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THEORY OF RAYLEIGH SCATTERING OF LIGHT IN LIQUIDS

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A molecular theory is developed to describe the spectrum and intensity of Rayleigh scattering of light in liquids or dense gases; this analysis does not make use of the thermodynamic theory of fluctuations. The spectral density of the scattered light is found to be the four-dimensional Fourier transform of a space-time molecular correlation function of the scattering system. This same function can be used to describe the kinetic characteristics of the system, i.e., the correlation and autocorrelation functions of the density fluctuations. This correlation function can itself be expressed in terms of an inverse four-dimensional Fourier transform of the spectral density of the scattered light. Using single-isotope lamps or lasers as light sources it should be possible, in practice, to transform the scattered light spectrum into a space-time correlation function and thus to obtain detailed information on molecular structure and molecular motion in liquids.

1. INTRODUCTION

THE theory of Rayleigh scattering of light in gases and liquids has been treated at great length (cf. reviews and monographs [1-4]). As applied to liquids the existing theory is essentially thermodynamic and is not directly connected with the details of the interaction and motion of the molecules or the molecular ordering. This approach is valid because wavelengths in the visible light region are appreciably greater than intermolecular distances or the dimensions of the regions of approximate order in liquids. However, it is still desirable to formulate a more detailed molecular theory which, in principle, would provide the possibility of obtaining detailed information on the molecular structure of liquids from experimental data on the intensity and spectral composition of the scattered light.

In the present work we have developed a molecular theory to describe the spectrum of Rayleigh scattered light in liquids and dense gases. It will be shown that the experimental data can be used to obtain the extremely important space-time correlation function of the system particles.

The present work was stimulated by a paper by van Hove [5] on the scattering of neutrons in liquids. In some sense the present work is a "translation" of van Hove's analysis from the language of neutron scattering to the language of light scattering. A translation of this kind is extremely desirable because recent developments in optics provide the possibility of precise optical spectral measurements that are not possible in neutron spectroscopy.

2. VAN HOVE CORRELATION FUNCTIONS

Below we shall require the two special space-time correlation functions for the particles in a fluid, introduced in [5]. We first define briefly these functions and determine their basic properties. For simplicity we assume everywhere in the present work that the molecules of the liquid are spherically symmetric and that the molecular positions are given completely by coordinates of the molecular center of mass. The liquid as a whole is assumed to be in equilibrium.

Assume that there are N molecules in a volume V and let $\mathbf{R}_i(0)$ $(i = 1, 2, \ldots)$ denote the position of a particle at some initial time and $\mathbf{R}_i(t)$ the positions at some other time. We consider the two functions

$$G_1(\mathbf{r}, t \mid \mathbf{r}_0, 0) = \frac{1}{N}\left\langle \sum_{1 \leqslant i \leqslant N} \delta(\mathbf{r} - \mathbf{r}_0 - \mathbf{R}_i(t) + \mathbf{R}_i(0))\right\rangle, \tag{1}$$

$$G_2(\mathbf{r}, t) \mid \mathbf{r}_0', 0) = \frac{2V}{N(N-1)}\left\langle \sum_{1 \leqslant i < k \leqslant N} \delta(\mathbf{r} - \mathbf{r}_0' - \mathbf{R}_i(t) + \mathbf{R}_k(0))\right\rangle, \tag{2}$$

where the angle brackets $\langle\ \rangle$ denotes an average over a Gibbs ensemble for the initial (i.e., $t = 0$) state of the system. It is evident that as a consequence of the isotropy of the liquid (neglecting surface effects)

$$G_1(\mathbf{r}, t \mid \mathbf{r}_0, 0) = G_1(|\mathbf{r} - \mathbf{r}_0|, t),$$

$$G_2(\mathbf{r}, t \mid \mathbf{r}'_0, 0) = G_2(|\mathbf{r} - \mathbf{r}'_0|, t). \tag{3}$$

The function $G_1(\mathbf{r}, t)$ describes the mean translational motion of a single particle, i.e., its self-diffusion. By the definition in (1) it represents the conditional probability density that an arbitrary particle of the system will be at point $\mathbf{r}$ at time t if it is at $\mathbf{r}_0$ at time t_0, regardless of the positions of the other particles:

$$dw(\mathbf{r}, t \mid \mathbf{r}_0, 0) = G_1(|\mathbf{r} - \mathbf{r}_0|, t)\, d\mathbf{r}, \tag{4}$$

where the following normalization holds

$$\int_{(V)} G_1(|\mathbf{r}|, t)\, d\mathbf{r} = 1. \tag{5}$$

The definition of $G_1(\mathbf{r}, t)$ also implies certain limiting properties:

$$\begin{aligned} &G_1(|\mathbf{r}|, t) \to \delta(\mathbf{r}) \text{ for } t \to 0, \\ &G_1(|\mathbf{r}|, t) \to 1/V \text{ for } t \to \infty \text{ or } |\mathbf{r}| \to \infty. \end{aligned} \tag{6}$$

In similar fashion the function G_2 is proportional to the conditional probability density that a particle will be at $\mathbf{r}$ at time t if some other particle is at $\mathbf{r}'_0$ at t = 0, regardless of the positions of the other particles:

$$dw(\mathbf{r}, t \mid \mathbf{r}'_0, 0) = V^{-1} G_2(|\mathbf{r} - \mathbf{r}'_0|, t)\, d\mathbf{r}, \tag{7}$$

where the following normalization holds

$$\frac{1}{V} \int_{(V)} G_2(|\mathbf{r} - \mathbf{r}'_0|, t)\, d\mathbf{r} = 1. \tag{8}$$

The function $G_2(|\mathbf{r}|, t)$ is a time-dependent generalization of the radial distribution function $G(|\mathbf{r}|)$ well-known in statistical theory[6,7] and, in fact, approaches the latter as $t \to 0$:

$$G_2(|\mathbf{r}|, t) \to g(|\mathbf{r}|) \text{ for } t \to 0. \tag{9}$$

At long times or large distances

$$G_2(|\mathbf{r}|, t) \to 1 \text{ for } t \to \infty \text{ or } |\mathbf{r}| \to \infty. \tag{10}$$

We also note that as a consequence of the reversibility of the equations of mechanics the functions G_1 and G_2 exhibit the property

$$G_1(|\mathbf{r}|, -t) = G_1(|\mathbf{r}|, t),\ G_2(|\mathbf{r}|, -t) = G_2(|\mathbf{r}|, t). \tag{11}$$

Below we shall encounter the sum

$$G(|\mathbf{r}|, t) = G_1(|\mathbf{r}|, t) + \frac{N-1}{V} G_2(|\mathbf{r}|, t). \tag{12}$$

To order N^{-1} this quantity represents the conditional probability density of finding a particle at time t at some point, a distance $\mathbf{r}$ from the location of any (the same particle or any other) particle at t = 0.

The function $G(\mathbf{r}, t)$ is a very important characteristic of the kinetic properties of a system; using this function we can find the correlation functions and autocorrelation functions of additive functions of particle coordinates and velocities.

3. DERIVATION OF THE BASIC EQUATION FOR THE SPECTRAL INTENSITY OF THE SCATTERED LIGHT

Suppose that on our system is irradiated by a plane monochromatic light wave with electric vector

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 e^{i(\mathbf{k}_0\mathbf{r} - \omega_0 t)}\ . \tag{13}$$

This wave produces a dipole moment density given by

$$\mathbf{p}(\mathbf{r}, t) = \alpha \mathbf{E}(\mathbf{r}, t) \sum_{1 \leqslant i \leqslant N} \delta(\mathbf{r} - \mathbf{R}_i(t)), \tag{14}$$

where α is some effective polarizability of a single molecule in the field of neighboring molecules; α is assumed to be independent of frequency (or weakly dependent) near ω_0. The field of the scattered wave can be described by the Hertz vector $\mathbf{Z}(\mathbf{R}, t)$:

$$\mathbf{E}'(\mathbf{R}, t) = \operatorname{grad}\operatorname{div} \mathbf{Z} - \frac{1}{c^2} \frac{\partial^2 \mathbf{Z}}{\partial t^2} \tag{15}$$

where

$$\Delta \mathbf{Z} - \frac{1}{c^2} \frac{\partial^2 \mathbf{Z}}{\partial t^2} = -4\pi \mathbf{p}. \tag{16}$$

The solution of this equation in terms of retarded potentials is

$$\mathbf{Z}(\mathbf{R}, t) = \int_{(V)} d\mathbf{r}' \int_{-\infty}^{\infty} dt' \frac{\mathbf{p}(\mathbf{r}', t')}{|\mathbf{r}' - \mathbf{R}|} \delta\left(t' - t + \frac{|\mathbf{r}' - \mathbf{R}|}{c}\right). \tag{17}$$

If the δ-function is expanded in a Fourier integral, using (15) and (17) we find in the wave zone

$$\begin{aligned} \mathbf{E}'(\mathbf{R}, t) = {} & \frac{\alpha}{2\pi c^2 R} \left(\mathbf{E}_0 - \frac{(\mathbf{E}_0\mathbf{R})\mathbf{R}}{R^2}\right) \int_{(V)} d\mathbf{r} \int_{-\infty}^{\infty} dt' \int_{-\infty}^{\infty} d\omega'\ \omega'^2 e^{i(\mathbf{k}_0\mathbf{r} - \omega_0 t')} \\ & \times \exp\left\{i\omega'\left(t' - t + \frac{R}{c} - \frac{\mathbf{R}\mathbf{r}}{cR}\right)\right\} \sum_{1 \leqslant i \leqslant N} \delta(\mathbf{r} - \mathbf{R}_i(t')). \end{aligned} \tag{18}$$

As is well-known,[3] the spectral intensity of the scattered light is related to the Fourier component of the expansion

$$\mathbf{E}'(\mathbf{R}, t) = \int_{-\infty}^{\infty} d\omega e^{i\omega t}\, \mathbf{E}(\mathbf{R}, \omega) \tag{19}$$

by the relation

$$I'(\mathbf{R}, \omega) = \frac{c}{2T} |\mathbf{E}'(\mathbf{R}, \omega)|^2, \tag{20}$$

where T is the time of arrival of the light. Carrying out the required calculations in (18), substituting the results in (20), and averaging both sides of (20) over a Gibbs ensemble for the initial (i.e., t = t′) particle distribution we find (recalling the definitions of the functions G_1, G_2, and G)

$$I'(\mathbf{R},\omega)=\frac{\alpha^2\omega^4N}{2\pi c^4R^2}I_0\sin^2\gamma\int\limits_{(V)}d\mathbf{r}\int\limits_{-\infty}^{\infty}dt \times\exp\left\{i\left(\mathbf{k}_0-\frac{\omega\mathbf{R}}{cR}\right)\mathbf{r}-i(\omega_0-\omega)t\right\}G(|\mathbf{r}|,t), \tag{21}$$

where I_0 is the intensity of the incident radiation and $\cos\gamma=|\mathbf{E}_0\cdot\mathbf{R}|/R|\mathbf{E}_0|$.

After simple substitution for the time variable we write the inner integral in the form

$$\int\limits_{-\infty}^{\infty}dt\exp\left\{i\left(\mathbf{k}_0-\frac{\omega_0\mathbf{R}}{cR}\right)\mathbf{r}-i(\omega_0-\omega)t\right\}G\left(|\mathbf{r}|,t+\frac{\mathbf{rR}}{cR}\right), \tag{22}$$

and expand G in powers of $(\mathbf{r}\cdot\mathbf{R}/cR)$. As a consequence of the properties given in (11) it is found that the first correction to I′ is of order $(\bar{v}/c)^2$, where $\bar{v}$ is the mean velocity of the molecular motion. Since the leading term in I′ gives a very small effect (scattering of light on a pure liquid) it is clear that the corrections can be neglected completely. Introducing the notation

$$\varkappa=\omega_0\mathbf{R}/cR-\mathbf{k}_0,\quad\Omega=\omega-\omega_0, \tag{23}$$

in place of (21) we have

$$I'(\mathbf{R},\omega)=\frac{\alpha^2\omega^4N}{2\pi c^4R^2}I_0\sin^2\gamma\int\limits_{(V)}d\mathbf{r}\int\limits_{-\infty}^{\infty}dt\,e^{i\Omega t-i\varkappa\mathbf{r}}G(|\mathbf{r}|,t). \tag{24}$$

The difference between (21) and (24) is the fact that κ and Ω are independent in the latter.

Thus, to within a constant $I'(\mathbf{R},\omega)/\omega^4\sin^2\gamma$ is the four-dimensional Fourier-transformed correlation function of van Hove. If we eliminate scattering at zero angle ($\kappa=0$) in Eq. (24) the function G can be replaced by G − 1. After this it is convenient to extend the integration over $d\mathbf{r}$ over all space; this procedure is possible because $|G(|\mathbf{r}|,t)-1|$ falls off rapidly with increasing $|\mathbf{r}|$ for all t. Finally, carrying out the integration over angle we find

$$I'(\mathbf{R},\omega)=\frac{2\alpha^2\omega^4N}{c^4R^2}I_0\sin^2\gamma\int\limits_0^{\infty}r^2dr\frac{\sin\varkappa r}{\varkappa r} \times\int\limits_{-\infty}^{\infty}dt\,(G(r,t)-1)\,e^{i\Omega t}. \tag{25}$$

It is interesting to compare this result with the results of the static theory, in which the time dependence of the correlation functions is ignored. If $G(\mathbf{r},t)$ is replaced by $G(\mathbf{r},0)$ in (24) or (25), we find from (6) and (9)

$$G(\mathbf{r},0)=\delta(\mathbf{r})+g(|\mathbf{r}|)/v, \tag{26}$$

where v = V/N; then we obtain in place of (25) the familiar result[6,7]

$$I'(\mathbf{R},\omega)=\frac{\alpha^2\omega^4N}{c^4R^2}I_0\sin^2\gamma\delta(\omega-\omega_0) \times\left\{1+\frac{4\pi}{v}\int\limits_0^{\infty}(g(r)-1)\frac{\sin\varkappa r}{\varkappa r}r^2dr\right\}. \tag{27}$$

Thus the static theory does not exhibit a change in the frequency of the light in scattering whereas the present dynamic theory leads to a finite width of the scattered light spectrum. It can be shown that to order $(\bar{v}/c)^2$ both expressions (25) and (27) yield the same total scattered light intensity.

This last result can be used to obtain a better value for α in our expressions. For visible light the function $(\sin\kappa r)/\kappa r$ is essentially equal to unity over the entire region in which $g(r)-1$ is nonvanishing. Hence, we set $(\sin\kappa r)/\kappa r$ equal to unity in (27); then, using the well-known expression[6]

$$\beta_T=\frac{v}{k_BT}\left\{1+\frac{4\pi}{v}\int\limits_0^{\infty}(g(r)-1)\,r^2\,dr\right\}, \tag{28}$$

where β_T is the isothermal compressibility of the system, in place of (27) we have

$$I'(\mathbf{R},\omega)=\frac{\alpha^2\omega^4}{c^4R^2}\frac{Nk_BT\beta_T}{v}I_0\sin^2\gamma\delta(\omega-\omega_0). \tag{29}$$

Comparing this with the familiar result of the phenomenological theory[1-3] we find

$$\alpha=\frac{v^2}{4\pi}\left(-\frac{\partial\varepsilon}{\partial v}\right)_T, \tag{30}$$

where ϵ is the dielectric constant, whose temperature dependence is neglected.

4. DISCUSSION OF RESULTS

At the present time the function $G(|\mathbf{r}|,t)$ cannot be computed theoretically because of the usual difficulties arising in the solution of the exact kinetic equations for the correlation functions in a liquid. Hence, in the general case a theoretical calculation of the scattered light spectrum by Eq. (25) is still not possible. For purposes of illustration, however, we can consider the case of a rarefied gas. If particle collisions are neglected completely, then $G_2=1$ and G_1 can be obtained directly from the Maxwellian molecular velocity distribution

$$G_1(|\mathbf{r}|,t)=\left(\frac{m}{2\pi k_BTt^2}\right)^{3/2}\exp\left\{-\frac{m|\mathbf{r}|^2}{2k_BTt^2}\right\}, \tag{31}$$

where k_B is the Boltzmann constant and T is the temperature. Substituting in (25) we find

$$I'_{\text{gas}}(\mathbf{R}, \omega) = \frac{\alpha^2\omega^4 N}{\pi c^4 R^2} I_0 \sin^2\gamma \left(\frac{\pi m}{2k_{\text{B}}T}\right)^{1/2} \frac{1}{\varkappa} \times \exp\left\{-\frac{m(\omega-\omega_0)^2}{2k_{\text{B}}T\varkappa^2}\right\}. \qquad (32)$$

This is the correction expression for the scattering of light in an ideal gas (taking account of the Doppler effect) and can be easily obtained from elementary considerations.

In our opinion, the true importance of (25) for condensed media is not that the spectrum of scattered light can be computed from $G(\mathbf{r}, t)$, but rather the fact that the inverse problem can be solved. Using the notation

$$I'(\mathbf{R}, \omega)/I_0 N\omega^4 \sin^2\gamma = S(\varkappa, \omega), \qquad (33)$$

and (25) (after eliminating scattering ar zero angle) we find the inverse Fourier transformation

$$G(|\mathbf{r}|, t) - 1 = \frac{c^4}{(2\pi)^3\alpha^2}\int d\boldsymbol{\varkappa} \int_{-\infty}^{\infty} d\Omega e^{-i(\Omega t - \boldsymbol{\varkappa}\mathbf{r})} S(\boldsymbol{\varkappa}, \omega) \qquad (34)$$

or, integrating over all directions κ,

$$r(G(|\mathbf{r}|, t) - 1) = \frac{2c^4}{(2\pi)^2\alpha^2}\int_0^{\infty} \varkappa d\varkappa \sin\varkappa r \int_{-\infty}^{\infty} d\Omega e^{-i\Omega t} S(\varkappa, \Omega). \qquad (35)$$

All the presently available information on molecular structure (approximate order) for actual simple liquids is based primarily on the interpretation of x-ray patterns of liquids in terms of the radial distribution function $g(r)$.[6,7] The corresponding equations, which relate $g(r)$ with the intensity of x rays scattered at a given angle, are obtained from (34) by going to the static case $t = 0$. Our results in (34) or (35) appear as a natural dynamic extension of this familiar static theory.

Just as the Fourier transformation of the angular dependence of the intensity of the scattered x rays gives us the equilibrium radial particle distribution function for the liquid $g(r)$, the double Fourier transform for the angular and frequency dependence (35) of the scattered light can give the space-time correlation function $G(|\mathbf{r}|, t)$. The latter contains much more information concerning structure of the liquid and the thermal motion of the molecules. The role of this function in kinetic theory has already been noted above in Sec. 2.

Equation (35) can be used directly for practical calculations. Unfortunately, techniques available until recently did not provide reliable measurements of spectral line shapes because the instrumental widths of available "monochromatic" light sources were approximately an order of magnitude greater than the line widths in scattered light spectra.[1,2] However, the situation has now changed radically because of the availability of single-isotope lamps and the rapid development of the laser as a laboratory tool. It thus appears that it will soon be practical to use (34) in the interpretation of the kinetics of molecular motion in simple liquids.

Van Hove[5] has shown that the function $G(|\mathbf{r}|, t)$ can be determined by measuring the angle-energy dependence of the slow-neutron scattering cross sections. However, the accuracy of spectral measurements in neutron spectroscopy is not nearly adequate for carrying out this program at the present time.

The method developed in the present paper can also be used for more complicated systems, for example, liquids with optically anisotropic molecules, liquid, gas mixtures, etc. The authors hope to consider these problems.

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