THE SCATTERING OF LIGHT AND ITS APPLICATIONS TO CHEMISTRY

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CONTENTS

I. INTRODUCTION

When a beam of light falls upon matter, the electric field associated with the light induces periodic oscillations of the electrons in the material. The material then serves as a secondary source of light and radiates light in the form of scattered radiation with a wave length equal to that of the incident light.[1] The intensity, polarization, angular distribution, and fine structure of the scattered radiation are determined by the size, shape, optical constants, and interactions of the molecules in the scattering material. Conversely, from a knowledge of the light-scattering properties of a given system, the chemist can, with the aid of the electromagnetic theory of radiation and the kinetic theory of matter, obtain a detailed molecular picture of that system.

The use of light scattering to study molecular systems has the added advantage that the system under study is not affected by the measurement (except in the rare instances in which the incident light induces photochemical changes) and that changes in the system which take place rapidly can be easily followed.

In this review no attempt will be made to discuss all the problems to which light scattering has been (or could be) applied, since such a discussion would

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[1] In this paper we shall not consider the relatively small amount of light which is re-emitted with an altered wave length when the molecules are raised to higher energy states by the incident light, i.e., the Raman effect (compare Section III,5).

encompass nearly every branch of science. We shall, instead, confine ourselves to the physical principles of light scattering and to the chemical problems to which it has been applied and shall indicate some further possible uses for it in the field of chemistry.

II. INDEPENDENT PARTICLES

Independent particles are defined as particles located randomly in space, as are molecules in a perfect gas or solute molecules in an ideal solution. For a system of independent particles, the intensity of the light scattered is the sum of the contributions from each of the scattering particles of the system. Since the particles are randomly disposed, the light scattered by any one particle bears no fixed relationship to that for any other particle, i.e., there is incoherent scattering, and the total intensity of scattered light is the sum of the intensities from all the particles. If, however, the scattering elements lie close together in a regular array, as in a perfect crystal at zero absolute temperature, there is destructive interference between the scattered wavelets because of the fixed phase relationships, i.e., there is coherent scattering, and the intensity of scattered light is zero. Because of the imperfect correlation which exists between the positions of molecules in a liquid, a liquid will scatter light with intensity intermediate between that for the same weight of a gas and that for a crystal.

In the case of particles which possess a linear dimension comparable to or greater than the wave length of incident light, the scattering from different parts of the same particle must be considered. Because there are fixed phase relationships between the wavelets scattered from the scattering elements of the same particle, there is for large particles some destructive interference with a consequent decrease in efficiency of scattering. Nevertheless, the intensity of light scattered by a system of large particles randomly disposed will be the sum of the contributions of the light scattered from each of the particles.

A. SMALL PARTICLES

1. Isotropic particles

Lord Rayleigh in 1871 (172) laid the foundation of light scattering by his application of electromagnetic theory to the problem of light scattering by molecules in a gas. He subsequently (173) used his results to account for the observed intensity, color, and polarization of light from the sky. According to Rayleigh (172, 173) the oscillating electric field of the light incident upon a transparent optically isotropic particle whose radius is small compared with the wave length of the light induces an oscillating electric moment in the particle. The particle, acting as a linear electrical oscillator, does not radiate light in the direction of the vibrations. Along other directions, however, it radiates light and the scattered light is perfectly plane polarized when viewed at right angles to the incident beam whether the incident light is polarized or unpolarized. The first detailed observations on the polarization of scattered light were made by Tyndall (208).

The character of the scattered light from particles small compared with the wave

length of the incident light is given by the formula for the intensity of radiation from a Hertzian dipole antenna which is derived in most textbooks of theoretical physics (see, for example, Slater and Frank (190, Chapter 25)). It is shown that the intensity of scattered light is proportional to the inverse fourth power of the wave length. Thus, when white light is made to fall on a system of such particles, the blue component of the white light is scattered much more than is the red; and the system has a blue color when viewed at right angles to the incident beam of light. When viewed in the direction of the transmitted beam, the system appears yellow in color since the blue component has been removed by scattering.

The complete equation for the intensity of light scattered by ν (per unit volume) independent small isotropic scatterers is derived in detail in treatises on electromagnetic theory (Born (19, Chapter 7, Section 81); Stratton (199, Chapter 8, Section 8.5 and Chapter 9, Section 9.27)) and is given by

$$\frac{i}{I} = \frac{8\pi^4 \nu \alpha^2}{\lambda'^4 r^2} (1 + \cos^2 \theta) \tag{1}$$

i is the intensity of scattered light per unit volume of the scattering system, I is the intensity of the incident beam, r is the distance of the observer from the scattering system, θ is the angle between the observer and the proceeding incident beam, λ' is the wave length of the light falling on the particles ($\lambda' = \lambda/n_0$, where λ is the wave length of light incident upon the system and n_0 is the index of refraction of the medium), and α is the polarizability or induced dipole moment per unit electrical field strength of the small isotropic particles. Equation 1 is for unpolarized incident light; the $\cos^2 \theta$ term in the parentheses refers to the component of the scattered light whose electric vector lies in the plane defined by the incident and scattered beams (the plane of the page in figure 1) and the unity term in the parentheses refers to the component of the scattered light whose electric vector is perpendicular to this plane. Figure 1 shows the angular distribution of intensity and polarization of the light scattered from a small isotropic scatterer. The scatterer is at the origin, and the length of the line drawn from the origin to a point on the curve is proportional to the intensity of scattered light. The dotted curve refers to the $\cos^2 \theta$ term, that is, to the component which is horizontally polarized, and the outer curve refers to the component which is vertically polarized. It is seen from figure 1 that the light scattered at 90° is completely vertically plane polarized. The total intensity of scattered light is the sum of the horizontally and vertically polarized components given by equation 1. The spacial distribution of the intensity of the scattered light is given by the surface formed by rotating the curves in figure 1 about the vertical axis.

When a beam of light traverses a light-scattering system, its intensity is decreased by virtue of the energy withdrawn from the beam in the form of scattered radiation. The energy lost is given by the time average of Poynting's vector integrated over the surface of a sphere of radius r. For small isotropic scatterers the angular intensity distribution is symmetrical; i.e., the intensity of scattered light in the forward directions is equal to that in the backward directions, and

the fractional decrease in intensity of the incident light scattered in all directions can be calculated. The logarithm of the fractional decrease in transmitted intensity, I, is given by the turbidity τ (also called the attenuation or extinction coefficient due to scattering) where $I = I_0 e^{-\tau l}$ and l is the path length in the scattering system. Such a calculation (Born (19, page 377); Stratton (199, page 436)) shows that for i perpendicular to the incident beam ($\theta = 90°$)

$$\tau = \frac{16}{3} \pi r^2 \frac{i}{I} \tag{2}$$

and on combining with equation 1 we obtain for the turbidity:

$$\tau = \frac{128\pi^5 \nu \alpha^2}{3\lambda'^4} \tag{3}$$

Since by equation 3 the turbidity for independent particles is proportional to the number of particles per unit volume, ν, equation 3 is a statement of Beer's law where the attenuation in intensity of the incident light is due to scattering.
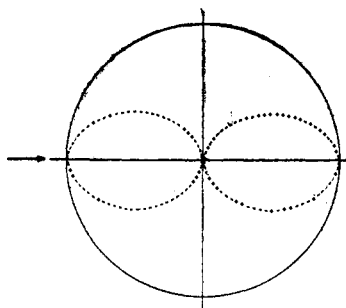

FIG. 1. Angular scattering diagram for small isotropic particle (dipole scattering). See text for explanation.

The polarizability of an isotropic molecule is proportional to the volume of the molecule; therefore from equations 1 and 3 the intensity of scattering is proportional to the number concentration, ν, of the particles and the square of their volumes. Because of the strong dependence of the intensity of scattering on the volume of the particles, it is important in scattering measurements to eliminate large extraneous particles (usually dust) which scatter a considerable amount of light even though they are present in relatively small concentrations. The practically complete elimination of dust particles in gases for light-scattering studies was first achieved by Cabannes in 1915 (23).

In order to relate equations 1 and 3 to experimental quantities, it is necessary to introduce the optical constants of the system. For a mixture of ν isotropic particles (per unit volume) of polarizability α immersed in a medium of optical dielectric constant ϵ_0 (the optical dielectric constant of transparent material is equal to the square of its refractive index) the following relation holds

$$\frac{\epsilon - \epsilon_0}{\epsilon_0} = 4\pi\nu\alpha \tag{4}$$

where ϵ is the optical dielectric constant of the mixture. Equation 4, which is due to Maxwell (see Jeans (90a, Chapter 5)), is valid regardless of the shape of the isotropic particles and requires no assumptions concerning the electric field on the particles (the local field). Inserting equation 4 into equations 1 and 3, we obtain for the intensity (per unit volume) and turbidity of the small isotropic particles (note that $\lambda = n_0\lambda'$)

$$\frac{i}{I_0} = \frac{\pi^2(\epsilon - \epsilon_0)^2}{2\lambda^4 \nu r^2} (1 + \cos^2 \theta) \tag{5}$$

and

$$\tau = \frac{8\pi^3(\epsilon - \epsilon_0)^2}{3\lambda^4 \nu} \tag{6}$$

Cabannes (24) has made quantitative measurements on the intensity of light scattered by argon. He was able to determine the number of gas molecules per unit volume, ν, from equation 5 where $\epsilon_0 = 1$ (empty space). Since $\nu = Nc/M$, where N is Avogadro's number, c the weight concentration, and M the molecular weight, Cabannes obtained a value for Avogadro's number.

Inserting Nc/M for ν in equations 5 and 6 we obtain expressions relating the intensity of scattering (per unit volume) and the turbidity to the molecular weight of the scatterers, or

$$\frac{i}{I_0} = \frac{\pi^2 Mc}{2\lambda^4 r^2 N} \left(\frac{\epsilon - \epsilon_0}{c}\right)^2 (1 + \cos^2 \theta) \tag{7}$$

and

$$\tau = \frac{8\pi^3 Mc}{3\lambda^4 N} \left(\frac{\epsilon - \epsilon_0}{c}\right)^2 \tag{8}$$

The specific dielectric increment, $\epsilon - \epsilon_0/c$, may be expressed in terms of the specific index of refraction increment, $n - n_0/c$, where n and n_0 are the indices of refraction of the mixture and medium, respectively, by

$$\frac{\epsilon - \epsilon_0}{c} = \frac{n^2 - n_0^2}{c} \simeq \frac{\partial n^2}{\partial c} \simeq 2n_0 \left(\frac{n - n_0}{c}\right) \tag{9}$$

For most substances the specific index of refraction increment is a constant independent of the concentration and depends on the index of refraction of the solute and of the medium. In the extreme case in which the index of refraction of the medium is equal to that of the solute, the refractive index increment is zero and no scattering will take place. The index of refraction of isotropic solute particles may be determined by adjusting the refractive index of the medium until no scattering occurs (Heller (84)).

Putzeys and Brosteaux (154, 155) have determined the relative intensity of scattering from dilute solutions of a few proteins. They found that the intensities were proportional to the known molecular weights of these proteins, in agreement with equation 7. By their studies, Putzeys and Brosteaux were the first

to establish the light-scattering method as a useful means of determining the molecular weights of large molecules in solution. Putzeys and Brosteaux (155) also determined the pH stability range of some proteins by measuring the relative intensity of scattering as a function of pH. In principle, they could have determined the absolute molecular weights from equation 8. In order to use this equation, however, it is necessary to know the volume of the scattering sample and the distance, r, very accurately. On the other hand, the absolute value of the turbidity can, for a sufficiently turbid sample, conveniently be measured in a colorimeter or spectrophotometer and only the thickness of the sample need be known (see below).

From equation 8, using the approximation of equation 9, the molecular weight of the small isotropic colorless solute particles is related to the turbidity for very dilute solutions (the turbidity of the solvent is subtracted) by

$$M = \frac{\tau}{Hc} \tag{10}$$

where

$$H = \frac{32\pi^3 n_0^2}{3N\lambda^4} \left(\frac{n - n_0}{c}\right)^2$$

Equation 10 is essentially Rayleigh's equation (equation 3) and is the result obtained from the more general expression due to Einstein (48) (see Debye (32, 33, 34) and Section III,2 of this paper), by extrapolating to infinite dilution. According to equation 10, the molecular weight of small isotropic particles can be determined from a knowledge of (1) the turbidity of a dilute solution of the material, (2) the concentration of the solution, and (3) the specific index of refraction increment.

An application of equation 10 was the determination of the molecular weights of tomato bushy stunt virus and influenza virus by the use of a spectrophotometer (Oster (138)). It was necessary to determine the turbidity as a function of wave length so as to use the turbidity in that wave-length region where the inverse fourth power of the wave-length relationship of Rayleigh was obeyed. The particles were large enough to give intense scattering where Beer's law was obeyed, so that the solutions were ideal. In figure 2 are shown the results for very dilute solutions of tomato bushy stunt virus. The turbidity given in terms of the optical density, D ($\tau = 2.303D$), obeys Rayleigh's inverse fourth power law over the visible range, but at shorter wave lengths there is real light absorption due to the presence of ultraviolet-absorbing chemical groups. The molecular weight calculated from the slopes of the curves, together with the index of refraction increments, gave values for the virus particles in agreement with those determined by other methods. The turbidity of the pure solvent is automatically taken care of when the turbidity of the solvent is taken as the zero reading in a spectrophotometer. The light-scattering method gives the molecular weights of the dry protein, since the water of hydration of the protein has nearly the same index of refraction as the solvent water. Recently Bardwell and

Sivertz (9) have determined the size of latex particles by the spectrophotometric method and obtained results in agreement with other methods.

The equations given above and the cases to which they were applied are those of monodispersed systems. Frequently, for high-polymeric and colloidal solutions, one does not deal with monodispersed systems. For a polydispersed system of ν_j (per unit volume) small isotropic particles of volume v_j, equation 3 for the turbidity is given by

$$\tau = A \sum_j \nu_j v_j^2 \tag{11}$$

where A is a function of the wave length and the proportionality constant (a function of the index of refraction) between the polarizability and the volume
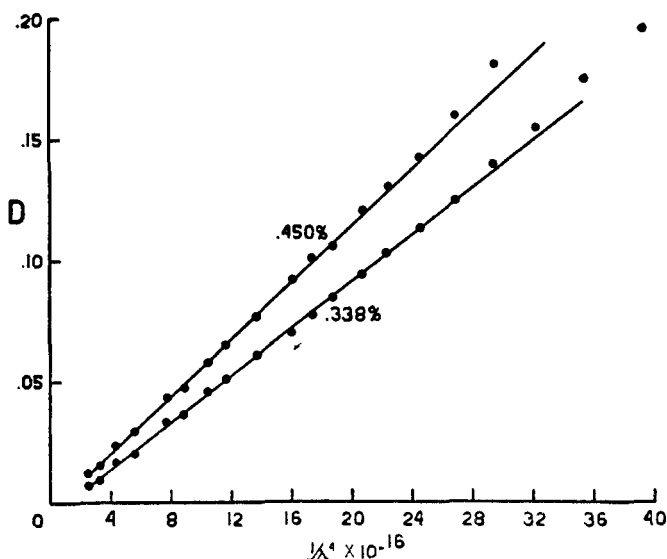

FIG. 2. Optical density as a function of inverse fourth power of the wave length for bushy stunt virus in water (Oster (138)).

of the particles (see equation 18). Equation 11 may be used to obtain an expression for the turbidity as a function of time for some kinetic processes. For a solution of high-polymeric molecules or colloidal particles in which polymerization or coagulation is taking place, the system at any instant is polydispersed. If we know the number of j-mers, ν_j, as a function of time we can calculate the change in light scattering with time for the polymerization or coagulation process (Oster (139)). Since the volume of the j-mers is j times the volume of the monomers, v_0, equation 11 becomes

$$\tau = A v_0^2 \sum_j j^2 \nu_j \tag{12}$$

The problem is now reduced to the mathematical one of evaluating the sum where ν_j is known for various polymerization and coagulation processes. Calculation shows (139) that (a) in linear condensation polymerization, the turbidity

(or intensity of scattering) increases linearly with time with a slope determined by the rate constant of the elementary step reaction, (b) in depolymerization of linear polymers, the turbidity decreases with time as the hyperbolic cotangent of the time, (c) in addition polymerization, the turbidity increases quadratically in time with a curvature determined by the rate constant of the elementary step reaction, (d) in coagulation of colloidal particles, the turbidity increases linearly in time with a slope proportional to the square of the weight concentration of the colloid. The last case was confirmed from experiments on the turbidity of coagulating systems during the period in the process when the coagulating particles scattered light according to Rayleigh's law.

2. Anisotropic particles

In the previous discussion we considered optically isotropic particles, that is, particles whose polarizability, α, is independent of direction in the particle. For small isotropic particles, the direction of the electric field associated with the incident light always coincides with the direction of the induced moment, and the scattered light is perfectly plane polarized in the direction $\theta = 90°$. For anisotropic particles, however, in which the polarizabilities along the various directions in the particle are not equal, in that there are different refractive indices along different directions, the direction of the incident electric field may not coincide with the direction of the induced moment. As a consequence, the light scattered at 90° will not be perfectly plane polarized perpendicular to the plane of the incident beam and the direction of the observation, and will exhibit a weak component in the horizontal direction. Rayleigh (177) calculated the depolarization, i.e., the ratio of the intensity of the horizontally polarized light to that of the vertically polarized light, in terms of the polarizabilities, α_1, α_2, α_3, along the principal axes of the polarizability ellipsoid by resolving the induced dipole moments along these principal axes and integrating over all possible orientations of the particle. The expression for the depolarization, ρ_u, of the light scattered at 90° from unpolarized incident light is given by

$$\rho_u = \frac{2(\alpha_1^2 + \alpha_2^2 + \alpha_3^2 - \alpha_1\alpha_2 - \alpha_2\alpha_3 - \alpha_1\alpha_3)}{4(\alpha_1^2 + \alpha_2^2 + \alpha_3^2) + \alpha_1\alpha_2 + \alpha_2\alpha_3 + \alpha_1\alpha_3} \tag{13}$$

For such small anisotropic molecules, the intensity of light scattered will be more than that for particles which are of the same volume but which are isotropic. According to Cabannes (25), the intensity of scattered light given by equations 5 and 7 must be, for $\theta = 90°$, multiplied on the right-hand side by the factor

$$\frac{1 + \rho_u}{1 - \frac{7}{6}\rho_u} \tag{14}$$

For directions other than $\theta = 90°$ a more elaborate factor is required (Martin (122)). The turbidity also depends on the depolarization, and equations 6 and 8 for the turbidity must be multiplied on the right-hand side by the factor:

$$\frac{1 + \frac{1}{2}\rho_u}{1 - \frac{7}{6}\rho_u} \tag{15}$$

The derivations of these formulae are quite involved, and for a detailed treatment the reader is advised to see any of the numerous treatments of the subject (for example, Born (19), Gans (68), Stuart (201), and Bhagavantam (13)).

The depolarization of the scattered light may be determined visually by the Cornu method adapted by Cabannes (25). This method consists in dividing the scattered light into its horizontal and vertical polarized components with a double prism (Wollaston prism). The two components are then made to pass through an analyzer (nicol prism or polaroid); if the analyzer is rotated through the angle ϕ which makes the brightness of the two components equal, the depolarization is given by $\tan^2 \phi$ (see, for example, Woods (220, page 340)). For most systems the depolarization is small and the intensity of the horizontal component is difficult to measure visually except by the Cornu method. With the recent development and general availability of extremely sensitive photoelectric cells, particularly the photomultiplier cell, the depolarization can be measured directly by measuring photoelectrically the intensity of the scattered light when it passes through the analyzer with plane of polarization in the vertical and horizontal positions.

Cabannes (25) has discussed the conditions under which the depolarization can be accurately determined. They include the use of parallel light as the incident beam, the observations made exactly at 90° to the incident beam, and the elimination of dust which, as we shall see, can make a large contribution to the depolarization. Another precaution is the elimination of secondary scattering, whose contribution to the depolarization will be discussed later.

The maximum depolarization which can be theoretically obtained for a particle small compared with the wave length of incident light is that of scattered light from an infinitely thin rod. Then $\alpha_1 \neq 0$ and $\alpha_2 = \alpha_3 = 0$, so from equation 13 the depolarization is 0.5, and from equation 14 and 15, respectively, the intensity is 3.6 times and the turbidity 3.0 times that for isotropic particles of the same volume. For all the gases which have been measured, however, the depolarization is considerably less than one-half. Bhagavantum (13, pages 54 and 55) has compiled a table of the depolarization of seventy-six common gases and vapors. The values range from 0 for argon to 0.125 for nitrous oxide, corresponding to $\alpha_1 = \alpha_2 = \alpha_3$ for the former and $\alpha_1/\alpha_2 = \alpha_1/\alpha_3 = 2.61$ for the latter. The aromatic compounds show greater depolarization than do the corresponding aliphatic series, and the depolarization increases as one goes from ethane through ethylene to acetylene. If the molecules are highly optically active, the interpretation of the depolarization is difficult (Gans (63)). The depolarization of scattered light from liquids is complicated by the fact that the particles are not independent and the problem will be treated in detail later. For the very dilute solutions of proteins studied by Putzeys and Brosteaux (154) the depolarization was observed to be negligibly small (see Section II,B,4).

Under the influence of a strong electric field, most liquids and gases will exhibit a feeble birefringence. This phenomenon, called the Kerr effect after its discoverer (94), has been shown by Langevin (112) to be due, for anisotropic non-polar gases, to the partial alignment of the molecules with their axes of greatest

polarizability along the direction of the applied electric field. Langevin related the Kerr constant (the birefringence per unit field strength) to the polarizabilities of the molecules. Thus the depolarization can also be obtained from the Kerr effect (Raman and Krishnan (158)). The depolarization obtained from the scattered light and that calculated from the observed Kerr effect are in good agreement for non-polar anisotropic gas molecules, but for polar molecules the Kerr effect is largely due to the Debye orientation effect, and one must incorporate the theory of Born (18) for such molecules with assumptions concerning the angle which the permanent dipole makes with the axes of the polarizability ellipsoid (for review, see Stuart (201)).

<center>B. LARGE PARTICLES</center>

In the treatment given above we have considered the light scattered from small transparent particles as that of the radiation from an oscillating dipole. If, however, the particles possess a linear dimension greater than about one-tenth the wave length of the incident light, or if the particles are metallic, they cannot be considered optically small and the character of the light scattered is more complicated than that given by the dipole radiator theory of Rayleigh. For large particles the scattered light will be the superposition of the wavelets from various parts of the same particle. In the general case the phase and intensity of the wavelets will bear complicated relationships to each other. The solution of this problem is obtained by solving the boundary value problem of a plane wave incident upon a particle of arbitrary size, shape, orientation, and index of refraction. This general case has not been solved because of mathematical difficulties. For spheres, however, whether transparent or metallic, the problem has been solved by Mie (125), and important contributions have also been made by Debye (31) and by Rayleigh (175). Some attempts have been made to extend the Mie theory to other than spherical particles (see Gans (62) and Möglich (126)), but the problem is far from completely solved.

When the index of refraction of the particle is nearly that of the medium, then as will be shown, the problem reduces to that of calculating the phase relationships between the wavelets scattered from a fixed array of dipole oscillators making up the particle. The mathematical problem is then identical with that of the analogous x-ray-scattering case. Because of the mathematical simplicity of this problem, it is useful to separate this case from that of particles with arbitrarily high index of refraction. We shall also treat separately the special case of metallic particles, since metals have complex indices of refraction for the visible wave-length region of light.

<center>1. *Large spheres*</center>

Mie (125) (see also Debye (31) and Rayleigh (175)) obtained as a mathematical solution for the intensity of scattered light incident upon a sphere of arbitrary size and index of refraction a series expression in terms of spherical harmonics. The coefficients of the series are functions of the ratio, m, of the index of refraction of the particle and that of the medium and of the parameter $x = 2\pi R/\lambda'$,

where R is the radius of the sphere and λ' is the wave length of the light in the medium. The series is the sum of the contributions to the scattering by the electric and magnetic multipoles of the oscillating electric charges.

For particles with radii comparable or large compared to the wave length of incident light, i.e., $x \geq 1$, and with index of refraction ratio, m, differing somewhat from unity, say, for example, $m \geq 1.3$, the calculations of the Mie series are lengthy, and for details the reader is referred to the original papers of Mie (125), Debye (31), and Rayleigh (175) and to the reviews by Epstein (50), Stratton (199, Chapter 9), and van der Hulst (211). The mathematical problem of the Mie theory is very similar to that of wave-mechanical collision processes in which the effective size of the particle is given in terms of the collision cross section and the wave length of the radiation is given in terms of the De Broglie wave length of the particles (see, for example, Mott and Massey (128, Chapter 2)).

In the case of very small spherical particles of finite index of refraction, i.e., for particles for which $mx \rightarrow 0$, Mie's theory reduces to the Rayleigh problem. For somewhat larger particles of finite index of refraction, say $m = 1.33$ and $x = 1$ (e.g., water droplets in air with radii about one-sixth the wave length of the incident light), the Mie series expression can be expressed with sufficient accuracy as the sum of terms involving the contributions to the scattering by the electric dipole and quadripole moments and the magnetic dipole moment. The intensities of the vertical and horizontal polarized components, i_1 and i_2, respectively, are given in this case by

$$i_1 = \frac{\lambda'^2}{8\pi r^2} \left| \frac{a_1}{2} + \frac{(a_2 + p_1)}{2} \cos \theta \right|^2$$

$$i_2 = \frac{\lambda'^2}{8\pi r^2} \left| \frac{a_1}{2} \cos \theta + \frac{a_2}{2} \cos 2\theta + p_1 \right|^2 \tag{16}$$

Equations 16 refer to unpolarized incident light of unit intensity. a_1 and a_2 are the electric dipole and quadripole contributions, p_1 is the magnetic dipole contribution, and they are given by

$$a_1 = 2x^3 \frac{m^2 - 1}{m^2 + 2} \qquad a_2 = -\frac{x^5}{6} \frac{m^2 - 1}{m^2 + 3/2} \qquad p_1 \simeq -\frac{x^5}{15} (m^2 - 1)$$

When the radius of the particle is small, only the electric dipole term, a_1, is important, and equation 16 reduces to the Rayleigh expression (equation 1) for the total intensity, $i_1 + i_2$, for unit intensity of unpolarized incident light: namely, to

$$i_1 + i_2 = \frac{\lambda' x^6}{8\pi^2 r^2} \left(\frac{m^2 - 1}{m^2 + 2} \right)^2 (1 + \cos^2 \theta) \tag{17}$$

where the polarizability, α, of the sphere is given by

$$\alpha = \frac{m^2 - 1}{m^2 + 2} \left(\frac{\lambda' x}{2\pi} \right)^3 = \frac{m^2 - 1}{m^2 + 2} R^3 \tag{18}$$

For larger particles than those to which equation 16 refers, the intensity will be

given by an expression involving the contributions to the scattering by higher multipoles. Equation 16 shows that the scattering is not symmetrical about $\theta = 90°$, but that more light is scattered in the forward than in the backward directions. Furthermore, the light scattered at $90°$ is not perfectly plane polarized, although the particles are taken as being isotropic.

Debye (31) has obtained asymptotic expressions for the terms in the series of the form of equation 16, and several authors have calculated the series numerically for various-size particles with various indices of refraction.[2] For example, Shoulejkin (186) has calculated the Mie terms for spherical particles of index of refraction ratio $m = 1.33$ (applicable to, for example, water droplets in air, or, with a minor transformation, air bubbles in water) for x equal to 1, 3, and infinity. Blumer (17) and Caspersson (27) have computed the Mie terms for several values of m and x. Engelhard and Freiss (49), Paranjpe, Naik, and Vaidya (144), and Ruedy (181) have calculated the Mie terms for large values of x and have compared the calculated values of the angular dependence of scattering with those from artificial aerosols made by adiabatic expansions of vapors, as is done in a Wilson cloud chamber. The agreement of the observed results with those calculated constitutes a confirmation of the Mie theory.

In figure 3 are illustrated angular scattering diagrams from Blumer's calculations (17) for spheres for which $m = 1.25$ and x equals 0.8 and 4.0, respectively. For $x = 4.0$ the large area of forward scattering is not shown. As in figure 1, the dotted curves represent the intensity of the horizontal component of the scattered light and the smooth curves represent the intensity for the vertical polarized component. For both these cases more light is scattered in the forward directions than in the backward directions, in contrast to Rayleigh scattering (figure 1) which is symmetrical about $90°$. The larger particle has a complicated scattering diagram which is typical of large particles, especially those with large index of refraction. The maxima and minima in the diagram increase in complexity as the size and index of refraction of the particle are increased and correspond to the increasing importance of the higher multipoles with their associated higher spherical harmonics in the Mie series. The complicated scattering diagram which is essentially the diffraction pattern of the large particles, reduces, in the limiting case of particles which are very large compared to the wave length of light, to the ordinary refraction and reflection diagram of geometrical optics together with the superimposed diffraction.

If white light is incident upon a monodispersed system of particles of large size and high index of refraction ratio, each color component of the white light will have its own complicated scattering pattern and the scattering system will exhibit vivid colors when viewed at various angles. Ruedy (181), for example, has examined the transmitted color and the colored rings about the transmitted beam of light in artificial fogs of water droplets. Keen and Porter (92) noted that sulfur sols exhibited changes in transmitted colors as the sols aged, that is,

[2] *Added in proof:* The most complete calculations to date are those carried out by A. Lowan and his associates. They are available from the U. S. Department of Commerce Office of Publications Board, Washington, D. C.

as the particles increased in size.   Ray (171) (see also Raman and Ray (165)) found that sulfur sols exhibited a few orders of colors when viewed at various angles with respect to the incident beam.   A detailed study of this phenomenon has recently been carried out by La Mer and his coworkers.   La Mer and Barnes (107) made a special effort to obtain monodispersed sulfur sols and were able to see as high as nine orders of colors in angular scattering.   It is necessary to obtain nearly monodispersed systems, since a mixture of particles of various sizes will not give distinct color bands.   Johnson and La Mer (91a) have shown that as the monodispersity is increased the color bands become more distinct, and propose that this effect may be used as a test of homogeneity of the size of the particles.   They have measured the position and ratio of the intensities of the red to green colors of sulfur sols of known particle sizes and obtained good agreement with the Mie theory.   It should be remembered, however, that sulfur has a high index of refraction ($m \simeq 1.5$ in water) and for particles of low refractive

$$m = 1.25$$
$$x = 0.8$$

A

$$m = 1.25$$
$$x = 4.0$$

B

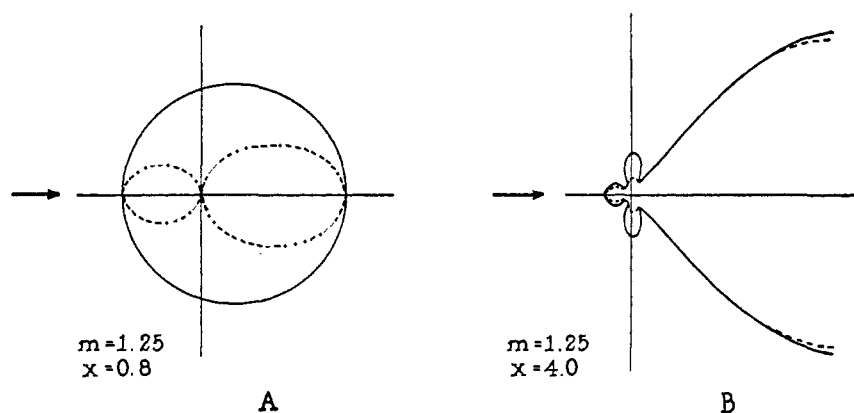Fig. 3. Angular scattering diagrams for spheres (from calculations by Blumer (17))

index of refraction, say, for example, protein material ($m \simeq 1.15$ in water), in order to exhibit colors the particles must be so large that they can easily be seen in a light microscope.   Nevertheless, for large-size protein-containing substances such as blood cells or bacteria, small changes in size due to drying can be easily followed by studying changes in the angular color pattern or diffraction pattern of suspensions of these particles (for review, see Ponder (152)).

    In order to calculate the turbidity or extinction coefficient for a scattering system, it is necessary to integrate the intensity of scattered light over all angles. Rayleigh scattering gives a symmetrical angular pattern and the integration is easy to perform.   For larger particles, however, the angular distribution is given by the Mie series, and the integration is difficult to perform.   Jobst (91) obtained an approximate value for the sum of the Mie series by utilizing the asymptotic expressions for the terms in the series obtained by Debye (31). While for small particles the extinction coefficient is proportional to the sixth power of the radius and inversely proportional to the fourth power of the wave length of incident light, Jobst finds, for particles comparable to the wave length

of light, that the extinction coefficient is proportional to the fourth power of the radius and inversely proportional to the square of the wave length. For very large particles, the extinction coefficient is proportional to the square of the radius and is independent of the wave length. Since the extinction coefficient or turbidity becomes less dependent on wave length as the particles are increased in size, a system of large particles will, when illuminated with white light, appear whitish when viewed at 90° instead of bluish as for Rayleigh scattering. An estimation of the size of particles can be made by determining spectrophotometrically the dependence of the turbidity on the inverse power of the wave length (see Heller, Klevens, and Oppenheimer (85), Heller and Vassy (86), and Doty (42)).
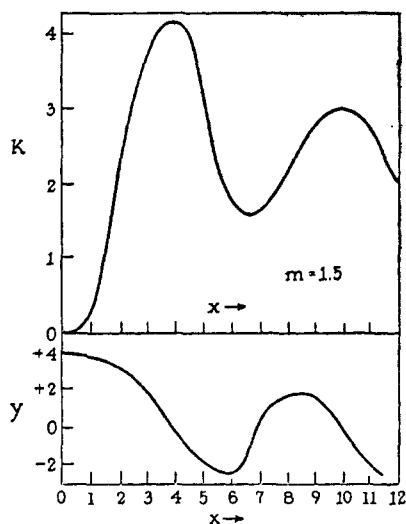

FIG. 4. Upper: extinction coefficient per cross-sectional area as a function of size of sphere. Lower: power of x/λ as a function of size of sphere (La Mer (106)).

For the purposes of this discussion it is convenient to consider the scattering area coefficient, K, which is the extinction coefficient per cross-sectional area of the particle and which may be written quite generally as:

$$K = Q\left(\frac{x}{\lambda}\right)^{y} \qquad (19)$$

Q is a function of m, and y varies from 4 for a Rayleigh scatterer to 0 for a particle large compared to the wave length. For some intermediate particle sizes y can be negative as may be seen in figure 4, calculated by La Mer (106) from the Mie theory. Figure 4 and similar curves by Stratton and Houghton (198), by van der Hulst (211), and by Sinclair (187) show that the extinction coefficient per cross section increases in the Rayleigh region as x^4 and reaches a maximum of from about 3 to 5, depending on the value of m, while for large x it oscillates with diminishing amplitude about the value 2 as x increases. That is, as the

geometrical optical region is approached, the extinction becomes equal to twice the cross-sectional area of the particle.   This result, which follows from computations of the higher Mie terms for very large particles, appears to be twice as great as one would expect from geometrical optics, to which the Mie theory must reduce for very large particles.   This apparent paradox has been explained in detail by van der Hulst (211, Chapter 5; see also Sinclair (187)), who showed that even in geometrical optics a sphere will extinguish twice the amount of light striking it.   Half this amount of light is scattered in a narrow peak of only slightly deviating rays on the exit beam.   If the incident plane wave comes from a distant source and if the observation is made at a sufficiently great distance from the particle, the extinction will be twice the cross-sectional area of the particle.   In the usual experiments in geometrical optics, however, the particle may be of macroscopic dimensions and the light source and observer are not at sufficiently great distances to observe this phenomenon.   An example of the large distances required is given in the transmission experiments of Sinclair (187) with lycopodium spores (radius equal to 15 microns).   At an observation distance of 6 in. from the spores the extinction coefficient was found to be equal to the cross-sectional area and only at a distance of 18 feet or greater was the extinction coefficient equal to twice the cross-sectional area.   The applications of the theory of turbidity of large spherical particles are very important to the problem of visibility in astronomy and meteorology and the reader is referred to the book of Middleton (124), which contains a few hundred references on this problem.

As indicated earlier, the turbidity is less dependent on the size of the particle for very large particles than for small ones.   For a given weight (or volume) of material which is monodispersed into particles of very small size so that Rayleigh's law is obeyed, the turbidity will increase as the third power of the radius, since the number of particles per unit volume of the system decreases inversely as the third power of the radius, while the scattering of each particle increases as the sixth power of the radius, and the turbidity is the product of these quantities.   When the particles are comparable in size to the wave length of incident light, the scattering per particle is proportional to the fourth power of the radius, and the scattering for a given weight of material will increase linearly with the radius.   For still bigger particles the scattering is proportional to the square of the radius, so that the scattering of the system will actually decrease with increasing radius of the particles.   Thus, maximum scattering will occur for a given weight of material when the particles are about equal in size to the wave length (i.e., when the particles have a diameter nearly equal to the resolving power of the light).   In figure 5 are shown curves for the dependence of the extinction coefficient of a given weight of material on the particle diameter.   The data are taken from the work of Caspersson (27), who calculated them from the Mie theory.   Note that the particle size for which the maxima occur is independent of the refractive index ratio.   The position does depend, however, on the index of refraction of the medium, which determines the resolving power. Paint manufacturers have learned by experience that the maximum spreading

power of colorless material is achieved by grinding the material to a size corresponding to the resolving power of the light.   Clewell (29) (see also Barnett (10), Andreason (3), Bailey (7), and de Vore and Pfund (38)) has examined suspensions of highly refracting substances and found the maximum in turbidity given in figure 5.   The curves also show that for certain sizes (in figure 5, particles with a diameter of 380 mμ) the longer wave length will be scattered more than the shorter one, a result which is the reverse of that in Rayleigh scattering.

2. Metallic particles

The vivid colors exhibited by metal sols are due mainly to selective absorption of the light by the metals.   For sufficiently large particles, however, scattering can also play a rôle in determining the color of the sol.   The color phenomena
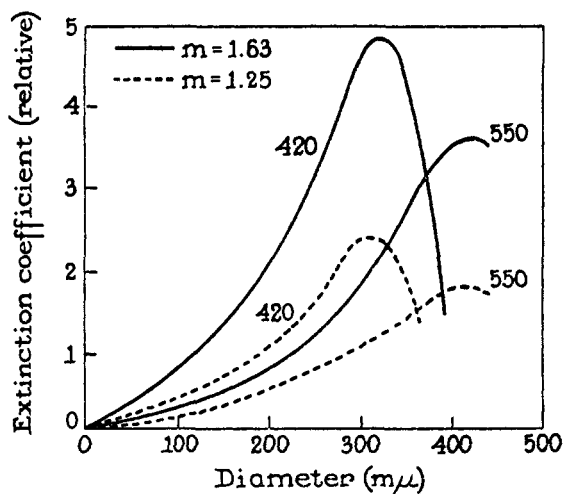

FIG. 5. Relative extinction coefficient as a function of diameter of spheres for constant weight concentration of scattering material (from calculations by Caspersson (27)).

of metal sols are described in detail by Wo. Ostwald (143), by Svedberg (204, page 193 et seq.), and by Freundlich (57, Volume 2, page 26 et seq.), who also give extensive bibliographies.

According to Mie (125), the color of metal sols may be deduced from his theory when the index of refraction of the metal, n', is given in complex form

$$n' = n - ik \qquad (20)$$

where n is the ordinary index of refraction and $4\pi k/\lambda$ is the absorption coefficient of the metal.   For all metals in the visible region of the spectrum, n and k are nearly equal and are of the order of unity.   Both quantities vary considerably with the wave length in a manner characteristic for each metal (see, for example, Mott and Jones (129, Chapter 3, sections 7 and 8).   At long wave lengths (infrared wave lengths or greater) n and k are equal and are large compared to unity. For such long wave lengths there is considerable reflection of the incident light in the backward directions.

Steubing (196) examined the transmission and the 90° scattering of gold sols in some detail. He found that sols of small particle size (radius about 25 mμ) strongly absorbed green light and thus appeared red on transmission and showed very little scattering. For larger particles, the absorption band is broader and shifts toward the red and there is considerable right-angle scattering. Such sols appear blue on transmission. Mie (125) showed that the phenomena reported by Steubing are explainable in a quantitative fashion by his theory.

For each metallic sol the absorption coefficient and index of refraction of the metal as a function of wave length must be known in order to explain the color of the sol. Further complications are introduced if the metallic particles are not spherical (see Gans (61)) or homogeneous in size. The polarization of scattered light from metallic spheres is similar to that expected for transparent spheres.

The theory of the light scattering from metallic particles has been used in the study of the transmission of light through interstellar space. Recent work indicates that much of the matter in interstellar space is in the form of particles comparable in size to the wave length of light. From an analysis of the absorption coefficient, estimates can be made of the distribution of these particles in interstellar space (the work up to 1940 has been summarized by Schoenberg and Lambrecht (185)).

3. Particles with relative index of refraction near unity

Particles which are comparable in size to the wave length of incident light and which possess a high relative index of refraction exhibit a complicated scattering pattern. This pattern, given by the Mie series, is determined not only by the interferences between the wavelets scattered by the volume elements of the same particle, but also by the distortions in phases and electric field associated with the incident and outgoing light brought about by the electromagnetic interactions of the field and the polarizable scattering elements. As indicated above, even for such a simple shape as a sphere, the solution of the problem is quite complicated. For particles with relative index of refraction m near unity, however, the distortion effect on the primary and scattered waves is small; and, to a first approximation, only the relative phases of the wavelets from the scattering elements, treated as dipole oscillators, need be considered. The relative phase relationships of the wavelets from various parts of the same particle are determined by the relative positions of the scattering elements, that is, by the shape of the particle, and therefore the problem is identical mathematically with the analogous problem in x-ray and electron scattering by molecules.

The treatment of the scattering of large particles as that of an assembly of independent dipole oscillators will be valid if the condition $2x(m-1) << 1$ is satisfied. Thus for particles, such as bacteria in water, which have a low relative refractive index but are large compared with the wave length of light, this simplified picture will not apply. In general, however, chemists are interested in particles which are too small to be seen in the light microscope. For protein molecules and most high polymers in solution the relative index of refraction is

less than 1.2; and since these particles possess a linear dimension equal to or less than the wave length of light, the simplified treatment is applicable. In cases where the index of refraction of the particle is quite high, the relative index of refraction can be reduced by dissolving some highly refractive substance into the suspending medium.

For a particle with a dimension equal to the wave length of light or greater than it and having a relative index of refraction nearly unity, each volume element of the particle will scatter light according to the Rayleigh relation given by equation 1. The wavelets will interfere, because the phase relationships between the wavelets coming from the various volume elements of the same particle are fixed. There will be more light scattered in the forward directions than in the backward directions, since wavelets from particles along the incident beam will be approximately in phase, but in the backward direction they will generally be out of phase with some destructive interference and a consequent loss in intensity. The radiation envelope will be smooth, as for the particle in figure 3A, and the larger the particle the greater will be the forward scattering. The $1 + \cos^2 \theta$ factor of Rayleigh scattering of unpolarized incident light is symmetrical about 90° to the incident beam and can be omitted from the discussion, since we shall consider observations made at angles symmetrical about this direction. As P. Debye (32) and P. P. Debye (36) have pointed out, intensity measurements made at two equal angles on either side of 90° define the shape of the radiation envelope and allow for a determination of the size of the scattering particle. The ratio of the intensity of light scattered in some forward angle ($\theta < 90°$) to that scattered at its supplementary angle, $180° - \theta$, is called the dissymmetry of the scattering system. We shall now consider the dependence of dissymmetry on the size of the particle for three types of particles frequently encountered in high-polymer chemistry,—namely, for spheres, random coils, and rods.

Just as for x-ray and electron scattering, the intensity of light scattered from an assembly of light-scattering elements making up the particle is proportional to

$$\sum_i \sum_j \frac{\sin\left(\frac{4\pi r_{ij}}{\lambda'} \sin\frac{\theta}{2}\right)}{\frac{4\pi r_{ij}}{\lambda'} \sin\frac{\theta}{2}} \qquad (21)$$

where λ' is the wave length of light in the medium and r_{ij} is the distance between the elements i and j. This formula may be expressed in integral form in terms of the vector distance separating two volume elements and the density of pairs of such elements. This latter function—the radial density—is determined by the arrangement of the scattering elements, that is, by the shape of the large particle. Equation 21 and its integral representation are derived in detail in most treatments of x-ray and electron scattering by molecules (see, for example, Compton and Allison (30, Chapter 3) and Pirenne (149, Chapter 7)).

For spherical particles the scattering elements are spherically symmetrically distributed. The radial density function is a constant for such an arrangement

of scattering centers. The integral representation of equation 21 for a sphere of diameter L leads to the following expression for the angular dependence of the scattered light intensity when normalized (intensity is unity for $\theta = 0$)

$$\left[\frac{3}{z^3} (\sin z - z \cos z) \right]^2$$

where

$$z = \frac{2\pi L}{\lambda'} \sin \frac{\theta}{2} \qquad (22)$$

This formula was first derived by Rayleigh (176) (see also Gans (65)) and is identical with that obtained by Landshoff (108) for light scattering from spherical
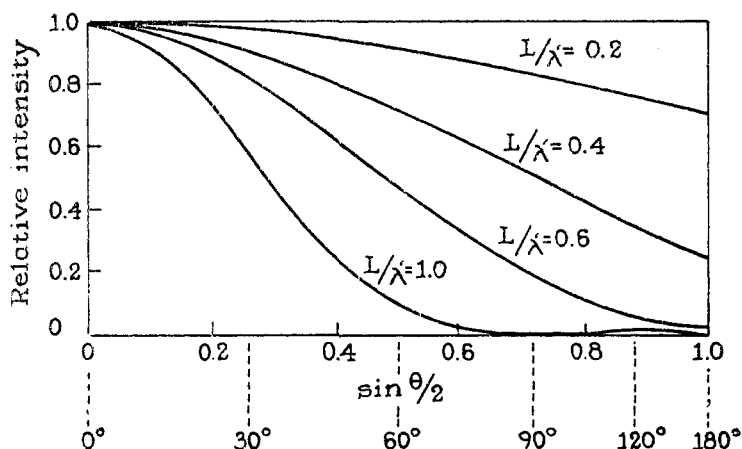

Fig. 6. Relative intensity of scattering as a function of angle for spheres of low relative index of refraction (P. P. Debye (37)).

aggregates of small particles. The same expression was obtained by Debye and Menke (35) in their study of the x-ray diffraction of liquid mercury. For x-ray scattering by liquids this term has importance only for angles extremely close to the main beam and is, therefore, neglected in most x-ray studies. This small angle scattering of x-rays is important, however, in the case of finely divided powders; and for carbon black the size of the clusters of the tiny particles can be determined by equation 22 from the angular distribution of the radiation scattered at small angles (Biscoe and Warren (16)). The Mie theory reduces to the same result as equation 22 for spherical particles which have sufficiently small relative index of refraction and size (van der Hulst (211, Chapter 4). In figure 6 is illustrated (P. P. Debye (37)) the expression of equation 22 as a function of angle for spheres of various sizes. Incidentally, equation 22 is expressible by the Bessel function of the 3/2 order, $J_{3/2}(z)$, and is equal to

$$\frac{9\pi}{2z^3} J^2_{3/2}(z)$$

Tables for this Bessel function are available.[3]   As can be seen from the curves, the intensity of scattering is greater in the forward directions than in the backward directions.   The curves show that for these particles the radiation envelopes are smooth and that only for the comparatively large sphere $L = \lambda'$ at an angle close to the main beam is there any deviation from a simple behavior.   In figure 7 is illustrated the ratio of the intensities of the scattered light for observations made at 45° on either side of 90° to the incident beam.   The dissymmetry rises very rapidly with increase in particle diameter.

The dissymmetry for spheres may be illustrated by the results obtained for influenza virus by the reviewer.   Measurements were made at 45° and 135° in a light-scattering photometer developed by Speiser and Brice (193).[4]   The
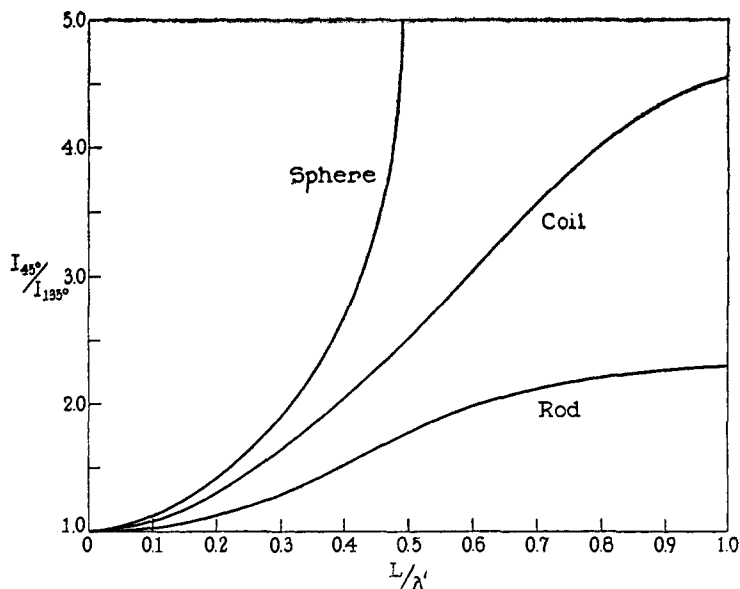

FIG. 7. Dissymmetry as a function of L/λ' for spheres, coils, and rods of low relative index of refraction.

apparatus consists essentially of a mercury lamp with monochromatic filters, a lens for projecting a narrow beam through the center of the scattering cell, a sensitive phototube mounted on an arm capable of rotation about a vertical axis, and a removable polarizer and analyzer for determining depolarization. If a rectangular cell is used, it is necessary to correct the angles for refraction at the solution–glass–air interfaces (Debye (36); see also Stein and Doty (194)). Such a correction may be eliminated by using a cell whose faces are normal to the outgoing scattered beam.   A spherical cell with radius large compared to the

[3] *Tables of Spherical Bessel Functions*, Vol. I.   Columbia University Press, New York (1947).

[4] The author is indebted to Dr. B. A. Brice of the Eastern Regional Research Laboratory, U. S. Department of Agriculture, Philadelphia, Pennsylvania, for the use of this apparatus.

cross-sectional area of the scattered beam has been found satisfactory by the reviewer. By introducing a mirror which can be rotated in a rectangular cell P. P. Debye (36, 37) insures that the scattered light is always normal to the face of the cell so that no correction need be made in the angles. The results for the scattering of blue light from a solution of a highly purified sample of influenza virus (PR8 strain) in 1 N phosphate buffer at pH 7 are shown in figure 8. On extrapolating to infinite dilution the dissymmetry is found to be equal to 2.6. This dissymmetry corresponds in figure 7 to a ratio of diameter to wave length of 0.39; and since the blue light was obtained with a filter having a maximum transmission at 436 mμ, the diameter of the particles is calculated to be (0.39)(436)/1.33 or 128 mμ. This value is 28 per cent higher than that obtained from spectrophotometric measurements of the turbidity (Oster (138)). The discrepancy in values obtained by the two methods may be due to the fact that,
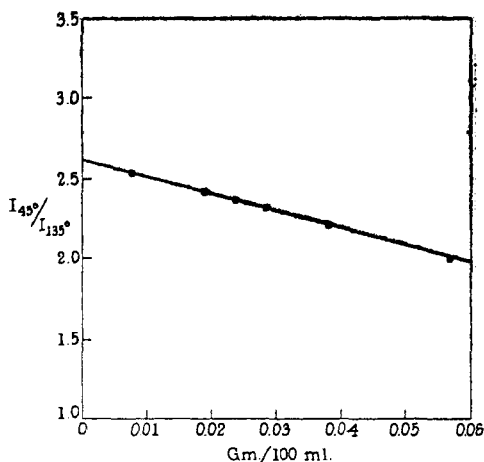

FIG. 8. Dissymmetry (λ = 436 mμ) of aqueous solutions of the PR8 strain of influenza virus.

since the blue filter allows some light of wave lengths shorter than 436 mμ to be transmitted and since the dissymmetry for spheres of this size range rises rapidly with a slight decrease in wave length, the observed dissymmetry is higher than that which might be obtained if purely monochromatic light had been employed. Because of the high sensitivity of dissymmetry to particle size the dissymmetry method may be conveniently employed to study the swelling of spheres. Molecules which clump together to give spheres of these sizes show large dissymmetry; and Doty, Wagner, and Singer (45) have studied the association of polyvinyl chloride in dioxane by this method (see also Landshoff (108)).

For randomly coiled polymers the radial density function is given by the Gaussian distribution employed by Kuhn (104); namely, by

$$\left(\frac{3}{2\pi L^2}\right)^{3/2} e^{-3/2(r^2/L^2)} \tag{23}$$

L is the root mean square distance between the ends of the polymer and is given

in terms of the number of links in the polymer chain, s; each link is of length l and can rotate freely, making an angle ϕ with its nearest neighbors. The mean square distance between the ends is given by Kuhn as:

$$L^2 = sl^2 \frac{1 + \cos \phi}{1 - \cos \phi} \qquad (24)$$

When the links are not able to rotate freely with respect to one another, more elaborate expressions in terms of the energy of the hindered rotation barrier may be used (Bresler and Frenkel (21), Sadron (182), and Taylor (204a)). When the radial density function of equation 23 is substituted into the integral representation of equation 21, the intensity when normalized (intensity is unity for $\theta = 0$) becomes,

$$\frac{2}{t^2} [e^{-t} - (1 - t)] \qquad (25)$$

where

$$t = \frac{2}{3} \left(\frac{2\pi L}{\lambda'} \sin \frac{\theta}{2} \right)^2$$

This formula, first obtained by Debye (32), is derived in detail in the paper by Zimm, Stein, and Doty (225). In figure 7 the dissymmetry for θ equal to 45° and 135° is given as a function of the ratio of L to the wave length of light in the medium. The degree of coiling of a polymer chain can conveniently be determined by studying the deviations of the dissymmetry from that given by equation 25. Thus, P. P. Debye (37) found that latex particles gave a higher dissymmetry than that expected for randomly coiled chains. The particles are tightly coiled and give a dissymmetry calculated for spheres. Stein and Doty (194), on the other hand, found that cellulose acetate molecules with a molecular weight below 80,000 exhibited in acetone less dissymmetry than that calculated for a random coil and gave values closer to that expected for a rigid rod (see below). The cellulose acetate molecules of higher molecular weights show dissymmetry corresponding to a more kinked condition. It is seen that the dissymmetry method provides a means for studying changes in the shape of high-polymeric molecules in solution. Such changes can be brought about by variations of the type of solvent or variation of the temperature and can be followed as a function of time. The dissymmetry studies of Doty, Affens, and Zimm (43) on polystyrene show that these molecules are in the randomly coiled state in solution. In their measurements, the authors of these latter two papers obtained accurate results with an extraordinarily simple dissymmetry apparatus developed by them. Light scattered at two equal angles on either side of 90° was reflected from mirrors into a comparator photometer and the two light beams were equalized visually.

A thin stiff rod of low relative refractive index may be regarded as a linear array of dipole scatterers. The normalized intensity for a thin rod of length L is given by

$$\frac{1}{z} \int_0^{2z} \frac{\sin w}{w} \, dw - \left(\frac{\sin z}{z} \right)^2 \tag{26}$$

where

$$z = \frac{2\pi L}{\lambda'} \sin \frac{\theta}{2}$$

This formula was derived independently by Neugebauer (134) and by Debye (32). A detailed derivation is also given in the paper by Zimm, Stein, and Doty (225). The definite integral (w is a variable over which the integration is taken) in equation 26, called Si ($2z$) in the mathematical literature, is given as a function of $2z$ in certain tables of special functions.[5] Oster, Doty, and Zimm (142) give values for the dissymmetry as a function of angle for various rod length to wave length ratios. In figure 7 the dissymmetry at θ equal to 45° and 135° is given as a function of the ratio of the length of the rod to the wave length in the medium. The dissymmetry for rods is less than for spheres or coils of comparable size. For particle lengths of the size of the wave length or greater, the dissymmetry increases relatively slowly with increase in particle length. To study particles of such great lengths, the intensities at angles closer to the main beam of light should be measured. However, if angles too close to the main beam are chosen, there is a danger of picking up stray scattered light. In figure 9 is shown the angular distribution of scattered light as measured in the apparatus of Speiser and Brice (193) for two dilute solutions of tobacco mosaic virus particles. Figure 9A shows the relative intensity of light ($\lambda = 546$ mμ) scattered at angles from 45° to 135° in 5° intervals for a sample which had been rendered nearly biologically inactive by having been subjected to very strong sound irradiation for 64 min. This sample has been shown (Oster (140)) by direct examination in the electron microscope to consist of rod-like particles of one-half the length of normal biologically active virus or shorter. The angular scattering of the normal particles is given in figure 9B. From figure 9 the dissymmetry at 45° and 135° is 1.20 and 2.06 for the shorter and longer particles, respectively. From figure 7 the average length of the particles is calculated to be 103 mμ and 275 mμ. The type of average for a system of many particle lengths which the dissymmetry determines depends on the length of the particles for, as seen in figure 7, particles of very great length do not show a dissymmetry much greater than shorter particles which are still great in length. In the intermediate regions, however, for L/λ' from about 0.3 to 0.6, the dissymmetry increases approximately linearly with the length of the particles, so that the dissymmetry for a polydispersed sample of rods of lengths lying in this range will be determined by the mean length of the particles. It should be emphasized that the particle-length region where the dissymmetry is approximately linear with the length of the particles depends on the scattering angles which one chooses. As seen in figure 9A, the angular light scattering for the shorter particles is nearly sym-

[5] See, for example, The British Association for the Advancement of Science, *Mathematical Tables*, Vol. I, London (1931).

metrical with a minimum near 90°. For unpolarized incident light the curve for a single dipole scatterer is given by $1 + \cos^2 \theta$, and figure 9A is this curve with a slight forward dissymmetry superimposed on it. The virus particles of normal size, however, show a strong forward scattering. The particle length calculated for the dissymmetry at 45° and 135° is in good agreement with that found by
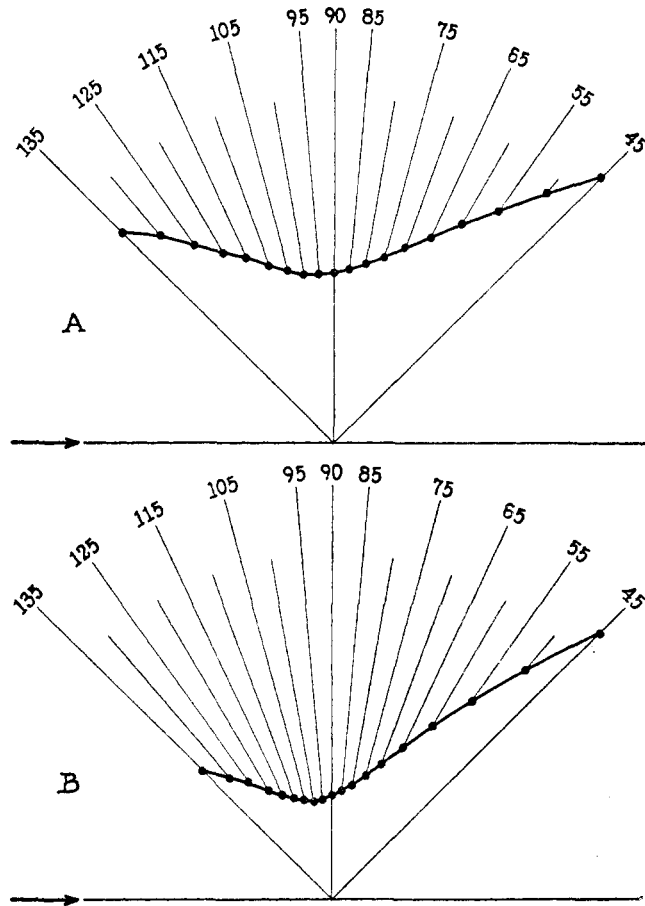

FIG. 9. Angular scattering ($\lambda = 546 \, m\mu$) for solutions (protein concentration of 0.01 g./100 ml. buffered at pH 7.0) of (A) tobacco mosaic virus which had been subjected to sonic irradiation for 64 min. and (B) normal freshly purified tobacco mosaic virus.

Oster, Doty, and Zimm (142), who studied the dissymmetry of a similar sample at two different angles in the visual photometer described earlier. These authors determined the particle length by viscosity and electron microscope studies and obtained close agreement with that determined by the dissymmetry method with the same sample. The reviewer (141) has been able to determine by the dissymmetry method the particle length of long rods of tobacco mosaic virus particles which have been made to aggregate end-to-end and which exceed 1

micron in length. This method should prove of value for studying the end-to-end aggregation of other fibres, particularly those encountered so frequently in biology. The dissymmetry method is perhaps superior to stream birefringence and viscosity methods for determining the lengths of elongated particles, since it determines the length of the particles as they exist in solution under equilibrium conditions. The latter two methods, however, involve subjection of the particles to a shear gradient in order to make them flow; and this process can in some cases distort the normal shape of the particles (Kuhn (105), Frenkel (55)). Doty (42) has integrated numerically the angular scattering curves for rods of several lengths. From these results he is able to determine the particle length of rods from the dependence of the turbidity on wave length as determined in a spectrophotometer. This method is similar to that described for spheres in the previous section.

From figure 7 it appears that the dissymmetry for rods or coils approaches limiting values as L/λ' increases. If the dissymmetry is determined at two angles symmetrical about 90°, then it may be shown from equation 26 that for rods the dissymmetry approaches $\cot \theta/2$ for large values of L/λ' (note that Si $(2z) \rightarrow \pi/2$ and $(\sin z/z) \rightarrow 0$ for large z). Similarly it may be shown that for coils the dissymmetry approaches $\cot^2 \theta/2$ and for spheres the dissymmetry oscillates about $\cot^4 \theta/2$ for large values of L/λ'. Since the dissymmetries for rods, coils, and spheres approach quite different values, the general shape of the particle can be determined from the limiting value of the dissymmetry.[6] Stein (195) has suggested that the limiting value of the dissymmetry could be determined by measuring the dissymmetry for continuously decreasing wave lengths (and therefore increasing values of L/λ'), using a variable monochrometer as a light source.

The molecular weight of spheres of known density can be found from the dissymmetry, since this method determines the diameter of the particles. For coils and rods, however, only the length of the long dimension is determined, so that another measurement must be made in order to find the molecular weight of the particles. Because of the destructive interference among the wavelets scattered from particles comparable in size to the wave length of light, the turbidity will be less, per unit volume of scattering material, for such large particles than for very small particles. In making molecular weight determinations of such large particles the turbidity must be corrected by a factor greater than unity to account for this decrease in scattering. If the turbidity is determined in the transverse direction, it must be multiplied by the reciprocal of relative intensity given by equations 22, 25, or 26, depending on the shape of the particle, for $\theta = 90°$ and L/λ' determined by the dissymmetry measurement. This corrected value for the turbidity, for sufficiently dilute solutions, gives from equation 10 the molecular weight of the particles. By applying this correction, determined graphically from the dissymmetry measurements, to their measure-

[6] *Added in proof:* These ideas have recently been utilized by W. K. Jordan and G. Oster (Science **108**, 188 (1948)) in their light-scattering studies of changes in shape of the very long fibrillar muscle protein, actomyosin.

ments of the turbidity of solutions of tobacco mosaic virus, Oster, Doty, and Zimm (142) obtained a molecular weight for these particles which agreed closely with that obtained from other methods.

The dissymmetry of a system of particles is very sensitive to particle interactions. Thus Oster, Doty, and Zimm (142) found that the dissymmetry of scattering from very dilute solutions of tobacco mosaic virus in water decreased markedly with increase in virus concentration. In buffer at pH 7.0, however, the dissymmetry was found to be independent of concentration in this low concentration region. The reviewer has investigated this system further (141) and has found that for much higher virus concentrations the dissymmetry of solutions of the virus in the buffer at pH 7.0 also decreased with increasing virus concentration, but that the solutions of the virus in water show a much steeper decrease and beyond a certain concentration show an increase in dissymmetry with concentration. The concentration for the minimum in dissymmetry is correlated with a maximum in turbidity and with the formation of the liquid crystalline state (see reference 141 for details). Zimm (223) has developed an approximate theory which attempts to correlate the concentration dependence of the dissymmetry with certain thermodynamic quantities which express the extent of the deviation of the solution from ideality. This problem will be discussed later in this review when non-independent particle systems are considered. There can be, however, a decrease in dissymmetry with concentration which is not due to particle interactions. The reviewer (141) has studied the dissymmetry of solutions of tobacco mosaic virus as a function of virus concentration for two wave lengths. When extrapolated to infinite dilution the curve for the shorter wave length ($\lambda = 436$ mμ) gives a higher dissymmetry than that for the longer wave length ($\lambda = 546$ mμ) and both correspond from figure 7 to that for a rod 275 mμ in length. For concentrations above 0.03 per cent, however, there is a reversal in relative values of the dissymmetries. The dissymmetry measured with the blue light now becomes less than that for the green light, and the difference between the dissymmetries for the two colors becomes more pronounced as the concentration of the virus is increased. This anomalous behavior may be due to several causes which depend on the geometrical arrangement, size, and convergence of the incident beam of light and on the turbidity of the sample. This problem will be considered in detail in the discussion of anomalous depolarization given below. In general, it is difficult to correct for these effects; and for most systems the dissymmetry is easily interpretable only when it is extrapolated to infinite dilution, as is done for influenza virus in figure 8.

4. Depolarization by large particles

The character of the polarization of the light scattered by a system of particles is determined by the size and the optical anisotropy of the particles. As discussed earlier, small isotropic particles exhibit complete vertically polarized scattered light at 90°, while small anisotropic particles show some depolarization in this direction. Spherical particles which are comparable in size to the wave

length of light also exhibit depolarization, although these particles may not be anisotropic. Thus, depolarization studies enable one to determine the size range and anisotropy of the scattering particles.

The intensities of the horizontal and vertical components of the light scattered at 90° are usually denoted by H and V, respectively. The subscripts u, h, and v denote unpolarized, horizontally polarized, and vertically polarized incident light, respectively. In terms of the quantities V_v, H_v, V_h, and H_h, the depolarizations are given by

$$\rho_v = \frac{H_v}{V_v} \tag{27a}$$

$$\rho_h = \frac{V_h}{H_h} \tag{27b}$$

$$\rho_u = \frac{H_h + H_v}{V_h + V_v} = \frac{H_u}{V_u} \tag{27c}$$

Some authors define ρ_h as the reciprocal of that given in expression 27b—namely, by H_h/V_h—and this is occasionally a source of confusion. The components for four types of scattering particles—small isotropic, small anisotropic, large isotropic spheres, and large anisotropic non-spherical particles—will now be considered.

Optically isotropic particles which are small enough to show Rayleigh scattering give a scattering diagram exhibited by a dipole oscillator. This diagram (figure 1) shows that if the incident light is horizontally polarized, the intensity of light scattered at 90° is zero. If the incident light is vertically polarized, all the light scattered at 90° is vertically polarized. This condition is expressed by

$$V_v \neq 0 \quad H_v = V_h = H_h = 0 \quad \rho_v = 0 \quad \rho_h = 1 \quad \rho_u = 0 \tag{28}$$

Small anisotropic particles, however, exhibit depolarization at 90° when the incident light is either vertically polarized or is unpolarized. For these particles, the plane of polarization of the incident light may not lie in the direction of the induced moment and, as can be shown (see Gans (68)), give rise to the following values for the components:

$$V_v \neq H_v = V_h = H_h \neq 0 \quad \rho_v \neq 0 \quad \rho_h = 1 \quad \rho_u \neq 0 \tag{29}$$

Large isotropic spherical particles should, according to Mie (125), exhibit depolarization at 90°. As the particle size is increased the terms corresponding to the higher electric and magnetic multipoles increase in importance (see equation 16), with a resultant increase in ρ_u. Blumer (17) has calculated the depolarization, ρ_u, for spheres of various sizes and indices of refraction, and the theory has been confirmed by the light-scattering studies of Pokrowski (151) and Lange (111) with colloidal solutions and of van dem Borne (210) with aerosols. The components of the light scattered at 90° for large spherical isotropic particles are given by

$$V_v \neq 0 \quad H_v = V_h = 0 \quad H_h \neq 0 \quad \rho_v = 0 \quad \rho_h = 0 \quad \rho_u \neq 0 \tag{30}$$

The depolarization of light scattered from large anisotropic particles has been calculated by Gans (62). The components for such particles are the superposition of those for the small anisotropic and for the large isotropic particles, or

$$V_v \neq 0 \quad H_v = V_h \neq 0 \quad H_v \neq 0 \quad \rho_v \neq 0 \quad \rho_h \neq 0 \quad \rho_u \neq 0 \qquad (31)$$

In all four cases the relation $H_v = V_h$ holds. This is a statement of the reciprocity theorem of optics due to Rayleigh (174) and was found by experiment to be valid for light-scattering systems by Krishnan (97). Perrin (146) has examined the theorem in great detail for light-scattering systems and concludes that the relation is valid for a system of a large number of particles which have no preferred orientation in space. The reciprocity theorem together with equation 27c gives the important relation due to Krishnan (97):

$$\rho_u = \frac{1 + \dfrac{1}{\rho_h}}{1 + \dfrac{1}{\rho_v}} \qquad (32)$$

Thus if two of the depolarizations are known, the third may be calculated. This is particularly important in the determination of ρ_h, which is often difficult to measure directly. The Krishnan relation (equation 32) has been confirmed by several investigators with various scattering systems (Krishnan (100), Mueller (132), Boutaric and Breton (20), Hoover, Putnam, and Wittenberg (88), Subbaramaija (202), Ramaiah (156), Gehman and Field (70)).

As seen in equations 28, 29, 30, and 31, a system of isotropic particles irrespective of size gives $\rho_v = 0$ and if the particles are anisotropic, then $0 < \rho_v < 1$. For random coils containing anisotropic segments the net anisotropy of the coils is decreased as the number of segments is increased (Neugebauer (134), Strauss (200), and Kuhn (103)). For small particles irrespective of anisotropy and shape $\rho_h = 1$, but when the particles are comparable in size to the wave length of light and are isotropic $\rho_h < 1$. In the special case of thin rods which are comparable in length to the wave length of light and whose index of refraction along the long axis differs from that perpendicular to it, Gans (69) (compare Vrkljan and Katalinis (216)) calculates that $\rho_h > 1$ (see, however, the recent review by Doty (41)).

The depolarizations can be conveniently determined by the Cornu method described earlier. Another method, due to Krishnan (98), employs two Wollaston prisms. The first divides the incident beam of light into its horizontal and vertical polarized components. The second prism placed at right angles to the scattering cell divides the two scattered beams into the four polarized components V_v, H_v, V_h, and H_h, which may be photographed and compared in intensity (for a detailed discussion of errors of measurement, see Volkmann (215)). Raman (157) has proposed the use of the Babinet compensator (for a general description see, for example, Woods (220, page 356)) to determine the state of polarization of liquids. This method is particularly useful for the determination of ρ_h when ρ_v is small and has been employed by Balakrishnan (8). It

has been the reviewer's experience, however, that the direct measurement of the polarization components can successfully be made with two polaroids or nicols acting as polarizer and analyzer and with a photomultiplier to determine the intensity.

There are two troublesome factors in depolarization measurements which reduce, somewhat, the usefulness of the method. These are the errors due to secondary or multiple scattering and those due to the convergence of the incident light beam. If light scattered from one particle is rescattered, this secondary scattering can result in large values of ρ_u and ρ_v and small values of ρ_h irrespective of the size, shape, or anisotropy of the particles. This problem has been investigated in detail by several workers, including Tichanowsky (205), Rousset (180), and Strauss (200). Tichanowsky (205) applied his theory to light scattering from the sky, which gives a depolarization apparently due to secondary scattering. According to Rousset (180), as a result of secondary scattering the value of ρ_h will depend on the shape of the illuminated volume of the scattering system and will be greater the closer the shape of the volume approaches a cube. The theory has been fully confirmed by Rousset (180) and by Mookerjee (127) in their depolarization studies of liquid mixtures at the critical mixing temperature. Mookerjee (127) has criticized Krishnan for his failure to take secondary scattering into account in his studies of liquids and liquid mixtures (Krishnan (97)). The problem of scattering from liquids and solutions will be considered in detail later in this review. Krishnan has also been criticized by Parthasarathy (145) (see, however, Krishnan (102)) for not correcting his depolarization values for convergence. Because of the finite size of the light source it is impossible to achieve perfectly parallel light in the incident beam. According to Gans (67), the convergence of the incident beam increases ρ_u and ρ_v by a term which is proportional to the square of the angle of convergence. ρ_h is decreased by a term proportional to the square of the convergence angle and inversely proportional to ρ_v, and therefore when there is convergence ρ_h is less than unity although the scattering particles may be of small size. According to Rao (169) (see Bhagavantum (13, Chapter 4)), no convergence correction is necessary if the scattered light comes from a point at the focus of the converging incident beam. In the theory of Strauss (200) the depolarization, ρ_u, for a dilute solution of spheres increases approximately linearly with the turbidity of the sample. The constant of proportionality increases as the size of the incident beam is increased. These results are in agreement with those obtained by Lonti (118). In figure 10 are shown Lonti's depolarization measurements at two different wave lengths for solutions of the hemocyanin of *Helix pomatia*. The turbidity and therefore the depolarization is greater for the shorter wave length. The depolarization, as does the turbidity, increases with increasing concentration (figure 10A). Figure 10B shows that the depolarization increases nearly linearly with the diameter of the incident beam. For this system, at least, in order to obtain the true depolarization it is necessary to extrapolate to infinite dilution and to small beam diameter. An indication of secondary scattering is usually given when the depolarization of a system is strongly de-

pendent on concentration and wave length. For less turbid systems than that studied by Lonti, secondary scattering may be less important. The necessity of working with extremely dilute solutions in making depolarization measurements of colloidal solutions is clearly shown in the work of Hoover, Putnam, and Wittenberg (88) with bentonite and ferric oxide sols (see also Singh (189)).

In nearly all cases of high-polymeric molecules in solution ρ_v is found to be small (natural rubber, Gehman and Field (70); synthetic rubbers, Tsvetkoff and Frisman (207); cellulose acetate, polyvinyl chloride, and polystyrene, Doty and Kaufman (44); myosin, Lotmar (120); and tobacco mosaic virus, Doty (42) and Oster (141)). This indicates that the molecules are nearly isotropic in solution. It is difficult to evaluate results obtained for ρ_h, since in most cases not enough measurements were taken in the low concentration range to allow
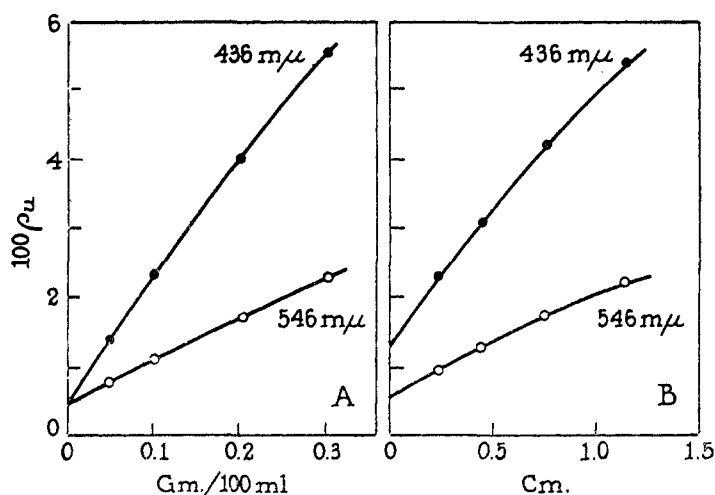

FIG. 10. Depolarization of light scattered at 90° from solutions of hemocyanin (*Helix pomatia*): (A) depolarization as a function of protein concentration; (B) depolarization as a function of incident beam diameter (Lonti (118)).

an extrapolation to infinite dilution (see, however, Gehman and Field (70), Lotmar (120), Doty (42), and Oster (141)). In his studies of ionic solutions, Hogrebe (87) found that the depolarization ρ_u (and therefore ρ_v, since $\rho_h \simeq 1$) when extrapolated to infinite dilution was considerable for unsymmetrical ions. Even symmetrical ions showed a slight depolarization, which Hogrebe attributes to the formation of anisotropic scattering units due to the interaction of the ions and the surrounding water molecules.

The depolarization of scattered light from large colloidal particles oriented by flowing in a tube has been examined by Diesselhorst and Freundlich (39). By making observations of the scattered polarized light perpendicular to and in the direction of flow, they were able to distinguish between spherical, disc-shaped, and rod-shaped colloidal particles (see Freundlich (57, Volume 2, page 81)). In some ways this resembles the method of flow birefringence (for review, see Edsall (47)). Depolarization studies have also been made on col-

loidal particles which are oriented with an electric or magnetic field (see, for example, Krishnan (101), Errera, Overbeck, and Sack (51), Mueller (132), Lauffer (113), and Subrahmanya, Doss, and Rao (203)). The theory and experimental results of the electrooptical properties of colloids have been discussed in detail by Heller (83) and by Mueller and Sackmann (133).

III. Non-Independent Particles

In the treatment for independent particles given above the particles were considered to be in random positions with respect to one another. For liquids and non-ideal solutions, however, the thermal movements of the constituent members of the scattering system are not independent, and it cannot be expected that the total intensity of scattered light will be the mere summation of the intensities from the individual particles. Some destructive interference will occur and result in a decrease in intensity of scattered light from that expected for the same weight of independent particles. In principle, the phase relationships between the wavelets scattered by the various elements of a condensed system can be computed; however, the mathematical difficulties are circumvented by considering the problem as one in fluctuations. The elementary ideas of the theory of fluctuations have been given by Landau and Lifshitz (109, Chapter 6), Tolman (206, Section 114), and Slater (191, Chapter 7). More complete treatments are given by Fürth (58) and especially by Leontovich (115, Chapter 3). It was clearly shown by Gibbs (71; see especially Chapters 7, 8, and 15) that thermodynamic quantities which are usually measured represent time averages over a large number of molecules. If, however, we consider a small volume in a system, the thermodynamic state of the system described by some thermodynamic quantity x may differ at any instant from the average value $\bar{x}$. The time average of this deviation, $x - \bar{x}$, may be zero, but if the volume is chosen small enough so as to include only a small number of molecules, the time average of the square of the deviations, or fluctuation, may differ considerably from zero. Also, according to Gibbs, the average value of any quantity in a small volume is the same whether the averaging is taken over a long period of time in the one volume element or whether the instantaneous value for a great number of such volume elements is averaged.

Smoluchowski (192) used the concept of thermodynamic fluctuations to explain the great intensity of scattering observed for liquids near their critical temperatures. According to Smoluchowski, the molecules in a liquid are not distributed uniformly, but rather in any small volume of the liquid the number of particles varies from instant to instant as a consequence of their thermal motions. This local fluctuation in density of particles will give local inhomogeneities in the index of refraction and will scatter light. In the case of liquids, the fluctuations in density are increased as the compressibility is increased and at the critical temperature the light scattering should theoretically be infinite. Smoluchowski's theory was further extended by Einstein (48) for liquid mixtures to include inhomogeneities in the refractive index due to fluctuations in concentration.

The elementary principles of the theory of fluctuations will now be briefly

reviewed, since much of the light-scattering phenomena to be discussed can be explained in terms of this theory.

In order to bring about a change in a given system of some thermodynamic quantity from its average value $\bar{x}$ to some value x, a certain amount of free energy must be expended. The probability of such a change is proportional to

$$e^{-\Delta A/kT} \tag{33}$$

where A is the Helmholtz free energy and $\Delta A = A(x) - A(\bar{x})$. k is Boltzmann's constant, and T is the absolute temperature. Boltzmann's definition of entropy is a special case of equation 33 in which the energy and volume are kept constant. The temperature is assumed constant throughout the fluctuation process. According to equation 33, the probability of a deviation in x decreases rapidly the greater the deviation. If only small deviations about the average value are considered, the free energy difference ΔA may be expanded in a Taylor series in the deviation $\Delta x = x - \bar{x}$, or

$$\Delta A = \left(\frac{\partial A}{\partial x}\right)_{x=\bar{x}} \Delta x + \frac{1}{2!}\left(\frac{\partial^2 A}{\partial x^2}\right)_{x=\bar{x}} (\Delta x)^2 + \frac{1}{3!}\left(\frac{\partial^3 A}{\partial x^3}\right)_{x=\bar{x}} (\Delta x)^3 + \cdots \tag{34}$$

But $\left(\dfrac{\partial A}{\partial x}\right)_{x=\bar{x}}$ is zero, since the free energy of a closed system of constant temperature is a minimum at equilibrium. For small deviations, terms higher than the squared term are small, so the free energy difference is given by

$$\Delta A \simeq \frac{1}{2}\left(\frac{\partial^2 A}{\partial x^2}\right)_{x=\bar{x}} (\Delta x)^2 \tag{35}$$

Insertion of this value into equation 33 gives a Gaussian distribution whose second moment or average value (averaged over Δx) of the square of the deviation is

$$\overline{(\Delta x)^2} = \frac{kT}{\left(\dfrac{\partial^2 A}{\partial x^2}\right)_{x=\bar{x}}} \tag{36}$$

It can further be shown that the average value of the product of deviations of independent quantities is zero, that is:

$$\overline{\Delta x_i \Delta x_j} = 0 \tag{37}$$

1. Pure liquids

Following Smoluchowski (192) (see also Einstein (48)) we shall consider light scattered from an element of volume δV of the liquid which is small compared with the wave length of the incident light, yet which is sufficiently large to include a great number of molecules (the exact dimensions of the volume element are unimportant for the discussion). The fluctuation in the number of particles in the volume element will result in a fluctuation in the optical dielectric constant. Any particular volume element may be likened to a small particle with optical

dielectric constant different from that of the surrounding homogeneous medium in which it is immersed. From equation 4 it is seen that the effective square of the polarizability for the volume δV is given by

$$\frac{(\delta V)^2}{16\pi^2 \epsilon_0^2} \overline{(\Delta\epsilon)^2} \tag{38}$$

The inhomogeneities in density of particles are randomly distributed throughout the total volume of the liquid, so that the total intensity of scattering is the sum of the contributions from each of the volume elements. The intensity per unit volume of scattering material is then obtained by inserting the expression for the square of the polarizability, equation 38, into equation 1 and dividing by the sum of the volume elements, or

$$\frac{i}{I_0} = \frac{\pi^2}{2\lambda^4 r^2} \overline{(\Delta\epsilon)^2} \delta V (1 + \cos^2\theta) \tag{39}$$

and the turbidity is

$$\tau = \frac{8\pi^3}{3\lambda^4} \overline{(\Delta\epsilon)^2} \delta V \tag{40}$$

The optical dielectric constant ϵ is a function of the density σ and the temperature, i.e.

$$\Delta\epsilon = \left(\frac{\partial\epsilon}{\partial\sigma}\right)_T \Delta\sigma + \left(\frac{\partial\epsilon}{\partial T}\right)_\sigma \Delta T \tag{41}$$

For liquids $\left(\dfrac{\partial\epsilon}{\partial T}\right)_\sigma$ is about 10^{-5} (Levin (117)) and therefore the second term on the right of equation 41 is negligible compared with the first term, since $\left(\dfrac{\partial\epsilon}{\partial\sigma}\right)_T$ is of the order of unity. The fluctuation in the optical dielectric constant is then given by

$$\overline{(\Delta\epsilon)^2} = \left(\frac{\partial\epsilon}{\partial\sigma}\right)_T^2 \overline{(\Delta\sigma)^2} \tag{42}$$

With the use of well-known thermodynamic relations the fluctuation in density for the volume element δV may be shown from equation 36 $(x = \sigma)$ to be

$$\overline{(\Delta\sigma)^2} = \frac{kT\beta\sigma^2}{\delta V} \tag{43}$$

where β is the isothermal compressibility. From equation 39 the intensity per unit volume and the turbidity are given by

$$\frac{i}{I_0} = \frac{\pi^2}{2\lambda^4 r^2} \left(\sigma \frac{\partial\epsilon}{\partial\sigma}\right)_T^2 kT\beta(1 + \cos^2\theta) \tag{44}$$

and by

$$\tau = \frac{8\pi^3}{3\lambda^4} \left(\sigma \frac{\partial\epsilon}{\partial\sigma}\right)_T^2 kT\beta \tag{45}$$

It is necessary to relate the optical dielectric constant to the density in order to give a value for $\sigma(\partial\epsilon/\partial\sigma)$ in terms of conveniently observable quantities. The optical dielectric constant of a liquid is conventionally related to the density by the Clausius–Mossotti equation. This equation is derived by considering the electric field in a small region of the liquid as that given by the Lorentz local field (Lorentz (119, page 303)), which is a mathematical device and is subject to criticism on physical grounds (for a critique of Lorentz's theory, see Van Vleck (212)). A more physically plausible treatment of the local field is given by Onsager (135), according to whom the field in a small region of the liquid is that given by the field in a real cavity imbedded in a medium of homogeneous dielectric constant. According to Onsager

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} = K\sigma \qquad (46)$$

where K is a constant for a given liquid. The reviewer has found (unpublished calculations) that equation 46 holds better for liquids and liquid mixtures than does the Clausius–Mossitti equation (for recent data on the variation of index of refraction of liquids and liquid mixtures with density, see Rosen (179)). Equation 46 gives:

$$\sigma \frac{\partial\epsilon}{\partial\sigma} = (\epsilon - 1)\left(\frac{2\epsilon^2 + \epsilon}{2\epsilon^2 + 1}\right) \qquad (47)$$

Since ϵ is usually less than 2 for most liquids, the second factor in parentheses on the right may, to a close approximation, be taken as unity. The intensity per unit volume and the turbidity then become

$$\frac{i}{I_0} = \frac{\pi^2}{2\lambda^4 r^2} (\epsilon - 1)^2 kT\beta(1 + \cos^2\theta) \qquad (48)$$

$$\tau = \frac{8\pi^3}{3\lambda^4} (\epsilon - 1)^2 kT\beta \qquad (49)$$

A similar result was obtained by Ramanathan (167), using a different and somewhat questionable physical argument.

Equations 48 and 49 must be further modified to correct for the depolarization of the scattered light. According to Ramanathan (166, 167) equations 48 and 49 must be multiplied by the Cabannes factors equations 14 and 15, respectively, to account for the fluctuations in orientation. The depolarization ρ_u used is that observed for the liquid.

The early work of Keesom (93) on ethylene and the later work of Ramanathan (166), Venkateswaran (214), Martin and Lehrman (123), Krishnan (96), Raman and Ramanathan (161), Cabannes (25, part 1), Peyrot (147), and Rao (170) on several other liquids shows general agreement with equation 48. Rao (170) has studied a few liquids over a wide range of temperatures. He found that equation 48 with its appropriate depolarization factor held very closely up to temperatures a few degrees below the critical temperature. Use of the Clausius–

Mossotti equation relating the optical dielectric constant and the density gave, however, values of the intensity which were greater than those observed.

In general, the depolarization for liquids is five or more times greater than that exhibited by the molecules in the gaseous state. The depolarization for normal alcohols increases with increasing length and greater anisotropy of the carbon chain, but for fatty acids there are alternations in the depolarization with increasing carbon chain length which resemble the marked alternation in melting points and dissociation constants exhibited by these compounds. More recent data on the depolarization by liquids have been compiled by Cabannes and Rousset (26) (see Peyrot (148), who also discusses error of measurement). The larger values of the depolarization of the molecules in the liquid state are attributed by Raman and Krishnan (159, 160) to the polarizability induced by the surrounding medium. If the inner field is treated as homogeneous and of the Lorentz type, the calculated depolarization for liquids is too high. Raman and Krishnan (159, 160) therefore treat the molecules and their immediate surrounding fluid as polarizable ellipsoids and calculate depolarizations for some long-chain hydrocarbons which are in fair agreement with observed values. They also apply these concepts to the Kerr effect for non-polar liquids. Mueller (131) has criticized the treatment of Raman and Krishnan for its failure to consider the possibility of hindered rotation between molecules in the condensed state. The theory of Mueller has, however, certain drawbacks, since it is based on the Lorentz inner field and on the cybotactic theory of liquids. According to the cybotactic theory due to Stewart (197) there are, at any instant in the liquid, groups of as many as a hundred molecules which are in a relatively ordered array and which are rapidly exchanging members with the continuous region between them. Although it is possible that for liquids consisting of long-chain molecules (and particularly those investigated by Stewart which contain OH and COOH groups) there exist such groups (see Frenkel (56, Chapter 5, Section 10) for the conditions of stability of cybotactic groups), more recent x-ray data of ordinary liquids (Warren (218), Ginrich (72)) indicate that in most liquids only local order exists and extends over mainly the first shell of nearest neighbors (for a critical discussion see Prins (153), and especially Bernal (11)). In view of the criticisms discussed earlier by Mookerjee (127) and by Parthasarathy (145) of the depolarization results of R. S. Krishnan, it cannot be claimed at the present time that the depolarization studies prove the existence of cybotactic groups. In the case of liquid crystals, however, Chatelain (28) (see also Zwetkov (227)) in his light-scattering studies has shown the presence of molecular groupings comparable in size to the wave length of the incident light. The theory of dielectrics of Onsager (135) has been extended by Kirkwood (95) to include the case of hindered rotation of the molecules, so that the means are at hand to develop a complete theory of depolarization of non-polar and polar liquids. The theory would also be suitable to explain the Kerr effect for these liquids. In the case of highly elongated molecules it would be necessary to modify the Onsager local field.

2. Non-ideal solutions

The extension by Einstein (48) of Smoluchowski's theory (192) to include liquid mixtures is suitable for any solution as long as the particles are small compared to the wave length of the incident light. If they are not, a correction factor for the dissymmetry of the scattering must be applied. According to Einstein (48) fluctuations in the concentration in an element of volume δV will be large; and since, in general, the optical dielectric constants of the solute and the solvent differ, the resultant fluctuation in the optical dielectric constant will cause light to be scattered. The fluctuation in concentration may be determined from equation 36 (see Gibbs (71, Chapter 15)). The fluctuation in dielectric constant is related to the fluctuation in concentration of the solute (for convenience the concentration of the solute c is given in grams per milliliter of solution) by

$$\overline{(\Delta\epsilon)^2} = \left(\frac{\partial\epsilon}{\partial c}\right)^2 \overline{(\Delta c)^2} \tag{50}$$

where

$$\overline{(\Delta c)^2} = \frac{kT}{\left(\dfrac{\partial^2 A}{\partial c^2}\right)_{\bar{c},V}}$$

Now

$$\left(\frac{\partial A}{\partial c}\right)_{\bar{c},V} = \mu_0 \frac{\partial\nu_0}{\partial c} \tag{51}$$

where μ_0 is the Gibbs chemical potential of the solvent and ν_0 is the number of solvent molecules per milliliter of solution. For the volume element δV, the variation in number of solvent molecules with the variation in the concentration of the solute is given closely by

$$\frac{\partial\nu_0}{\partial c} = -\frac{N\delta V}{\bar{V}_0 \bar{c}} \tag{52}$$

where N is Avogadro's number and $\bar{V}_0$ is the partial molal volume of the solvent. Insertion of equation 50 with equations 51 and 52 into equation 40 gives for the turbidity (at this point the average solute concentration will be written as c)

$$\tau = \frac{8\pi^3}{3\lambda^4} \frac{RT\bar{V}_0 c}{N\left(-\dfrac{\partial\mu_0}{\partial c}\right)} \left(\frac{\partial\epsilon}{\partial c}\right)^2 \tag{53}$$

where R is the gas constant. If the system exhibits depolarization, equation 53 must be multiplied by the Cabannes factor (equation 15).

Equation 53 gives the light scattering in terms of the thermodynamic properties of the solvent. The osmotic pressure P of a solution is related to the chemical potential of the solvent by $P\bar{V}_0 = -N\mu_0$ and gives for equation 53:

$$\tau = \frac{8\pi^3}{3\lambda^4} \frac{RTc}{N\left(\dfrac{\partial P}{\partial c}\right)} \left(\frac{\partial\epsilon}{\partial c}\right)^2 \tag{54}$$

Equation 54 is in the form given by Raman and Ramanathan (161) and by Debye (33, 34). For dilute solutions, the osmotic pressure may be written in terms of the molecular weight M of the solute and of the solute concentration by

$$P = \frac{c}{M} RT + Bc^2 \tag{55}$$

where B is a measure of the deviation from ideality. In the limit of $c \to 0$ we obtain for ideal solutions, after the contribution of the scattering of the solvent has been subtracted (the contribution from density fluctuations of the solute is negligible),

$$H \left(\frac{c}{\tau} \right)_{c=0} = \frac{1}{M} \qquad \text{where} \qquad H = \frac{8\pi^3}{3N\lambda^4} \left(\frac{\partial \epsilon}{\partial c} \right)^2 \tag{56}$$

which is identical with equation 10. For dilute solutions the turbidity may be written in the form

$$H \frac{c}{\tau} = \frac{1}{M} + \frac{2Bc}{RT} \tag{57}$$

A plot of $H(c/\tau)$ versus c gives a straight line whose intercept is the reciprocal of the molecular weight of the solvent and whose slope is determined by B. Doty, Zimm, and Mark (46) have determined the molecular weights of fractions of polystyrene and cellulose acetate by this method and obtain results which are in agreement with direct osmotic-pressure measurements of these samples. Similar studies have been made by P. P. Debye (37) of polymers which had been subject to milling. In their work on cellulose acetate, Stein and Doty (194) corrected the molecular weights obtained by extrapolation with the dissymmetry factor. A similar procedure was adopted by Oster, Doty, and Zimm (142), who obtained a molecular weight for tobacco mosaic virus in agreement with that obtained by other methods.

As shown by Zimm and Doty (224), the molecular weight obtained by the light-scattering method is the weight-average molecular weight, because, as may be seen directly from Rayleigh's equation, the intensity of scattering is proportional to the number of scatterers and to the square of their volumes or molecular weights. According to Zimm and Doty (224) the curvature of the $H(c/\tau)$ versus c curve is determined by the higher moments of the molecular weights of the sample. In principle, the spread of the molecular weight distribution could be determined from the curvature. In practice, however, this is not feasible because of the relatively poor ability of the light-scattering method to resolve different sizes (Waser, Badger, and Schomaker (219)). The slope of the linear portion of the curve determines the value of B, which can be related to the size and shape of the solute molecules and to their interactions with each other and with the solvent. In general, the greater the solubility and the more the particles deviate from spherical shape, the greater the slope. If the molecular weight of the polymer is the same in different solvents, the curves should converge at zero concentration of the polymer. Ewart, Roe, Debye, and McCartney (52) have found, however, that this is not the case for polystyrene in various mixtures of

benzene and methanol (see figure 11).   These workers attribute the lack of convergence at infinite dilution to selective absorption of benzene by the polystyrene and not to any changes in the molecular weight of polystyrene in the various solvent mixtures.   The alcohol serves as a precipitant, and the turbidity is increased considerably by its presence in small quantities well below the concentration necessary for two-phase separation.   Ewart, Roe, Debye, and McCartney have shown that the magnitude of the selective absorption can be determined by turbidity measurements.   In the case of a solvent–precipitant pair, such as butanone and 2-propanol, which have nearly equal refractive indices, or in the case of a pure liquid solvent or a solvent mixture in which no selective absorption by the solute occurs, the $H(c/\tau)$ *versus* c curves converge at infinite dilution.   For further discussion of applications to high-polymeric systems see the recent review by Mark (121a).
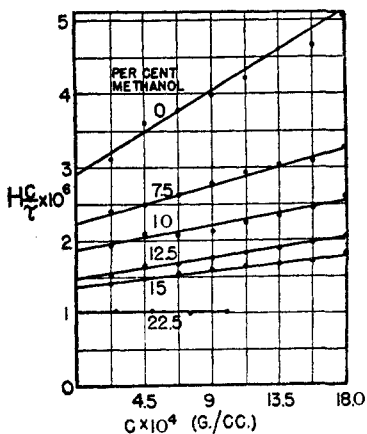

Fig. 11. Reciprocal specific turbidity as a function of concentration of polystyrene in benzene–methanol mixtures (Debye (34); Ewart, Roe, Debye, and McCartney (52)).

3. Liquids at the critical temperature

When a liquid is brought to its critical temperature or when a liquid mixture is brought to its critical temperature of mixing, it assumes a milky opalescence on illumination with white light.   The theories of Smoluchowski (192) and of Einstein (48) properly explain the large scattering exhibited by such systems near the critical temperature but predict too high an intensity of scattering for systems very close to or at the critical temperature.   Furthermore, several authors have found that in addition to there being less scattering than is to be expected from equation 48, the scattering is proportional to $1/\lambda^2$ rather than to $1/\lambda^4$ (Zernicke (221), Andant (2), and Bhattacharya (14)).   Ornstein and Zernicke (136) attribute the discrepancy with the Smoluchowski–Einstein theory to failure to consider the influence of deviations of density or concentration in one volume element on those in another volume element.   According to Ornstein and Zernicke (137) the mean value of the product of the deviations in one volume element and those in another is not zero as in equation 37, but is proportional to the

radial distribution of the molecules about any one molecule (compare Zimm (222)). In place of equation 48, Ornstein and Zernicke obtain for the intensity of scattering per unit volume

$$\frac{i}{I_0} = \frac{\pi^2(\epsilon - 1)^2}{2\lambda^4 r^2} \frac{kT(1 + \cos^2\theta)}{\frac{1}{\beta} + \left(\frac{2\pi g}{\lambda}\sin\frac{\theta}{2}\right)^2} \tag{58}$$

where g is a measure of the size of the sphere of influence of the intermolecular forces. At temperatures below the critical temperature the second term in the denominator is negligible compared to $1/\beta$ and equation 58 reduces to equation 48. Very close to or at the critical temperature, however, the compressibility, β, is very great, and the second term in the denominator predominates; and therefore the intensity becomes proportional to $1/\lambda^2$. The quantity g can be obtained from experiment and has been given in terms of the radial distribution function by Ornstein and Zernicke (137). Some objections to the more explicit definition of g have been raised by Placzek (150) and by Rocard (178); however, equation 58 reproduces the general features of the scattering at the critical temperature. Mueller (131) has extended the theory to take into account non-independent fluctuations in the orientation of anisotropic molecules.

Rousset (180) has examined several liquid mixtures at the critical mixing temperature. He has observed the dissymmetry in scattering which is predicted by equation 58 when the second term in the denominator predominates.

The light-scattering method is also useful for studying phase changes besides those which occur at the critical temperature. It could be used, for example, to detect possible premelting at temperatures just below the melting point of a solid (Ubbelohde (209); for theory, see Frenkel (56, chapter 7, Section 3)) and to determine the kinetics of phase changes. The light-scattering method has been used by Donnan and Krishnamurti (40) to study sol–gel transformations. They found that for agar solutions the intensity and depolarization of scattered light increase markedly when the sol is transformed into a gel on cooling. These authors attribute this change in scattering to the formation of micelles in the gel. Tobacco mosaic virus gels, however, show less scattering than that of the sols because the gel is an ordered structure (Bernal and Fankuchen (12), Oster (141)).

4. Interfaces

It was early recognized by Smoluchowski (192) that there should be increased scattering by the surface of a liquid as the critical temperature is approached, because of the increased density fluctuations. Mandelstam (121) soon after developed a theory of the scattering of surfaces which is the two-dimensional analog of the volume scattering of Ornstein and Zernicke (136, 137). According to Mandelstam, at temperatures below the critical temperature the intensity of scattering from a surface, i_s, per unit area of surface is given by

$$\frac{i_s}{I_0} = \frac{4kT(\epsilon - 1)^2}{\gamma\lambda^2 r^2} f \tag{59}$$

where f is a function of the angles of incidence and of observation and depends on the degree of polarization of the incident beam and γ is the interfacial tension. As the surface tension is decreased, the density fluctuations at the surface increase and the intensity of scattering increases. The theory has been extended by Gans (64) to include liquid metal surfaces and the general theory has been modified slightly by Gans (66) and by Andronov and Leontovich (4). Detailed investigations by Raman and Ramdas on the intensity of light scattered from surfaces of metallic liquids (162), of transparent liquids (163), and of liquid carbon dioxide near the critical temperature (164) show good agreement with Mandelstam's theory. The scattered light which is usually observed close to the beam reflected from the surface does not, however, show exact agreement in angular distribution predicted by the theory (Ramdas (168); see also Jagannathan (89) and Hariharan (82)).

Raman and Ramdas (164) found that the intensity of scattering increased when surface-active agents were applied to water. The light-scattering method affords a convenient method for studying surface films especially as regards their continuity (see Zocher and Stiebel (226) and Adams (1)) and could also be used to study the orientation of molecules at surfaces. Schaeffer (183) has studied the light-scattering properties of monolayers on metallic surfaces. Since in equation 59 γ refers to the interfacial tension, the light-scattering method provides a simple way to determine the interfacial tension.

5. Fine structure of the Rayleigh line

Fine structure was first observed by Gross (75) in an examination, under high resolution, of light scattered at 90° by liquids. In general, one observes with a spectroscope or interferometer that the scattered light consists of three lines: an undisplaced center line and two lines on either side with wave lengths slightly different from that of the incident light. Usually these lines can be distinguished from the Raman scattering of the liquid. The displaced lines can be attributed to the Doppler shift of the scattered radiation which is reflected from the system of Debye sound waves excited by thermal energy (Brillouin (22), Leontovich and Mandelstam (116); see also Frenkel (56, Chapter 4, Section 8)).[7] According to Landau and Placzek (110), the undisplaced line, which in general is brighter, is due to entropy fluctuations which vary relatively slowly with time. The ratio of the intensity of the center undisplaced line, I_c, to the intensities of the displaced doublets, $2I_d$, is given by Landau and Placzek (110) as

$$\frac{I_c}{2I_d} = \frac{C_p - C_v}{C_v} \tag{60}$$

where C_p and C_v are the specific heats at constant pressure and volume, respectively. A complete derivation of this formula is given by Gross (78). The

[7] *Added in proof:* A. B. Bhatia and K. S. Krishnan (Proc. Roy. Soc. (London) **A192**, 181 (1948)) have shown that the intensity of the displaced lines is given by the same expression derived by I. Waller (Uppsala Univ. Årssk. (1925)) for x-ray scattering from substances when thermal vibrations are taken into account.

ratio of the intensities of the central line to that of the doublets is given by the ratio of the contributions to the fluctuations in the optical dielectric constant due to fluctuations in entropy and those due to fluctuations in pressure associated with ordinary sound waves, or

$$\frac{I_c}{2I_d} = \frac{\left(\frac{\partial v}{\partial s}\right)_p^2 \overline{(\Delta S)^2}}{\left(\frac{\partial v}{\partial p}\right)_s^2 \overline{(\Delta p)^2}} \tag{61}$$

With the aid of equation 36 and some well-known thermodynamic relations, equation 61 leads to the Landau and Placzek formula, equation 60. Gross (76) and Birus (15) (see also Meyer and Ramm (123a) and Ramm (168a)) found that this formula held for a few liquids. For some substances, for example water and quartz, $C_p \simeq C_v$, so the center line is very feeble. However, for a number of other liquids, e.g., benzene, the center line has a greater intensity than that given by the Landau and Placzek formula (Gross (76), Venkateswaren (213)). The very intense center line can, in several cases, be attributed to orientation fluctuations by anisotropic molecules and is highly depolarized (Gross (77), Venkateswaran (213)). The intensity of the center line is increased with increasing viscosity, that is, with increasing rotational relaxation time of the anisotropic molecules (see Leontovich (114)). However, it has been found by Gross and Siromyatnikov (81) and by Bai (6) that for very viscous liquids which do not contain anisotropic molecules, the center line is of greater intensity than that predicted by the Landau and Placzek formula and is not depolarized. This result is as yet not completely explained, but even in the absence of a complete theory it is clear that the ratio of intensities of the center line to that of the doublets is a measure of the amount of thermal energy apportioned between the pressure and the entropy fluctuations. A study of the Rayleigh scattering lines for certain solids gives some information about molecular rotation in solids (Gross and Raskin (79)).

According to Ginsburg (74), the widths of the lines must be considered when their intensities are determined. He has related the width of the central line to the heat conductivity and the width of the doublets to the absorption of sound in the liquid. Recent work by Gross and Raskin (79), by Fabelinsky (53), and by Vuks (217) on the detailed structure of the Rayleigh lines indicates confirmation of Ginsburg's theory.

In view of the extraordinary physical properties of helium II, especially its ability to propagate two types of sound waves, it might be expected that this substance would show unusual fine structure of the Rayleigh scattering (for discussion, see Ginsburg (73) and Argawala and Chowdri (5)), but no experimental results on the fine structure have as yet been reported. Jakovlev (90) has found that the intensity of scattering by helium II below 2° A. is that given by equation 48. As Ginsburg (73) has pointed out, the observed intensity is that expected from Landau's theory of helium II and is less by a factor of ten thousand than that for a condensed Bose–Einstein gas calculated by Fusov, Belinsky, and

Galanin (59) (see also Singh (188), Schiff (184), and Galanin (60)).   Incidentally, Fusov, Belinsky, and Galanin (59) have also calculated the light scattering from a Fermi–Dirac gas and derive results which explain the incoherent part of the scattering of x-rays by metals (see also the interesting treatment by Frenkel (54, Chapter 6, Section 35) of electrical conductivity as a problem in fluctuation scattering).   In their theoretical treatment of the fluctuations they use the Bose–Einstein and Fermi–Dirac distributions instead of the Maxwell–Boltzmann distribution given by equation 33.

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