k T) + (2 \times \frac{1}{2} k T) + (2 \times (3 n - 5) \times \frac{1}{2} k T)$$

For a non-linear n-atomic molecule

$$\epsilon_{\text{total}} = (3 \times \frac{1}{2} k T) + (3 \times \frac{1}{2} k T) + (2 \times (3 n - 6) \times \frac{1}{2} k T)$$

Validity of Equipartition principle:

This principle has been established from classical point of view, that the energy levels are continuous.

QM treatment tells that energy levels are discrete and quantized. $[\epsilon_{tr} = \frac{n^2 h^2}{8 m l^2}]$, where m is mass of the molecule, l is the dimension of the container, n is the translational quantum number.

If l is in the order of a few cm, $\Delta n = 1$, then $\Delta \epsilon_{tr}$ i.e. the gap between adjacent translational levels is in the order of 10^{-30} erg.

Similarly, $\Delta \epsilon_{rot}$ i.e. the energy gap between two adjacent rotational levels is in the order of 10^{-15} erg.

$$[E_{rot} = \frac{h^2}{8 \pi^2 I} J (J + 1) \quad \text{where } I = \text{moment of inertia, } J = \text{rotational quantum number}]$$

Similarly, $\Delta \epsilon_{vib}$ is in the order of 10^{-13} erg.

$$[E_{vib} = (v + \frac{1}{2}) h \omega \quad \text{where } v = \text{vibrational quantum number, } \omega = \text{frequency of collision}]$$

How much is kT ? At 27°C , kT is in the order of 10^{-14} erg.

Principle of equipartition of energy is valid as long as the colliding molecules can exchange freely the thermal energy between various modes of motion.

This condition is satisfied both for translational and rotational modes of motion as the gap between the adjacent levels is less than kT (at room temperature). Therefore, at room temperature w.r.t. thermal energy, translational and rotational levels can be considered as continuous while vibrational (and electronic) levels can't be considered as continuous. Hence, equipartition principle in general at room temperature is not valid for vibrational modes of motions.

However, the gap between adjacent vibrational levels decreases gradually as the vibrational quantum number increases due to anharmonic oscillation. With increase in temperature the population at higher vibrational level will increase. Hence at higher temperature, the magnitude of kT will be higher than the vibrational energy gap. Thus, at higher temperature equipartition principle is also valid for vibrational levels (but still not for electronic levels).

Thus, at higher temperature equipartition principle is valid for all modes of motion i.e. translational, rotational and vibrational modes of motion.

Heat capacity: (C_p , C_v etc.)

For monoatomic gas:

$$\langle E \rangle = 3 \times \frac{1}{2} k T \times N_A = \frac{3}{2} R T \quad [\text{Average energy per mole}]$$

$$C_v = \left(\frac{dQ}{dT} \right)_v = \frac{dE}{dT} = \frac{3}{2} R$$

$$C_p - C_v = R \quad [\text{Proof will be given in thermodynamics class}]$$

$$\Rightarrow C_p = \frac{5}{2} R$$

$$\Rightarrow \gamma \text{ (heat capacity ratio)} = \frac{C_p}{C_v} = \frac{5}{3} = 1.667$$

For diatomic gas or linear polyatomic gas:

$$C_v = \frac{5}{2} R \quad \text{and} \quad C_p = \frac{7}{2} R \quad [\text{only translational and rotational, no vibrational contribution}]$$

$$\Rightarrow \gamma \text{ (heat capacity ratio)} = \frac{C_p}{C_v} = \frac{7}{5} = 1.4$$

For non-linear polyatomic gas [no vibrational contribution]:

$$C_v = 3R \quad \text{and} \quad C_p = 4R$$

$$\Rightarrow \gamma \text{ (heat capacity ratio)} = \frac{C_p}{C_v} = \frac{4}{3} = 1.33$$

Maxwell Boltzmann Distribution:

The density of air and hence the pressure decreases with altitude due to earth's gravitational field.

Let us consider a vertical column of air of a unit cross-sectional area.

Let us assume pressure at height h is p and at a height $(h + dh)$ is $(p - dp)$

Then $(-)\ dp = \rho\ g\ dh$ [when ρ = density of air at altitude h and at temperature T]

Assuming ideal gas behaviour of a particular gas of molar mass = M (and temperature remaining constant in the column, i.e. average kinetic energy of molecules remains same at different altitudes).

$$(-)\ dp = \rho\ g\ dh = \frac{pM}{RT}\ g\ dh \quad \left[\rho = \frac{M}{V} = \frac{M \cdot p}{R \cdot T} \right]$$

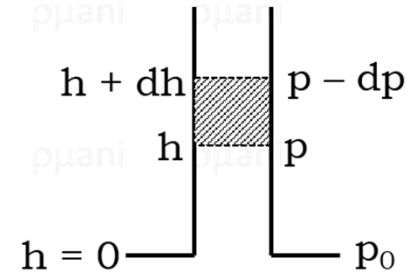
$$\Rightarrow (-)\ \frac{dp}{p} = \frac{M}{RT}\ g\ dh$$

If pressure at height $h = 0$ be p_0 and at height h be p , then

$$\int_{p_0}^p (-)\ \frac{dp}{p} = \frac{Mg}{RT} \int_0^h dh$$

$$\Rightarrow (-)\ \ln \frac{p}{p_0} = \frac{Mg}{RT} h$$

$$\Rightarrow \boxed{p = p_0 \cdot e^{-\frac{Mg}{RT} h}} \Rightarrow \boxed{\text{Barometric formula}}$$



At a given temperature, pressure is proportional to the number of gas molecules,
i.e. $p \propto n$

Thus, the above equation becomes, $\frac{n}{n_0} = e^{-\frac{Mgh}{RT}}$ or $n = n_0 \cdot e^{-\frac{Mgh}{RT}}$

This is (one form of) Boltzmann distribution.

(Mgh) is the potential energy (E_P) of one mole of gas of molar mass M at an altitude h in the earth's gravitational field

Therefore, the fraction of molecules possessing potential energy greater than (or equal to) E_P is given by

$$\frac{n}{n_0} = e^{-\left(\frac{E_P}{RT}\right)} = e^{-\left(\frac{\epsilon_P}{kT}\right)}$$

For Maxwell distribution we know,

$$dn_c = 4\pi n \cdot \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \cdot c^2 \cdot e^{-\frac{mc^2}{2kT}} \cdot dc$$

Combining these two equations we get,

$$dn_c = 4\pi n_0 \cdot \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \cdot c^2 \cdot e^{-\frac{(\epsilon_K + \epsilon_P)}{kT}} \cdot dc \quad \left[\epsilon_K = \frac{1}{2} m c^2\right]$$

$\Rightarrow dn_c = 4\pi n_0 \cdot \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \cdot c^2 \cdot e^{-\frac{\epsilon}{kT}} \cdot dc$, where $\epsilon (= \epsilon_P + \epsilon_K)$ is the total energy of a molecule at a height h . The above equation is known as Maxwell-Boltzmann distribution.

Question: Derive Boltzmann distribution from Maxwell distribution.