

❖ The Stokes-Einstein Relation

Albert Einstein realized that an ion moving in an electrolytic solution is somewhat analogous to a macroscopic sphere moving in a liquid medium. A macroscopic sphere can travel very fast if it is outside of water or any other liquid; however, its velocity will definitely be affected if it is put in some liquid. The reduced velocity of the sphere in liquid can be attributed to an opposing force exerted upon it by the diameter of the sphere (d), viscosity of the medium (η), density of the medium (ρ) and the speed of the ion itself (v). All these factors are correlated mathematically to give “Reynolds number (R_e)” as

$$R_e = vd \frac{\rho}{\eta} \quad (59)$$

If the hydrodynamics has a profile that makes the $R_e \ll 1$, Stokes proved that the dragging force (F) on the sphere can be formulated by the following relation.

$$F = 6\pi r\eta v \quad (60)$$

Which is the famous Stokes’ law.

Now although the equation (60) is very useful in case of a macroscopic sphere moving in water or in any other liquid, the applicability of the same to microscopic ions requires some testing first. One condition that must be satisfied for the practicality of Stokes law to ion in solution is the very small value of Reynolds number i.e. $R_e \ll 1$. After using the ionic diameter and typical drift velocity of ion, it is found that Reynolds number is very small in comparison to unity, and therefore, suggests that Stokes law can be applied to ionic movement. However, equation (60) would show deviations from experimental results if the ions tagged are not completely spherical, and therefore, should be modified for such particles. It has been shown that for cylindrical particles, the factor 6π must be replaced by 4π to get reasonable results. It is also worthy to note that the Stokes law fails to explain the viscous drag on extremely small ions, justifying the need for some other advanced models. Furthermore, besides the viscous drag, the presence of other ions also creates collisions and stop-start zig-zag movement which makes it very difficult to apply Stokes’ law.

Albert Einstein developed a modified approach to correlate the viscosity with the diffusion coefficient by suggesting that a driving force ($-d\mu/dx$) operates on the particles during diffusion which can be formulated as given below.

$$-\frac{d\mu}{dx} = 6\pi r\eta v_d \quad (61)$$

Where v_d is the steady-state velocity of the ion under consideration. The right-hand side of the above equation means that the driving force we assumed must be opposed by an equal and opposite resistive force given by Stokes’ law.

Besides, when a charged particle moves in a polar solvent, solvent dipoles surround it from oppositely charged ends; and this surrounding environment is destroyed and built up again and again due to movement,

and takes time for it. In this relaxation process, a relaxation force is in operation which can be considered as an additional frictional force on the tagged ion. Therefore, the dragging force expression is modified to

$$F = 6\pi\eta vr - 6\pi\eta v \frac{s}{\epsilon} \quad (62)$$

Where $s = (4/9)(\tau/6\pi\eta)e_0^2/r^3$ whereas ϵ represents the dielectric constant of the solvent. The correction factor sometimes can be very large but will be neglected for the simplicity of the derivation Stokes-Einstein law. Now, from the definition of absolute mobility, i.e.,

$$\bar{u}_{abs} = \frac{v_d}{\vec{F}} \quad (63)$$

The drift velocity can be divided either by the diffusional driving force or by the equal and opposite viscous force given by Stokes law. Therefore, using equation (61) in equation (63), we get

$$\bar{u}_{abs} = \frac{v_d}{-d\mu/dx} = \frac{v_d}{6\pi r\eta v_d} = \frac{1}{6\pi r\eta} \quad (64)$$

At this stage, recall the famous Einstein's relation between the absolute mobility and diffusion coefficient, i.e.,

$$D = \bar{u}_{abs} kT \quad (65)$$

Substituting the value of \bar{u}_{abs} from equation (64) in the above expression, we have

$$D = \frac{kT}{6\pi r\eta} \quad (66)$$

Which is the famous Stokes-Einstein's relation between the viscosity and diffusion coefficient.

The Stokes-Einstein relation inspired the pioneering work of Perrin who studied the random walk of a colloidal particle using an ultramicroscope and found that the mean square distance ($\langle x^2 \rangle$) covered in 't' time is correlated with the diffusion coefficient as given below.

$$D = \frac{\langle x^2 \rangle}{2t} \quad (67)$$

From the knowledge of the weight of colloidal particles and corresponding density, the magnitude of radius r can be obtained, which in turn can be employed (along with medium's viscosity) to find the value of Boltzmann constant from the rearranged form of equation (66)

$$k = \frac{6\pi r\eta D}{T} \quad (68)$$

Since $k = R/N_A$, the value of the Avogadro number can be obtained from $N_A = R/k$. Furthermore, the Stokes-Einstein law can also be used to find the value of conventional ionic mobility (\bar{u}_{conv}). To do so, recall the expression for conventional mobility i.e.

$$\bar{u}_{conv} = \bar{u}_{abs} z_i e_0 \quad (69)$$

Now using the value of \bar{u}_{abs} from equation (64), we have

$$\bar{u}_{conv} = \frac{z_i e_0}{6\pi r \eta} \quad (70)$$

The mobility given is typically labeled as Stokes mobility. The physical significance of the above equation lies in the fact that it shows the correlation of conventional mobility with the charge on the ion, radius of the ion and viscosity of the solvent used. It should also be noted that the equation does not explain the concentration dependence of ion-ion interaction, and therefore, is an oversimplified approach.

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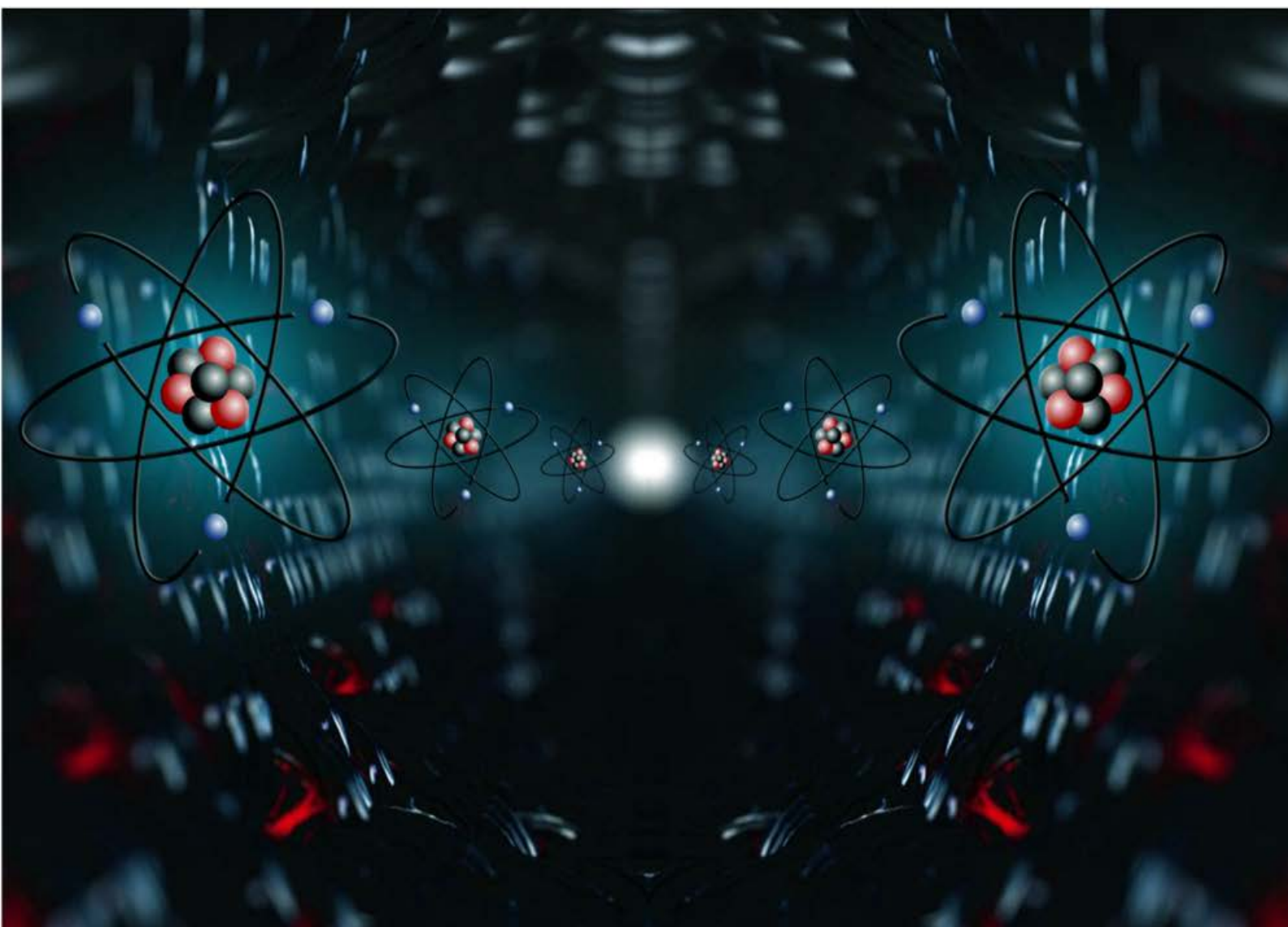
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MANDEEP DALAL



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