Finite-Size Effects in Rayleigh Scattering

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Experimental studies of Rayleigh scattering show an asymmetrical scattering cross section which has been attributed to the finite size of the scattering volume. The scattering cross section is computed as an asymptotic series in a size parameter and it is shown that finite-size effects cannot account for the experimental results.

I. INTRODUCTION

INTENSE light beams of the laser have made possible the experimental measurement of the differential cross section for scattering of light from gas molecules. Such measurements have been made by George, Goldstein, Slama, and Yokoyama.[1,2] The experimentally determined differential cross sections for argon and xenon show a pronounced deviation from the form predicted by the simple linear theory due to Rayleigh.[3] The Rayleigh theory predicts azimuthal symmetry about the polarization vector of the incident beam while the experimental results show a forward enhanced asymmetry which is greater for xenon than argon. The intensity of scattered light was found to vary linearly with the pressure and therefore with density in agreement with the Rayleigh theory.

On the basis of the preliminary report given in Ref. 1, a theoretical explanation was offered by Theimer.[4] The scattered intensity was computed as a function of the relative wave vector $\boldsymbol{\mu}=\mathbf{k}_0-\mathbf{k}$ between the incident and scattered wave. The finite dimensions of the scattering volume and the detector relative to the observation distance were then taken into account simultaneously by averaging the scattered intensity over a range of $\boldsymbol{\mu}$. This amounted to simultaneously summing the contributions to the scattered intensity from the various subvolumes of the scattering volume over the subsurfaces of the detector. In principle such a procedure is not correct for coherent scattering and would be indicated only if the light being scattered from the various subvolumes were incoherent. Since the scattering is coherent one must first sum the contributions to the scattered electric field. Only then should the intensity be computed and summed over the face of the detector. The purpose of the present work is to compute the scattered intensity in this manner. Furthermore in the calculation of Ref. 4 the finite-size correction is obtained only approximately with no estimate of the accuracy of the approximation. The present calculation will make systematic use of the asymptotic expansion of integrals so that the magnitude of the next correction can be estimated.

The correction to the Rayleigh theory computed in Ref. 4 is an additive asymmetric factor which arises from the interference of light scattered from different atoms of the gas. The asymmetric factor is quadratic in the density and when normalized by the Rayleigh term depends only on the number density of scattering particles and the geometry of the scattering volume. This is not in agreement with the observed linear dependence of the scattering cross section on density. Furthermore, it cannot account for the increased asymmetry of the scattering from xenon over argon since under the conditions of the experiment the number density of atoms was less for xenon than argon. Finally, it should be noted that although no other differential-cross-section measurements have been made for elements of high atomic number, light-scattering experiments for other gases and liquids[5-7] have failed to observe any deviation from the Rayleigh theory. Nevertheless, it seems appropriate that finite-size effects be carefully evaluated since all experimental equipment is of necessity finite in size.

II. DERIVATION OF THE SCATTERED INTENSITY

For the purpose of this calculation three assumptions are made:

(i) The irradiated gas or liquid is in thermal equilibrium. The special case where the gas is ideal will be considered in more detail.

(ii) The induced electric-dipole moment per unit volume is given by the linear theory

$$\mathbf{p}(\mathbf{r},t)=\alpha n(\mathbf{r},t)\mathbf{E}(\mathbf{r},t)\,, \qquad (1)$$

where α is the effective single-particle polarizability and

$$n(\mathbf{r},t)=\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{R}_i(t)) \qquad (2)$$

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[1] T. V. George, L. Goldstein, L. Slama, and M. Yokoyama, Phys. Rev. Letters 11, 403 (1964).

[2] T. V. George, L. Goldstein, L. Slama, and M. Yokoyama, Phys. Rev. 137, A369 (1965).

[3] J. W. Strutt, Phil. Mag. 41, 107 (1871); 41, 274 (1871); 41, 447 (1871).

[4] O. Theimer, Phys. Rev. Letters 13, 622 (1964).

[5] R. C. C. Leite, R. S. Moore, S. P. S. Porto, and J. E. Ripper, Phys. Rev. Letters 14, 7 (1965).

[6] R. D. Watson and M. K. Clark, Phys. Rev. Letters 14, 1057 (1965).

[7] R. R. Rudder, D. R. Bach, and R. K. Osborn, Bull. Am. Phys. Soc. 12, 891 (1967).

is the number density of atoms. $\mathbf{R}_i(t)$ is the position vector of atom i at time t.

(iii) The incident laser light is well represented by the electric field of a plane wave

$$\mathbf{E}(\mathbf{r},t)=\mathbf{E}_0 e^{i(\mathbf{k}_0\cdot\mathbf{r}-\omega_0 t)}. \tag{3}$$

The first two assumptions are supported by experimental evidence reported in Ref. 2. The density of the irradiated gas and the amplitude of the incident laser light were varied without measurable changes in the differential scattering cross section. The third assumption depends on several experimentally observed properties of the incident ruby-laser beam.[8] Among these are the spatial and temporal coherence, the time which characterizes the spontaneous fluctuations in the intensity, and the dispersion of the incident wave vector in direction and magnitude. Since the scattered intensity depends on the square of the scattered electric field, only second-order coherence[9] is of importance here. That the second-order spatial coherence properties of the ruby-laser beam are in agreement with a plane-wave description was demonstrated by Nelson and Collins[10] for spatial separations of 0.0054 cm and by Hercher[11] for separations of 0.35 cm. Temporal coherence is of importance because of the time delay due to the different path lengths of light scattered to the detector from different subvolumes of the scattering volume. Berkley and Wolga[12] have shown that the double slit diffraction pattern for a path difference of 700 cm shows little deviation from the pattern obtained with no path difference. Thus for a path difference of only 1 or 2 cm one expects the second-order temporal coherence properties of the beam to be well represented by the plane wave. The intensity of the ruby laser is known to pulsate with somewhat irregular time intervals.[8] However these time intervals are of the order of 1 or 2 μsec. The frequency of the principal line is about 4.3×10^{14} sec^{-1} and thus the field oscillates about 10^8 times during each spontaneous pulsation of the intensity. This means that the fluctuations of the amplitude of the wave can be treated as adiabatic relative to the plane-wave oscillations of the field which in turn are being treated as adiabatic oscillations relative to the electronic motions in the scattering atom. The apparatus used in Ref. 2 allowed for incident wave vectors which had a maximum half-angular spread of less than 2°. Thus the dispersion in the direction of $\mathbf{k}_0$ is comparable to the half-angle subtended by the detector and negligible compared to the 15° intervals at which the intensity is measured. The detector was fitted with an interference filter centered about 14 400 cm^{-1} and 100–125 cm^{-1} wide. The filter prevented all the lines reported by Porto and Wood[13] except the lattice band lines near 14 400 cm^{-1} from reaching the detector. The linewidth of the lattice band lines of the ruby laser is reported to be very narrow, of the order of 0.2 cm^{-1} or less,[8] compared to a wave number of about 14 400 cm^{-1} for the principle line. Thus for a discussion of light intensity the incident laser beam is well represented by a monochromatic plane wave.

The scattered electric field at the observation point $\mathbf{R}$ is given by

$$\mathbf{E}(\mathbf{R},t)=\text{grad div}\mathbf{Z}(\mathbf{R},t)-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{Z}(\mathbf{R},t), \tag{4}$$

where the Hertz potential $\mathbf{Z}(\mathbf{R},t)$ is determined from[14]

$$\nabla^2\mathbf{Z}(\mathbf{R},t)-\frac{1}{c^2}\frac{\partial^2}{\partial t^2}\mathbf{Z}(\mathbf{R},t)=-4\pi\mathbf{p}(\mathbf{R},t). \tag{5}$$

The solution can be written in the form

$$\mathbf{Z}(\mathbf{R},t)=\frac{1}{2\pi}\int_V d\mathbf{r}\int_{-\infty}^{\infty}dt'\int_{-\infty}^{\infty}d\omega \times\frac{\mathbf{p}(\mathbf{r},t')}{|\mathbf{R}-\mathbf{r}|}e^{i\omega[t'-t+(1/c)|\mathbf{R}-\mathbf{r}|]}, \tag{6}$$

where V is the scattering volume. Making use of this result along with Eqs. (1), (3), and (4) one obtains an expression for the scattered electric field

$$\mathbf{E}(\mathbf{R},t)=\frac{\alpha}{2\pi c^2}\int_V d\mathbf{r}\int_{-\infty}^{\infty}dt'\int_{-\infty}^{\infty}d\omega \times\frac{\omega^2 n(\mathbf{r},t')}{|\mathbf{R}-\mathbf{r}|}\left\{\mathbf{E}_0-\frac{[\mathbf{E}_0\cdot(\mathbf{R}-\mathbf{r})](\mathbf{R}-\mathbf{r})}{|\mathbf{R}-\mathbf{r}|^2}\right\} \times e^{i[\mathbf{k}_0\cdot\mathbf{r}+(\omega-\omega_0)t'-\omega t+(\omega/c)|\mathbf{R}-\mathbf{r}|]}. \tag{7}$$

In deriving Eq. (7) terms of order $\lambda\!\!\!^{-}/|\mathbf{R}-\mathbf{r}|$ compared to 1 have been dropped from the integrand, where $\lambda\!\!\!^{-}=c/\omega$ is the wavelength of the scattered field divided by 2π.

The intensity of scattered light at the point $\mathbf{R}$ is

[8] For a review of the ruby laser see the article by V. Evtuhov and J. K. Neeland, in *Lasers*, edited by A. K. Levine (Marcel Dekker, Inc., New York, 1966), Vol. 1.

[9] For a discussion of the coherence properties of optical fields see L. Mandel and E. Wolf, Rev. Mod. Phys. 37, 231 (1965).

[10] D. F. Nelson and R. J. Collins, J. Appl. Phys. **32**, 739 (1961).

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[13] S. P. S. Porto and D. L. Wood, J. Opt. Soc. Am. **52**, 251 (1962).

[14] W. Panofsky and M. Phillips, *Classical Electricity and Magnetism* (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1955).

given by

$$I'(\mathbf{R})=\frac{c}{8\pi}\lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{T}dt\,\langle|\mathbf{E}(\mathbf{R},t)|^2\rangle$$
$$=\frac{c}{8\pi}\lim_{T\to\infty}\frac{1}{2T}\int_{-T}^{T}dt\frac{\alpha^2}{4\pi^2c^4}\int_V d\mathbf{r}\int_V d\mathbf{r}'\int_{-\infty}^{\infty}dt'\int_{-\infty}^{\infty}dt''\int_{-\infty}^{\infty}d\omega\int_{-\infty}^{\infty}d\omega'\omega^2\omega'^2\frac{\langle n(\mathbf{r},t')n(\mathbf{r}',t'')\rangle}{|\mathbf{R}-\mathbf{r}|\,|\mathbf{R}-\mathbf{r}'|}$$
$$\times\left\{\mathbf{E}_0-\frac{[\mathbf{E}_0\cdot(\mathbf{R}-\mathbf{r})](\mathbf{R}-\mathbf{r})}{|\mathbf{R}-\mathbf{r}|^2}\right\}\cdot\left\{\mathbf{E}_0-\frac{[\mathbf{E}_0\cdot(\mathbf{R}-\mathbf{r}')](\mathbf{R}-\mathbf{r}')}{|\mathbf{R}-\mathbf{r}'|^2}\right\}\exp\left\{i\left[\mathbf{k}_0\cdot(\mathbf{r}-\mathbf{r}')+\frac{\omega}{c}|\mathbf{R}-\mathbf{r}|-\frac{\omega'}{c}|\mathbf{R}-\mathbf{r}'|\right.\right.$$
$$\left.\left.+(\omega-\omega_0)t'-(\omega'-\omega_0)t''-(\omega-\omega')t\right]\right\},\quad(8)$$

where $\langle\,\rangle$ denotes an ensemble average appropriate to the thermodynamic state of the gas or liquid.

The Van Hove space-time correlation functions[15] are defined by

$$G_1(\mathbf{r},t;\,\mathbf{r}',t')=\frac{1}{N}\left\langle\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{R}_i(t))\delta(\mathbf{r}'-\mathbf{R}_i(t'))\right\rangle,$$
$$G_2(\mathbf{r},t;\,\mathbf{r}',t')=\frac{1}{N}\left\langle\sum_{i\neq j}\delta(\mathbf{r}-\mathbf{R}_i(t))\delta(\mathbf{r}'-\mathbf{R}_j(t'))\right\rangle,\quad(9)$$

where $N=n_0V$ is the number of atoms in the volume V and n_0 is the average density. In terms of these functions

$$G(\mathbf{r},t;\,\mathbf{r}',t')=\langle n(\mathbf{r},t)n(\mathbf{r}',t)\rangle$$
$$=N\{G_1(\mathbf{r},t;\,\mathbf{r}',t')+G_2(\mathbf{r},t;\,\mathbf{r}',t)\}.\quad(10)$$

Komarov and Fisher[16] have used these functions to discuss the theory of Rayleigh scattering in liquids neglecting finite-size effects.

For a system in thermal equilibrium the Van Hove functions are functions only of the differences $|\mathbf{r}-\mathbf{r}'|$ and $(t-t')$. In particular, it can easily be shown that for an ideal gas

$$G_1(|\mathbf{r}-\mathbf{r}'|,\,(t-t'))=\frac{1}{V}\left[\frac{1}{\pi}\frac{\beta m}{2(t-t')^2}\right]^{3/2}$$
$$\times e^{-[\beta m/2(t-t')^2](\mathbf{r}-\mathbf{r}')^2},\quad(11)$$
$$G_2(|\mathbf{r}-\mathbf{r}'|,\,(t-t'))=\frac{n_0}{V},$$

where β^{-1} is the product of the Boltzmann constant and the absolute temperature and m is the atomic mass. Using the difference property of the function $G(|\mathbf{r}-\mathbf{r}'|,(t-t'))$ and the change of variables

$$s=t'-t'',\quad s'=t'+t'',$$

the s' integration of Eq. (8) can be done. The result is $2\pi\,\delta(\omega-\omega')$, which allows one to perform the ω' integration. This drops all t dependence of the integrand making it possible to perform the t integration and the $T\to\infty$ limit. The result is

$$I'(\mathbf{R})=\frac{\alpha^2}{2\pi c^4}\frac{c}{8\pi}\int_V d\mathbf{r}\int_V d\mathbf{r}'\int_{-\infty}^{\infty}ds\int_{-\infty}^{\infty}d\omega$$
$$\times\frac{\omega^4G(|\mathbf{r}-\mathbf{r}'|,\,s)}{|\mathbf{R}-\mathbf{r}|\,|\mathbf{R}-\mathbf{r}'|}\left\{\mathbf{E}_0-\frac{[\mathbf{E}_0\cdot(\mathbf{R}-\mathbf{r})](\mathbf{R}-\mathbf{r})}{|\mathbf{R}-\mathbf{r}|^2}\right\}$$
$$\cdot\left\{\mathbf{E}_0-\frac{[\mathbf{E}_0\cdot(\mathbf{R}-\mathbf{r}')](\mathbf{R}-\mathbf{r}')}{|\mathbf{R}-\mathbf{r}'|^2}\right\}$$
$$\times e^{i[\mathbf{k}_0\cdot(\mathbf{r}-\mathbf{r}')+(\omega/c)(|\mathbf{R}-\mathbf{r}|-|\mathbf{R}-\mathbf{r}'|)+(\omega-\omega_0)s]}.\quad(12)$$

The retardation factor which appears in the exponential can be expanded in powers of R^{-1}. The finite observation distance R relative to the linear dimensions of the scattering volume is taken into account by keeping terms first order in R^{-1}

$$|\mathbf{R}-\mathbf{r}|-|\mathbf{R}-\mathbf{r}'|=-\hat{R}\cdot(\mathbf{r}-\mathbf{r}')$$
$$+(1/2R)\{(\mathbf{r}+\mathbf{r}')-[\hat{R}\cdot(\mathbf{r}+\mathbf{r}')]\hat{R}\}\cdot(\mathbf{r}-\mathbf{r}').\quad(13)$$

This is in contrast to the usual radiation zone approximation which neglects finite-size effects by keeping only the first term on the right.

The remaining part of the integrand of Eq. (12) can also be expanded in powers of R^{-1}. When terms to first order are retained the result can be written in the form

$$I'(\mathbf{R})=(N\alpha^2I_0/c^4R^2)\,|\hat{\epsilon}-(\hat{\epsilon}\cdot\hat{R})\hat{R}|^2\{J_1+J_2\},\quad(14)$$

where for $j=1,\,2$

$$J_j=\frac{1}{2\pi}\int_V d\mathbf{r}\int_V d\mathbf{r}'\int_{-\infty}^{\infty}dt\int_{-\infty}^{\infty}d\omega\,\omega^4G_j(|\mathbf{r}-\mathbf{r}'|,\,t)$$
$$\times e^{i(\omega-\omega_0)t}\,e^{i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}')/\chi_0}\left\{1+\frac{2}{|\hat{\epsilon}-(\hat{\epsilon}\cdot\hat{R})\hat{R}|^2}\right.$$
$$\left.\times[(\hat{\epsilon}\cdot\mathbf{R})\hat{\epsilon}+\hat{R}-2(\hat{\epsilon}\cdot\hat{R})^2\hat{R}]\cdot\left(\frac{\mathbf{r}+\mathbf{r}'}{2R}\right)\right\}.\quad(15)$$

[15] L. Van Hove, Phys. Rev. **95**, 249 (1954). Actually the functions defined by Van Hove are obtained from those used here by integrating over the relative coordinates $(\mathbf{r}+\mathbf{r}')$ in the limit of large volume, neglecting finite-size corrections in Eq. (8). For this reason the normalization of the G functions differ by a factor of V^{-1}.

[16] L. I. Komarov and I. Z. Fisher, Zh. Eksperim. i Teor. Fiz. **43**, 1927 (1962) [English transl.: Soviet Phys.—JETP **16**, 1358 (1963)].

Here, $I_0=cE_0^2/8\pi$ is the incident light intensity, $\hat{\epsilon}=\mathbf{E}_0/|E_0|$ is the electric polarization, and

$$\mathbf{K}=\mathbf{k}_0-\frac{\omega}{\omega_0}\hat{R}+\frac{\omega}{\omega_0}\left\{\left(\frac{\mathbf{r}+\mathbf{r}'}{2R}\right)-\left[\hat{R}\cdot\left(\frac{\mathbf{r}+\mathbf{r}'}{2R}\right)\right]\hat{R}\right\}. \quad (16)$$

In Eq. (14) the direct scattering term J_1 is the contribution to the scattered intensity which results from the self-interference of the electric field which is scattered by each individual atom. The interference term J_2 is due to the interference of the electric fields scattered by two different atoms.

If the scattering gas or liquid is static so that the individual atoms are at rest, the function $G_1(|\mathbf{r}-\mathbf{r}'|,t)$ reduces to $(1/V)\delta(|\mathbf{r}-\mathbf{r}'|)$ and the evaluation of the direct scattering term is simplified, yielding just the Rayleigh result ω_0^4. The term linear in $(\mathbf{r}+\mathbf{r}')/2R$ contributes nothing in the static limit. Furthermore, the finite-size corrections of this term will be reduced relative to the unit term by a factor proportional to the linear dimensions of the scattering volume divided by the observation distance and hence may be neglected. In the dynamic case the integral over $G_1(|\mathbf{r}-\mathbf{r}'|,t)$ takes into account the thermal motion of the atoms during the scattering process. Since collisions tend to restrict the range of atomic motion, the ideal gas provides a system for an estimate of an upper bound on the size of corrections due to thermal motion. To make this estimate it is convenient to introduce the dimensionless variables

$$\tau=\omega_0 t,\quad \psi=(\omega-\omega_0)/\omega_0. \quad (17)$$

Experimentally a filter is often used to restrict the range of frequencies which contribute to the scattered intensity. The range $\Delta\omega$ is assumed centered about ω_0. The dimensionless parameters

$$\sigma=|\Delta\omega/\omega_0|,\quad M=\tfrac{1}{2}\beta mc^2 \quad (18)$$

have typical values of $\sigma=4\times10^{-3}$ for the experimental setup of Ref. 2 and $M=7.2\times10^{11}$ for argon at room temperature. In terms of these quantities the direct scattering term for an ideal gas can be written in the form

$$J_1=\frac{\omega_0^4}{2\pi V\bar{\lambda}_0^3}\int_V d\mathbf{r}\int_V d\mathbf{r}'\int_{-\infty}^{\infty}d\tau\int_{-\sigma}^{\infty}d\psi(1+\psi)^4e^{i\psi\tau}\times\left[\frac{1}{\pi}\frac{M}{\tau^2}\right]^{3/2}e^{-M/\tau^2\left(\frac{\mathbf{r}-\mathbf{r}'}{\bar{\lambda}_0}\right)^2}e^{i\mathbf{K}\cdot[(\mathbf{r}-\mathbf{r}')/\bar{\lambda}_0]}. \quad (19)$$

The volume integrations are more easily done in terms of the relative coordinates $\mathbf{r}-\mathbf{r}'$ and $\mathbf{r}+\mathbf{r}'$. To the extent that the dimensions of the scattering volume are infinite compared to the wavelength of the incident light, the $\mathbf{r}-\mathbf{r}'$ integration is just the Fourier transform of a normalized Gaussian, which gives $e^{-K^2\tau^2/4M}$. The finite-size corrections are of the order of the wavelength divided by a linear dimension of the scattering volume and can be neglected. The same result is obtained if the radiation zone approximation and the thermodynamic limit are made simultaneously, i.e., if the linear dimensions of the scattering volume and the observation distance R are allowed to become infinite with the corresponding ratios held fixed at the experimental values. It should be emphasized that not all finite-size effects are lost in this limit since relative directions are preserved. In this approximation the τ integration can be done exactly to give

$$J_1=\frac{\omega_0^4}{V}\int_V d\mathbf{r}\int_{-\sigma}^{\sigma}d\psi(1+\psi)^4[M/\pi K^2(\mathbf{r},\psi)]^{1/2}\times\exp[-M\psi^2/K^2(\mathbf{r},\psi)]. \quad (20)$$

For scattering angles of interest for the purpose of measurement and reasonable frequency ranges σ, the function

$$K^2(\mathbf{r},\psi)=\left|\hat{k}_0+(1+\psi)\left\{\left(\frac{\mathbf{r}+\mathbf{r}'}{2R}\right)-\hat{R}-\left[\hat{R}\cdot\left(\frac{\mathbf{r}+\mathbf{r}'}{2R}\right)\right]\hat{R}\right\}\right|^2 \quad (21)$$

is well behaved and the ψ integration can be evaluated as an asymptotic series in M^{-1}. Because of the extremely large value of M the only significant term of the series is the first, for which the remaining volume integration is easily done to give the simple Rayleigh result $J_1=\omega_0^4$. As already mentioned, this is exactly the result one gets for the static system neglecting finite-size effects. The interference term J_2 is somewhat more interesting in this respect.

The direct scattering term J_1 has given the entire Rayleigh expression with negligible corections of the order of $\bar{\lambda}_0/R$ and M^{-1}. Since finite-size corrections to the Rayleigh results are being sought, it will suffice to consider only the first term of the integrand of Eq. (15) for the interference term J_2.

Except for a factor of V^{-1}, the function $G_2(|\mathbf{r}-\mathbf{r}'|,t)$ gives the average density of particles at the point $\mathbf{r}'$ at time t excluding one particle under the circumstance that the excluded particle was initially at the point $\mathbf{r}$. It follows from the defining Eq. (9) that

$$\int_V d\mathbf{r}\int_V d\mathbf{r}'\,G_2(|\mathbf{r}-\mathbf{r}'|,t)=N-1, \quad (22a)$$

$$\lim_{t\to 0}G_2(|\mathbf{r}-\mathbf{r}'|,t)=(1/V)g(|\mathbf{r}-\mathbf{r}'|), \quad (22b)$$

where g is the well-known pair distribution function, normalized so that it is equal to the average density n_0 in the case of an ideal gas. For large spatial separations or long times t, $G_2(|\mathbf{r}-\mathbf{r}'|,t)\to n_0/V$ for arbitrary fluids which are not near the critical point or in a state of collective motion.[17] Except in these cases, where long-

[17] For a discussion of these important cases see the article by R. D. Mountain, Rev. Mod. Phys. 38, 205 (1966).

range correlations may be established, the function $[g(|\mathbf{r}-\mathbf{r}'|)-n_0]$ is short range and vanishes for $|\mathbf{r}-\mathbf{r}'|$ greater than a few times the range of the intermolecular forces. Even in the case of collective motion, as, for example, the passage of a sound wave through the fluid, the deviation of $g(|\mathbf{r}-\mathbf{r}'|)$ from a constant background density is either short range or small compared to the average density n_0. For these reasons one expects the magnitude of the interference term to be well estimated if $G_2(|\mathbf{r}-\mathbf{r}'|,t)$ is replaced by the ideal gas value n_0/V. In this approximation the t and ω integrations of Eq. (15) can be done immediately to give

$$J_2=\omega_0\frac{n_0}{V}\int_V d\mathbf{r}\int_V dr'\, e^{i\mathbf{K}_0\cdot(\mathbf{r}-\mathbf{r}')/\bar{\lambda}_0}, \qquad (23)$$

where

$$\mathbf{K}_0=\hat{k}_0-\hat{R}+\left(\frac{\mathbf{r}+\mathbf{r}'}{2R}\right)-\left[\hat{R}\cdot\left(\frac{\mathbf{r}+\mathbf{r}'}{2R}\right)\right]\hat{R}. \qquad (24)$$

The volume integrations of Eq. (23) are made specific if the scattering volume is approximated by a parallelepiped as shown in Fig. 1 as the intersection of the incident and scattered beam. In this approximation

$$\int_V d\mathbf{r}\rightarrow\int_{-A_3}^{A_3}dr_3\int_{-A_2}^{A_2}dr_2\int_{-(A_1/\sin\phi)+r_2\cot\phi}^{(A_1/\sin\phi)+r_2\cot\phi}dr_1,$$

and the scattering volume is $V=8A_1A_2A_3/\sin\phi$. The three integrations composing the integration over the scattering volume are made independent by the linear transformation

$$\rho_1=r_1\sin\phi-r_2\cos\phi,\quad \rho_2=r_2,\quad \rho_3=r_3. \qquad (25)$$

For the purpose of later comparison it is interesting to compute the interference term in the radiation zone approximation $R\rightarrow\infty$. In this limit $\mathbf{K}_0\cdot\mathbf{r}=f(\rho_1-\rho_2)$, where

$$f=(1-\cos\phi)/\sin\phi. \qquad (26)$$

If the infinite volume limit is also taken the resulting expression for the interference term is proportional to a δ function in the forward direction $\delta(f)$ and contributes nothing to the observed scattering. However, the finite volume integrations can be done exactly to give

$$J_2=\omega_0^4n_0\bar{\lambda}_0^3(8A_3\bar{\lambda}_0/A_1A_2)(\csc\phi/f^4)\times\sin^2(fA_1/\bar{\lambda}_0)\sin^2(fA_2/\bar{\lambda}_0).$$

The intensity measured by the photomultiplier tube is obtained by averaging this expression over a small range $\Delta\phi$ or by a change of variable over an interval $\Delta f=f\csc\phi\Delta\phi$. Using the relation $\sin^2x=\frac{1}{2}(1-\cos 2x)$ it is clear that owing to the extreme size of $A_1/\bar{\lambda}_0$ the major contribution to the average comes from the two factors of $\frac{1}{2}$ to give

$$\bar{J}_2=\omega_0^4n_0\bar{\lambda}_0^3(2A_3\bar{\lambda}_0/A_1A_2)(\csc\phi)/f^4. \qquad (27)$$

From Eq. (23) one expects this result to be a good approximation to the observed intensity when $\exp(ir^2/\bar{\lambda}_0R)\simeq 1$ for all points r in the scattering volume. This means $A^2/\bar{\lambda}_0R<1$, where A is a typical dimension of the scattering volume. In the experimental arrangement of Ref. 2 the dimensions of the scattering volume can be estimated from the half-width of the response curve for the photomultiplier tube (Fig. 15 of Ref. 2) and the cross section of the laser beam. The approximate values are $A_1=A_3=0.18$ cm, $A_2=0.20$ cm, $R=2.65$ cm and for the ruby laser $\bar{\lambda}_0=1.105\times10^{-5}$ cm. For these values $A^2/\lambda_0R\simeq1.3\times10^3$ which does not meet the requirement and hence Eq. (27) does not apply.

The large size of the parameter $A^2/\bar{\lambda}_0R$ suggests that one use the methods of asymptotic series to evaluate the integrals of Eq. (23). Since the variables $\mathbf{r}$ and $\mathbf{r}'$ and thus $\boldsymbol{\rho}$ and $\boldsymbol{\rho}'$ appear only in the combination of sum and difference it is convenient to make a second transformation to the dimensionless variables

$$\mathbf{y}=(\boldsymbol{\rho}+\boldsymbol{\rho}')/2R,\quad \mathbf{x}=(\boldsymbol{\rho}-\boldsymbol{\rho}')/\bar{\lambda}_0. \qquad (28)$$

In terms of these variables

$$\frac{1}{V}\int_V d\mathbf{r}\int_V d\mathbf{r}'\rightarrow\frac{\bar{\lambda}_0\csc\phi}{a_1a_2a_3}\prod_{j=1}^{3}\int_{-a_j}^{a_j}dy_j\int_{-(2R/\lambda_0)(a_j-|y_j|)}^{(2R/\lambda_0)(a_j-|y_j|)}dx_j,$$

where $a_j=A_j/R$. The x integration can be done to give

$$J_2=\omega_0^4\frac{n_0\bar{\lambda}_0^3\csc\phi}{a_1a_2a_3}\prod_{j=1}^{3}Q_j, \qquad (29)$$

where

$$Q_j=\int_{-a_j}^{a_j}\frac{dy_j}{K_j'}\sin\frac{2R}{\bar{\lambda}_0}K_j'(a_j-|y_j|). \qquad (30)$$

Here $K_j'=(f+y_1,-f,y_3)$ is the image of K_0 under the change of variables and f is given by Eq. (26).

If one simultaneously makes the radiation zone approximation and takes the thermodynamic limit, as described in the discussion of the direct scattering term

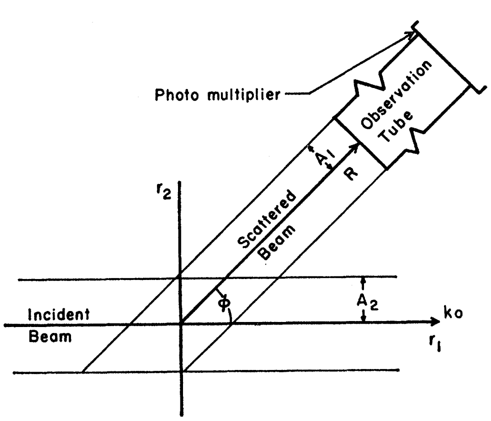

FIG. 1. Geometry of the scattering volume for scattering angle ϕ. The polarization vector is along $\mathbf{k}_0\times\mathbf{R}$.

by letting $R\to\infty$ with a_j held fixed the resulting expression for the interference term is again proportional to a δ function in the forward direction $\delta(f)$. In this limit the interference term does not contribute to the observed scattering.

For finite scattering volume and observation distance the integrals Q_j can be evaluated as asymptotic expansions in $(R/\lambda_0)^{-1}$, the first terms of which are obtained in the Appendix. When these expressions are substituted into Eq. (29) and averaged over $\Delta\phi$ the oscillatory factors contribute little to the observed intensity given by

$$\bar{J}_2=\omega_0^4 n_0\lambda_0^3\frac{\pi(\lambda_0/R)^2}{a_1a_2a_3}\frac{\csc\phi}{f^2}\frac{f^2+a_1^2}{(f^2-a_1^2)^2}. \qquad (31)$$

As discussed in the evaluation of Q_1 this result applies only for scattering angles ϕ for which $f>a_1$; a condition which is well satisfied for angles greater than 15° in the experimental arrangement of Ref. 2 where $a_1=a_2=0.068$, $a_2=0.076$. The next correction to Eq. (31) is of the order of $(a^2R/\lambda_0)^{-1}=(A^2/\lambda_0R)^{-1}\sim 1/1300$.

Using the experimental parameters already given, the relative contribution of the interference term

$$\bar{J}_2/\bar{J}_1=\bar{J}_2/\omega_0^4$$

at room temperature of 300°K is given in Table I for argon at 1 atm and xenon at 140 mm Hg.

III. CONCLUSIONS

By evaluating the integrals Q_j asymptotically instead of passing to the limit $R\to\infty$, the forward-direction δ function is spread over the forward hemisphere. However, the contribution of the interference term is still negligible for scattering angles greater than 60° and thus cannot account for the reduced intensity in the backward direction relative to that at right angles. The situation is even worse for xenon where the interference term gives a correction of less than 5% for all experimentally observed scattering angles. This is in contrast to the experimental results which show an increased scattering asymmetry for xenon. It should be noted that the numerical results of this calculation as expressed in Table I depend on the size of the scattering volume. Increasing the effective dimensions of the scattering volume decreases the effect of the interference term for angles greater than 45° ($f\geq 0.4$) as long as $a_1\leq 0.2$. Since $a_1=A_1/R=0.068$ was determined from the half-width of the relative response curve for the photomultiplier tube, one expects the numerical values given here to serve as an upper bound to the experimental values.

TABLE I. Relative contribution of the interference term (J_2/ω_0^4) for argon at 1 atm and xenon at 140 mm Hg.

ϕ(degrees)	$f(\phi)$	Ar	Xe
45	0.414	0.275	0.05
60	0.577	0.057	0.01
75	0.768	0.016	0.003
90	1.00	0.005	0.001
105	1.302	0.0007	0.0001
120	1.732	0.0006	0.0001
135	2.414	0.0002	0.00004

More generally, the results expressed by Eqs. (27) and (31) take on a common angular dependence when $f^2\gg a_1^2$. In terms of the scattering volume $V=8A_1A_2A_3\times\csc\phi$ these two results can be written in the form

$$J_2=2\omega_0^4 n_0\lambda_0^3\chi\cot^2(\tfrac{1}{2}\phi)\csc^4(\tfrac{1}{2}\phi),$$

where

$$\chi=2A_3^2\lambda_0/V,\qquad A_3^2/\lambda_0R\ll 1$$
$$=\pi R\lambda_0^2/V,\qquad A_3^2/\lambda_0R\gg 1.$$

This suggests that neglecting the volume effect, the angular dependence of the interference term is given by $\cot^2(\frac{1}{2}\phi)\csc^4(\frac{1}{2}\phi)$ in all cases. This angular distribution does not fit the shape suggested by the data of Ref. 2.

As indicated by the results given in Table I, the effect of the interference term for light scattering in gases is small for all but the smaller scattering angles. Since the relative effect of this term is proportional to the number density of scattering molecules one expects the interference term to give measurable contributions to light scattering from liquids provided the geometrical factor χ is not too small. The theory cannot be compared with published results such as those given in Ref. 5 since the dimensions of the scattering volume are not provided. However, it is a simple matter to determine if either Eq. (27) or Eq. (31) applies to a given experimental apparatus, and if so, to compute the interference term once the geometry is determined.

ACKNOWLEDGMENTS

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APPENDIX

Write the integral

$$Q_1=\int_{-a}^{a}\frac{dy}{f+y}\sin\frac{2R}{\lambda_0}(f+y)(a-|y|)$$

in the form

$$Q_1=F(f)+F(-f)$$

with

$$F(f)=\int_0^a\frac{du}{b+u}\sin\frac{2R}{\lambda_0}u(b+u),$$

where f is given by Eq. (26), $u=a-y$, and $b=f-a$. $F(f)$ is the imaginary part of the integral

$$H(f)=\int_0^a\frac{du}{b+u}\exp\left\{i\frac{2R}{\lambda_0}u(b+u)\right\},$$

which by contour integration can be written in the form

$$H(f)=i\int_0^\infty \frac{dZ}{b+iZ}\exp\left\{i\frac{2R}{\lambda_0}Z(Z+ib)\right\}$$
$$-i\exp\left\{i\frac{2R}{\lambda_0}a(b+a)\right\}\int_0^\infty \frac{dZ}{b+a+iZ}$$
$$\times\exp\left\{-\frac{2R}{\lambda_0}Z(b+2a+iZ)\right\}.$$

For scattering angles greater than 45° $(2R/\lambda_0)b\geq 1.5\times 10^5$; the exponential factors are rapidly decreasing and $H(f)$ can be approximated by

$$H(f)=\frac{i}{b}\int_0^\infty dZ\exp\left\{-\frac{2Rb}{\lambda_0}Z\right\}+\frac{i}{b+a}\exp\left\{i\frac{2R}{\lambda_0}a(b+a)\right\}$$
$$\times\int_0^\infty dZ\exp\left\{-\frac{2R}{\lambda_0}(b+2a)Z\right\}.$$

The resulting integrals can be evaluated and the imaginary part taken to give

$$F(f)=\frac{\lambda_0}{2R}\left\{\frac{1}{b^2}-\frac{\cos(2R/\lambda_0)a(b+a)}{(b+a)^2}\right\}+O\left(\frac{\lambda_0}{2R}\right)^2.$$

Thus to first order in λ_0/R

$$Q_1(f)=\frac{\lambda_0}{R}\left\{\frac{f^2+a^2}{(f^2-a^2)^2}-\frac{1}{f^2}\cos\frac{2R}{\lambda_0}af\right\}.$$

For smaller angles this expression diverges as $f\rightarrow a$. Returning to the original integral expression one sees that as $f\rightarrow a$, a point of stationary phase approaches the range of integration. This means that the resulting value of the integral will contain one less factor of $(\lambda_0/R)^{1/2}$ and thus will be somewhat larger but nevertheless remains finite. This region is not of much experimental interest since for most arrangements $a<f$ for all experimentally observed scattering angles.

The second integral can be evaluated directly:

$$Q_2=\int_{-a}^{a}\frac{dy}{f}\sin\frac{2R}{\lambda_0}f(a-|y|)$$
$$=\frac{\lambda_0}{R}\frac{1}{f^2}\left\{1-\cos\frac{2R}{\lambda_0}fa\right\}.$$

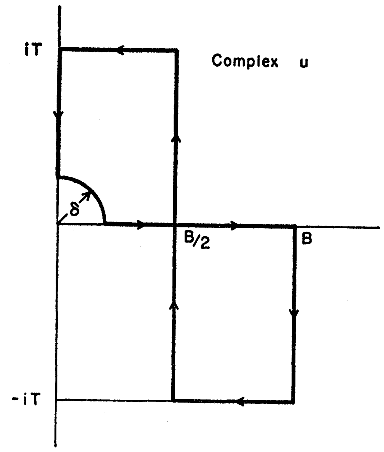

FIG. 2. Contour for the evaluation of the integral Q_3.

The third integral

$$Q_3=\int_{-a}^{a}\frac{dy}{y}\sin\frac{2R}{\lambda_0}y(a-|y|)$$

can be written in the form

$$Q_3=2\,\mathrm{Im}\int_0^B\frac{du}{u}e^{iu(B-u)},$$

where $B=a(2R/\lambda_0)^{1/2}$ and $u=(2R/\lambda_0)^{1/2}y$. Using the contour shown in Fig. 2 and taking the limits $\delta\rightarrow 0$, $T\rightarrow\infty$ an exact expression for Q_3 is obtained:

$$Q_3=\pi-B\int_{-\infty}^{\infty}\frac{du}{u^2+(\frac{1}{2}B)^2}\cos[u^2+(\tfrac{1}{2}B)^2]$$
$$+2\int_0^\infty du\left\{\frac{\sin u^2}{u}+\frac{B\cos u^2-u\sin u^2}{B^2+u^2}\right\}e^{-Bu}.$$

In the case of interest $B=(2A_3{}^2/\lambda_0R)^{1/2}\gg 1$ and the remaining integrals can be evaluated by the method of stationary phase. To first order in B^{-1} the result is

$$Q_3=\pi-\frac{2(2\pi)^{1/2}}{a}\left(\frac{\lambda_0}{R}\right)^{1/2}\left\{\cos\frac{a^2R}{2\lambda_0}-\sin\frac{a^2R}{2\lambda_0}\right\}.$$