

Molecular Theory of the Scattering of Light in Fluids

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Now

$$\partial\phi/\partial x_i = (\partial\phi/\partial a)(x_i/a)$$

and

$$\frac{\partial^2\phi}{\partial x_i^2} = \frac{d^2\phi}{da^2} \frac{x_i^2}{a^2} + \frac{1}{a} \left(1 - \frac{x_i^2}{a^2} \right) \frac{d\phi}{da}$$

Replacing x_i/a and x_i^2/a^2 by their average values 0, and $\frac{1}{3}$ respectively,

$$\frac{\partial\bar{\phi}}{\partial x_i} = 0,$$

$$\frac{\partial^2\bar{\phi}}{\partial x_i^2} = \frac{2}{3} \left(\frac{1}{2} \frac{d^2\phi}{da^2} + \frac{1}{a} \frac{d\phi}{da} \right).$$

Then

$$\bar{\phi} = \phi(a^1) = \sum_i \frac{1}{2} \left[\frac{2}{3} \left(\frac{1}{2} \frac{d^2\phi}{da^2} + \frac{1}{a} \frac{d\phi}{da} \right) \right]_{a^1} dx_i^2,$$

since the average of a sum is the sum of the individual

averages. Defining

$$\sum_i dx_i^2 = da^2 \text{ as } r^2,$$

$$\bar{\phi} = \phi(a^1) + \frac{1}{2} \left[\frac{2}{3} \left(\frac{1}{2} \frac{d^2\phi}{da^2} + \frac{1}{a} \frac{d\phi}{da} \right) \right]_{a^1} r^2.$$

When $\bar{\phi}$ is multiplied by $\frac{1}{2}$ the number of nearest neighbors, C , there is obtained

$$U = U_0 + \frac{1}{2} \left[\frac{2}{3} \left(\frac{1}{2} \frac{d^2U_0}{da^2} + \frac{1}{a} \frac{dU_0}{da} \right) \right] r^2.$$

Now if U is expanded as a function of r

$$U = U_0 + \frac{1}{2} (d^2U/dr^2)_0 r^2,$$

it will be seen that

$$\begin{aligned} \frac{1}{2} \left(\frac{d^2U}{dr^2} \right)_0 &= 2\pi^2 m v^2 \\ &= \frac{1}{2} \left[\frac{2}{3} \left(\frac{1}{2} \frac{d^2U_0}{da^2} + \frac{1}{a} \frac{dU_0}{da} \right) \right], \end{aligned}$$

which is identical with Eq. (18).

Molecular Theory of the Scattering of Light in Fluids*

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A molecular theory of the scattering of light by fluids of isotropic molecules is developed, utilizing recent advances in the statistical mechanics of condensed phases. The results are shown to be the same in first approximation as those of the continuous theory based on fluctuations originally proposed by Smoluchowski and Einstein. Higher approximations of the molecular theory are especially applicable to the study of critical opalescence and fluids consisting of very large molecules.

INTRODUCTION

THE theoretical calculation of the intensity of the light scattered by the molecules of a transparent substance is an old problem. Nearly half a century ago, Lord Rayleigh¹ developed the theory of the scattering of light by single isotropic molecules and extended it, with some success, to perfect gases. It was soon found, however, that the intensity of scattering by condensed phases was less than that predicted by the formula by more than one order of magnitude. This effect was rightly attributed to destructive interference between the wave trains scattered from different molecules, but the means of

calculating the extent of the interference were not available at that time.

Subsequently the difficulty was elegantly circumvented by Smoluchowski² and Einstein,³ who considered the liquid as a continuous medium troubled by small statistical fluctuations in density. The extent of these fluctuations could be calculated from the macroscopic compressibility of the medium, and the intensity of the scattered light was obtained without discussing the individual molecules at all.

It is now possible, however, as a result of recent advances in statistical mechanics, to obtain the Einstein-Smoluchowski formula from a molecular

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¹ Lord Rayleigh, *Phil. Mag.* **47**, 375 (1899).

² M. Smoluchowski, *Ann. d. Phys.* **25**, 205 (1908).

³ A. Einstein, *Ann. d. Phys.* **33**, 1275 (1910). An error, which introduced a factor of $(\mu^2+2)^2/9$ in the formula (24), is corrected by later authors. See references (7) and (8).

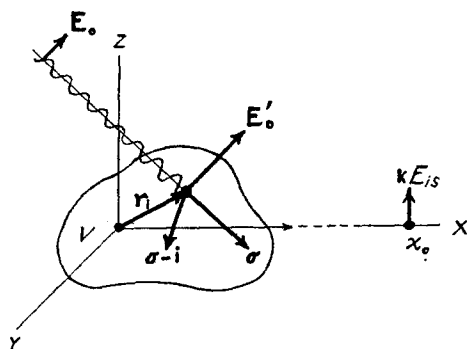


FIG. 1. Geometrical relations between light, system, and observation point.

point of view. The treatment is also applicable in the neighborhood of the critical point, where the Einstein-Smoluchowski method encounters serious difficulties. This molecular development is the subject of the present paper.

FUNDAMENTAL EQUATIONS

We consider a system of N identical molecules, which are smaller than the wave-length of light, in a compact volume V ; N , V , and the temperature, are such that the system consists wholly of one fluid phase. (See Fig. 1.) The system is exposed to a train of monochromatic, plane, and plane-polarized light waves whose electric field is given as a function of time and space by the equation:

$$\mathbf{E}(t, \mathbf{r}) = \mathbf{E}_0 \cos \frac{2\pi}{\lambda} (\boldsymbol{\sigma} \cdot \mathbf{r} - ct), \quad (1)$$

where $\boldsymbol{\sigma}$ is a unit vector in the direction of propagation, λ the wave-length in vacuum, c the velocity in vacuum, and t the time.

In passing through the system, this wave train is modified to

$$\mathbf{E}'(t, \mathbf{r}) = \mathbf{E}_0' \cos \frac{2\pi}{\lambda} (\mu \boldsymbol{\sigma} \cdot \mathbf{r} - ct), \quad (2)$$

where μ is the refractive index of the system and \mathbf{E}' , the "effective" field, is in general different from \mathbf{E} in magnitude and direction. In each of the molecules of the system, the effective field induces a dipole moment $\mathbf{p}(t, \mathbf{r})$:

$$\mathbf{p}(t, \mathbf{r}) = \alpha \cdot \mathbf{E}'(t, \mathbf{r}) = \alpha \cdot \mathbf{E}_0' \cos \frac{2\pi}{\lambda} (\mu \boldsymbol{\sigma} \cdot \mathbf{r} - ct). \quad (3)$$

The polarizability tensor, α , is a molecular constant. We shall discuss in this paper only the case in which the molecules are isotropic; that is, where α may be adequately represented by a scalar. In addition, we shall not concern ourselves with variations in the value of \mathbf{E}_0' from point to point in the system, but shall assume it constant. The first restriction is for convenience only, to avoid an unduly cumbersome result; the second is forced upon us by the present lack of a complete theory of the effective field \mathbf{E}' .

Under these restrictions $\bar{\mathbf{p}}$ is the same as the average moment per molecule, $\bar{\mathbf{p}}$, of a part of the system containing many molecules, but in which the value of $\boldsymbol{\sigma} \cdot \mathbf{r}$ does not change appreciably, which is known to be

$$\bar{\mathbf{p}}(t, \mathbf{r}) = \bar{\alpha} \mathbf{E}(t, \mathbf{r})$$

$$= \frac{(\mu^2 - 1) V \mathbf{E}_0}{4\pi N} \cos \frac{2\pi}{\lambda} (\boldsymbol{\sigma} \cdot \mathbf{r} \mu - ct). \quad (4)$$

Here $\bar{\alpha} = [(\mu^2 - 1) V / 4\pi N]$ is the average polarizability per molecule of the system to the external field, \mathbf{E} .

The light scattered by the system is observed at a point on the x -axis, x_0 , with the distance x_0 large compared to $V^{1/3}$. Observation is made through an analyzer which only transmits light polarized in the z -direction.

Consider a molecule, small compared to λ , located within V at $\mathbf{r}_i = ix_i + jy_i + kz_i$. If \mathbf{i} , \mathbf{j} , and \mathbf{k} are the usual unit vectors in the x , y , and z directions, the z -component of the electric field, measured at x_0 , of the light scattered by this molecule is given by⁴

$$E_{iz} = \frac{1}{x_0 c^2} \mathbf{k} \cdot \left\{ \mathbf{i} \times \left[\mathbf{i} \times \frac{\partial^2}{\partial t^2} \mathbf{p} \left(t - \frac{\mu(x_0 - x)}{c}, \mathbf{r}_i \right) \right] \right\}$$

$$= \frac{\pi (\mathbf{E}_0 \cdot \mathbf{k}) (\mu^2 - 1) V}{x_0 N \lambda^2} \cos \frac{2\pi}{\lambda}$$

$$\times [\mu (\boldsymbol{\sigma} - \mathbf{i}) \cdot \mathbf{r}_i + \mu x_0 - ct]. \quad (5)$$

The z -component of the electric field, E_z , of the total light scattered by all the molecules is the sum of their individual contributions:

$$E_z = \sum_i E_{iz}. \quad (6)$$

⁴ M. Born, *Optik* (Verlagsbuchhandlung, Julius Springer, Berlin, 1933), Chap. VII, Sec. 81.

The intensity of the scattered light, I_s , is the time average (over an integral number of cycles) of the square of E_s . The integral over time may be performed immediately, and the constant x_0 may be eliminated in the process:

$$I_s = \left[\frac{\pi(\mathbf{E}_0 \cdot \mathbf{k})(\mu^2 - 1)V}{x_0 N \lambda^2} \right]^2 \frac{1}{t'} \oint_0^{t'} dt \sum_i \sum_j \cos \frac{2\pi}{\lambda} \times [(\boldsymbol{\sigma} - \mathbf{i}) \cdot \mathbf{r}_i \mu + \mu x_0 - ct] \cdot \cos \frac{2\pi}{\lambda} [(\boldsymbol{\sigma} - \mathbf{i}) \cdot \mathbf{r}_j \mu + \mu x_0 - ct] \\ = \left[\frac{\pi(\mathbf{E}_0 \cdot \mathbf{k})(\mu^2 - 1)V}{x_0 N \lambda^2} \right]^2 \left\{ \sum_i \cos^2 \frac{2\pi\mu}{\lambda} (\boldsymbol{\sigma} - \mathbf{i}) \cdot \mathbf{r}_i + 2 \sum_{i>j} \cos \frac{2\pi\mu}{\lambda} (\boldsymbol{\sigma} - \mathbf{i}) \cdot \mathbf{r}_i \cos \frac{2\pi\mu}{\lambda} (\boldsymbol{\sigma} - \mathbf{i}) \cdot \mathbf{r}_j \right\}. \quad (7)$$

The sums in (7) may be expressed and evaluated as integrals, provided certain distribution functions giving the probability of occurrence of specified values of the \mathbf{r}_i are known. The successful use of these functions is the kernel of this paper, and is possible only because of recent advances in the statistical mechanics of condensed systems.*

Mathematically, the argument is this: the sum of a function, $f(\mathbf{r})$, over a large number of discrete values of the independent variable, $\mathbf{r}_1, \mathbf{r}_2, \dots$, etc. may be expressed as an integral over \mathbf{r} provided the number of discrete values occurring in the interval between \mathbf{r} and $\mathbf{r} + d\mathbf{r}$ is known. This latter number is the probability of a value between \mathbf{r} and $\mathbf{r} + d\mathbf{r}$, and is represented in the notation used by J. E. Mayer^{6,6} as $(N/V)F_1(\mathbf{r})$.

$$\sum_i f(\mathbf{r}_i) = \frac{N}{V} \int_V F_1(\mathbf{r}) f(\mathbf{r}) d\mathbf{r}. \quad (8)$$

* A treatment of the problem in terms of a continuous rather than a molecular theory, which, however, makes use of the radial distribution function, has been given by L. S. Ornstein and F. Zernicke, *Physik. Zeits.* **27**, 261 (1926).

⁶ J. E. Mayer and E. Montroll, *J. Chem. Phys.* **9**, 2 (1941).

⁶ J. E. Mayer, *J. Chem. Phys.* **10**, 629 (1942).

A similar theorem holds for double sums:

$$\sum_{i>j} f(\mathbf{r}_i) f(\mathbf{r}_j) = \frac{N(N-1)}{2V^2} \times \int_V \int_V F_2(\mathbf{r}_1, \mathbf{r}_2) f(\mathbf{r}_1) f(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \quad (9)$$

Here $[N(N-1)/2V^2]F_2(\mathbf{r}_1, \mathbf{r}_2)$ is the probability of the simultaneous occurrence of a value of both coordinates between $\mathbf{r}_1, \mathbf{r}_2$, and $\mathbf{r}_1 + d\mathbf{r}_1, \mathbf{r}_2 + d\mathbf{r}_2$.

DISTRIBUTION FUNCTIONS

The distribution functions of the coordinates of the molecules, $(N/V)F_1(\mathbf{r})$ and $[N(N-1)/2V^2]F_2(\mathbf{r}_1, \mathbf{r}_2)$, already defined in terms of probabilities, are so normalized that their average values in the coordinate space are respectively the number and number of pairs of molecules:

$$\int_V \left(\frac{N}{V} \right) F_1(\mathbf{r}) d\mathbf{r} = N. \quad (10)$$

$$\int_V \int_V \frac{N(N-1)}{2V^2} F_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \frac{N(N-1)}{2}. \quad (11)$$

For fluids, where long range order is absent, $F_1(\mathbf{r})$ is a constant, equal to unity, and $F_2(\mathbf{r}_1, \mathbf{r}_2)$ is a function only of the relative values of \mathbf{r}_1 and \mathbf{r}_2 , that is:

$$F_2(\mathbf{r}_1, \mathbf{r}_2) = F_2(\mathbf{r}_{12}), \quad (12)$$

where $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ is introduced.

For the same reason, $F_2(\mathbf{r}_{12})$ approaches a constant when \mathbf{r}_{12} becomes large. Another useful function is then defined by

$$g_2(\mathbf{r}_{12}) = F_2(\mathbf{r}_{12}) - \lim_{\mathbf{r}_{12} \rightarrow \infty} F_2(\mathbf{r}_{12}). \quad (13)$$

The integral, divided by twice the volume, of $g_2(\mathbf{r}_{12})$ over the coordinates of the two molecules is a constant, written as b_2 :

$$b_2 = \frac{1}{2V} \int_V \int_V g_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \frac{1}{2} \int g_2(\mathbf{r}_{12}) d\mathbf{r}_{12}. \quad (14)$$

The second half of the equation follows from (12).

EVALUATION OF I_s

In the present case, the $f(\mathbf{r})$ of Eqs. (8) and (9) is $\sin(2\pi\mu/\lambda)(\boldsymbol{\sigma}-\mathbf{i})\cdot\mathbf{r}$. Using this, the sums in Eq. (7) may be changed to integrals

$$I_s = \left[\frac{\pi(\mathbf{E}_0 \cdot \mathbf{k})(\mu^2 - 1)V}{x_0 N \lambda^2} \right]^2 \times \left\{ \frac{N}{V} \int F_1(\mathbf{r}) \cos^2 \frac{2\pi\mu}{\lambda} (\boldsymbol{\sigma}-\mathbf{i}) \cdot \mathbf{r} d\mathbf{r} + \frac{N(N-1)}{V^2} \iint F_2(\mathbf{r}_1, \mathbf{r}_2) \cos \frac{2\pi\mu}{\lambda} (\boldsymbol{\sigma}-\mathbf{i}) \cdot \mathbf{r}_1 \cos \frac{2\pi\mu}{\lambda} (\boldsymbol{\sigma}-\mathbf{i}) \cdot \mathbf{r}_2 d\mathbf{r}_1 d\mathbf{r}_2 \right\}. \quad (15)$$

Since $F_1(\mathbf{r}) = 1$, the first term is merely $N/2$, if edge effects be neglected.

$$\frac{N}{V} \int F_1(\mathbf{r}) \cos^2 \frac{2\pi\mu}{\lambda} (\boldsymbol{\sigma}-\mathbf{i}) \cdot \mathbf{r} d\mathbf{r} = \frac{N}{2}. \quad (16)$$

The evaluation of the second term is less trivial. Writing \mathbf{r}_1 in terms of \mathbf{r}_1 and \mathbf{r}_{12} so that $\mathbf{r}_2 = \mathbf{r}_1 + \mathbf{r}_{12}$, $d\mathbf{r}_1 d\mathbf{r}_2 = d\mathbf{r}_1 d\mathbf{r}_{12}$, we can write the integral as

$$\frac{N(N-1)}{V^2} \iint F_2(\mathbf{r}_{12}) \cos \frac{2\pi\mu}{\lambda} (\boldsymbol{\sigma}-\mathbf{i}) \cdot \mathbf{r}_1 \cos \frac{2\pi\mu}{\lambda} (\boldsymbol{\sigma}-\mathbf{i}) \cdot \mathbf{r}_{12} d\mathbf{r}_1 d\mathbf{r}_{12}. \quad (17)$$

This may be integrated over \mathbf{r}_1 , if the second cosine is rewritten in terms of products of cosines and sines of \mathbf{r}_1 and \mathbf{r}_{12} ; the integral over \mathbf{r}_1 of terms containing a cosine or sine of \mathbf{r}_1 to the first power is zero, and to the second power is $V/2$, so that (17) becomes

$$\frac{N(N-1)}{2V} \int F_2(\mathbf{r}_{12}) \cos \frac{2\pi\mu}{\lambda} (\boldsymbol{\sigma}-\mathbf{i}) \cdot \mathbf{r}_{12} d\mathbf{r}_{12}. \quad (18)$$

A form more convenient for our purpose, is obtained by using (13) for $F_2(\mathbf{r}_{12})$. If, as usual we neglect edge effects,** the integral of

** This neglect may be justified by writing out the limits of both integrals in Eq. (16), and noting that the contribution to the integral of the surface is negligible.

$\cos(2\pi\mu/\lambda)(\boldsymbol{\sigma}-\mathbf{i}) \cdot \mathbf{r}_{12} d\mathbf{r}_{12}$ over V is zero and the cross term finally becomes

$$\frac{N(N-1)}{2V} \int g_2(\mathbf{r}_{12}) \cos \frac{2\pi\mu}{\lambda} (\boldsymbol{\sigma}-\mathbf{i}) \cdot \mathbf{r}_{12} d\mathbf{r}_{12}. \quad (19)$$

In the commonly met special case in which the Einstein-Smoluchowski treatment is useful, the integral (19) may be still further simplified. It may be seen from (13) that $g_2(\mathbf{r}_{12})$ becomes zero when \mathbf{r}_{12} is large. Indeed, for ordinary fluids not in the vicinity of the critical point, it is well known that $g_2(\mathbf{r}_{12})$ is only different from zero at values of \mathbf{r}_{12} less than several molecular diameters. If the molecules are small, $\cos(2\pi\mu/\lambda)(\boldsymbol{\sigma}-\mathbf{i}) \cdot \mathbf{r}_{12}$ may be replaced by unity within this region, and (19) becomes simply b_2/V :

$$\frac{1}{2V} \int g_2(\mathbf{r}_{12}) d\mathbf{r}_{12} = \frac{b_2}{V}. \quad (20)$$

A value for b_2 , involving no significant approximations, has been recently obtained by Mayer.⁶ The derivation is too long to repeat here, but, from a generalized form of the grand partition function, he was able to arrive directly at the value***

$$b_2 = -\frac{z^2 V^2}{2N^2 k T} \left(\frac{\partial^2 p}{\partial z^2} \right)_T, \quad (21)$$

where z is the fugacity of the substance, normalized in terms of molecules per unit volume, and p is the pressure. By making use of the thermodynamic equation

$$(\partial p / \partial z)_T = N k T / z V, \quad (22)$$

we can transform (21) to the more usable form

$$b_2 = -\frac{1}{2} \left[k T \left(\frac{\partial \ln V}{\partial p} \right)_T + \frac{V}{N} \right]. \quad (23)$$

*** The $F_2(\mathbf{r}_{12})$ used here differs from that employed by Mayer in reference (6), in that the latter defines his $F_2(\mathbf{r}_{12})$ over an infinite system, whereas ours is defined over a finite system. In Mayer's case, $\lim_{\mathbf{r}_{12} \rightarrow \infty} F_2(\mathbf{r}_{12}) = 1$, but in our case for molecules of finite size, the limit differs from unity by a term of the order of magnitude of $1/N$. Nevertheless, the $g_2(\mathbf{r}_{12})$ and b_2 as defined by (13) and (14) are identical with those used by Mayer.

It should be noted that the only approximations involved in (21) and (23) are those inherent in the fundamental theorems of the semi-classical statistical mechanics.

If we now use (16) and (23) in (15), and overlook the truly negligible difference between N and $N-1$, we get the final expression for I_s in the case of fluids of small molecules not near the critical point as

$$I_s = \frac{\pi^2(\mathbf{E}_0 \cdot \mathbf{k})^2(\mu^2 - 1)^2 k T V}{2x_0^2 \lambda^4} \left(-\frac{\partial \ln V}{\partial p} \right)_T. \quad (24)$$

A useful related quantity is the "turbidity," τ , the extinction coefficient in Lambert's law,

$$I = I_0 e^{-\tau l}. \quad (25)$$

It may also be defined as the total intensity scattered per unit volume divided by the incident intensity, $I_0 = \frac{1}{2} E_0^2$. Integration of (24) over all angles of the direction of the primary light (the details are given by Born⁴) yields

$$\tau = \frac{8\pi^3(\mu^2 - 1)^2 k T}{3\lambda^4} \left(-\frac{\partial \ln V}{\partial p} \right)_T. \quad (26)$$

This formula is in complete agreement with that derived by the usual Einstein-Smoluchowski methods.^{7, 8}

⁷ S. Bhagavantam, *The Scattering of Light and Raman Effect* (Andhra University, Waltair, India, 1940).

⁸ J. Cabannes, *La Diffusion Moléculaire de la Lumière* (Les Presses Universitaires de France, Paris, 1929).

CONCLUSION

In general, the approximation of replacing the cosine by unity in (19) will not be valid. In the neighborhood of the critical point, for example, or for fluids or glasses composed of very large molecules, $g_2(\mathbf{r}_{12})$ will not fall to zero at values of \mathbf{r}_{12} less than the wave-length of light, and here use must be made of the complete form (19) rather than (20). The expression for I_s then is

$$I_s = \frac{\pi^2(\mathbf{E}_0 \cdot \mathbf{k})^2(\mu^2 - 1)^2 V}{2x_0 \lambda^4} \times \left\{ \frac{V}{N} + \int_V g_2(\mathbf{r}_{12}) \cos \frac{2\pi\mu}{\lambda} (\boldsymbol{\sigma} - \mathbf{i}) \cdot \mathbf{r}_{12} d\mathbf{r}_{12} \right\}. \quad (27)$$

The first term is just the light scattered by N isolated molecules, while the second term describes the interference resulting from correlations in position of the molecules. It will be noted that the second term is essentially the Fourier transform, as a function of the angles between illumination and observation, of $g_2(\mathbf{r}_{12})$, in close analogy to the well known formulas for the scattering of X-rays.

The extension of this method to many-component systems is straight-forward and will be reported in a later paper.

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