

CHAPTER II



EINSTEIN'S THEORY

Macroscopic thermodynamics (3) is known not to base on atomic model in deriving its principles. Microscopic thermodynamics explains a phenomenon on the basis of statistical mechanics and Einstein's theory (1) demanded this molecular statistical picture. Einstein first showed that, in molecular kinetic theory of heat aspect ; solute molecules dissolved in a liquid and small suspended particles in the liquid behave identically in producing osmotic pressure (11) at great dilution, where as pure thermodynamics cannot give this result.

Next, he derived the diffusion coefficient of suspended particles D of spherical shape of radius a in liquid, on the basis that, the diffusion of these particles comes about by the irregular pushing action of the liquid molecules on the particles. He obtained the relation

$$D = \frac{kT}{6\pi\eta a} \quad ; \quad k = \frac{R}{N}$$

where k is the Boltzmann's constant, R the universal gas constant, N the Avogadro Number, η the viscosity of liquid and T the temperature of liquid.

Because of the statistical nature of Brownian motion, he derived for $f(x,t)$ the statistical distribution of number of particles per unit volume at position x and time t . Let the liquid has unit cross-sectional area perpendicular to the x -axis, from the diffusion equation.

$$\frac{\partial f(x,t)}{\partial t} = D \frac{\partial^2 f(x,t)}{\partial x^2}$$

He obtained

$$f(x,t) = \frac{n}{(4\pi D)^{1/2}} \frac{e^{-x^2/4Dt}}{\sqrt{t}}$$

where n is the total number of small suspended particles. The distribution $f(x,t)$ permitted him to calculate the mean square displacement in x -direction as

$$\lambda_x = (\overline{x^2})^{1/2} = \left\{ \frac{1}{n} \int_{-\infty}^{\infty} f(x,t) x^2 dx \right\}^{1/2} = \sqrt{2Dt}$$

Later, he generalized the previous results which considered only the translatory motion. He used more general method to develop the formula for the translational and the rotational movement in a single discussion. The method is supposing α to be a measurable parameter of a system which is in thermal equilibrium. Pure thermodynamics gives no reason why α should not remain constant, where as molecular kinetic theory of heat can explain the necessary change of α . He assumed that under the influence of the force $-\partial\phi/\partial\alpha$, the parameter α changes similarly to a heavy sphere in viscous fluid.

$$\Delta = -B(\partial\phi/\partial\alpha)t$$

where B is the mobility of the system with respect to α , Δ the change in α and ϕ the potential of force acting on the particle. He obtained by the laws of statistics, the relation

where $(\overline{\Delta^2})^{1/2}$ is the mean square change in α produced by irregular thermal

$$(\overline{\Delta^2})^{1/2} = (2kTBt)^{1/2}$$

process. This is the required general formula for the translatory and rotational motion of a suspended particle. For the translatory motion, from

$$B_t = \frac{1}{6\pi\eta a}$$

He got

$$(\overline{\Delta_t^2})^{1/2} = \left\{ \frac{2kTt}{6\pi\eta a} \right\}^{1/2} = (2Dt)^{1/2}$$

where B_t and $(\overline{\Delta_t^2})^{1/2}$ are the mobility for translatory motion and the root mean square translatory displacement of the particle. We can see that the result obtained is the same as the previous value λ_x , where as for the rotational motion, the corresponding formula becomes

$$(\overline{\Delta_r^2})^{1/2} = \left\{ \frac{kTt}{4\pi\eta a^3} \right\}^{1/2} \quad ; \quad B_r = \frac{1}{8\pi\eta a^3}$$

where B_r and $(\overline{\Delta_r^2})^{1/2}$ are the mobility for rotational motion and the root mean square angular displacement of the particle. He concluded from these results that the thermal rotation of the particle decreased, with increasing a , much faster than the translatory motion.

In the next chapters, we will concern more general and rigorous analysis using Langevin and Fokker-planck equations in obtaining the average displacement and velocity of Brownian particle.