CLASSICAL THEORY OF LIGHT SCATTERING FROM SOLUTIONS—A REVIEW

BRUNO H. ZIMM, R. S. STEIN, and PAUL DOTY,
Polytechnic Institute of Brooklyn

I. INTRODUCTION

G ENERAL INTEREST IN LIGHT SCATTERING has greatly increased in the last few years due largely to its application to the study of colloidal suspensions and polymer solutions. The chemist who wishes to acquaint himself with the theoretical background in this field finds that Cabannes' treatise (4), containing the best basic treatment of the subject, is out of print and essentially unobtainable. The only other book on this subject—Bhagavantam (1)—does not adequately cover a considerable portion of relevant material. Moreover, neither of these books treats the developments of the past decade or the special problems connected with large molecules. Finally, the initial work on light scattering from solutions of large molecules has not produced a literature adequate to provide one with a working knowledge of the subject.

In this stage of development it may be useful to summarize the main features of the classical theory of light scattering and the recent extensions of the theory that are applicable to solutions of large molecules. Because of limitations of space, practically no reference will be made to experimental work. The development begins with the treatment of scattering from an isolated vibrating dipole. By use of fluctuation theory and thermodynamics this treatment is extended to scattering from a binary mixture. The special problem of scattering from solutions of large molecules is then developed on the basis of relations between scattering and (1) molecular weight and (2) size and shape of the solute molecules. Finally, the theory of depolarization is treated together with a review of the useful information obtainable from measurements of depolarization with unpolarized and polarized light.

II. SCATTERING OF LIGHT FROM AN ISOLATED MOLECULE

Polarized, monochromatic light waves propagating in free space consist of an electromagnetic disturbance, having equal electric and magnetic fields, **E** and **H**, directed at right angles to one another varying in intensity sinusoidally with time; the wave travels perpendicularly to both of these components. These properties may be rigorously described in the form of solutions of Maxwell's electromagnetic equations (3). The energy density at any point is, of course, the sum of the energy densities of the respective fields; and, since the fields vary

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with time, energy flows from one place to another. Investigation shows that the *instantaneous* rate of flow of energy at any point is given by Poynting's vector, S, which is proportional to the vector product of the electric and magnetic fields at that point:

$$\mathbf{S} = \frac{c}{4\pi} \mathbf{E} \times \mathbf{H} \tag{1}$$

If this is averaged over time to obtain the average rate of flow of energy per square centimeter in the direction of propagation, that is, the intensity of the light beam, I, it is found that

$$I = \frac{c}{8\pi} E_0^2 \tag{2}$$

E_0 is the maximum value, or amplitude, of $\mathbf{E}$.

If a molecule of a transparent, nonabsorbing substance lies in the light beam, it will scatter energy from the beam, behaving as a source of secondary radiation. This secondary or scattered light depends in character on both the incident light and on the molecule itself, and so serves as a source of information about either. The classical theory of this effect will now be summarized.

For the present we will confine the discussion to small isotropic, spherical molecules, introducing the complicating factors of size and internal structure later. When such a molecule is placed in an electric field, such as a light wave, the negatively charged electrons are shifted slightly in one direction and the positively charged nuclei in the other, so that the molecule acquires an electric dipole moment. It is generally found, for fields of the intensities and frequencies we are here concerned with, that this induced moment is proportional to the field strength; if p is the dipole moment and E represents the magnitude of the electric field,

$$p = \alpha E \tag{3}$$

α is the proportionality constant called the polarizability.

The electric field of a light wave may be represented by a sine or cosine function of time and distance such as the following:

$$E = E_0 \cos \frac{2\pi}{\lambda} (x - ct) \tag{4}$$

λ is the wave length of the light, x is the distance in the direction of propagation, and E_0 is the amplitude of the light wave.

As this wave passes over a molecule placed at a certain position, x_0, in the path of the light, it will exert an oscillating electric force on the electrons in the molecule and these will respond to produce an oscillating dipole moment (see Fig. 1). The magnitude of the moment at any time is obtained from (3) and

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(4). Thus:

$$p = \alpha E_0 \cos \frac{2\pi}{\lambda} (x_0 - ct) \qquad (5)$$

According to classical electromagnetic theory, an oscillating dipole of this kind should radiate energy in the form of spherical waves of light. The strength of the electric field of these waves at a distance r from the vibrating dipole is given (3, 18, 20) by equation (6).

$$E' = \frac{1}{c^2 r} \frac{\partial^2 [p]}{\partial t^2} \cos \phi = \alpha E_0 \frac{4\pi^2}{\lambda^2 r} \cos \frac{2\pi}{\lambda} (x_0 - ct + r) \cos \phi \qquad (6)$$
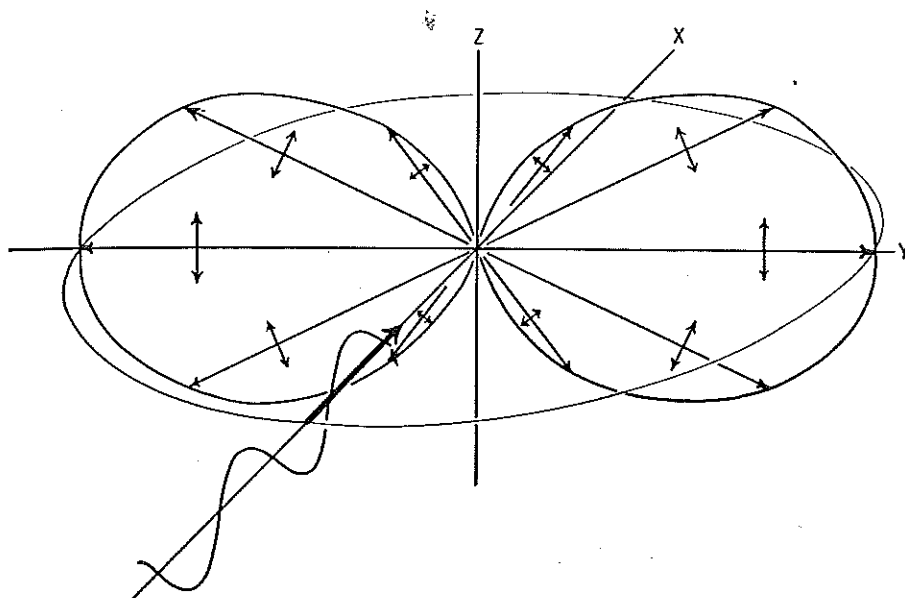

Fig. 1. Scattering from small particle with polarized incident light

[Light is scattered from a particle at the origin; the scattered intensity is indicated by the lengths of the vectors in the various directions and the polarization by the double-headed arrows. The scattering is completely polarized and symmetrically distributed around the Z axis.

In this equation the brackets around p indicate that, wherever t appears, it is to be replaced by the retarded time, $(t - r/c)$, to allow for the time it takes the scattered wave to travel the distance r from the molecule. Angle ϕ is the angle between the directions of vibration of the electric vectors in the incident and

scattered rays. This direction in the scattered ray is perpendicular to its direction of propagation, as it must be in any light beam, and always lies in the plane determined by the direction of the electric vector in the incident light and the direction of propagation of the scattered beam at the point in question.

The intensity of scattering in any direction, I', is given as usual by $c/8\pi$ times the square of the amplitude, E_0', of the vibration. If we recognize that the intensity of the incident beam, I_0, is $c/8\pi$ times the square of E_0, we obtain:

$$I' = \frac{16\pi^4\alpha^2 I_0 \cos^2\phi}{\lambda^4 r^2} \tag{7}$$

Thus it is found that the polarization and intensity of the scattered light depend in a regular way on the direction of scattering. These relations are diagrammed in Figure 1.
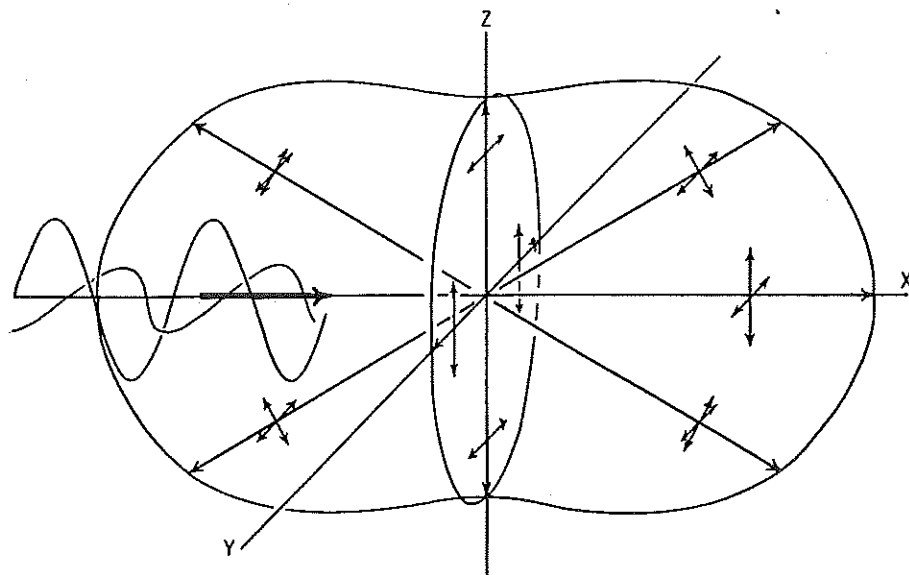

Fig. 2. Scattering from small particle with unpolarized incident light

The incident light is analyzed into two perpendicularly polarized beams out of phase. The scattered light, as indicated by the arrows, also generally contains two independent components, except for light in the $X-Y$ plane. The scattering is symmetrical around the X axis.

An unpolarized light beam may be thought of as the superposition of two polarized beams, polarized at right angles to each other, and incoherent in phase, that is, with phases which vary at random with respect to one another. Each one of these beams induces independent oscillations in the molecule and these

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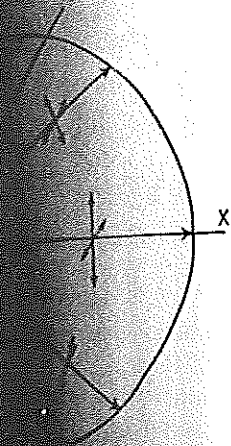
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scatter light independently of one another. A diagram of the resulting scattering is given in Figure 2. The light is now equally bright and completely polarized in all directions normal to the incident beam. However, it is twice as bright and completely unpolarized in both the forward and backward directions of the incident beam. This situation is represented by the equation:

$$I' = \frac{8\pi^4 \alpha^2 I_0 (1 + \cos^2 \theta)}{\lambda^4 r^2} \qquad (8)$$

θ is the angle between the incident beam and the direction of scattering.

III. SCATTERING FROM A SOLUTION

It has been shown that energy will be radiated in all directions from a polarizable molecule (or small particle) residing in the force field of a light wave. In most practical cases, however, since it is impossible to observe the scattering of a single molecule, it is necessary to study what happens when a number of molecules are simultaneously illuminated.

The simplest case is that of the perfect gas, where the molecules move at random and completely independently of one another. Hence each molecule may be considered as an independent source, and the intensity of the total scattered light will be the sum of the intensities from each of the individual molecules, as stated by Mariotte's law for independent sources.

However, in a condensed phase the molecules are far from being independent of one another; in fact, they are arranged in something approaching a regular manner. All molecules in a given part of the incident wave front will be vibrating with the same phase, but since they occupy nearly regular positions there will be interference between their scattered waves just as in a diffraction grating. The usual result is that the aggregate intensity is sharply reduced below the sum of the intensities which would come from each molecule alone if it were isolated. For this reason pure liquids, which have several hundred times as many molecules per unit volume as their vapors at atmospheric pressure, only scatter from ten to fifty times as much light.

There are several ways of calculating the extent of this interference. Perhaps the most direct (21) is to add up immediately the scattered wave trains from the different molecules, taking due account of their varying phases, and average over all positions of the scattering molecules. This method involves some rather recondite statistical mechanics and is not well suited to our present purposes. A simpler method is known as the *thermodynamic method*, originally used by Einstein (8) and more recently applied to polymer solutions by Debye (5). This treatment is less direct and tends to conceal some of the assumptions involved by its very elegance; nevertheless, it skillfully accomplishes a difficult task with small effort.

The Thermodynamic Method

The extreme opposite of a perfect gas, with its random molecular arrangement, is the perfect crystal, where the molecules are placed in absolute order at small distances from one another. Such a medium is completely homogeneous from an optical standpoint and scatters no light; this may be demonstrated readily with the aid of Figure 3. Let A and B be two members of a lattice of volume
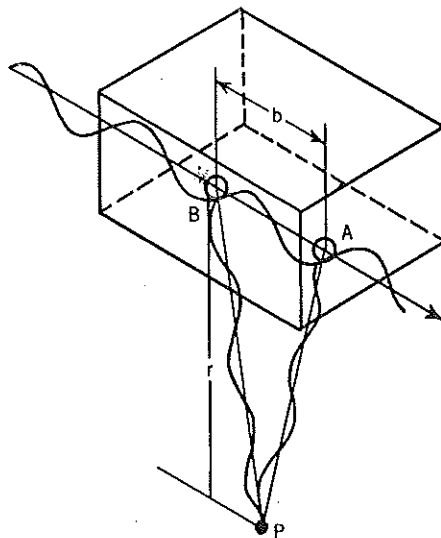

Fig. 3. Scattering from a homogeneous medium

elements, v_0, which are small as compared with the wave length and are regularly distributed throughout the medium. All the molecules in one of these elements may be considered as concentrated in a point source of radiation. The waves scattered by each will be given by equation (6), with the appropriate values of r.

If the medium is absolutely homogeneous, A and B scatter exactly the same amount of light and the electric fields from each at the observation point P have the same strength. The distance, b, between them, however, is arbitrary and may be chosen so that these fields act in opposite directions because of the difference in the values of r in equation (6). They will then cancel.

All of the elements of the medium may be paired in this manner (except those in thin layers near the surfaces which are negligible), and the total scattered intensity will be zero.

It is thus apparent that a perfectly homogeneous transparent medium would scatter no light. Actual transparent liquids are not completely homogeneous, however, as a result of the thermal motions of the molecules. If we consider a

small volume in a mass of fluid we will find that molecules are continually moving in and out of it as a result of their chance wanderings, with the result that the number in the volume, and hence the density, fluctuate at random about a mean value. If the liquid is a mixture, the concentrations in the small volume fluctuate in the same way as the density.

In most cases the refractive index of the material changes with the density and concentration, so that, as a result of the fluctuations of these two variables, the medium is rendered turbid by the presence of minute refracting inhomogeneities.

The probable extent of the fluctuations of density and concentration from their equilibrium value can be calculated by Boltzmann's theorem from statistical mechanics. If the increase of the Gibb's free energy of the fluid as a whole (at constant temperature and pressure) when the small volume changes from its equilibrium state to another state is ΔF, then the probability of this change is equal to:

$$W = Ce^{-\Delta F/kT} \qquad (9)$$

where C is a proportionality constant and k and T have their usual meanings.*

If then we know the relation between the refractive index and the density and concentration, and the relation between these two quantities and the free energy, we are in a position to calculate the probability of a deviation of the refractive index from the normal due to thermal fluctuations in any small volume. By the application of classical electrodynamic theory, we can then calculate the intensity of the light scattered from such a volume immersed in a fluid of normal refractive index. Because of the fortunate circumstance that the fluctuations in any one volume are random and independent of those going on around it, it is possible merely to add up the intensities from all the volume elements of the fluid to obtain the total scattering, since the coherence of phase necessary for abnormal interference is lacking here.

The details of the method will now be outlined before returning to the question of its significance and limitations.

Let us calculate the light scattered from a small element of volume, v_0, of refractive index, n, when immersed in a fluid of refractive index, n_0. By using equation (6), the radiation field at a distance r will be:

$$E' = \frac{4\pi^2 \cos \phi p v_0}{\lambda^2 r} \cos \frac{2\pi}{\lambda} (x_0 + r - ct) \qquad (10)$$

* The derivation of this rather unfamiliar form of Boltzmann's expression from the usual form which applies at constant volume and energy, $W = e^{\Delta S/k}$, is as follows. Consider a mass of fluid containing the small volume to be in thermal equilibrium with a large reservoir of material and the whole system to be isolated so that its energy and volume are constant. Now let a reversible change take place to produce the fluctuation in the small volume. The probability of the fluctuation will be the exponential of the entropy change of the system as a whole, ΔS_t, since the conditions are such that the above equation applies. But if ΔS_f and ΔS_r are the entropy changes in the fluid and reservoir, respectively, $\Delta S_t = \Delta S_f + \Delta S_r$. Since the change is reversible and ΔH_t must be zero, $\Delta S_r = \Delta H_r/T = -\Delta H_f/T$. Therefore, $\Delta S_t = \Delta S_f - \Delta H_f/T = -\Delta F_f/T$. Substitution in the first equation gives the desired relation. The demand that the change be reversible is equivalent to demanding that it take place at constant temperature and pressure.

where p is the dipole moment per unit volume and pv_0 is the moment induced in the volume element v_0. We will separate p into two parts: p_0, equal to the average moment per unit volume in the rest of the fluid; and Δp, the fluctuation from the mean, so that:

$$p = p_0 + \Delta p = (\alpha_0 + \Delta\alpha)E_e \tag{11}$$

where E_e is the effective incident field. Since the part of E' due to p_0 is exactly the radiation field which would be produced by a homogeneous medium of index n_0, this will be exactly cancelled by other fields as we have previously seen. The only part of E' which survives is that due to Δp. We therefore write:

$$E' = \frac{4\pi^2 \cos\phi\, \Delta\alpha E_e v_0}{\lambda^2 r} \cos\frac{2\pi}{\lambda}(x_0 + r - ct) \tag{12}$$

The intensity is c times the time average of the square of E' over 4π:

$$I' = \frac{2\pi^3 c \cos^2\phi}{\lambda^4 r^2}\overline{\Delta\alpha^2}E_{e0}^2 v_0^2 \tag{13}$$

This is the equation if the incident light is plane polarized. We will return to the unpolarized case later.

It is now necessary to calculate the mean square of the fluctuation in polarizability, $\overline{\Delta\alpha^2}$, which appears in equation (13). First of all, we note that the polarizability is a function of the density and concentration. In this paper we shall give the derivation making use of the concentration as the only fluctuating variable, since this is the more important one in polymer solutions. The calculation involving density fluctuations is not essentially different.

The polarizability is an approximately linear function of the concentration over a small range. It is therefore possible to write:

$$\Delta\alpha = \frac{\partial\alpha}{\partial g}\Delta g \tag{14}$$

for the fluctuation $\Delta\alpha$ in terms of the fluctuation Δg in the concentration. The polarizability of a volume, v_0, of material exposed to an external radiation field is related to the refractive index, n, of the material by:

$$\alpha = \frac{n^2 - 1}{4\pi} \tag{15}$$

Therefore

$$\frac{\partial\alpha}{\partial g} = \frac{n}{2\pi}\frac{\partial n}{\partial g} \tag{16}$$

and

$$\overline{\Delta\alpha^2} = \frac{n^2}{4\pi^2}\left(\frac{\partial n}{\partial g}\right)^2\overline{\Delta g^2} \tag{17}$$

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All quantities in this equation are measurable constants except $\overline{\Delta g}^2$. However, if the relation between g and the free energy is known, $\overline{\Delta g}^2$ can be calculated with the aid of equation (9).

Consider an element containing w_2 grams of solute in a volume v_0 at its equilibrium state. At the fluctuation state, these w_2 grams of solute will be contained in the volume v_0' of solution. Then the fluctuation in concentration, Δg, is:

$$ \Delta g = g' - g_0 = \frac{w_2}{v_0'} - \frac{w_2}{v_0} \qquad (18) $$

If the weight of solvent in the volume element in the equilibrium state is w_{10} and in the fluctuation state is w_1', and the density of the solution (assumed to be constant) is ρ, then

$$ v_0 = \frac{w_{10} + w_2}{\rho} \qquad (19) $$

and

$$ v' = \frac{w_0' + w_2}{\rho} \qquad (20) $$

so that

$$ \Delta g = \frac{w_2 \rho}{w_0' + w_2} - \frac{w_2 \rho}{w_{10} + w_2} \qquad (21) $$

or

$$ \Delta g = \frac{w_2 \rho (w_{10} - w_1')}{(w_1' + w_2)(w_{10} + w_2)} \qquad (22) $$

Let us define

$$ \Delta w_1 = w_1' - w_{10} \qquad (23) $$

Then

$$ \Delta g = \frac{-w_2 \rho (\Delta w_1)}{(w_{10} + w_2)^2 + \Delta w_1 (w_{10} + w_2)} \qquad (24) $$

But $\Delta w_1 (w_{10} + w_2)$ in the denominator is small as compared with $(w_{10} + w_2)^2$ and may be neglected. Then:

$$ \Delta g = \frac{-w_2 \rho (\Delta w_1)}{(w_{10} + w_2)^2} = -\frac{\Delta w_1 g_0}{\rho v_0} \qquad (25) $$

If n_1 represents the number of moles of solvent; that is

$$ n_1 = w_1 / M_1 \qquad (26) $$

where M_1 is the molecular weight of the solvent, we may substitute in equation (25) and obtain:

$$ \Delta g = -\frac{M_1 g_0 (\Delta n_1)}{\rho v_0} \qquad (27) $$

The free energy change accompanying this concentration fluctuation is equal to the differences in the free energy changes involved in removing the n_1 moles of solvent from the solution at its equilibrium concentration, g_0, and adding it to the solution contained in the element (of instantaneous concentration, g) reversibly. At the end of this process, the concentration of the solution in the element should equal the fluctuation value of g'. Therefore:

$$\Delta F = \int^{g'} \left\{ \left(\frac{\partial F}{\partial n_1} \right)_g - \left(\frac{\partial F}{\partial n_1} \right)_{g_0} \right\} d(\Delta n_1) \tag{28}$$

But,

$$\left(\frac{\partial F}{\partial n_1} \right)_g - \left(\frac{\partial F}{\partial n_1} \right)_{g_0} = \frac{\partial^2 F}{\partial n_1^2} (\Delta n_1) \tag{29}$$

Since the fluctuations are small, higher order terms may be neglected. Also, the partial molar free energy, $\overline{F}_1$, is defined as:

$$\overline{F}_1 = \left(\frac{\partial F}{\partial n_1} \right) \tag{30}$$

Therefore:

$$\Delta F = \frac{1}{2} \left(\frac{\partial \overline{F}_1}{\partial n_1} \right) (\Delta n_1)^2 \tag{31}$$

Substituting in the value of Δn_1 from equation (27):

$$\Delta F = \frac{\rho v_0}{2 g_0 M_1} \left(- \frac{\partial \overline{F}_1}{\partial g} \right) (\Delta g)^2 \tag{32}$$

We may then find the probability of such a fluctuation in concentration from the Boltzmann expression, equation (9). This is:

$$W(\Delta g) d(\Delta g) = C \exp \left[- \frac{\rho v_0}{2 g_0 M_1 kT} \left(- \frac{\partial \overline{F}_1}{\partial g} \right) (\Delta g)^2 \right] d(\Delta g) \tag{33}$$

The mean square of Δg is evaluated from the integral which defines it:

$$\overline{\Delta g^2} = \int_{-\infty}^{\infty} W(\Delta g)(\Delta g)^2 d(\Delta g), \tag{34a}$$

$$= \frac{kT M_1 g_0}{\rho v_0 \left(- \dfrac{\partial \overline{F}_1}{\partial g} \right)} \tag{34b}$$

The intensity of the scattered light for unpolarized incident light is now:

$$I' = \frac{\pi c \cos^2 \phi n^2 \left(\dfrac{\partial n}{\partial g} \right)^2 kT M_1 g v_0 E_o^2}{2 \lambda^4 r^2 \rho \left(- \dfrac{\partial \overline{F}_1}{\partial g} \right)} \tag{35}$$

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All the factors in this equation are directly measurable except E_e, the "effective" field. This is the field due not only to the incident light, but also that resulting from the displaced charges in the rest of the medium. Since E_e is proportional to p, and p is proportional to the external field, E, proportionality must exist between E_e and E.

$$E_e = \xi E \tag{36}$$

An exact evaluation of the factor ξ would involve an integration over the fields produced by all the rest of the medium. To date, this has not been accomplished, except by the use of the following rather drastic approximation due to Lorentz (12): the medium is assumed to be a continuous, uniform fluid, enclosing a cavity in which the volume element whose scattering we are studying is placed. It is then found that the factor is strongly dependent on the shape of the cavity, ranging in value from n^2 for a needle-shaped space parallel to the field to unity for a pillbox or disk cutting across the field. For a sphere, the value is $(n^2 + 2)/3$. The situation is further complicated by the possibility that the part of E_e due to polarization may fluctuate and that there may be a correlation between these fluctuations and those in v_0.

At present, then, only a rather unsatisfactory statement may be made concerning ξ; it is a factor depending on the constitution of the material whose value probably lies between n^2 and unity, perhaps near $(n^2 + 2)/3$.

If we note that the intensity of the incident light is $I_0 = (c/8\pi)E_0^2$, the scattering from one volume element is:

$$I' = \frac{4\pi^2 \cos^2 \phi \, \xi^2 n^2 \left(\dfrac{\partial n}{\partial g}\right)^2 kTM_1 g v_0 I_0}{r^2\lambda^4\rho \left(-\dfrac{\partial \overline{F}_1}{\partial g}\right)} \tag{37}$$

We can now add up the scattering from all volume elements to get the total intensity with polarized incident light. Since the sum of all the values of v_0 is V, the total volume, the total scattering is:

$$I' = \frac{4\pi^2 \cos^2 \phi \, \xi^2 n^2 \left(\dfrac{\partial n}{\partial g}\right)^2 kTM_1 g V I_0}{r^2\lambda^4\rho \left(-\dfrac{\partial \overline{F}_1}{\partial g}\right)} \tag{38a}$$

If the incident light is unpolarized, a formula corresponding to (8) is obtained:

$$I' = \frac{2\pi^2(1 + \cos^2 \theta)\xi^2 n^2 \left(\dfrac{\partial n}{\partial g}\right)^2 kTM_1 g V I_0}{r^2\lambda^4\rho \left(-\dfrac{\partial \overline{F}_1}{\partial g}\right)} \tag{38b}$$

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The "turbidity," τ, is the fraction of the incident light scattered per cubic centimeter in all directions. This is found by integration to be:

$$\tau = \frac{32\pi^3\xi^2 n^2 \left(\dfrac{\partial n}{\partial g}\right)^2 kTM_1 g}{3\lambda^4 \rho \left(-\dfrac{\partial \overline{F}_1}{\partial g}\right)} \tag{39}$$

This is the expression for the turbidity due to concentration fluctuations.

To these equations should be added a term which results from the density fluctuations, and is essentially equal to the turbidity of the pure solvent, in order to obtain an expression for the turbidity of the solution. For polymer solutions, this term is small. Including it, the complete formula for the turbidity is (7):

$$\tau = \frac{32\pi^3\xi^2 n^2 kT}{3\lambda^4} \left\{ \beta\rho^2 \left(\frac{\partial n}{\partial \rho}\right)^2 + \frac{M_1 g}{\rho\left(-\dfrac{\partial \overline{F}_1}{\partial g}\right)} \left(\frac{\partial n}{\partial g}\right)^2 \right\} \tag{40}$$

where β is the compressibility, $-\left(\partial \ln V/\partial P\right)_r$.

We have now obtained a formula relating the intensity of the scattered light from a solution with the derivative of refractive index with respect to concentration and the free energy of one component (the solvent). The principal use of the equation is in obtaining the latter quantity from the first two.

In dilute solutions van't Hoff's law applies, and the molecular weight of the solute may be obtained from equation (41):

$$-\frac{\partial \overline{F}_1}{\partial g} = \frac{\overline{V}_1 RT}{M_2} \tag{41}$$

where V_1 is the partial molar volume of the solvent.

In polymer solutions the deviations from van't Hoff's law are frequently serious. In this case, the molecular weight may be obtained by extrapolating the results to infinite dilution. At the same time, the deviations from ideality, which are themselves of considerable interest in the theory of solutions, may be obtained by studying the scattering as a function of concentration. For advantageous methods of handling such data the reader is referred elsewhere (7, 19).

Discussion

In this way the use of the theory of fluctuation phenomena avoids the complications encountered in a direct summation of the radiation fields from an assembly of molecules. One may reasonably question, however, the exactness of the assumption that the fluctuations in one volume, v_0, are independent of those in the surrounding volumes. The answer to this question was given by

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Ornstein and Zernicke (15). The assumption is valid if the range of the intermolecular forces is of a smaller order of magnitude than the light wave length. The same conclusion has been reached from a treatment of the problem by the direct summation method by one of the authors (21). For polymer solutions, in which some of the molecules themselves are larger than the wave length, the assumption may not always hold. The theory of this effect will be discussed later in connection with the scattering from large molecules, but it may be remarked here that it offers a possible method of studying the internal structure of such solutions.

The least certain part of the derivation was that concerned with the internal field factor, ξ. Theoretically, it seems most likely that it should have the value appropriate for a sphere, $(n^2 + 2)/3$, but the only experimental results (7, 19) available indicate a value of nearly unity. More work on this point is imperative.

IV. SCATTERING OF LIGHT FROM LARGE MOLECULES

If a scattering particle is small as compared with the wave length of the light, it may be considered as a point source of radiation. It has been previously shown that the dependency of the intensity of the scattered light on the angle of observation would then be entirely a function of the projection of the induced dipole moment on a normal to the direction of observation, and would, for unpolarized incident light, vary as $(1 + \cos^2 \theta)$. In Figure 2 (page 93), a polar plot of this angular distribution is shown. It is seen that the intensities are symmetrically distributed about the 90° axis.

If, however, a linear dimension of the molecule approaches the magnitude of the wave length (greater than $1/10$ to $1/20$ of the wave length), the radiation from all of its component dipoles would vary in phase, and the molecule could not be considered in its entirety as a simple point source. Since the radiation from the component parts of any one molecule will be coherent, the resulting scattered intensity will then be proportional to the square of the vector sum of the amplitudes of the scattered rays from all of the scattering elements. This process will result in an interference pattern which is characteristic of the size and shape of the particle.

This phenomenon may be readily illustrated with the aid of a simple example. The sphere in Figure 4 represents a scattering particle of dimensions which are of the order of magnitude of the wave length. Consider two scattering volume elements of the particle at A and B, and two incident rays, R_1 and R_2, which are in phase at plane P. In reaching the observation point, O_1, ray R_1, which goes the longer distance to reach element A, goes the longer distance AO_1; while ray R_2, which goes the shorter distance to the element, goes the shorter distance to the observation point. Thus, the differences in path lengths are partially compensated for, and the rays do not get very much out of phase.

For observation point O_2, however, the situation is reversed; the ray which goes the longer distance from the plane to the element goes the longer distance to the observation point. If, as in this illustration, the molecular dimensions
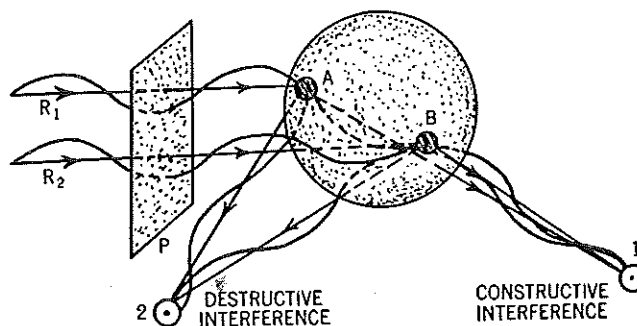

Fig. 4.   Scattering from a large particle

are something less than a wave length, the path difference will be such as to produce a phase lag that will result in destructive interference of the two rays. Therefore, it may be seen that, as a result of this interference effect, there will be an all-around decrease in the scattered intensity. Since destructive interference will be more probable between rays scattered in the backward direction, the radiation envelope will no longer be symmetrical.
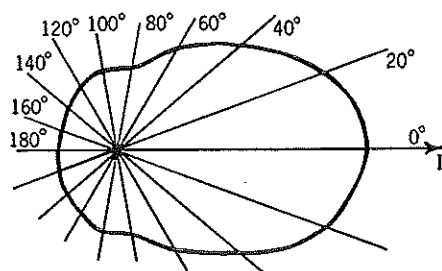

Fig. 5.   Radiation diagram for scattering from a large particle

A typical first-order interference pattern of this type is shown in Figure 5. For still larger particles, path differences of greater than one-half wave length will be produced and higher order interference will occur. More than one intensity maximum will then be experienced (3).

The evaluation of this interference effect for particles of simple geometric shape has been studied by Mie (14). Its exact evaluation is difficult, however, when the refractive index of the particle is much different from that of the me-

... is reversed; the ray which
... element goes the longer distance
... the molecular dimensions

CONSTRUCTIVE
INTERFERENCE

... particle
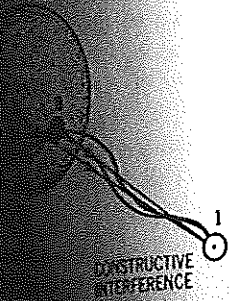
... will be such as to pro-
... ference of the two rays.
... some effect, there will be
... destructive interference
... backward direction, the

... particle

... in Figure 5.
... wavelength will
... intensity

... geometric
... however,
... the me-

dium in which it resides. The problem which then arises involves the determination of the effect of the polarization charges on the surface of the particles on the electric field acting upon a particular dipole as a function of the position of that dipole in the particle. A solution of Maxwell's equations under these conditions, even for particles of simple geometric shape, usually leads to complicated expansions, the application of which is difficult. Blumer (2) has obtained integrated solutions of this type for spheres.

P. P. Debye and P. Debye (5) have shown that a treatment in which the approximation of no refractive index is made is sufficiently accurate for many purposes. They have obtained solutions for particles having such shapes as spheres, rods, and random coils. The last two shapes most nearly correspond to those of high polymer molecules and they are considered here.

The method of solution is to consider the large molecule to be made up of a large number of submolecules, each of which is small as compared with the wave length and may be considered as a point source of radiation. The polarizability of one of these submolecules is then simply equal to the algebraic sum of the polarizabilities of its constituent dipoles.
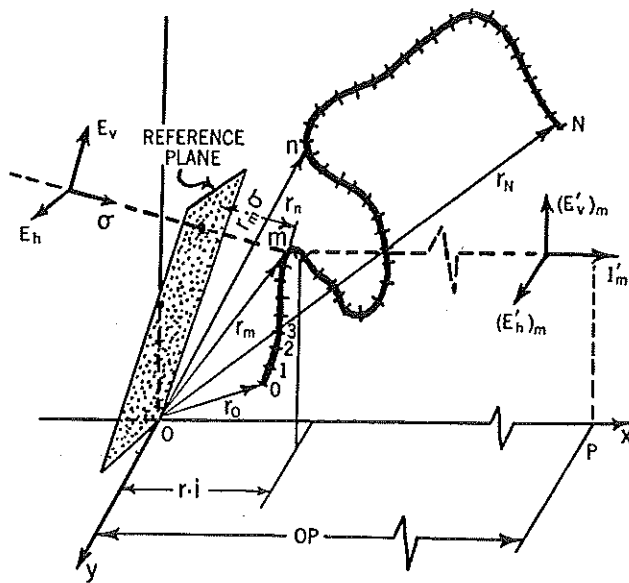

Fig. 6. Scattering from an element of a large polymer molecule

Consider a molecule, ON, residing in the field of the light wave (Fig. 6). It is located by the Cartesian coordinates, OX, OY, and OZ, and is divided into a large

number of elements $(0, 1, 2, 3, \ldots m, \ldots n, \ldots N)$. Let $\mathbf{r}_0, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_m \ldots \mathbf{r}_n \ldots \mathbf{r}_N$ be vectors, drawn from the origin, O, and $\mathfrak{d}$ be a unit vector pointing in the direction of propagation of the incident light. The observation point, P, is located far out on the X axis. As before, $\mathbf{E}_h$ and $\mathbf{E}_v$ are the horizontally and vertically polarized components of the electric field vector of the incident light; $\mathbf{E}_h'$ and $\mathbf{E}_v'$ are the components for the scattered light, and I' is its intensity.

The field of a scattered ray from the mth submolecule is given by equation (6) and is:

$$(E_h')_m = K \cos \frac{2\pi}{\lambda} (c'l - d_m) \tag{42}$$

where K is a constant involving the incident amplitude and frequency, the polarizability of the submolecule, and the distance from the molecule to the point of observation*; λ and c' are the wave length and velocity of the light in the medium in which the scattering takes place; and d_m is the sum of the distance from an arbitrary reference plane to the mth element and the distance from that element to the observation point. That is:

$$d_m = \mathbf{r}_m \cdot \mathfrak{d} - (OP - \mathbf{r}_m \cdot \mathbf{i}) \tag{43}$$

Since OP represents an arbitrary constant phase increment for all of the elements, it may be neglected. Then:

$$d_m = \mathbf{r}_m \cdot (\mathfrak{d} - \mathbf{i}) = \mathbf{r}_m \cdot \mathfrak{d}' \tag{44}$$

so that

$$(\mathbf{E}_h')_m = K \cos \frac{2\pi}{\lambda} (c'l - \mathbf{r}_m \cdot \sigma') \tag{45}$$

The intensity, I_h, due to these horizontal components may be obtained with the aid of Poynting's vector and is (the bar represents a time average):

$$I_h' = \frac{c}{4\pi} \overline{(\mathbf{E}_h')^2} = \frac{c}{4\pi} \overline{\left\{ \sum_{m-0}^{N} (\mathbf{E}_h')_m \right\}^2} \tag{46}$$

By substituting:

$$I_h' = \frac{c}{4\pi} \frac{1}{T} \int_0^T \left\{ \sum_{m-0}^{N} K \cos \frac{2\pi}{\lambda} (c'l - \mathbf{r}_m \cdot \mathfrak{d}') \right\}^2 dl \tag{47}$$

where T is the period of vibration (λ/c'). By expanding and carrying out the time integration, it is seen that:

$$I_h' = \frac{cK^2}{8\pi} \left\{ \frac{N}{2} + \sum_{m-0}^{N} \sum_{n-0}^{N}{}' \cos \frac{2\pi}{\lambda} [(\mathbf{r}_m - \mathbf{r}_n) \cdot \mathfrak{d}'] \right. \tag{48}$$

* For all points in the molecule, this distance may be considered essentially constant in this term.

Let $\mathbf{r}_0, \mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \ldots, \mathbf{r}_m \ldots$
... be a unit vector pointing in
... the observation point, P, is
... are the horizontally and
... of the incident light;
... and I' is its intensity.
... is given by equation (6)

$$\tag{42}$$

... amplitude and frequency, the
... from the molecule to the
... and velocity of the light in the
... is the sum of the distance
... and the distance from that

$$\tag{43}$$

... increment for all of the ele-

$$\tag{44}$$

$$\tag{45}$$

... may be obtained with
... average):

$$\tag{46}$$

$$\tag{47}$$

... out the

$$\tag{48}$$

The double summation may be evaluated as an integration if there are a large number of terms. This is true in this case. From a modification of the fundamental theorem of integral calculus, it may be shown that:

$$\sum_i \sum_j {'} a(i, j) = \int_i \int F(i, j) \, a(i, j) \, di \, dj$$

where $F(i, j)$ is the number of terms between i and $(i + di)$, and j and $(j + dj)$. Therefore:

$$I'_h = \frac{cK^2}{8\pi}\left\{\frac{N}{2} + \int_{m=0}^{N}\int_{n=0}^{N} F(\mathbf{r}_m, \mathbf{r}_n) \cos \frac{2\pi}{\lambda}\left[(\mathbf{r}_m - \mathbf{r}_n)\cdot\mathbf{\delta}'\right]d\mathbf{r}_m \, d\mathbf{r}_n \right. \tag{49}$$

Since, however, the molecule is free to move about at random, the probability of finding any particular submolecule at any particular place in solution will be constant, so that the probability function actually depends only on the separation of m and n. Therefore, the double integration may be reduced to a single integration over the vector differences between the r values, so that:

$$I'_h = \frac{cK^2}{8\pi}\left\{\frac{N}{2} + V\int_{(r_m - r_n)} F(\mathbf{r}_m - \mathbf{r}_n) \cos \frac{2\pi}{\lambda}\left[(\mathbf{r}_m - \mathbf{r}_n)\cdot\mathbf{\delta}'\right]d(\mathbf{r}_m - \mathbf{r}_n)\right. \tag{50}$$

and $F(\mathbf{r}_m - \mathbf{r}_n)$ is the number of pairs of submolecules separated between the distances of $(\mathbf{r}_m - \mathbf{r}_n)$ and $(\mathbf{r}_m - \mathbf{r}_n) + d(\mathbf{r}_m - \mathbf{r}_n)$. The nature of this function is determined by the size and shape of the molecule. Let us first consider the case of a rod-shaped molecule.

The Rod-Shaped Molecule

The probability function for a rod is relatively easy to evaluate. It may immediately be seen that the chance of finding pairs of elements close together is greater than that of finding them far apart. Furthermore, it may be seen that this relationship is linear.* Therefore, it follows that the number of elements separated by the distance, r, is proportional to $(L - r)$. The proportionality constant may be evaluated by integrating this expression over all values of r and equating to the total number of possible pairs, $N(N - 1)/2$. That is:

$$\int_0^L C(L - r) \, dr = \frac{N(N - 1)}{2} \tag{51}$$

so that $C = [N(N - 1)]/L^2$.

This equation will give the number of elements separated between the scalar distances of r and $(r + dr)$, while it is required by equation (50) to have a distribution function of the vector separation, $F(\mathbf{r}_m - \mathbf{r}_n)$. This function must be of such a nature that its integral over possible orientations in space reduces to the

---

* If L is the length of the rod, there will be one pair of submolecules, 0 and N, separated by the distance L; two pair, 0 and $(N - 1)$, and 1 and N, separated by the distance $(L - a)$ (where a is the length of a submolecule); three pair by $(L - 2a)$; etc.

function of the scalar separation. Since it is obvious that the function will be independent of the angle of orientation, this may readily be accomplished by dividing the scalar function by $4\pi r^2$. Therefore:

$$F(\mathbf{r}_m - \mathbf{r}_n) = \frac{N(N-1)}{L^2} \frac{(L-r)}{4\pi r^2} \tag{52}$$

Substituting into equation (50) gives:

$$I_h' = \frac{c'K^2}{8\pi} \left\{ \frac{N}{2} + \frac{N(N-1)}{L^2} \int_{(r_m - r_n)} \frac{(L-r)}{4\pi r^2} \cos \frac{2\pi}{\lambda} \times \right.$$
$$\left. [(\mathbf{r}_m - \mathbf{r}_n)\cdot\boldsymbol{\delta}']d(\mathbf{r}_m - \mathbf{r}_n) \right\} \tag{53}$$

By substituting for $(\mathbf{r}_m - \mathbf{r}_n)\cdot\boldsymbol{\delta}'$, its definition $r\delta' \cos \phi$, where ϕ is the angle between $(\mathbf{r}_m - \mathbf{r}_n)$ and $\boldsymbol{\delta}'$, and by integrating over the spherical volume differential, $2\pi r^2 \sin \phi d\phi dr$, one finds that:

$$I_h' = \frac{cK^2N(N-1)}{16\pi} \left\{ \frac{1}{x} \int_0^{2x} \frac{\sin u}{u} \, du - \left(\frac{\sin x}{x} \right)^2 + \frac{2}{N-1} \right\} \tag{54}$$

where $x = \pi L\sigma'/\lambda$. But $2/(N-1) \ll 1/x$. Therefore, by normalizing so that $I_h' = 1$ when $\sigma' = 0$, it is seen that:

$$I_h' = \frac{1}{x} \int_0^{2x} \frac{\sin u}{u} \, du - \left(\frac{\sin x}{x} \right)^2 \tag{55}$$

The vector, $\boldsymbol{\delta}'$, may be readily related to the angle, θ, between the unit propagation vector, $\boldsymbol{\delta}$, and the propagation vector of the scattered light, $\mathbf{i}$. A simple consideration of its geometry shows that its magnitude is:

$$\sigma' = 2 \sin \theta/2 \tag{56}$$

If the total scattered intensity, $(I_h' + I_r')$, is considered, then the angular dependency of intensity as given by equation (55) would have to be multiplied by the factor $(1 + \cos^2 \theta)$ resulting from the resolution of the polarized components of the incident light.

The Randomly Coiled High Polymer Chain

The randomly coiled high polymer chain differs from the rigid rod in that a link of the chain usually makes a definite angle with the preceding link, and is free to rotate (on a cone-shaped locus) with respect to a plane determined by the preceding two links. The probability of finding two particular submolecules a given distance apart in the resulting snakelike configuration would have to be given by a more complex type of distribution function.

24

is obvious that the function will be
may readily be accomplished by di-
re:

$$\cdots 1)\ \frac{(L - r)}{4\pi r^2} \tag{52}$$

$$\cdots \cos \frac{2\pi}{\lambda} \times$$

$$[(\mathbf{r}_m - \mathbf{r}_s)\cdot \boldsymbol{\sigma}']d(\mathbf{r}_m - \mathbf{r}_n)\Big\} \tag{53}$$

on $r\boldsymbol{\sigma}' \cos \phi$, where ϕ is the angle be-
over the spherical volume differential,

$$\cdots du = \left(\frac{\sin x}{x}\right)^2 + \frac{2}{N - 1}\Big\} \tag{54}$$

Therefore, by normalizing so that

$$\cdots du = \left(\frac{\sin x}{x}\right)^2 \tag{55}$$

the angle, θ, between the unit propa-
of the scattered light, i. A simple
its magnitude is:

$$\sin \theta/2 \tag{56}$$

If N is considered, then the angular de-
(58) would have to be multiplied by
resolution of the polarized components

Some matters from the rigid rod in that a
with the preceding link, and is
in a plane determined by the
particular submolecules a
ration would have to be

This problem is similar to the classical statistical problem of the "random walk," and has been studied, for example, by Kuhn (11). The distribution function for a molecule containing a large number of links may be approximated by an exponential type of function, and is:

$$P(\mathbf{r})d\mathbf{r} = \left(\frac{3}{2\pi R^2}\right)^{3/2} e^{-\frac{3}{2}\frac{r^2}{R^2}} d\mathbf{r} \tag{57}$$

where $P(\mathbf{r})d\mathbf{r}$ is the probability of finding two particular links a vector distance apart between $\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$; and R^2 is the mean r^2. This function is normalized so that $\int P(\mathbf{r})d\mathbf{r} = 1$.

R^2 may be related to the physical characteristics of the chain, and is given by the relationship:

$$R^2 = n\left(\frac{1 - \cos \phi}{1 + \cos \phi}\right) A^2 \tag{58}$$

where n is the number of links between the two links that are separated by the mean square distance, R^2; ϕ is the angle between the two links; and A is the length of a link. Therefore, it is seen that $R^2 = kn$.

The total number of links separated by vector distance between $\mathbf{r}$ and $\mathbf{r} + d\mathbf{r}$, $F(\mathbf{r}_m - \mathbf{r}_n)$ may be found by summing equation (57) over all values of n.

$$F(\mathbf{r}_m - \mathbf{r}_n) = \sum_n \left(\frac{3}{2\pi kn}\right)^{3/2} e^{-\frac{3}{2}\frac{r^2}{kn}} = \int_0^N F(n) \left(\frac{3}{2\pi kn}\right)^{3/2} e^{-\frac{3}{2}\frac{r^2}{kn}} dn \tag{59}$$

where N is the total number of links in the chain, and $F(n)dn$ is the number of values of n between n and $n + dn$. It is similar to the distribution function for a rigid rod, and proves to be:

$$F(n) = (N - n + 1) \tag{60}$$

By substituting this value of $F(\mathbf{r}_m - \mathbf{r}_n)$ into equation (50), it follows that:

$$I_\lambda' = \frac{cK^2}{8\pi}\Bigg\{\frac{N}{2} + \int_{r_m - r_n}\Bigg[\cos\frac{2\pi}{\lambda}(\mathbf{r}_m - \mathbf{r}_n)\cdot \boldsymbol{\sigma}'\Bigg]\times$$

$$\Bigg[\int (N - n + 1)\left(\frac{3}{2\pi kn}\right)^{3/2} e^{-\frac{3}{2}\frac{r^2}{kn}}\, dn\Bigg]d(\mathbf{r}_m - \mathbf{r}_n)\Bigg\} \tag{61}$$

On converting to Cartesian coordinates and integrating one finds that:

$$I_\lambda' = \frac{cK^2}{8\pi}\Bigg\{\frac{N}{2} + \frac{N(N - u)}{u^2}\,[e^{-u} - (1 - u)]\Bigg\} \tag{62}$$

where $u = \dfrac{2}{3}\left(\dfrac{\pi R \sigma'}{\lambda}\right)^2$

Since $N \gg u$, the $N(N - u)$ term in the multiplier approximately equals N^2. Then, normalizing so that $I'_h = 1$ when $u = 0$:

$$I'_h = \frac{2}{u^2} [e^{-u} - (1 - u)] \tag{63}$$

The angular dependency of the intensity of the light scattered from large high polymer molecules shaped like rigid rods and like randomly coiled chains ha been computed. These are the two extreme cases. The links of actual high polymer molecules are usually not completely free to orient at random on the cone-shaped locus formed by the valence angle, but there is "restricted rotation" and the potential energy varies as a function of the position on this cone.
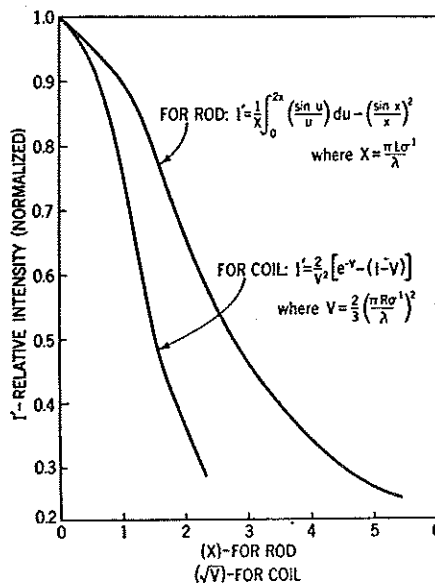

Fig. 7. Angular intensity distribution for a rod and a coil

Debye (5) has derived the equation relating the mean distance between two particular links with the number of links between the two, the valence angle, the length of a link, and the amount of restriction of the rotation. This equation is:

$$R^2 = n \frac{\left(\dfrac{1 - \cos \phi}{1 + \cos \phi}\right) + q}{1 - q} A^2 \tag{64}$$

where q is a factor characterizing the restricted rotation. It is equal to the ratio

... approximately equals N^2.

(63)

... scattered from large high ... randomly coiled chains has ... The links of actual high ... to orient at random on the ... there is "restricted rotation" ... position on this cone.

... two ... angle, the ... ation is:

(64)

... the ratio

of the time average to the static value of the projection of a link on the base of the right circular cone which forms its locus of rotation. (For free rotation, all positions will be equally probable, and the time average projection will be zero.)

Plots of equations (55) and (63) are presented in Figure 7.

The derivations of this section were made on the assumption that the dissymmetry originates from isolated molecules, and that the interference resulting in the angular dependency is among rays scattered from parts of any single molecule. It is possible, however, that radiation from adjacent molecules in more concentrated solutions is also coherent and will contribute to the interference. This intermolecular interaction is related, theoretically, to the interference of the scattering from an assembly of small molecules of a binary mixture which has been previously discussed. Therefore, it should be possible to relate the concentration dependency of dissymmetry to the concentration dependency of the intensity of the scattering at any particular angle. This relationship has not as yet been published.

Discussion

By an appropriate summation of the scattered amplitudes from large scattering particles of various shapes, it has been possible to express the relative intensity of scattered light at any angle for a particularly shaped particle as a function of: (1) the ratio of a characteristic dimension of the particle to the wave length of the light in solution; and (2) the angle of observation. It has been shown that these relationships represent a decrease in the all-around scattered intensity and a modification of the small particle scattering laws is in order.

This relative intensity distribution may be readily expressed in terms of absolute intensities, for a re-examination of Figure 4 (page 103) shows that no path difference, and hence no destructive interference, result between rays scattered in the forward direction at 0° regardless of the separation or distribution of scattering elements in the particle. Therefore, both large and small particle scattering laws must correspond for scattering in this direction; and since we have normalized our relative intensity equations to unity at 0° ($\sigma' = 0$), the absolute scattering at any angle may be found by simply multiplying the relative intensity by that predicted by the small particle law (Rayleigh scattering). In the determination of molecular weights from 90° scattering measurements, the observed intensity must be divided by this relative intensity in order to correct the scattering resulting from concentration fluctuations for the reduction due to intramolecular interference.

In view of the lack of knowledge regarding molecular size and shape, it is usually necessary to characterize the angular distribution curve experimentally. For the usual first-order interference for scattering from particles of homogeneous size, the angular distribution curve may be adequately characterized by measuring the ratio of the intensities at two angles symmetrically located about 90°. This

simplification is possible because the form of the intensity distribution curve is quite similar for any molecular model if the largest dimension is somewhat less than the wave length of light. An extrapolation of this *dissymmetry ratio* to infinite dilution of the scattering solution serves to eliminate the *inter*molecular effect.

The angular distribution of intensity is also indicative of the size and shape of the scattering particle in solution. It is possible, for a particular shaped particle, to plot a curve relating the dissymmetry ratio to a characteristic size of the molecule. Thus, if one assumes a model for the molecule, a dimension may be determined. The correctness of the model chosen may be tested by comparing this size with one computed for the model from such information as the degree of polymerization and length of a monomer unit in the case of polymer molecules. The application of this procedure with respect to both molecular weight and size for the case of cellulose acetate is the subject of a current paper (19).

V. DEPOLARIZATION OF SCATTERED LIGHT

In the treatment of scattering developed in the first part of this article it was considered that a periodic wave incident upon a molecule induces a forced oscillation of bound charges synchronous with the applied field. Since the bound charges oscillated in the same direction as the electric vector in the incident light, the transversely scattered light should be completely polarized in the vertical direction. However, light scattered at 90° from solutions, as well as gases and pure liquids, is found in general to be incompletely polarized, that is, there is both a horizontal and vertical component, the ratio of which is called the depolarization value. The quantitative consideration of this effect is necessary for two reasons. First, all the horizontally polarized light and a small amount of the vertically polarized light originate, not at the expense of the scattered light previously considered, but from a new effect. Consequently, the absolute intensity of scattered light is greater than that calculated by equation (39) and is not directly proportional to the square of the polarizability. It is clear that this effect must be taken into account when measured turbidities are used for molecular weight determinations. Second, since the explanation of depolarization must lie in the fact that the scattering centers, the molecules, are asymmetric and anisotropic, it is reasonable to expect that, if the relation between cause and effect can be determined, depolarization measurements will contribute to our knowledge of the size and shape of molecules. These two aspects of depolarization of scattered light will now be discussed in turn.

Increased Intensity of Scattered Light Due to Molecular Anisotropy (1, 4)

Let us recall that the intensity of scattered light is proportional to the square of the induced moment, which, in turn is proportional to the square of the polariz-

the intensity distribution curve is
largest dimension is somewhat less
of this *dissymmetry ratio* to in-
to eliminate the *intermolecular*

indicative of the size and shape
possible for a particular shaped par-
ratio to a characteristic size of the
the molecule, a dimension may be
be tested by comparing
from such information as the degree
in the case of polymer molecules.
both molecular weight and size
of a current paper (19).

SCATTERED LIGHT

the first part of this article it was
a molecule induces a forced oscilla-
applied field. Since the bound
electric vector in the incident light,
polarized in the vertical
vibrations, as well as gases and
polarized, that is, there is
which is called the de-
this effect is necessary for
and a small amount of
of the scattered light
the absolute inten-
equation (39) and is not
It is clear that this
are used for molecu-
of depolarization
are asymmetric
cause and
contribute to our
of depolariza-

anisotropy (1, 4)

the square
the polariz-

ability for a given field, E. That is, $p = \alpha E$. The induced moment will have the same direction as the incident electric vector only if the polarizability is independent of direction; this situation can only occur in the case of spherical, isotropic molecules.* In the general case, α depends on the direction and is actually a tensor. It will always be possible to find a rectangular coordinate system for which the nondiagonal terms of the tensor vanish. The three axes of such a coordinate system correspond to the three principal polarizabilities of the molecule A, B, C. An electric vector incident along any of the axes will induce a moment parallel to itself. This situation may be described by:

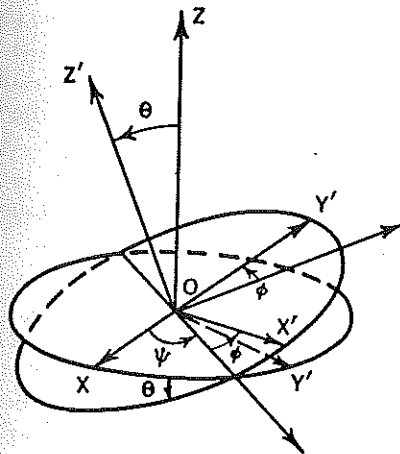$$p_{X'} = AE_{X'}; \quad p_{Y'} = BE_{Y'}; \quad p_{Z'} = CE_{Z'} \tag{65}$$

Fig. 8.   Eulerian angles

But, of course, generally the incident electric vector does not coincide with the principal polarizabilities, and consequently the direction of vibration of the scattered light will be slightly inclined to the light vector, and a weak horizontal component may be detected in the transversely scattered light.

We now consider quantitatively the general case of an asymmetric and/or anisotropic molecule whose principal axes of polarizability, A, B, C, determine a set of coordinates, X, Y, Z, which have a common origin with the X', Y', Z' axes. The orientation of the molecule is fixed by the system of three angles which orients the common type of geographic globe. The angles, known as the Eulerian angles, are shown in Figure 8. Axis Z' may be regarded as a polar axis, which is oriented by giving angle θ, between it and axis Z. To fix completely the orientation of axis Z' requires one more angle, ψ. This is taken as the angle between the fixed X axis and line ON, in

	X	Y	Z
X'	$\cos \psi \cos \psi \cos \theta - \sin \psi \sin \phi$	$\sin \psi \cos \phi + \cos \psi \sin \phi \cos \theta$	$- \sin \theta \cos \phi$
Y'	$- \sin \psi \cos \phi \cos \theta - \cos \psi \sin \phi$	$\cos \psi \cos \phi - \sin \psi \sin \phi \cos \theta$	$\sin \theta \sin \psi$
Z'	$\sin \theta \cos \phi$	$\sin \theta \sin \phi$	$\cos \theta$

* This development assumes the molecules to be small. A spherical, isotropic molecule, so large that the electric vector changes appreciably in passing through the particle, will give rise to a horizontal component in the scattered light as will be shown in the next section. This component is formed at the expense of the vertical component and hence does not affect the total scattered intensity to the degree of approximation considered here.

which $X'Y'$ plane intersects the XY plane; the orientation of the molecule is then specified completely by giving the angle ϕ that X' makes with ON. The cosines of the various angles between the different axes are given in the table on page 112.

If the tensor components referred to the fixed coordinates are denoted by α_{xy}, their values are given by:

$$\alpha_{xy} = \sum_{x'y'} \alpha'_{xy} \cos XX' \cos YY' \tag{66}$$

α'_{xy} is the value of α_{xy} when the two coordinate systems coincide. Thus the nondiagonal terms, α'_{xy}, α'_{yz}, etc., are zero. The diagonal terms are equal to the principal polarizabilities, that is, $\alpha'_{xx} = A$, $\alpha'_{yy} = B$, and $\alpha'_{zz} = C$. With the help of these relations and the table of cosines, the tensor components may be evaluated by means of equation (66). Now that we have obtained the polarization tensor components, the induced moments in the X, Y, and Z directions may be calculated. It is a ratio of these moments that is equal to the depolarization value.

Consider E_x, E_y, and E_z as the components of the incident electric vector, $\mathbf{E}$, in the directions X, Y, and Z. Then a component of the induced moment, say p_z, will be given by:

$$p_z = \alpha_{zx}E_x + \alpha_{zy}E_y + \alpha_{zz}E_z \tag{67}$$

The square of this component of the induced moment, p_z^2, will be a measure of the intensity of that part of the scattered beam in which the vibrations are restricted to the OZ direction. But in a large number of randomly oriented molecules the light scattered is uncorrelated in phase and the average intensity per molecule is obtained from the following expression for such an average:

$$\overline{p_z^2} = \frac{\int_0^\pi \int_0^{2\pi} \int_0^{2\pi} p_z^2 \sin\theta \, d\theta \, d\phi \, d\psi}{\int_0^\pi \int_0^{2\pi} \int_0^{2\pi} \sin\theta \, d\theta \, d\phi \, d\psi} \tag{68}$$

Carrying out the designated integrations leads to:

$$\overline{p_z^2} = E_z^2\{{}^1\!/_5(A^2 + B^2 + C^2) + {}^2\!/_{15}(AB + BC + AC)\} + (E_x^2 + E_y^2)\{(A^2 + B^2 + C^2 - AB - BC - AC)\} \tag{69a}$$

A similar treatment for p_y shows that:

$$\overline{p_y^2} = E_y^2\{{}^1\!/_5(A^2 + B^2 + C^2) + {}^2\!/_{15}(AB + BC + AC)\} + (E_x^2 + E_y^2)\{{}^1\!/_{15}(A^2 + B^2 + C^2 - AB - BC - AC)\} \tag{69b}$$

The depolarization value for incident unpolarized light ($E_x = E$, $E_y = 0$, $E_z = E$) is given, of course, by the ratio of the horizontal to the vertical components. The horizontal component is made up of equal contributions from both E_x and E_z. Each of these contributions is proportional to p_y^2. E_z makes a similar contribu-

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tion to the vertical component which is dominated by the large contribution from E_t which is proportional to p_z, thus;

$$\rho = \frac{\overline{p}_y^2 + \overline{p}_y^2}{\overline{p}_y^2 + \overline{p}_z^2} = \frac{2(A^2 + B^2 + C^2 - AB - BC - AC)}{4(A^2 + B^2 + C^2) + AB + BC + AC} \tag{70}$$

If we equate $(A + B + C)/3$ to α, the mean polarizability of the molecule, and denote by γ^2 the quantity $(A^2 + B^2 + C^2 - AB - BC - AC)$, the expression for ρ may be reduced to the following:

$$\rho = \frac{6/45\gamma^2}{\alpha^2 + 7/45\gamma^2} \tag{71}$$

From this it may be seen that the vertical component, whose intensity is proportional to the denominator, is no longer proportional to α^2 but to $\alpha^2 + 7/45\gamma^2$. Moreover, the intensity is further increased by the horizontal component. The net effect is that the scattered intensity, originally calculated as being proportional to α^2 for isotropic molecules, is for anisotropic molecules proportional to $\alpha^2 + 13/45\gamma^2$. From the previous equation:

$$\frac{13}{45}\gamma^2 = \frac{13\rho\alpha^2}{6 - 7\rho} \tag{72}$$

Consequently, where α^2 has appeared in equations (8) and (13), a correction of:

$$\left(1 + \frac{13\rho}{6 - 7\rho}\right) = \frac{6 + 6\rho}{6 - 7\rho} \tag{73}$$

should be applied. Similarly, turbidities measured for molecular weight determinations should be divided by this factor since these turbidities correspond only to those arising from concentration fluctuations. In the next section, however, it will be demonstrated that this correction is applicable only if the entire depolarization comes from anisotropy of the molecules. It represents an overcorrection if depolarization also arises from the finite size of the molecules.

The Relation of Depolarization to Molecular Size and Anistropy (6, 10)

It is clear from the previous section that the depolarization, ρ_u, of light scattered from small molecules is intimately connected with their asymmetry and anisotropy. In general, the depolarization is a measure of the deviation of the scattering particles from isotropic spheres. However, if the scattering particles are about one-tenth of the wave length of light or more in their largest dimension, the effect of size, independent of anisotropy, will give rise to depolarization. Consequently, depolarization measurements on polymer solutions are likely to reflect a combined effect due to size and anisotropy (and/or asymmetry); the measurement of ρ_u alone will not yield very definite information (13).

In one of the early papers in this field, Mie (14) demonstrated that ρ_u increases with increasing particle diameter. Gans (9) has considered in detail the scattering from model particles such as ellipsoids and disks. Blumer (2) has made the most complete numerical investigation of the problem thus far for spheres of various diameters. The means of resolving the effects of size and anisotropy is due to Krishnan (10). The most satisfying theoretical treatment of depolarization in turbid media is that of Perrin (16) whose development is analytical in nature, independent of molecular theory.

By using polarized and unpolarized incident light, three depolarization values may be measured:

$$\rho_u = \frac{H_v + V_h}{V_v + V_h} = \frac{H_u}{V_u} \tag{74a}$$

$$\rho_v = \frac{H_v}{V_v} \tag{74b}$$

$$\rho_h = \frac{V_h}{H_h} \tag{74c}$$

H and V denote the intensities of the horizontal and vertical components of the scattered light and the subscripts refer to unpolarized and vertically and horizontally polarized incident light. All three depolarization values may be measured experimentally.

Krishnan has shown that, from the values of these three depolarizations, the scattering units may be classified on the basis of *size* and *anisotropy*. With respect to size, particles with dimensions less than 500 Å are considered small as compared to visible light waves. For convenience, from now on, anisotropy will be used to denote both the departure from spherical shape (asymmetry) and the
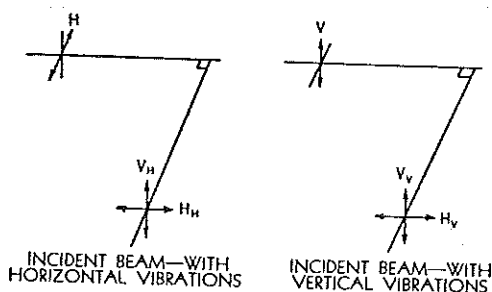

Fig. 9. Components of scattered light

intrinsic anistropy which signifies the presence of different properties in different directions. Now let us investigate the possible values of H_v, V_v, H_h, and V_h for

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four classes of particles: small isotropic, large isotropic, small anisotropic, and large anisotropic. Reference to Figure 9 will be helpful.

For all these classes of scattering particles, V_v will be finite since the predominant effect of the passage through the particle of vertically polarized incident light will be the forced vertical oscillations of the dipole. In the case of small isotropic particles, H_v, H_h, and V_h will be zero because the moment induced will be colinear with the incident electric vector, thus giving rise to only vertically polarized light.

A much more complicated problem faces us when we pass from a small spherical particle to a large one. The magnitude of the incident electric vector will vary throughout the particle. The solution (20) of the problem involves a detailed consideration of the effects of the different fields of all the oscillating di-
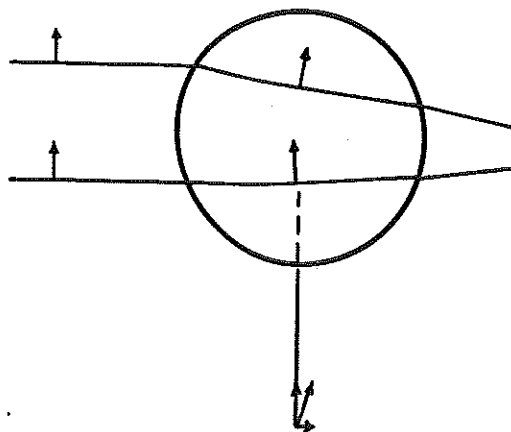

Fig. 10. Refraction of a plane polarized wave by a sphere

poles on each other. Mie (14) solved this problem with special reference to *metallic* particles. His solution is, however, too complicated to give here. Instead, the following crude picture is presented which demonstrates the essential features. A plane wave upon encountering a spherical particle of higher refractive index will behave as shown in Figure 10. Refraction causes the incident electric vector to pass through the particle at an angle so that the light scattered transversely in the plane of the paper will possess a horizontal component, H_h. Complete interference is not possible because the scattering from different parts of the plane shown in the figure will not be in phase. On the other hand, considering the sphere in three dimensions, many light rays will be refracted obliquely. This means that most of the induced dipoles will also give rise to a vertical component, V_h. But this kind of scattering will be destroyed by interference since,

for any dipole in the hemisphere in front of the plane of the paper, there will l a corresponding dipole in the hemisphere behind the paper and at the same di tance from the observer. Thus there is no V_h component. Similarly, there no H_v component. For large spherical particles, then, there is a H_h componen and the much larger V_v component.

For small isotropic particles (17), H_h will be finite for a different reason. Thi is evident from the discussion in the first part of the previous section. The scat tering units can be considered as point sources characterized by their polarizabil ity ellipsoids. The induced moment, which would be horizontal for the iso tropic particles, is in this case deflected approximately in the direction of the axis of greatest polarizability in the particle. Thus the induced moment will gen erally have an oblique orientation which gives rise to a horizontal component when the incident electric vector is horizontal. Exactly analogous reasoning applies to H_r and H_h; consequently, all these components are finite and equal.

Finally, for the large anisotropic particle, the magnitude of the various com ponents can be found by adding the results obtained for the two previous cases. Thus, H_r and V_h will be finite for the reasons mentioned in the foregoing para graph. This effect holds also for H_h, but to it must be added the effect that causes H_h to be finite for a large isotropic particle. Consequently, H_h is finite but larger than H_r or V_h.

All these results are summarized in the table below, together with the values of the three depolarizations that result. The plus sign denotes a positive value between zero and one for the depolarization.

An important principle is obvious from this table: the measurement of the three depolarization values permits the classification of the scattering units with respect to both size and anisotropy. Moreover, these depolarization values are monotonically increasing functions of size and anisotropy. This permits one to follow changes in size and anisotropy even though during all the changes the scat tering units remain within one of the above classes. Indeed, at present, this is one of the most promising uses of depolarization measurements, for in this man ner changes in size or anisotropy may be followed as a function of solvent, addi tion of precipitant to solution, molecular weight, and concentration. It should be noted that a further source of depolarization is that arising from secondary scattering from strongly turbid media. This is of no theoretical interest and should be eliminated by working at lower concentrations.

Depolarization Values for Various Classes of Scattering Units

Type of particle	H_r	V_v	H_h	V_h	ρu	ρv	ρh
Small isotropic	0	+	0	0	0	0	0
Large isotropic	0	+	+	0	+	0	0
Small anisotropic	+	+	+	+	+	0	I
Large anisotropic	+	+	++	+	+	+	+

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Further examination of the table shows another useful principle in the study of polymer solutions.   When ρ_r is finite, that is, in the case of anisotropic particles, deviations of ρ_h from unity may be used as a measure of particle size.   If the value of ρ_h is close to unity, then one may separate the contribution of anisotropy and size to ρ_u.   The portion due to anisotropy is given by $2\rho_r/1 + \rho_u$ and the remainder is due to size.

For all cases noted in the table, the relation $H_r = V_h$ holds.   This is merely an example of a general theorem which permeates classical physics.   It is known as the Law of Reciprocity since its establishment by Lord Rayleigh.   Although Krishnan made considerable use of this law, it remained for Perrin (16)' to demonstrate its range of applicability in the general phenomenon of scattering.   For polymer solutions, the law should be valid if there are a large number of particles having no preferred orientation in the plane containing the incident and scattered beams and if there are no optically active molecules in the solution.

The Law of Reciprocity may be combined with equations (74a), (74b), and (74c) to give a relation between the three depolarization values.   This important relation, known as Krishnan's relation, is:

$$\rho_u = \frac{1 + \dfrac{1}{\rho_h}}{1 + \dfrac{1}{\rho_v}} \tag{75}$$

It is useful because it permits the evaluation of one of the depolarization values when the other two are known, or it may be used to check experimental data. This relation is particularly valuable for the evaluation of ρ_h which is often extremely difficult to measure accurately.

We may now return to the question of the anisotropy correction discussed at the end of the previous section.   It is evident now that the ρ_u value for a polymer solution may in general contain a contribution from the effect of size alone. Thus, if the measured depolarization is used in equation (73), an overcorrection for the scattering due to fluctuation in orientation results.   The proper value of the depolarization for use in this correction would be $2\rho_r/(1 + \rho_r)$ based upon the value of ρ_r.

SUMMARY

In this short review, we have covered four main topics: the scattering of light from ideally small, isotropic molecules; the scattering from solutions composed of such molecules; the scattering from large chain molecules; and the scattering from anisotropic molecules, large and small.   From a measurement of the intensity of the scattered light, with suitable corrections if the molecules are large or anisotropic, one may determine molecular weights, and from a meas-

urement of the angular distribution of intensity, average linear dimensions of the molecules. Measurements of depolarization yield more qualitative information on size as well as data on the intrinsic molecular anisotropy.

The reader may note that no treatment has been given of concentrated solutions of molecules which are large with respect to the light wave. Such a theory is still in the formative stage. From it may be expected to come information on the arrangement of the molecules in the solution.

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