conclusion is in entire accord with experience; for example, the effect is measurable for nitrocellulose but not for poly(methyl methacrylate) even of very high molecular weight.[31] It can also be shown that for equilibrium eq. 25 is in agreement with special examples treated by Wippler and Benoit[31] and by Wallach and Benoit.[36]

Very recently Wallach and Benoit[36] have measured the effect in an alternating field for solutions of two nitrocellulose fractions in ethyl acetate, these having weight-average molecular weights of 1.5×10^5 and 4.0×10^5 and intrinsic viscosities of 2.55 and 9.1 dl./g., respectively. The observed relaxation times were about 60 and 200 μ sec., at concentrations of several tenths of a per cent. Since eq. 25 indicates the overwhelming importance of the first chain relaxation mode ($k = 1$) for this type of polymer, the above experimental values may be compared with calculations of π_1' based on eq. 17b, which yield about 6 and 55 μsec.[37] The effects of both concentration and polydispersity would be to augment these figures, so that the agreement between theory and experiment may be considered reasonable.

(36) M. L. Wallach and H. Benoit, private communication, 1963.

(37) By using a published viscosity–molecular weight relationship, such as that of M. L. Hunt, S. Newman, H. A. Scheraga, and P. J. Flory, *J. Phys. Chem.*, **60**, 1278 (1956), it is possible to increase the calculated values by a factor of three.

Clearly more experimental results would be welcome, but eq. 25 makes clear that the effects of polydispersity will require great care in the interpretation. Conversely, the effect when observable will according to the present theory yield no molecular information (other than polydispersity) that cannot be more conveniently obtained by less difficult techniques.

An ancient conversation with B. H. Zimm is gratefully recalled.

Appendix

For an alternating applied field of circular frequency ω, the second-order coefficient $c_k(t)$ of the distribution function of eq. 5 is given in real representation by the formula

$$8c_k(t) = P_k + Q_k \cos 2\omega t + R_k \sin 2\omega t$$

with

$$P_k = 2q^2 + a_k[1 + \omega^2(\tau_k')^2]^{-1}$$

$$Q_k = 2q^2[1 + \omega^2(\tau_k')^2]^{-1} +$$
$$a_k[1 - \omega^2(\tau_k')^2][1 + \omega^2(\tau_k')^2]^{-2}$$

$$R_k = 2q^2\omega t_k'[1 + \omega^2(\tau_k')^2]^{-1} +$$
$$2a_k\omega\tau_k'[1 + \omega^2(\tau_k')^2]^{-2}$$

On the Validity of the Einstein–Smoluchowski Theory of Light Scattering

BY ROBERT ZWANZIG

The molecular basis of the Einstein–Smoluchowski macroscopic theory of light scattering is investigated, using a generalization of Frölich's theory of dielectrics. The macroscopic and molecular theories differ by an experimentally negligible quantity, associated with the electric field dependence of the dielectric constant. A slight depolarization, not accounted for by the macroscopic theory, is associated with the same quantity. Because of the method of derivation, the results obtained here are valid only in the limit of long wave length and low frequency.

Introduction

The macroscopic theory of light scattering due to Smoluchowski[1] and Einstein[2] is based on a certain extremely plausible hypothesis: that the molecular nature of the scattering medium can be ignored, and that one can regard the light as being scattered by local fluctuations in the dielectric constant of a continuous medium.

In applications of this hypothesis, the dielectric constant is usually taken to be a function of local thermodynamic variables, so that the dielectric constant fluctuates solely because the local thermodynamic state fluctuates.[3]

Several attempts have been made to derive the Einstein–Smoluchowski theory from the principles of molecular physics. The most detailed investigation up to now is due to Fixman[4] and is a continuation of

(1) M. Smoluchowski, *Ann. Physik*, **25**, 205 (1908).

(2) A. Einstein, *ibid.*, **33**, 1275 (1910).

(3) Einstein considered only fluctuations in density and composition. It is customary, however, to refer to the more general theory involving fluctuations in all local thermodynamic variables as the Einstein–Smoluchowski theory.

(4) M. Fixman, *J. Chem. Phys.*, **23**, 2074 (1955).

earlier work by Yvon.[5]

Fixman restricted his analysis to a system of spherical polarizable atoms. He calculated the intensity of scattered light in the form of a power series expansion in the polarizability α of a single atom, keeping all terms of order α^2, α^3, and α^4, and omitting many terms of higher order.

Previously, Yvon had calculated the dielectric constant of the same system as a power series in α.

Fixman compared his results, found independently of the Einstein–Smoluchowski hypothesis, with the results that are obtained using this hypothesis. It should be noted that in this comparison, fluctuations in the dielectric constant were attributed entirely to fluctuations in density, and fluctuations in temperature (or local energy density) were ignored. Fixman found exact agreement between the two approaches in the α^2 and α^3 terms.

In the α^4 term, however, a certain "completely intractable" integral appeared. Fixman observed that this integral, whatever its magnitude, must give

(5) J. Yvon, "Actualités Scientifiques et Industrielles," No. 543. Hermann et Cie., Paris, 1937.

rise to some depolarization of the scattered light. From the experimental observation that little or no depolarization is found when the scattering molecules are isotropic, he then concluded the the integral is negligible.

This constitutes the basis of Fixman's claim[6] that "The Einstein–Smoluchowski theory of light scattering is shown to agree with the molecular theory of light scattering for a one-component system of isotropic scattering molecules."

Several unsatisfactory features of Fixman's work are evident. (1) The series expansion is not carried out to all orders in α; only the terms up to α^4 are treated completely. (2) Part of the α^4 contribution is estimated only by appeal to light scattering measurements, and there is no independent indication as to the size of this contribution. (3) The role of temperature fluctuations is completely ignored. For these reasons, Fixman's results cannot be regarded as definitive.

We have re-examined the question of the relation of the Einstein–Smoluchowski theory to the molecular theory, by means of an entirely different method. Our results are in essential agreement with Fixman's, and go considerably further. Because of certain limitations inherent in our method, however, our results cannot be regarded as definitive either.

We find that the Einstein–Smoluchowski theory is very nearly in agreement with molecular theory. A discrepancy exists: its magnitude is determined by the coefficient $\epsilon_{av}^{(2)}$ in the expansion of the average dielectric constant $\epsilon_{av}(E)$ of the system in powers of the electric field strength E

$$\epsilon_{av}(E) = \epsilon_{av}^{(0)} + \epsilon_{av}^{(2)}E^2 + \ldots \qquad (1)$$

and consequently is not observable in light scattering measurements of current accuracy.

We find also that dielectric saturation gives rise to some depolarization of the scattered light; but it should be noted that this is an entirely different effect from the familiar one, which is due to fluctuations in the off-diagonal elements of the dielectric tensor, and which is correctly accounted for by the Einstein–Smoluchowski hypothesis.

Our results are limited in two ways. First, they are valid only when the optical wave length is much greater than the correlation length of fluctuations in the medium. The second limitation is that the medium must be optically transparent, with its lowest dispersion frequency much higher than the frequency of the light wave. This comes from an assumption made in the course of the derivation that the system's electronic charge distribution is always in thermal equilibrium relative to the instantaneous electric field of the incident light wave. We hope to remove these limitations by a more careful investigation at some future time.

Our derivation deals explicitly with the same case discussed by Fixman, a system of spherical polarizable atoms. This is entirely a matter of convenience; the approach can be used equally well for a system of anisotropic molecules, with the same results.

Dielectric Constant and Scattering as Fluctuations

The method used here is based on the following observation. As is well known, the dielectric constant of

(6) Author's abstract in ref. 4.

a fluid is related to the mean squared fluctuation of the total electric dipole moment of a region of the fluid, *in the absence of any applied field*. The intensity of light scattered by the same region is determined by the same mean squared fluctuation, but now *in the presence of a field*. It is natural to suspect a connection between the two fluctuations; the derivation of this connection leads to the results stated in the Introduction.

To begin, we put the above statements into more explicit mathematical form. This is done along the lines of Fröhlich's theory of dielectrics.[7]

Consider a macroscopic spherical region, of volume V. (For convenience, we shall often refer to the region itself as V.) The radius of the sphere is chosen to be large compared with the correlation length of fluctuations in density, temperature, etc., so that light scattered from V will not interfere with light scattered from other parts of the system. The radius of V is also chosen to be small compared with optical wave lengths of interest, so that the electric field of the incident light wave is practically uniform over V.

In calculating the intensity of light scattered by V, we treat the substance inside V as molecules obeying classical statistical mechanics and the substance outside V as a uniform dielectric continuum.

The instantaneous electric dipole moment of the contents of V is denoted by $\mathbf{M}$. The actual value of $\mathbf{M}$ depends on the exact state of the system, and this varies with time.[8] The average value of $\mathbf{M}$, regarded either as an average over very long times or as an average over a grand canonical ensemble, is denoted by $\mathbf{M}_{av}$.

Because three different kinds of average appear in the following discussion, it is important to have a notation that distinguishes between them explicitly. The state of the system, *i.e.*, the contents of V, is specified by the set X of the coordinates of all molecules in V, by the total number N of molecules in V, and by the temperature T of V. An average over a canonical ensemble is then an average over all X for given N and T, denoted by

$$\text{canonical average of } A = \langle A;X \rangle \qquad (2)$$

In a grand canonical ensemble,[9] the average is taken over X, and also over N and T, denoted by

$$\text{grand canonical average of } A = \langle A;XNT \rangle \qquad (3)$$

Finally, we need averages of functions of N and T over the ensemble of fluctuations in N and T, denoted by

$$\text{fluctuation average of } A = \langle A;NT \rangle \qquad (4)$$

These averages are all taken in the presence of an applied electric field. The corresponding averages

(7) H. Frölich, "Theory of Dielectrics," Oxford University Press, London, 1949

(8) Connection with other theories, for example that of Yvon and Fixman, can be made by regarding the total electric moment as being due to instantaneous displacements of dispersion oscillators. It is well known that a system of dipole-coupled dispersion oscillators is identical with a system of interacting polarizable molecules.

(9) The name "grand canonical" is technically incorrect; a true grand canonical ensemble allows fluctuations in N and in the total energy content, rather than in N and the temperature. Since no other name appears to be available for the kind of ensemble wanted here, we have appropriated the name "grand canonical." More important than the name is the list of quantities following the semicolon in the angular bracket appearing in eq. 2, 3, and 4. In each case these are the quantities over which one performs the average.

when $E = 0$ will be indicated by a superscript zero, viz., $\langle\rangle^0$.

In this notation, the average electric dipole moment referred to above is

$$\mathbf{M}_{av} = \langle \mathbf{M} ; XNT \rangle \qquad (5)$$

As is well known, the electric field of the light scattered by the region V, observed at a point very far from V, is proportional to the instantaneous fluctuation of the electric dipole moment of V

$$\mathbf{E}_{scat} \sim \mathbf{M} - \mathbf{M}_{av} \qquad (6)$$

The coefficient of proportionality is a scalar quantity; we do not need to know its exact value here. If the scattered light is passed through a Nicol prism analyzer (so as to observe the degree of depolarization), and if the direction of the analyzer is specified by the unit vector u, then the observed component of the scattered field is

$$\mathbf{u} \cdot \mathbf{E}_{scat} \sim (\mathbf{M} - \mathbf{M}_{av}) \cdot \mathbf{u} \qquad (7)$$

The intensity I_{scat} of the light passing through the analyzer is proportional to the square of the field component in the direction of u

$$I_{scat} \sim |\mathbf{u} \cdot \mathbf{E}_{scat}|^2 \qquad (8)$$

Therefore the average scattered intensity I_{av} is proportional to the following quantity, denoted by S

$$I_{av} \sim S = \langle [(\mathbf{M} - \mathbf{M}_{av}) \cdot \mathbf{u}]^2 ; XNT \rangle \qquad (9)$$

This is the mean squared fluctuation, in the grand canonical ensemble, of a particular component of the total electric moment, in the presence of the exciting field.

At this point we show how S is calculated using the Einstein–Smoluchowski hypothesis. In mathematical form, this hypothesis may be stated as follows. The exact (i.e., the instantaneous) total moment $\mathbf{M}$ of the region V is replaced by its average value in the canonical ensemble, determined by specified parameters N and T

$$\mathbf{M} \to \langle \mathbf{M} ; X \rangle \qquad (10)$$

The canonical average moment is proportional to the total volume V and to the applied field $\mathbf{E}$

$$\langle \mathbf{M} ; X \rangle = \frac{V}{4\pi} (\epsilon^{(0)} - 1) \mathbf{E} \qquad (11)$$

where $\epsilon^{(0)}$ is the dielectric constant appropriate to the canonical ensemble. Observe that $\epsilon^{(0)}$ depends on N and T.[10] Only the low field limit (indicated by the superscript zero) is used.

The average moment in the grand canonical ensemble, $\mathbf{M}_{av}$, is found by averaging the canonical moment $\langle \mathbf{M} ; X \rangle$ over N and T. The average dielectric constant in the grand canonical ensemble, ϵ_{av}^0, is found in just the same way. Then the average of eq. 11 is

$$\mathbf{M}_{av} = \frac{V}{4\pi} (\epsilon_{av}^{(0)} - 1) \mathbf{E} \qquad (12)$$

where

$$\epsilon_{av}^{(0)} = \langle \epsilon^{(0)} ; NT \rangle^{(0)} \qquad (13)$$

In this notation, the scattering function $S(\text{macro})$ predicted by the Einstein–Smoluchowski theory is

$$S(\text{macro}) = \left(\frac{V}{4\pi}\right)^2 (\mathbf{u} \cdot \mathbf{E})^2 \langle (\epsilon^{(0)} - \epsilon_{av}^{(0)})^2 ; NT \rangle^0 \qquad (14)$$

This is a well known result in light scattering theory.

To conclude this section, we observe that the dielectric constant in the canonical ensemble can be expressed as a fluctuation[7]

$$\epsilon^0 - 1 = \frac{4\pi}{3} \frac{3\epsilon_{av}^{(0)}}{2\epsilon_{av}^{(0)} + 1} \frac{1}{VkT} \langle \mathbf{M}^2 ; X \rangle^0 \qquad (15)$$

The right-hand side contains $\epsilon_{av}^{(0)}$ and not $\epsilon^{(0)}$. This is because $\epsilon_{av}^{(0)}$ comes from the dielectric behavior of the surrounding continuous medium. We rederive this formula, and find its generalization to higher order in the field strength, in the following paragraphs.

Calculation of Fluctuations Induced by Light

In Fröhlich's theory of the static dielectric constant, the response of a system to a constant applied field is calculated by means of statistical thermodynamics. We propose to use the same method here to find the response of a system to a light wave.

The statistical thermodynamic method is justified when the medium is optically transparent (no dissipative energy transfer from electrons to nuclei) and when the frequency of the incident light is considerably smaller than the lowest optical dispersion frequency. Only then may we regard the electrons within V as being in thermal equilibrium with respect to a varying electric field.

This means that the dielectric constant that we deal with here is the "static" one, appropriate for describing the response of the system to light of low frequency. Our analysis is restricted to this limiting case.[11]

The potential energy of the molecules contained in V, taking into account also their interaction with the surrounding dielectric continuum, is denoted by U^0. When an electric field $\mathbf{E}(t)$ is applied, this energy is changed to $U(\mathbf{E})$

$$U(E) = U^0 - \frac{3\epsilon_{av}^{(0)}}{2\epsilon_{av}^{(0)} + 1} \mathbf{M} \cdot \mathbf{E}(t) \qquad (16)$$

Equation 16 is derived, for example, by Fröhlich.[7] His derivation was limited to fields that are constant in space and time; we use the same formula for fields that are almost constant in both respects. Therefore our results, obtained using eq. 16, are valid only in a limiting sense. The dielectric constant ϵ_{av} is that of the surrounding continuum, and is identical with the average, over a grand canonical ensemble, of the dielectric constant of the region V.

We have used in eq. 16 the low field limit of the dielectric constant, $\epsilon_{av}^{(0)}$. This is correct, strictly speaking, only for weak fields; and because we shall be concerned with the effects of strong fields, eq. 16 should be modified to allow for saturation. This has been

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(10) In the event that the system contains anisotropic molecules, we must add to N and T another parameter characteristic of the total degree of anisotropy of the contents of V. Then $\epsilon^{(0)}$ is a tensor and has off-diagonal elements depending on that parameter. In this way the theory presented here may be generalized easily to anisotropic systems.

(11) In generalizing the present theory to more complicated cases, e.g., polar molecules, one must remember that the frequencies of interest are only low in respect to electronic motions; they are still much higher than frequencies of nuclear (rotational and vibrational) motions.

done by Booth.[12] He finds that when the effects of saturation are taken into account at this point of the calculation, the resulting value of the coefficient $\epsilon_{av}^{(2)}$ is slightly changed. Because the principal result of our article is that the discrepancy between molecular and macroscopic theory is a term of order $\epsilon_{av}^{(2)}$, and because this is such a small quantity, a small error in its estimate will not cause trouble.

Average values in the canonical ensemble are given explicitly by

$$\langle A ; X \rangle = \frac{\int dX A \; \exp[-U(\mathbf{E})/kT]}{\int dX \; \exp[-U(\mathbf{E})/kT]} \qquad (17)$$

Together with eq. 16, this determines the electric field dependence of canonical averages. These averages may be expressed also as averages in the absence of the field, by means of the identity

$$\langle A ; X \rangle = \frac{\int dX A e^{-U^0/kT} e^{\lambda \mathbf{M} \cdot \mathbf{E}}}{\int dX e^{-U^0/kT} e^{\lambda \mathbf{M} \cdot \mathbf{E}}} = \frac{\langle A e^{\lambda \mathbf{M} \cdot \mathbf{E}} ; X \rangle^0}{\langle e^{\lambda \mathbf{M} \cdot \mathbf{E}} ; X \rangle^0} \qquad (18)$$

where for convenience we have abbreviated

$$\lambda = \frac{1}{kT} \frac{3\epsilon_{av}^{(0)}}{2\epsilon_{av}^{(0)} + 1} \qquad (19)$$

In particular, the average moment in the canonical ensemble is

$$\langle \mathbf{M} ; X \rangle = \langle \mathbf{M} e^{\lambda \mathbf{M} \cdot \mathbf{E}} ; X \rangle^0 / \langle e^{\lambda \mathbf{M} \cdot \mathbf{E}} ; X \rangle^0$$
$$= \frac{1}{\lambda} \nabla_E \log \langle e^{\lambda \mathbf{M} \cdot \mathbf{E}} ; X \rangle^0 \qquad (20)$$

To calculate the dielectric constant, we expand the exponential function, take the average of each term, and then find the logarithm of the sum. All terms containing odd powers of $\mathbf{M}$ will vanish because of the spherical symmetry of the system (for $\mathbf{E} = 0$). The result is

$$\log \langle e^{\lambda \mathbf{M} \cdot \mathbf{E}} ; X \rangle^0 = \frac{1}{2} \lambda^2 \langle (\mathbf{M} \cdot \mathbf{E})^2 ; X \rangle^0 +$$
$$\frac{1}{4!} \{ \lambda^4 \langle (\mathbf{M} \cdot \mathbf{E})^4 ; X \rangle^0 - 3[\langle (\mathbf{M} \cdot \mathbf{E})^2 ; X \rangle^0]^2 \} +$$
$$O(E^6) \quad (21)$$

Because of the spherical symmetry of the system, the electric field dependence of the average values can be calculated more explicitly as

$$\langle (\mathbf{M} \cdot \mathbf{E})^2 ; X \rangle^0 = \frac{1}{3} \langle M^2 ; X \rangle^0 E^2$$
$$\langle (\mathbf{M} \cdot \mathbf{E})^4 ; X \rangle^0 = \frac{1}{5} \langle M^4 ; X \rangle^0 E^4 \qquad (22)$$

Then the average moment is

$$\langle \mathbf{M} ; X \rangle = \frac{1}{3} \lambda \langle M^2 ; X \rangle^0 \mathbf{E} + \frac{1}{6} \lambda^3 \left\{ \frac{1}{5} \langle M^4 ; X \rangle^0 - \frac{1}{3} [\langle M^2 ; X \rangle^0]^2 \right\} E^2 \mathbf{E} + \dots \quad (23)$$

(12) F. Booth, J. Chem. Phys., 23, 453 (1955); for a somewhat different approach, see A. D. Buckingham, ibid., 25, 428 (1956).

On writing the canonical ensemble dielectric constant in the form of eq. 1

$$\epsilon(E) = \epsilon^{(0)} + \epsilon^{(2)} E^2 + \dots \qquad (24)$$

we find easily that the coefficients are

$$\epsilon^{(0)} = 1 + \frac{4\pi\lambda}{3V} \langle M^2 ; X \rangle^0 \qquad (25)$$

and

$$\epsilon^{(2)} = \frac{4\pi\lambda^3}{6V} \left\{ \frac{1}{5} \langle M^4 ; X \rangle^0 - \frac{1}{3} [\langle M^2 ; X \rangle^0]^2 \right\} \quad (26)$$

The zero field limit $\epsilon^{(0)}$ corresponds to eq. 15, and $\epsilon^{(2)}$ represents the lowest order effect of saturation. As was mentioned in the paragraph following eq. 16, our expression for $\epsilon^{(2)}$ is not exact; the true value may differ from this slightly.

Now the same analysis is repeated on the scattering function S. The average required here is taken over a grand canonical ensemble; we perform it in two steps, as an average over the ensemble of fluctuations in N and T

$$S = \langle (\mathbf{M} \cdot \mathbf{u})^2 ; X N T \rangle - (\mathbf{M}_{av} \cdot \mathbf{u})^2$$
$$= \langle R ; N T \rangle - (M_{av} \cdot u)^2 \qquad (27)$$

of the canonical average

$$R = \langle (\mathbf{M} \cdot \mathbf{u})^2 ; X \rangle \qquad (28)$$

The method used to calculate the canonical average of $\mathbf{M}$ can be used in just the same way to calculate the canonical average appearing in R. The calculation starts with the identity

$$R = \langle (\mathbf{M} \cdot \mathbf{u})^2 ; X \rangle = \frac{\langle (\mathbf{M} \cdot \mathbf{u})^2 e^{\lambda \mathbf{M} \cdot \mathbf{E}} ; X \rangle^0}{\langle e^{\lambda \mathbf{M} \cdot \mathbf{E}} ; X \rangle^0} \quad (29)$$

or, by differentiation

$$R = \frac{1}{\langle e^{\lambda \mathbf{M} \cdot \mathbf{E}} ; X \rangle^0} \left(\frac{1}{\lambda} \mathbf{u} \cdot \nabla_E \right)^2 \langle e^{\lambda \mathbf{M} \cdot \mathbf{E}} ; X \rangle^0 \quad (30)$$

But this can be rearranged algebraically to

$$R = \left[\frac{1}{\lambda} u \cdot \nabla_E \log \langle e^{\lambda \mathbf{M} \cdot \mathbf{E}} ; X \rangle^0 \right]^2 +$$
$$\left(\frac{1}{\lambda} u \cdot \nabla_E \right)^2 \log \langle e^{\lambda \mathbf{M} \cdot \mathbf{E}} ; X \rangle^0 \quad (31)$$

This rearrangement is in fact the decisive step in this article. The first term will be recognized as the square of the canonical average of $\mathbf{M}$ (see eq. 20). The second term is obtained easily from the derivative of the canonical average of $\mathbf{M}$; thus

$$\langle (\mathbf{M} \cdot \mathbf{u})^2 ; X \rangle = [\langle \mathbf{M} \cdot \mathbf{u} ; X \rangle]^2 +$$
$$\frac{1}{\lambda} u \cdot \nabla_E \langle \mathbf{M} \cdot u ; X \rangle \quad (32)$$

By the definition of the canonical ensemble dielectric constant

$$\langle \mathbf{M} ; X \rangle = (\epsilon - 1) \frac{V}{4\pi} \mathbf{E} \qquad (33)$$

this is equal to

$$\left(\frac{V}{4\pi}\right)^2 (\epsilon - 1)^2 (u\cdot E)^2 +$$

$$\frac{1}{\lambda} u\cdot \nabla_E \left[\frac{V}{4\pi} (\epsilon - 1) u\cdot E\right] \quad (34)$$

On expanding ϵ in powers of E, as in eq. 24, we get

$$\left(\frac{V}{4\pi}\right)^2 (\epsilon^{(0)} - 1)^2 (u\cdot E)^2 + \frac{V}{4\pi\lambda} (\epsilon^{(0)} - 1) +$$

$$\frac{V}{4\pi\lambda} \epsilon^{(2)} [E^2 + 2(u\cdot E)^2] + 0(E^4) \quad (35)$$

The first term is exactly what one obtains using the Einstein–Smoluchowski hypothesis. The second term is independent of the field strength. Although it is always present, it is of no interest in light scattering experiments. (One may regard this as the scattered light associated with black body radiation in the system.) The third term on the right-hand side of eq. 35 represents the error in the Einstein–Smoluchowski theory.

After averaging over the ensemble of fluctuations in N and T, and subtracting $(M_{av}\cdot u)^2$, we obtain our final result

$$S = S(\text{macro}) +$$

$$\frac{V}{4\pi\lambda} \epsilon_{av}^{(2)} [E^2 + 2(u\cdot E)^2] + 0(E^4) \quad (36)$$

This uses the notation of eq. 14. The term independent of E^2 has been dropped.

The extra term, containing $\epsilon_{av}^{(2)}$, is responsible for some depolarization. The empirical fact, referred to by Fixman, that small optically isotropic molecules usually show little or no depolarization is clearly related to the well known fact that such molecules show very little dielectric saturation.

Once more we mention that the coefficient $\epsilon_{av}^{(2)}$ appearing in the correction term in eq. 36 may be slightly in error, as a result of the neglect of saturation in calculating the cavity field. Because this correction is unobservably small in current light scattering experiments, a small error in its estimate is of no concern here.

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA]

Effects of Electron Correlation in X-Ray and Electron Diffraction[1]

By L. S. BARTELL AND R. M. GAVIN, JR.

The theory of X-ray and electron diffraction by atoms is examined from the standpoint of one-electron and two-electron operators. Elastic scattering depends on one-electron operators and hence, as is well known, may be used to determine the density of *electrons about nuclei*, a one-electron property. On the other hand, it is found that inelastic scattering by atoms possessing more than one electron depends on the distance between planetary electrons. Consequently, the mean density of *electrons about other electrons*, an important two-electron property, can also be determined from diffraction experiments. A procedure for deriving the electron–nuclear and electron–electron radial distribution functions $D(r_i)$ and $P(r_{ij})$ from scattered intensities is presented. It is shown how these functions, in turn, may be used to calculate electronic energies in atoms, *including correlation energy*. Properties of $D(r_i)$ and $P(r_{ij})$ are illustrated, using helium as an example. An extension of the treatment to molecules and crystals is briefly discussed. Comparisons are made of elastic and inelastic scattering factors calculated from Hartree–Fock wave functions and from wave functions explicitly including electron correlation. Effects of correlation on inelastic factors are found to be appreciable. The influence of correlation on elastic form factors and on Bragg reflection intensities for well-ordered crystals is insignificant, however. The relationship between Debye's 1915 picture of the X-ray scattering process and the very different picture developed in conventional treatments of X-ray crystallography is pointed out. This comparison helps to elucidate the role of electron correlation in X-ray and electron diffraction.

The purpose of this paper is to bring together a few simple ideas, most of which have received attention before, individually. In the aggregate, however, they cast a somewhat different light on X-ray and electron diffraction than the customary approach. Further, they illustrate how diffraction affords an experimental measure of two-electron properties of atoms and molecules in addition to the well-known measure of charge density, a one-electron property.[2] Indeed, as we shall

(2) n-Electron properties are properties depending on expectation values of n-electron operators. In general, n-electron operators are of the form $Q = \Sigma q(r_i, r_j \ldots r_s)$ in which each term in the sum depends on the coordinates of n electrons and in which the terms themselves cannot be written as the sum of m-electron operators with $m < n$. The operator of prime importance in this study is $[\Sigma \exp(is\cdot r_i)]$, a one-electron operator. The square of its absolute magnitude, which we also encounter, is a two-electron operator.

see, diffraction techniques even offer, in principle, a method for determining total electronic energies of molecules including electron–electron correlation energy. The basic theory for such chemically interesting ideas was developed many years ago but implications have not received the widespread recognition which their simplicity and power warrant. The main reason for this is that the enormous success of conventional X-ray crystallography, which is based on elastic scattering, has quite obscured the significant role of inelastic scattering.

In the following we shall outline those aspects of electron correlation and its effects on the scattering of radiation by atomic systems which seem of general interest to chemists. For sake of brevity and emphasis