Answer on Question #52204-Physics-Molecular Physics-Thermodynamics

a) What do you understand by mean free path of gas molecules? Derive an expression for the law of distribution of free paths.

b) What is Brownian motion? Give three examples of such a motion. Using Einstein's theory, obtain an expression for Einstein's formula for mean square displacement of a Brownian particle.

c) What is the transport phenomenon in gases? Obtain an expression for coefficient of viscosity of a gas if the average number of molecules crossing an area is given by $\Delta n = \frac{1}{4}nv$ and molecules make their last collision before crossing an imaginary surface at a distance of $\frac{2}{3}\lambda$ above or below it.

Solution

a) The mean free path is the average distance traveled by a moving molecule between successive collisions, which modify its direction or energy or other particle properties.

Consider a large number of molecules at a certain instant. As they travel they will collide among themselves and with other molecules. We wish to estimate the number that has not made a collision at some later time. Let the number of molecules surviving a collision in travelling distance r be N. If each molecule is allowed to travel a further distance dx, more collisions will occur. We assume that the number of collisions is proportional to the number of molecules N, and the distance dx. That is, the number of molecules removed by these collisions will be proportional to Ndx. Since the number of molecules decreases with increasing distance, we can write

$$dN = -P_c N dx$$

where P_c is a constant of proportionality and is called the Collision probability. One can rewrite the above equation as

$$\frac{dN}{N} = -P_c dx$$

This can be integrated to

$$N = N_0 e^{-P_c x}$$

where N_0 is the number of molecules at $x = 0$.

From this equation we find that number of molecules surviving a collision decreases exponentially. Further, the probability that a gas molecule will cover a distance x without making any collision is

$$\frac{N}{N_0} = f(x) = e^{-P_c x}.$$

This is the law of distribution of free paths.

$P_c = \frac{1}{l}$, where l is mean free path.

Thus

$$\frac{N}{N_0} = e^{-\frac{x}{l}}.$$

b) Brownian motion is the random movement of microscopic particles suspended in a liquid or gas caused by their collision with the quick atoms or molecules in the surrounding medium. Three examples of such a motion: motion of pollen grains in water, diffusion of "holes" through a semiconductor, motion of smoke in a glass box.

Let us obtain an expression for Einstein's formula for mean square displacement of a Brownian particle. When Brownian particle is move the net force F acts on it. Also on particle acts the friction force f caused by the medium viscosity and directed opposite to the force F.

Let us suppose that the particle has a spherical shape of radius a. Then the friction force f can be expressed by the Stokes' law:

$$f = 6\pi\eta a v,$$

where, η is the dynamic viscosity, v is the velocity of the particle.

So, we can write the equation of motion of the particle:

$$m\ddot{r} = F - 6\pi\eta a\dot{r}, (1)$$

where, m is a mass of the particle, r is the radius-vector of the particle relative to an arbitrary coordinate system, $\dot{r} = v$ is the velocity of the particle.

Let us consider the projection of the radius-vector on the axis X. Then the equation (1) looks like:

$$m\ddot{x} = F_x - 6\pi\eta a\dot{x}, (2)$$

where, F_x is the projection of the net force F on the axis X.

We need to obtain the displacement of the Brownian particle x, which caused by the collisions with the molecules. Mean displacement of the particle $\overline{x}$ would be equal to zero, because the displacements of the particle with equal probability can have both positive and negative values. But the mean square displacement $\overline{x^2}$ is not equal to zero, and we can rewrite the equation (2) so that it includes the value of x^2 (we multiply both sides of the equation on x):

$$mx\ddot{x} = F_x - 6\pi\eta a x\dot{x}. (3)$$

Let us use the next identities:

$$x\ddot{x} = \frac{1}{2}\frac{d^2(x^2)}{dt^2} - \left(\frac{dx}{dt}\right)^2, x\dot{x} = \frac{1}{2}\frac{d(x^2)}{dt}.$$

Substituting these identities into the equation (3) we obtain:

$$\frac{m}{2}\frac{d^2(x^2)}{dt^2} - m\left(\frac{dx}{dt}\right)^2 = -3\pi\eta a\frac{d(x^2)}{dt} + xF_x.$$

This equality is valid for any particle and because of that it is also valid for mean values that includes in it, so we can write:

$$\frac{m}{2}\frac{d^2\left(\overline{x^2}\right)}{dt^2} - m\overline{\left(\frac{dx}{dt}\right)^2} = -3\pi\eta a\frac{d\left(\overline{x^2}\right)}{dt} + \overline{xF_x}.$$

where $\overline{x^2}$ is the mean square displacement of the particle, $\overline{\left(\frac{dx}{dt}\right)^2}$ is the mean square velocity of the particle, the mean value of $\overline{xF_x}$ is equal to zero because for a large number of particles x and F_x equally takes both positive and negative values. Therefore, the equation (2) takes the next form:

$$\frac{m}{2}\frac{d^2\left(\overline{x^2}\right)}{dt^2} - m\overline{\left(\frac{dx}{dt}\right)^2} = -3\pi\eta a\frac{d\left(\overline{x^2}\right)}{dt}\,(4)$$

Because the motion of the particles is quite chaotic, then the mean squares velocity projections on all three coordinate axes must be equal to each other:

$$\overline{\left(\frac{dx}{dt}\right)^2} = \overline{\left(\frac{dy}{dt}\right)^2} = \overline{\left(\frac{dz}{dt}\right)^2}.$$

Also obvious, that the sum of this values must be equal to the mean square velocity of the particles $\overline{v^2}$:

$$\overline{\left(\frac{dx}{dt}\right)^2} + \overline{\left(\frac{dy}{dt}\right)^2} + \overline{\left(\frac{dz}{dt}\right)^2} = \overline{v^2}.$$

Therefore, we obtain:

$$\overline{\left(\frac{dx}{dt}\right)^2} = \frac{1}{3}\overline{v^2}$$

$$m\overline{\left(\frac{dx}{dt}\right)^2} = \frac{1}{3}m\overline{v^2} = \frac{2}{3}\frac{m\overline{v^2}}{2}.$$

Because the average kinetic energy of the Brownian particle must be equal to the average kinetic energy of the molecules of liquid (or gas), we can write:

$$\frac{m\overline{v^2}}{2} = \frac{3}{2}kT$$

$$m\overline{\left(\frac{dx}{dt}\right)^2} = \frac{2}{3}\frac{m\overline{v^2}}{2} = kT\ (5).$$

Substituting the equation (5) into the equation (4) we obtain:

$$\frac{m}{2}\frac{d^2\left(\overline{x^2}\right)}{dt^2} - kT = -3\pi\eta a\frac{d\left(\overline{x^2}\right)}{dt}.$$

This equation can be easily integrated. Let us denote $Z = \frac{d\left(\overline{x^2}\right)}{dt}$ and rewrite the equation:

$$\frac{m}{2}\frac{dZ}{dt} - kT = -3\pi\eta a Z.$$

After separation of variables we obtain:

$$\frac{dZ}{Z - \frac{kT}{3\pi\eta a}} = -\frac{6\pi\eta a}{m}dt.$$

Integrating the left-side of the equation within the limits from 0 to Z and the right side of the equation within the limits from 0 to t we get:

$$\int_0^Z \frac{dZ}{Z - \frac{kT}{3\pi\eta a}} = -\int_0^t \frac{6\pi\eta a}{m}dt$$

$$\ln\left(Z - \frac{kT}{3\pi\eta a}\right) - \ln\left(-\frac{kT}{3\pi\eta a}\right) = -\frac{6\pi\eta a}{m}t.$$

From this equation we can find Z:

$$Z = \frac{kT}{3\pi\eta a}\left(1 - e^{-\frac{6\pi\eta a}{m}t}\right) = \frac{d\left(\overline{x^2}\right)}{dt}.$$

The value of $e^{-\frac{6\pi\eta a}{m}t}$ is negligible, so we can write:

$$\frac{d\left(\overline{x^2}\right)}{dt} = \frac{kT}{3\pi\eta a}\ (6).$$

For the finite time intervals Δt and appropriate displacements $\Delta\overline{x^2}$ the equation (6) takes form:

$$\frac{\Delta\overline{x^2}}{\Delta t} = \frac{kT}{3\pi\eta a}.$$

Finally, we obtain an expression for Einstein's formula for mean square displacement of a Brownian particle:

$$\Delta\overline{x^2} = \frac{kT}{3\pi\eta a}\Delta t.$$

c) We have been able to relate quite a few macroscopic properties of gasses such as P, V, T to molecular behavior on microscale. We saw how macroscopic pressure is related to the molecular motion in case of perfect gasses. Is there anything else interesting one can learn from the kinetic theory of perfect gasses? Indeed there is.

So far we only considered macroscopic properties that can be termed as static. We shell now look at some properties that are not. Collectively they are termed transport phenomena and can be further subdivided in:

•Diffusion – molecular transport due to concentration gradients

•Thermal conduction – transport of energy

•Viscosity – transport of momentum

These are described by their corresponding coefficients: D for diffusion, K for thermal conduction and η for viscosity.

At a height $\frac{2}{3}\lambda$ above the surface, the flow velocity of the gas molecules will be $u + \frac{2}{3}\lambda\frac{du}{dy}$, where u is flow velocity at the surface. The momentum transported by a molecule moving with this velocity will be $m\left(u + \frac{2}{3}\lambda\frac{du}{dy}\right)$. So, the total momentum in direction of the flow carried across the surface per unit area per unit time by all the molecules crossing the surface from above will be

$$G^+ = \frac{1}{4}nvm\left(u + \frac{2}{3}\lambda\frac{du}{dy}\right).$$

Similarly, the total momentum flow carried across the surface per unit area per unit time by the molecules crossing it in upward direction from below will be

$$G^{-} = \frac{1}{4} nvm \left(u - \frac{2}{3} \lambda \frac{du}{dy} \right).$$

Hence, the net transport of momentum across the surface from below in the direction of mass motion per unit area per unit time, which is equal to the viscous force per unit area, is given by

$$G = G^{-} - G^{+} = -\frac{1}{3} mnv\lambda \frac{du}{dy}.$$

The coefficient of viscosity of a gas is given by

$$\eta = \frac{1}{3} mnv\lambda = \frac{1}{3} \rho v\lambda.$$