

Relation of Tyndall effect to osmotic pressure in colloidal solutions

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1. Introduction

Recent investigations have shown clearly* that the scattering of light in ordinary liquids arises from the local fluctuations in optical density due to molecular agitation. The simple Rayleigh theory of scattering, in which each molecule is regarded as an independent scattering particle, is valid only in the special case of an ideal gas and ceases to be applicable when, as in dense fluids, it is no longer permissible to postulate an absolutely chaotic ordering of the molecules in space. Likewise, in fluid mixtures and solutions,† the scattering observed is found to be due to local fluctuations of density and concentration and the varying orientations of the molecules. In view of these successes of the fluctuation theory in the region of molecular optics, it appears natural to apply it also in the field of colloid optics. Colloidal solutions often contain particles so numerous and finely divided that the Tyndall cone cannot be resolved into discrete specks of light and is very similar in general appearance to that observed in strongly scattering molecular solutions. Even when the separate particles can be resolved by the ultra-microscope, it does not follow that it would necessarily be justifiable to treat them as independent sources of scattered radiation. It must be remembered that the particles are only secondary sources scattering the same primary waves, and hence their aggregate effect is to be determined in accordance with the principles of interference and not by simple addition of intensities. The resultant effect may be greater than, equal to, or less than that of the individual particles taken separately, depending entirely on the distribution of the particles in space.

An excellent illustration of the effects of interference in colloid optics is furnished by the recent observations of Sogani‡ on the halos exhibited when a source of light is viewed through a chromatic emulsion which had been homogenized by settlement. He found that the source of light viewed through the emulsion appeared surrounded by sharply defined diffraction rings separated by

*C V Raman, *Molecular Diffraction of Light*, Calcutta University Press, Feb. 1922.

†C V Raman and K R Ramanathan, *Philos. Mag.* 1923, 45, 213.

‡C M Sogani, *Philos. Mag.* 1926, I, 321.

dark spaces; the emulsion, in fact, gave rise to effects which were analogous to those produced by a diffraction-grating and so were clearly due to a regularity in the space-grouping of the particles contained in it.

When the mean distance between neighbouring particles is sufficiently small, diffraction-rings will not arise, but the total intensity of the scattered light will be determined by the character of the space-grouping of the particles. If they are arranged with a high degree of regularity, the intensity of the Tyndall cone will be small, while on the other hand if they tend to form clusters or groups, the Tyndall effect would be greatly increased. The principle of interference, in fact, when applied to the determination of the aggregate effect of separate scattering particles, leads to results practically identical with those obtained from the application of the fluctuation theory to a *continuous* optical medium. Thus, there is reason to think that at least in the case of solutions in which the dispersed material exists in the form of very fine and numerous particles, the phenomena of colloid optics should show close analogies to those observed in molecular scattering of light and that we can apply to them thermodynamic reasoning of the same type.

2. Relation to osmotic pressure

The most convenient approach to the theory of fluctuations in a colloidal solution is by way of the osmotic pressure, which it may be remarked, also plays a fundamental role in Einstein's theory of the Brownian movement. We proceed to

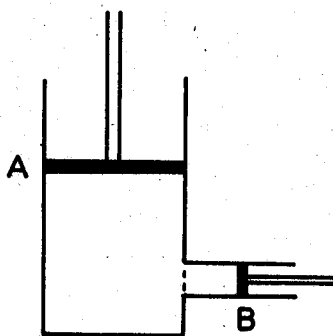


Figure 1

evaluate the work necessary to change the masses m_1 and m_2 respectively of the dispersal medium and the dispersed material present in unit volume of the solution, in an isothermal and reversible manner. This may be done in the following way. Consider a cylinder of very large volume with a small side-tube attached to it. The solution is enclosed between the two pistons A and B , the latter

being in the side-tube. Initially the whole solution is at uniform concentration and at atmospheric pressure, the pistons *A* and *B* being assumed to be held at rest by suitable external forces. The cylinder and side-tube are then separated by a semi-permeable septum through which only the dispersal medium can pass. The volume of solution present in the side-tube is initially taken to be unity. The piston *B* is then pushed in to an infinitesimal extent, and the piston *A* correspondingly pushed out so as to diminish the volume in the side-tube by Δv , and the mass of the dispersal medium present in it by Δm_1 . We write $\Delta m_1 = \rho_k \Delta v$. The concentration $k = m_2/m_1$ of the dispersed phase is increased in this process by Δk , and the resultant work done in this process is

$$\begin{aligned} \frac{1}{2} \frac{\partial P}{\partial k} \cdot \Delta k \cdot \Delta v &= \frac{1}{2} \frac{\partial P}{\partial k} \cdot \frac{m_1}{k \rho_k} (\Delta k)^2 \\ &= \frac{1}{2} \alpha (\Delta k)^2 \text{ (say)} \end{aligned} \quad (1)$$

where P is the osmotic pressure of the solution.

The semi-permeable septum is then replaced by a rigid and impermeable septum and the piston *B* is further pushed so as to compress the solution to an infinitesimal extent, the piston *A* being at the same time allowed to move at constant pressure so as to keep the total volume of the solution constant. The work done in this process is

$$\frac{1}{2} \beta (\Delta p)^2 \quad (2)$$

where β is the compressibility of the solution and Δp the increase of pressure in the side-tube produced by the compression. The total work done is thus

$$\left[\frac{1}{2} \alpha (\Delta k)^2 + \frac{1}{2} \beta (\Delta p)^2 \right]. \quad (3)$$

Following an argument very similar to that used in the paper on liquid mixtures by Raman and Ramanathan cited above, it is easily shown that in a direction at right angles to the incident beam, assumed to be unpolarised and of unit intensity, the intensity of the scattered light is

$$I = \frac{\psi}{r^2} \cdot \frac{\pi^2 RT}{2N\lambda^4} \cdot \left\{ \left(\frac{\partial \epsilon}{\partial k} \right)^2 / \alpha + \left(\frac{\partial \epsilon}{\partial p} \right)^2 / \beta \right\} \quad (4)$$

where ψ is the volume of the solution scattering light, r = the distance from it of the receiving screen, R/N = Boltzmann's constant, ϵ = the optical dielectric constant of the solution, $\alpha = (\partial p / \partial k) \cdot m_1 / k \rho_k$, β = compressibility of solution, ρ_k = reciprocal of shrinkage of volume of solution by removal of unit mass of dispersal medium, p = hydrostatic pressure and λ = the wavelength.

Instead of expressing the scattering in terms of the osmotic pressure of the dispersed material, we can of course, also express it in terms of the vapour pressure of the dispersal medium. For this purpose, we alter the concentration by evaporating a mass Δm_1 of the dispersal medium from a large volume of solution, and then condense the vapour isothermally and reversibly into a unit volume of solution and thus lower its concentration. The work gained in the first part of the process is

$$p(v - 1/\rho_k) \cdot \Delta m_1$$

where p is the pressure and v the specific volume of the vapour. In the second-half of the process, the work to be done would be

$$p(v - 1/\rho_k) \Delta m_1 + \frac{1}{2} \frac{\partial p}{\partial k} \cdot (v - 1/\rho_k) \cdot \Delta m_1.$$

The difference between the works done would be thus

$$\frac{1}{2} \left(- \frac{\partial p}{\partial k} \right) \cdot (v - 1/\rho_k) m_1 / k \cdot (\Delta k)^2.$$

We thus obtain as an alternative expression for α in (4)

$$\alpha = \left(- \frac{\partial p}{\partial k} \right) (v - 1/\rho_k) m_1 / k. \quad (6)$$

From equation (4), we see that the scattering consists of two parts, the first being due to fluctuations of concentration and the second due to fluctuations of density. The latter is inversely proportional to the compressibility of the solution, and in colloidal solutions should usually be quite negligible in comparison with the first. As in the theory of molecular scattering, we should also have to include a third type of scattering, which, unlike the two considered above, is practically *unpolarised* and is caused by the varying orientations of the molecules of the dispersal medium and of the colloidal particles. If the latter are highly unsymmetrical in shape, this term would be important, even when the particles are very finely dispersed.

Our equations (4) and (6) will be found to become identical with those given by Raman and Ramanathan in the paper on liquid mixtures already cited, when one of the components is assumed to be non-volatile. In making the comparison, it should be remembered that we have taken the concentration k to be the ratio of the mass of the non-volatile to the volatile component, while in the paper of Raman and Ramanathan, it is the reciprocal of this quantity that is denoted by k .

In another paper, we shall consider the application of the foregoing theory to the explanation of the optical behaviour of various actual colloids, of the influence of coagulating and peptising agents on the Tyndall effect, and specially

the influence of hydrogen-ion-concentration, temperature and other factors on the opalescence of protein solutions.

3. Summary

In this paper, it is proposed to apply the theory of fluctuations to the elucidation of the optical behaviour of colloidal solutions. It is pointed out that the treatment usually given, in which each particle is regarded as an independent source of scattered radiation, is based on the assumption of a completely random distribution of the dispersed material in space; such an assumption would not always be valid. An expression is derived from the light-scattering power in terms of the variations of osmotic pressure and refractive index with concentration.

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