Double-scattering correction in the interpretation of Rayleigh scattering data near the critical point of a binary liquid*

Alan J. Bray
Center for Theoretical Physics, Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742

R. F. Chang
Center of Materials Research, Department of Physics and Astronomy, University of Maryland, College Park, Maryland 20742
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Double-scattering contributions to the intensity of Rayleigh-scattered light near the critical point of a binary liquid are calculated for 90° scattering. We consider a family of sample geometries, namely cylinders with arbitrary length-to-radius ratio and cuboids with square cross sections and arbitrary length-to-side ratio. For binary liquids with nearly matched refractive indices, these terms can be sufficiently large that they affect the interpretation of data with respect to the value of the critical exponent η and the deviation of the correlation function from Ornstein-Zernike form, yet small enough that higher-order contributions can be neglected. Numerical results are presented for all temperatures above T_c together with analytical results in certain limiting cases. Near the critical point, the double-scattered intensity is comparable with that lost through extinction and these two effects cancel in leading order. Some analytical results are also obtained for the depolarization ratio. For example, if the height of the sample seen by the detector is small, the depolarization ratio is proportional to the differential cross section and to the sample height. The proportionality constant is $\pi/4$. Numerical results are presented for more general cases.

I. INTRODUCTION

Light-scattering experiments have been used extensively[1] for measuring the density-density (or concentration-concentration) correlation function of a simple (or binary) liquid near its critical point. According to the Ornstein-Zernike (OZ) theory,[2] the light-scattering intensity per unit length and per unit solid angle is given by

$$I(\theta, \Phi) = A\kappa_T(k=0)\sin^2\Phi/[1+(k\xi)^2] \;, \tag{1.1}$$

where for a simple liquid,

$$A=\pi^2\lambda^{-4}\left(\frac{\rho\partial\epsilon}{\partial\rho}\right)_T^2 k_B T \;,$$

$\kappa_T(k=0)$ is the static isothermal compressibility,

$$k=|\vec{k}_{\rm in}-\vec{k}_{\rm out}|=2k_0\sin(\tfrac{1}{2}\theta)$$

is the magnitude of the scattering wave vector, Φ is the angle between the polarization vector of the incident beam and the wave vector $\vec{k}_{\rm out}$ of the scattered beam, ξ is the correlation length, λ is the vacuum wavelength of incident light, and k_0 is the magnitude of the wave vector of the light in the medium. For a binary liquid the same expression holds except $(\rho\partial\epsilon/\partial\rho)_T$ is replaced by $(\partial\epsilon/\partial c)_T$ and

$$\kappa_T(k=0)=\left(\frac{\partial c}{\partial(n\mu)}\right)_T \;,$$

where c is the molar concentration of one component, μ the (relative) chemical potential, and n the molecular number density. By measuring the scattered intensity as a function of angle and/or temperature, Eq. (1.1) has been used[3-5] to determine the absolute values and the temperature dependences of $\kappa_T(k=0)\propto(T-T_c)^{-\gamma}$ and $\xi\propto(T-T_c)^{-\nu}$ and hence to determine the critical exponents γ and ν.

Sufficiently close to the critical point ($k\xi>1$) Eq. (1.1) is expected to fail, and has to be replaced by the more general form[6]

$$I(\theta,\Phi)=A\kappa_T(k=0)\sin^2\Phi f(k\xi) \;, \tag{1.2}$$

where $f(k\xi)$ is the "scaling function" with the properties $f(x)=1-x^2+O(x^4)$, $x\ll 1$ and $f(x)\propto x^{-(2-\eta)}$, $x\gg 1$, this last form defining the critical exponent η, related to γ and ν by the scaling law $\gamma=\nu(2-\eta)$. Light-scattering measurements may in principle be used to determine the exponent η and the functional form of $f(x)$.

A direct application of Eq. (1.1) or (1.2) to the measured scattered intensity requires that a given light ray be scattered at most once by the sample. As the critical point is approached, however, the scattering intensity grows so that eventually one may have to take multiple scattering effects into account when calculating the scattered intensity. For simple fluids such effects typically become significant in the critical region, making a detailed investigation of the scaling function close to the critical point impossible. Recently, however, the use of binary liquids with approximately equal refractive indices has become more common. For such mixtures the scattering intensity can be made sufficiently small that the single scattering formula, Eq. (1.1) or (1.2), will hold, without multiple scattering correction, until quite close to T_c. A price has to be paid in so far as the scattering from concentration fluctuations becomes too small in the "hydrodynamic" regime ($k\xi \ll 1$) for reliable data to be taken.

A system of this type which has been used by one of the authors is 3-methylpentane-nitroethane[3] with refractive indices 1.373 and 1.389 at 6328 Å, respectively. The scattered intensity is measured for $k\xi$ typically in the range $0.1 < k\xi < 10$. For the range of temperatures covered by the measurements the multiple scattering corrections were estimated, from turbidity measurements, to be negligible for $k\xi \simeq 0.1$, increasing to about 5% for $k\xi \simeq 10$. In this latter regime, which is where the scaling function differs most from the OZ form, the single-scattering formula is inaccurate by $\simeq 5\%$, which is of the same order as the difference between the exact scaling function and the OZ form, namely of the order of the critical exponent η. As pointed out in the investigation of double scattering by Oxtoby and Gelbart,[7] an apparent deviation of the scaling function from OZ can be induced by double scattering. Therefore, for a satisfactory interpretation of the data in terms of the critical exponent η which quantifies the deviation of the scaling function $f(x)$ from OZ form, it is necessary to take adequate account of the multiple scattering corrections.

In their investigation, Oxtoby and Gelbart assumed a spherical scattering sample with only its central region under illumination. Their geometrical configuration is physically unrealizable and their calculations are not applicable to an actual experimental situation. An investigation of double-scattering effects for a more realistic geometrical configuration is necessary in order to apply proper corrections to scattering-intensity measurements and this is the aim of this paper.

Customarily, data from scattering-intensity measurements are corrected for the extinction due to increased turbidity near a critical point. The turbidity τ is the total scattering intensity per unit length, and is given by the integral of $I(\theta, \Phi)$ over solid angle. The OZ form for $I(\theta, \Phi)$ is usually used, with the unknown parameters determined by measuring, as a function of temperature, the ratio of the intensity I of the unscattered beam to that I_0 of the incident beam and fitting to $I/I_0 = e^{-\tau L}$, where L is the path length in the sample of the unscattered beam. If the path length of the scattered beam is L', the turbidity correction consists of determining the intensity for single scattering $I_{\text{sing.}}$ from the measured intensity $I_{\text{meas.}}$ according to

$$I_{\text{meas.}} = I_{\text{sing.}}\, e^{-\tau L'} \; . \tag{1.3}$$

This approach treats all light scattered out of the incident beam, other than in the direction of the detector, as "lost." However, some of this light will be subsequently rescattered and eventually reach the detector. The goal of the present paper is to take such contributions accurately into account for the most common experimental geometry, namely a scattering volume which consists of either a cylinder or a cuboid with square cross section. We include double scattering only, which is adequate provided the turbidity correction is small.

Then Eq. (1.3) is modified to read

$$I_{\text{meas.}} = I_{\text{sing.}} - \tau L' I_{\text{sing.}} + I_{\text{double}} \; , \tag{1.4}$$

where I_{double} reflects the "gain" through double scattering whereas $\tau L' I_{\text{sing.}}$ reflects the "loss" due to turbidity, the exponential function being approximated by its linearized form for small $\tau L'$. The loss term and the gain term are of the same order of magnitude, so that application of a turbidity correction to the experimental data, without also taking double scattering into account, is a poor approximation.

While the motivation for the present work arose from the need to interpret the data of one of the authors, the results presented here have general applicability in situations where the multiple scattering corrections are small (but not negligible). In particular, the use of binary liquids with nearly matched refractive indices is an increasingly common experimental technique.

Our method for computing the double-scattering correction is simply to integrate over all possible double-scattering processes. In doing so, we will exploit the fact that, for typical experimental geometries, the width of the sample seen by the detector, Δw, is small compared to the dimension of the scattering volume. This assumption enables us to treat the integrand (the intensity for a given double-scattering process) as constant across the width Δw and greatly simplifies the computation of the double-scattering integral. Consequently, we are able to reduce the integral to that over a single variable and obtain certain analytical results in a few limiting cases.

This approach is to be contrasted with the recent calculation of Reith and Swinney[8] on the depolarization of light due to double scattering. Their computational problem is identical to that encountered here. In their calculation they chose to evaluate fourfold integrals using the Monte Carlo method. Their principle theoretical result is that the depolarization ratio (defined as the ratio of scattering intensity with cross polarization to that with parallel polarization with respect to the incident beam) is, for $k\xi \ll 1$, proportional to the differential cross section for single scattering, the height h of the sample seen by the detector, and a factor g, which is equal to $\frac{1}{4}\pi$ for small h and approximately equal to 0.77 for the range of h used in their experiment. By exploiting the smallness of the width Δw, we have been able to compute the factor g for the whole range of h and find that, in the limit of small h, g is equal to $\frac{1}{4}\pi$ plus corrections quadratic in h.

Section II contains a discussion of the geometries we will consider (which include the geometries used in the experiments of one of the authors and those of Reith and Swinney) and a derivation of the double-scattering correction as a triple integral over (essentially) the scattering volume. The calculation is carried out for the special case of 90° scattering, with the polarization of the incident beam perpendicular to the plane of scattering. Section III is devoted to an evaluation of this integral and a discussion of the results. It turns out that two of the three integrals may be evaluated analytically while the final integration must be carried out numerically except in certain limits. Depolarization effects are discussed in Sec. IV, where the function $g(h)$ introduced by Reith and Swinney is computed. The case where the polarization of the incident beam is parallel to the direction of scattering is also discussed. Double-scattering contributions dominate here since single scattering in the direction of polarization is forbidden. The ratio of the intensities for polarization perpendicular and parallel to the plane of scattering is a pure number, depending only on the sample geometry. Finally, Sec. V consists of a brief summary.

II. DOUBLE-SCATTERING CORRECTION

We will assume that the multiple scattering provides a small correction ($\lesssim 10\%$) to the single-scattering intensity, but must nevertheless be taken into account in order to determine the scaling function $f(x)$ and exponent η reliably from the data, since $f(x)$ differs from its OZ form $(1+x^2)^{-1}$ by an amount of the same order ($\sim\eta\sim 0.1$). To leading order, therefore, we need include only the double-scattering contribution to the multiple scattering correction. By the same token we are justified in using, for the double-scattering calculation, the OZ form Eq. (1.1) for the single-scattering intensity, since the resulting error will be second-order small in the final result.

Equation (1.1) may be written more conveniently as

$$I(\theta,\Phi)=B\sin^2\Phi/[\alpha^2+(2\sin\tfrac{1}{2}\theta)^2]\ , \qquad (2.1)$$

where $B=A\kappa_T(k=0)(k_0\xi)^{-2}$ and $\alpha=(k_0\xi)^{-1}$. The temperature dependence of B is (A has no critical variation) $B\sim(T-T_c)^{\nu\eta}\sim$ constant, since we may take $\eta=0$ in the present calculation for the reasons cited above. The turbidity is then[9]

$$\tau=\int d\Omega\, I(\theta,\Phi)$$
$$=\tfrac{1}{2}\pi B\left[(1+\beta)\ln\left(\frac{\sqrt{\beta}+1}{\sqrt{\beta}-1}\right)-2\sqrt{\beta}\right]\ , \qquad (2.2)$$

where

$$\beta=(1+\tfrac{1}{2}\alpha^2)^2\ . \qquad (2.3)$$

To calculate the double-scattering correction we specialize to the experimental arrangement shown in Fig. 1, which has been used by one of the authors.[3] The scattering volume is a cylinder of radius r_0 and height h, although identical results are obtained if the cross section is a square of side $2r_0$. The incident beam is directed along the positive y axis, polarized in the z direction, and assumed to have negligible width. The detector is placed on the positive x axis and "sees" just a narrow strip, of width Δw, of the scattering volume. Only light which is finally scattered inside this strip, and parallel to the x axis can reach the detector. The total intensity received by the detector is proportional to, for unit intensity in the incident beam,

$$I_{\text{meas.}}(\tfrac{1}{2}\pi,\tfrac{1}{2}\pi)=I_{\text{sing.}}(\tfrac{1}{2}\pi,\tfrac{1}{2}\pi)-\epsilon_{\text{out}}+\epsilon_{\text{in}}\ , \qquad (2.4)$$

the constant of proportionality being $(\Delta w)\,d\Omega$, where $d\Omega$ is the solid angle subtended by the detector at a point in the strip, and is assumed the same for every such point. The general assumption here is that the width Δw of the scattering volume seen by the detector is small compared to

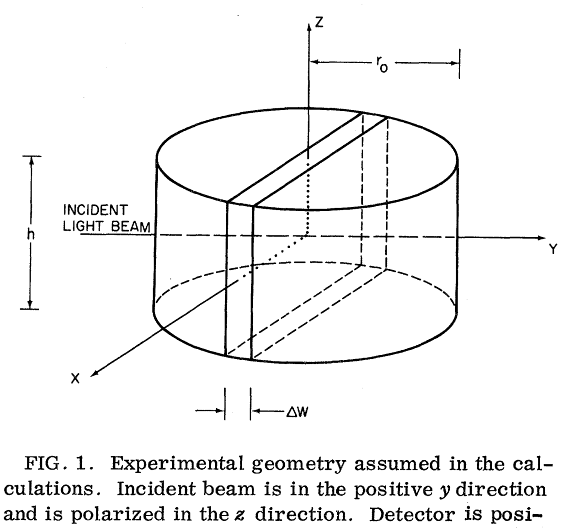

FIG. 1. Experimental geometry assumed in the calculations. Incident beam is in the positive y direction and is polarized in the z direction. Detector is positioned on the positive x axis. Only light which is finally scattered from the narrow strip of width Δw reaches the detector.

the dimension of the sample ($\Delta w \ll 2r_0$) and the detector is sufficiently far away from the sample. In Eq. (2.4), $I_{\text{sing.}}$ is given by Eq. (1.2), while ϵ_{out} is the correction for the light lost or scattered "out":

$$\epsilon_{\text{out}} = I(\tfrac{1}{2}\pi, \tfrac{1}{2}\pi)(1 - e^{-2r_0\tau})$$
$$\simeq [B/(\alpha^2+2)]2r_0\tau , \qquad (2.5)$$

where we have linearized in τ (for double scattering) and used Eq. (2.1) for $I(\pi/2, \pi/2)$. Use of Eqs. (2.2) and (2.3) yields

$$\epsilon_{\text{out}} = 2\pi r_0 B^2 \left[\frac{1+\beta}{4\sqrt{\beta}} \ln\left(\frac{\sqrt{\beta}+1}{\sqrt{\beta}-1}\right) - \frac{1}{2}\right]. \qquad (2.6)$$

Finally ϵ_{in} in Eq. (2.4) is the correction for light scattered "in" the direction of the detector, from the narrow strip of width Δw, after two scattering events. To compute ϵ_{in} we imagine that this strip is composed of a large number of narrower strips of infinitesimal width δw. We consider scattering from such a single strip and use the coordinate system of Fig. 1, but with the origin of the y coordinate shifted to the center of the given strip. The first scattering event occurs on the y axis between points $(0, y, 0)$ and $(0, y+dy, 0)$; the second scattering event occurs in an area $dx\,dz$ around the point $(x, 0, z)$. The solid angle for the first scattering event is then $dx\,dz \cos\theta/(x^2+y^2+z^2)$, and the path length is dy, while for the second scattering event the solid angle is $d\Omega$ and the path length $\delta w/\cos\theta$. With the normalization of Eq. (2.4), the scattered intensity from these two events becomes

$$\delta\epsilon_{\text{in}} = \frac{\delta w}{\Delta w}\frac{dy\,dx\,dz}{x^2+y^2+z^2}\, I(\theta, \Phi) I(\theta', \Phi') ,$$

where θ, θ' are the scattering angles for the first and second scattering events and Φ, Φ' are the corresponding angles between incident polarization and scattering direction. The full ϵ_{in} is now obtained by integrating over x, y, z for each infinitesimal strip and then summing over strips. Using the condition $\Delta w \ll 2r_0$ we may approximate the limits for the x and y integrations by $\pm r_0$ for every strip to give

$$\epsilon_{\text{in}} = \int_{-r_0}^{r_0} dy \int_{-r_0}^{r_0} dx \int_{-h/2}^{h/2} dz \frac{I(\theta, \Phi) I(\theta', \Phi')}{x^2+y^2+z^2} . \qquad (2.7)$$

The cosines of the angles θ, θ', and Φ are easily written down in terms of x, y, z:

$$\cos\theta = -y/(x^2+y^2+z^2)^{1/2} ,$$
$$\cos\theta' = x/(x^2+y^2+z^2)^{1/2} , \qquad (2.8)$$

and

$$\cos\Phi = z/(x^2+y^2+z^2)^{1/2} .$$

To determine Φ' let $\hat{k}_0, \hat{p}_0, \hat{k}_1, \hat{p}_1, \hat{k}_2, \hat{p}_2$ be unit vectors specifying the propagation direction and polarization direction of the incident, intermediate and final beams, respectively. Then

$$\cos\theta = \hat{k}_0 \cdot \hat{k}_1 ,$$
$$\cos\theta' = \hat{k}_1 \cdot \hat{k}_2 ,$$
$$\cos\Phi = \hat{p}_0 \cdot \hat{k}_1 .$$

The direction of $\hat{p}_1$ is given by the component of $\hat{p}_0$ which is perpendicular to $\hat{k}_1$. Normalizing gives

$$\hat{p}_1 = [\hat{p}_0 - (\hat{p}_0 \cdot \hat{k}_1)\hat{k}_1]/\sin\Phi . \qquad (2.9)$$

Hence

$$\cos\Phi' = \hat{p}_1 \cdot \hat{k}_2 = -\cos\Phi \cos\theta'/\sin\Phi ,$$

since $\hat{p}_0 \cdot \hat{k}_2 = 0$. Substituting for θ' and Φ from Eq. (2.8) yields

$$\cos\Phi' = -xz/(x^2+y^2+z^2)^{1/2}(x^2+y^2)^{1/2} . \qquad (2.10)$$

Substituting for θ, θ', Φ, Φ' from Eqs. (2.8) and (2.10) yields

$$\epsilon_{\text{in}} = \frac{2B^2}{\beta} \int_0^{r_0} dy \int_0^{r_0} dx \int_0^{h/2} dz \frac{(x^2+y^2)^2 + y^2z^2}{[x^2+z^2+(1-1/\beta)y^2][y^2+z^2+(1-1/\beta)x^2](x^2+y^2+z^2)} . \qquad (2.11)$$

The evaluation of this triple integral and the results obtained occupy Sec. III of this paper. Our final result will be written in the form

$$I_{\text{meas.}}(\tfrac{1}{2}\pi, \tfrac{1}{2}\pi) = I_{\text{sing}}(\tfrac{1}{2}\pi, \tfrac{1}{2}\pi) - \epsilon_{\text{out}}(1-R) , \qquad (2.12)$$

with

$$R = \epsilon_{\text{in}}/\epsilon_{\text{out}} . \qquad (2.13)$$

The quantity $(1-R)$ is the factor by which the turbidity correction must be muliplied to take account of scattering "in." It should also be noted that the same integral is obtained for Eq. (2.11) if the scattering volume has a square cross section of side $2r_0$.

To close this section we would like to mention that in our formulation, ϵ_{in} and ϵ_{out} are both second order in B, and $I_{\text{sing.}}$ is first order in B. Any effects that yield terms of higher than second order in B are neglected. Hence ϵ_{out} in Eq. (2.5) is linearized in τ and the turbidity is neglected in calculating ϵ_{in}. This approximation is valid in the temperature region in which $1 - e^{-\tau L'}$ can be approximated by $\tau L'$. In binary liquids with closely matched refractive indices this temperature range extends to within a millidegree of T_c.

In the spirit of the power series in B, it becomes clear that the turbidity correction alone applied to the experimental data without multiple scattering corrections is not sufficient. If the exponential function in the turbidity correction can not be adequately approximated by its linearized form, then still higher-order multiple scatterings must be taken into consideration.

III. EVALUATION OF ϵ_{in}: RESULTS AND DISCUSSION

The integral over z in Eq. (2.11) is readily performed by elementary techniques to give

$$\epsilon_{in}=2B^2\beta\int_0^{r_0}dy\int_0^{r_0}dx\left[\frac{(x^2+y^2)^2-y^2(x^2+(1-1/\beta)y^2)}{y^2(y^2-x^2)}\frac{1}{[x^2+(1-1/\beta)y^2]^{1/2}}\tan^{-1}\left(\frac{h/2}{[x^2+(1-1/\beta)y^2]^{1/2}}\right)\right.$$
$$-\frac{(x^2+y^2)^2-y^2[y^2+(1-1/\beta)x^2]}{x^2(y^2-x^2)}\frac{1}{[y^2+(1-1/\beta)x^2]^{1/2}}\tan^{-1}\left(\frac{h/2}{[y^2+(1-1/\beta)x^2]^{1/2}}\right)$$
$$\left.+\frac{(x^2+y^2)^{1/2}}{y^2}\tan^{-1}\left(\frac{h/2}{(x^2+y^2)^{1/2}}\right)\right]. \tag{3.1}$$

Introducing polar coordinates $y=r\cos\theta$, $x=r\sin\theta$ one finds that the integration over r is also elementary and gives

$$\epsilon_{in}=2r_0B^2\beta\int_0^{\pi/4}d\theta\left(\sec2\theta\left\{\frac{(1/\beta)+\sec^2\theta}{[1-(1/\beta)\cos^2\theta]^{1/2}}\left[\sec\theta\tan^{-1}\left(\frac{1}{\gamma}\frac{\cos\theta}{[1-(1/\beta)\cos^2\theta]^{1/2}}\right)\right.\right.\right.$$
$$\left.+\frac{1}{2\gamma}\frac{1}{[1-(1/\beta)\cos^2\theta]^{1/2}}\ln[1+\gamma^2(\sec^2\theta-1/\beta)]\right]$$
$$-\frac{(1/\beta)+\csc^2\theta}{[1-(1/\beta)\sin^2\theta]^{1/2}}\left[\sec\theta\tan^{-1}\left(\frac{1}{\gamma}\frac{\cos\theta}{[1-(1/\beta)\sin^2\theta]^{1/2}}\right)\right.$$
$$\left.\left.+\frac{1}{2\gamma}\frac{1}{[1-(1/\beta)\sin^2\theta]^{1/2}}\ln[1+\gamma^2(\sec^2\theta-\beta^{-1}\tan^2\theta)]\right]\right\}$$
$$\left.+\sec^2\theta\csc^2\theta[\sec\theta\tan^{-1}(\gamma^{-1}\cos\theta)+(1/2\gamma)\ln(1+\gamma^2\sec^2\theta)]\right), \tag{3.2}$$

where $\gamma=2r_0/h$ describes the shape of the scattering volume. The remaining integral over θ has to be performed numerically. A slightly more convenient form is obtained via the substitution $\tan\theta=t$:

$$\epsilon_{in}=2r_0B^2\beta\int_0^1dt\,(1+t^2)\left(\frac{1}{(1-t^2)}\left\{\frac{1+1/\beta+t^2}{(1-1/\beta+t^2)^{1/2}}\left[\tan^{-1}\left(\frac{1}{\gamma}\frac{1}{(1-1/\beta+t^2)^{1/2}}\right)\right.\right.\right.$$
$$\left.+\frac{1}{2\gamma}\frac{1}{(1-1/\beta+t^2)^{1/2}}\ln[1+\gamma^2(1-1/\beta+t^2)]\right]$$
$$-\frac{1+1/\beta+1/t^2}{[1+(1-1/\beta)t^2]^{1/2}}\left[\tan^{-1}\left(\frac{1}{\gamma}\frac{1}{[1+(1-1/\beta)t^2]^{1/2}}\right)\right.$$
$$\left.\left.+\frac{1}{2\gamma}\frac{1}{[1+(1-1/\beta)t^2]^{1/2}}\ln\{1+\gamma^2[1+(1-1/\beta)t^2]\}\right]\right\}$$
$$\left.+\frac{1}{t^2}\left[(1+t^2)^{1/2}\tan^{-1}\left(\frac{1}{\gamma}\frac{1}{(1+t^2)^{1/2}}\right)+\frac{1}{2\gamma}\ln[1+\gamma^2(1+t^2)]\right]\right). \tag{3.3}$$

The ratio $R=\epsilon_{in}/\epsilon_{out}$ may be computed from equations (3.3) and (2.6). Results are plotted against $\alpha=(k_0\xi)^{-1}$ over four decades, for five values of γ, in Fig. 2. The dashed curves refer to certain asymptotic forms which we will discuss later. For $\gamma\lesssim0.4$ the result is essentially independent of γ. For $0.4\lesssim\gamma\lesssim1$ variation with γ is slow while for $\gamma\gtrsim1$, R depends strongly on γ. This is to be expected on general grounds. The only light which contributes to ϵ_{in} is that which is scattered into the strip of thickness $\Delta\omega$, width $2r_0$, and height h. For $h < 2r_0$, this is limited by h while for $h > 2r_0$, the width $2r_0$ of the strip essentially limits the amount of light that can be intercepted. Increasing h further has little effect.

Notice that the ratio R is a function of the two parameters α and γ. It is interesting to discuss the various limiting cases separately.

In the hydrodynamic regime where $\alpha \gg 1$, ($\beta \gg 1$), the ratio R rapidly approaches its asymptotic limit. In this limit, Eq. (2.6) becomes

$$\epsilon_{out} = 2\pi r_0 B^2[2/3\beta + O(\beta^{-2})] , \tag{3.4}$$

and Eq. (3.2) becomes

$$\epsilon_{in} = \frac{2r_0 B^2}{\beta} \int_0^{\pi/4} d\theta \left[\tfrac{7}{8}\sec\theta \tan^{-1}\left(\frac{\cos\theta}{\gamma}\right) + \frac{1}{\gamma}\ln(1+\gamma^2\sec^2\theta) - \frac{1}{8\gamma}\frac{\gamma^2}{\gamma^2+\cos^2\theta}\right] + O(\beta^{-2}) , \tag{3.5}$$

where $O(\beta^{-2})$ denotes the terms of the order β^{-2} and higher. A numerical computation of $R_\infty \equiv (\epsilon_{in}/\epsilon_{out})_{\beta=\infty}$, as a function of γ, is shown in Fig. 3. For the limiting case of $\gamma = 0$, Eq. (3.5) simplifies greatly and the corresponding ratio $R_\infty(0)$ is given by the closed form:

$$R_\infty(0) = \tfrac{21}{32}\ln(1+\sqrt{2}) = 0.578 . \tag{3.6}$$

On the other hand, for the limiting case $\gamma \gg 1$, one obtains the asymptotic form

$$R_\infty(\gamma) = (3/4\gamma)(\ln\gamma + \tfrac{3}{8} + \ln 2 - 2G/\pi) + O(\gamma^{-3})$$
$$= (3/4\gamma)(\ln\gamma + 0.485) + O(\gamma^{-3}) , \tag{3.7}$$

where G is Catalan's constant. From Eqs. (3.4) and (3.5) one notes that the relative corrections to R_∞ are of the order β^{-1} which is equal to the order of α^{-4}. This explains why the asymptotic limits are approached so rapidly.

In the critical regime where $\alpha \ll 1$, the ratio R approaches unity. This may be seen analytically as follows. In this limit, Eq. (2.6) becomes

$$\epsilon_{out} = 2\pi r_0 B^2[\ln(1/\alpha) + O(1)] . \tag{3.8}$$

The dominant contribution to ϵ_{in} [Eq. (3.3)] for $\alpha \ll 1$ comes from the region $t \sim \alpha$. Expanding $\beta \sim 1 + \alpha^2$ and keeping only the leading terms yields

$$\epsilon_{in} = 2r_0 B^2 \int_0^1 dt \frac{2}{(\alpha^2+t^2)^{1/2}} \frac{\pi}{2}$$
$$= 2\pi r_0 B^2[\ln(1/\alpha) + O(1)] . \tag{3.9}$$

Hence

$$R = 1 + O([\ln(1/\alpha)]^{-1})$$

or

$$1 - R = O([\ln(1/\alpha)]^{-1}) . \tag{3.10}$$

This result may also be seen on general physical grounds, starting from Eq. (2.7). For $\alpha \ll 1$, the scattered beam is strongly concentrated in the forward direction, with characteristic angle α. The whole of the scattered beam therefore intercepts the strip and, being nearly in the forward direction, may be scattered through an angle close to 90° to arrive at the detector. In computing the scattered intensity from such a process, the factor $I(\theta', \Phi')$ may be evaluated at $\theta' = \pi/2 = \Phi'$ and taken outside the integral in Eq. (2.7). For small angles we can set $dx\,dz/(x^2+y^2+z^2)$ equal to the solid angle for the first scattering process. The integral over x and z of $I(\theta, \Phi)$ then gives just the turbidity while

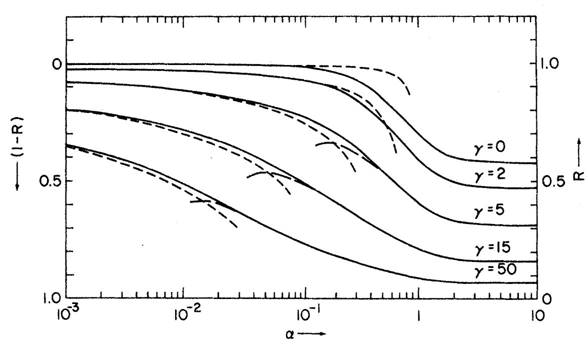

FIG. 2. Ratio $R = \epsilon_{in}/\epsilon_{out}$ of scattering "in" to scattering "out" terms in the double-scattering intensity, plotted against $\alpha = (k_0\xi)^{-1}$ for five values of $\gamma = 2r_0/h$, according to Eqs. (2.6) and (3.3). Short-dash curves represent the asymptotic form for small α, given by Eq. (3.15). Long-dash curves represent the asymptotic form for large γ, given by Eqs. (2.6) and (3.25).

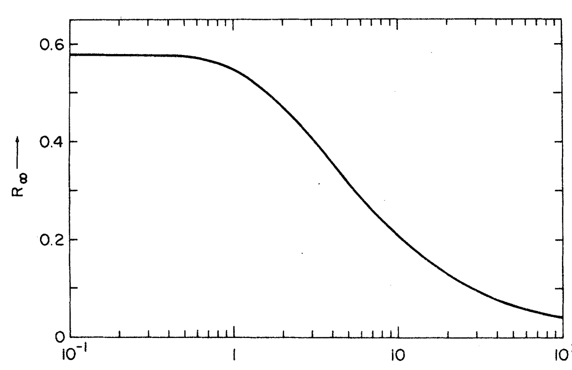

FIG. 3. Asymptotic value R_∞ of R as $\alpha = (k_0\xi)^{-1} \to \infty$, plotted as a function of $\gamma = 2r_0/h$, according to Eqs. (3.4) and (3.5). Behavior for $\gamma > 10^2$ is accurately described by Eq. (3.7).

the integral over y from $-r_0$ to 0 gives a factor r_0. Hence the contribution to ϵ_{in} from processes in which scattering through a small angle is followed by scattering through an angle close to 90° is $\tau r_0 I(\frac{1}{2}\pi, \frac{1}{2}\pi) = \frac{1}{2}\epsilon_{out}$. A little thought convinces one that an equal contribution comes from processes in which scattering through an angle close to 90° is followed by scattering through a small angle, to give a net result $\epsilon_{in} = \epsilon_{out}$ for $\alpha \ll 1$, or $R=1$. The above line of argument also indicates that the result breaks down if h is so small that the whole of the scattered beam is no longer intercepted by the strip. This happens when $\frac{1}{2}h \sim \alpha r_0$ or $\alpha \sim \gamma^{-1}$ so that the condition $\alpha \ll 1$ for the result $R=1$ should strictly be replaced by $\alpha \ll \min(1, \gamma^{-1})$. From Fig. 2 it is clear that the asymptotic limit is approached more slowly for large γ.

One further notes, from Eq. (2.12), that the total contribution to the measured scattering intensity from double-scattering processes is equal to

$$\delta I_{\text{meas.}} = -\epsilon_{out}(1-R) , \tag{3.11}$$

which, according to Eqs. (3.8) and (3.10) saturates to a constant value as $\alpha \to 0$, in contrast to the logarithmic divergence associated with a simple turbidity correction.

In order to determine the saturation value of $\delta I_{\text{meas.}}$ it is necessary to evaluate the $O(1)$ terms in Eqs. (3.8) and (3.9). The first of these is simple

$$\epsilon_{out} = 2\pi r_0 B^2[\ln(1/\alpha) + \ln 2 - \tfrac{1}{2} + O(\alpha)] . \tag{3.12}$$

To obtain the $O(1)$ term in ϵ_{in} one may add and subtract in the integrand of Eq. (3.3) the term responsible for the leading $\ln(1/\alpha)$ behavior. In the remainder, $\alpha = 0$ may be used to $O(1)$ accuracy. This procedure gives

$$\epsilon_{in} = 2\pi r_0 B^2[\ln(1/\alpha) + \ln 2 + A(\gamma) + O(\alpha)] , \tag{3.13}$$

where

$$A(\gamma) = \frac{1}{\pi}\int_0^1 dt(1+t^2)\Bigg(-\frac{\pi}{t} + \frac{1}{1-t^2}\Bigg\{\frac{2+t^2}{t}\left[\tan^{-1}\left(\frac{1}{\gamma t}\right) + \frac{1}{2\gamma t}\ln(1+\gamma^2 t^2)\right] - (2+1/t^2)[\tan^{-1}(1/\gamma) + (1/2\gamma)\ln(1+\gamma^2)]\Bigg\} + \frac{1}{t^2}\left[(1+t^2)^{1/2}\tan^{-1}\left(\frac{1}{\gamma}\frac{1}{(1+t^2)^{1/2}}\right) + \frac{1}{2\gamma}\ln[1+\gamma^2(1+t^2)]\right]\Bigg). \tag{3.14}$$

Thus,

$$1 - R = C(\gamma)/\ln(1/\alpha) + O[\alpha/\ln(1/\alpha)] , \tag{3.15}$$

with

$$C(\gamma) = -[A(\gamma) + \tfrac{1}{2}] . \tag{3.16}$$

Numerical evaluation of $A(\gamma)$ gives the form for $C(\gamma)$ plotted in Fig. 4. The value for $\gamma = 0$ is

$$C(0) = 3\ln 2 + \tfrac{1}{4}\sqrt{2} - \tfrac{3}{4}\ln(1+\sqrt{2}) - \tfrac{7}{4} = 0.022 , \tag{3.17}$$

while for large γ the asymptotic form is

$$C(\gamma) = \ln\gamma - \tfrac{3}{2} + O[(1/\gamma)\ln\gamma] . \tag{3.18}$$

The short-dash lines in Fig. 2 are plots of Eq. (3.15) which is asymptotically exact for small α. In this limit, the double scattering contribution to $I_{\text{meas.}}$ saturates at a value

$$\delta I_{\text{meas.}}(\alpha = 0) = -2\pi r_0 B^2 C(\gamma) . \tag{3.19}$$

The dependence of $\delta I_{\text{meas.}}$ on α is given by

$$\delta I_{\text{meas.}} = -2\pi r_0 B^2 F(\gamma, \alpha) , \tag{3.20}$$

with

$$F(\gamma, \alpha) = [(1-R)/2\pi r_0 B^2]\epsilon_{out} . \tag{3.21}$$

Plots of F vs α for five values of γ are shown in Fig. 5. The dash-dot curve labeled $\gamma = \infty$ corresponds to the limit $h = 0$, for which case $\epsilon_{in} = 0$. This curve, therefore, represents a simple turbidity correction. The amount by which the other curves deviate from the $\gamma = \infty$ limit is a measure of the importance of the scattering "in" terms.

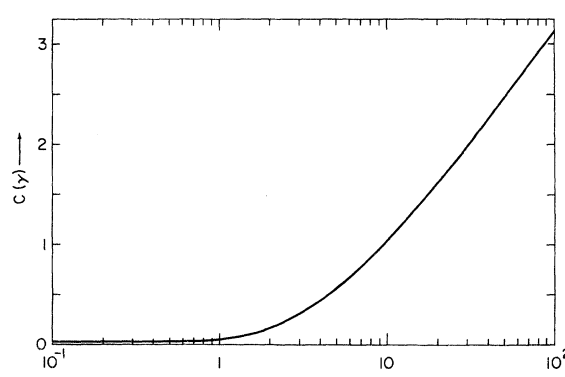

FIG. 4. Function $C(\gamma)$, defined by Eqs. (3.14) and (3.16). Behavior for $\gamma > 10^2$ is accurately described by Eq. (3.18).

Finally we wish to discuss the limiting case of large γ, in which the height of the cylindrical scattering volume is small compared to its radius. This is a good geometry for experiments since the double-scattering correction is a much smoother function of temperature than for small values of γ. A large γ can be obtained easily by reducing the height h but note that our initial assumptions require that h still be large compared to the incident beam width. In the limit $\gamma \gg 1$ we can expand the right hand side of Eq. (3.3) to terms of order $(1/\gamma)\ln\gamma$ and $1/\gamma$. The $O[(1/\gamma)\ln\gamma]$ term is

$$2r_0 B^2\beta \frac{1}{\gamma}\ln\gamma \int_0^1 dt\,(1+t^2)\left[\frac{1}{t^2}+\frac{1}{1-t^2}\left(\frac{1+1/\beta+t^2}{1-1/\beta+t^2}-\frac{1+1/\beta+1/t^2}{1+(1-1/\beta)t^2}\right)\right], \tag{3.22}$$

which may be integrated using elementary methods to give

$$2\pi r_0 B^2 \frac{1}{\gamma}\ln\gamma \frac{1}{(2\beta-1)(1-1/\beta)^{1/2}} . \tag{3.23}$$

The $O(1/\gamma)$ contribution is

$$2r_0 B^2\beta \frac{1}{\gamma}\int_0^1 dt\,(1+t^2)\left[\frac{1}{1-t^2}\left(\frac{1+1/\beta+t^2}{1-1/\beta+t^2}\left[1+\tfrac{1}{2}\ln(1-1/\beta+t^2)\right]-\frac{1/\beta+1+1/t^2}{1+(1-1/\beta)t^2}\left\{1+\tfrac{1}{2}\ln[1+(1-1/\beta)t^2]\right\}\right)\right.$$
$$\left.+(1/t^2)\left[1+\tfrac{1}{2}\ln(1+t^2)\right]\right], \tag{3.24}$$

which has to be evaluated numerically. It is convenient to express the result in the form

$$\epsilon_{\rm in}=\frac{2\pi r_0 B^2}{(2\beta-1)(1-1/\beta)^{1/2}}\,\frac{1}{\gamma}\,[\ln\gamma+D(\alpha)]+O(\gamma^{-3}),\quad \gamma\gg 1,\ \alpha^{-1} . \tag{3.25}$$

The function $D(\alpha)$ is plotted in Fig. 6. The $\alpha=\infty$ limit $D(\infty)=0.485$ has already been calculated in Eq. (3.7). For $\alpha \ll 1$ one may use the asymptotic form

$$D(\alpha)=\ln(2\alpha)+1,\quad \alpha \ll 1 . \tag{3.26}$$

The result of using Eq. (3.25) to calculate R is shown for $\gamma=5$, 15, 50 by dashed lines in Fig. 2. The approximation is extremely accurate until, as indicated in Eq. (3.25), it begins to go bad when $\alpha \sim \gamma^{-1}$.

If h becomes so small that it is comparable to the width of the incident beam, the above results have to be modified. The resulting corrections are small, as is shown in the Appendix.

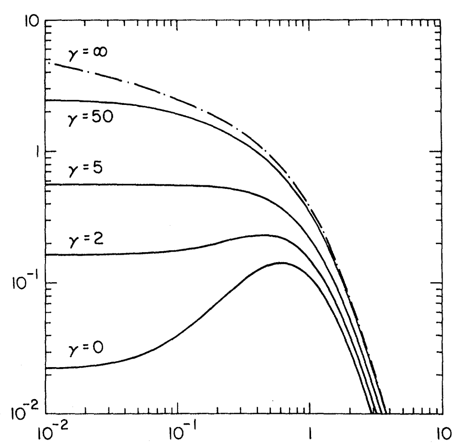

FIG. 5. Function $F(\alpha)$ which describes the total contribution to the measured scattering intensity from double-scattering processes according to Eq. (3.20), for five values of γ. Curve labeled $\gamma=\infty$ represents the result of correcting for turbidity alone.

IV. DEPOLARIZATION RATIO

The purpose of Sec. IV, which is not restricted to binary liquids, is to extract from our general result, Eq. (2.11), that part of the double-scattered intensity which has polarization perpendicular to that of the incident beam. This is the "depolarized" intensity. We may then make contact with

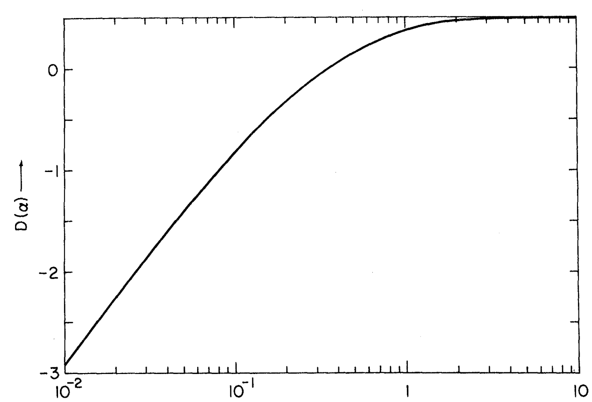

FIG. 6. Function $D(\alpha)$, defined by Eqs. (3.25) and (3.26). Behavior for $\alpha < 10^{-2}$ is accurately described by Eq. (3.26).

the work of Reith and Swinney.[8]

In complete analogy to Eq. (2.9), the polarization vector after the second scattering process is given by

$$\hat{p}_2 = [\hat{p}_1 - (\hat{p}_1 \cdot \hat{k}_2)\hat{k}_2]/\sin\Phi' \ . \tag{4.1}$$

The fraction of the scattered intensity which is depolarized is

$$1 - (\hat{p}_0 \cdot \hat{p}_2)^2 = 1 - \sin^2\Phi/\sin^2\Phi' = y^2 z^2/[(x^2+y^2)^2 + y^2 z^2] \ . \tag{4.2}$$

The depolarized intensity from double scattering is obtained by multiplying the integrand of Eq. (2.11) by this depolarization factor:

$$I_{\rm VH} = \frac{2B^2}{\beta}\int_0^{r_0} dy \int_0^{r_0} dx \int_0^{h/2} dz \frac{y^2 z^2}{[x^2+z^2+(1-1/\beta)y^2][y^2+z^2+(1-1/\beta)x^2](x^2+y^2+z^2)} \ . \tag{4.3}$$

The evaluation of $I_{\rm VH}$, for all values of $\gamma = 2r_0/h$ and $\beta = (1+\frac{1}{2}\alpha^2)^2$ may be carried out in complete analogy to that of $\epsilon_{\rm in}$ in Sec. III. For comparison with the results of Reith and Swinney, however, it is sufficient to consider the limit $\beta \simeq \frac{1}{4}\alpha^4 \to \infty$ appropriate to the regime $k\xi \ll 1$.[10] In this limit Eq. (2.1) becomes

$$I(\theta, \Phi) = \sigma_0 \sin^2\Phi \ , \tag{4.4}$$

where $\sigma_0 = B/\alpha^2$ is the differential cross section per unit volume, and is independent of θ. Then the intensity from single scattering, which has polarization parallel to that of the incident beam, is $I_{\rm VV} = \sigma_0$. Thus, for $k\xi \ll 1$,

$$\frac{I_{\rm VH}}{I_{\rm VV}} = 8\sigma_0 \int_0^{r_0} dy \int_0^{r_0} dx \int_0^{h/2} dz \frac{y^2 z^2}{(x^2+y^2+z^2)^3} \ , \tag{4.5}$$

$$\frac{I_{\rm VH}}{I_{\rm VV}} = \sigma_0 g h \ , \tag{4.6}$$

where the last line defines the function $g(h/2r_0)$. As in Sec. III the integration over z may be performed by elementary methods. Introducing polar coordinates $y = r\cos\theta$, $x = r\sin\theta$, and then integrating over r yields

$$g = \tfrac{1}{2}\gamma \int_0^{\pi/4} d\theta \left[\frac{1}{\cos\theta}\tan^{-1}\!\left(\frac{1}{\gamma}\cos\theta\right) + \frac{\gamma}{\gamma^2+\cos^2\theta}\right], \tag{4.7}$$

where $\gamma = 2r_0/h$ as usual. As pointed out by Reith and Swinney, measurements of $I_{\rm VH}/I_{\rm VV}$ determine, if g is known, the value of σ_0 and thence the constant B. By varying h the "collision-induced" contribution to $I_{\rm VH}$, which is due to single scattering from anisotropic clusters of molecules and therefore independent of h, may be removed.

A plot of g vs $\gamma^{-1} = h/2r_0$ is presented in Fig. 7. The range of γ^{-1} covered by Reith and Swinney's experiment and Monte Carlo calculations is indicated by the arrows. This range is expanded in the inset with the results of Ref. 8 superimposed, and we have taken $2r_0 = 6$ mm as given in Ref. 8. In this range, an expansion of Eq. (4.7) to order γ^{-2},

$$g = \tfrac{1}{4}\pi - \tfrac{1}{6}(1+\tfrac{1}{2}\pi)\gamma^{-2} + O(\gamma^{-4}) \ , \tag{4.8}$$

is accurate to about $\frac{1}{2}\%$ everywhere and is indicated by the dash-dot line in Fig. 7. In Ref. 8, a constant value $g = 0.77$ was used for the range of h used in the experiment. In the limit $\gamma \to 0$, g has the asymptotic form

$$g = \tfrac{1}{4}\pi \ln(1+\sqrt{2})\gamma + O(\gamma^3) \ , \tag{4.9}$$

which is indicated by the dashed line in Fig. 7.

The product gh appearing in Eq. (4.6) varies linearly with h with slope $\frac{1}{4}\pi$, for small h, and then bends over as $h/2r_0$ increases to the order of unity and eventually saturates, according to Eq. (4.9), at a value $r_0(\pi/2)\ln(1+\sqrt{2})$. Departures from linearity should be observable if the experiments of Ref. 8 were extended to somewhat larger values of h.

For very small h one has to take into account

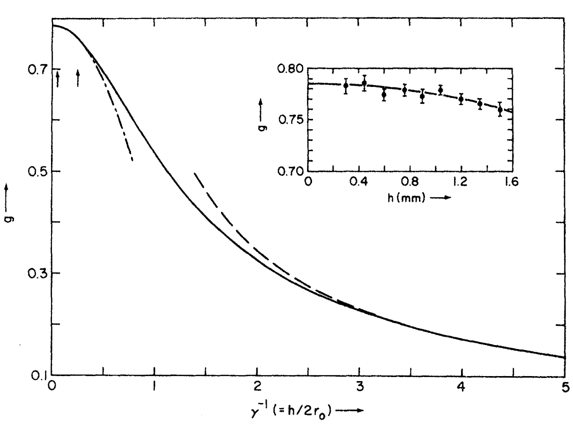

FIG. 7. Function $g(\gamma^{-1})$ vs γ^{-1} according to Eq. (4.7). Dot-dash and dashed curved are the asymptotic forms for small and large γ^{-1} as given by Eqs. (4.8) and (4.9), respectively. Arrows indicate the range of γ^{-1} covered by the Monte Carlo calculations of Ref. 8. Region is expanded in the inset and the results of Ref. 8, where $2r_0 = 6$ mm, are superimposed. Error bars represent the standard deviation of thirteen Monte Carlo calculations for each value of h.

the finite width w_B of the incident beam. However, we show in the appendix that the resulting corrections are totally negligible provided $(w_B/2r_0) \ll 1$.

Finally it is interesting to consider the case where the incident beam is polarized horizontally, i.e., in the x direction. Then all of the light received by the detector has undergone double (or higher-order) scattering. Neglecting the higher-order scattering, which is justified (even for simple fluids) in the hydrodynamic regime $k\xi \ll 1$ sufficiently far from the transition temperature, the ratio I_{HV}/I_{HH} of the scattered intensities polarized vertically and horizontally is a pure number which depends only on the sample geometry. We proceed to calculate this ratio.

In the hydrodynamic regime $k\xi \ll 1$, $I(\theta, \Phi)$ is given by Eq. (4.4) so that Eq. (2.7) becomes

$$\epsilon_{in} = 8\sigma_0^2 \int_0^{r_0} dy \int_0^{r_0} dx \int_0^{h/2} dz \, \frac{\sin^2\Phi \sin^2\Phi'}{x^2+y^2+z^2} . \tag{4.10}$$

The angle Φ is given by, instead of Eq. (2.8),

$$\cos\Phi = x/(x^2+y^2+z^2)^{1/2} . \tag{4.11}$$

From Eq. (2.9), Φ' is determined from

$$\cos\Phi' = \hat{p}_1 \cdot \hat{k}_2 = (1 - \cos\Phi \cos\theta')/\sin\Phi , \tag{4.12}$$

since $\hat{p}_0 \cdot \hat{k}_2 = 1$ for the present case. Using Eq. (2.8) for $\cos\theta'$ and Eq. (4.11) for $\cos\Phi$ yields

$$\cos\Phi' = (y^2+z^2)^{1/2}/(x^2+y^2+z^2)^{1/2} . \tag{4.13}$$

Hence

$$\epsilon_{in} = 8\sigma_0^2 \int_0^{r_0} dy \int_0^{r_0} dx \int_0^{h/2} dz \, \frac{x^2(y^2+z^2)}{(x^2+y^2+z^2)^3} \tag{4.14}$$

This is the total intensity from double scattering. The fraction polarized horizontally is, for a given double-scattering process, given by $(\hat{p}_2 \cdot \hat{k}_0)^2$. Using Eq. (4.1) for $\hat{p}_2$ and Eq. (2.9) for $\hat{p}_1$ yields

$$\hat{p}_2 \cdot \hat{k}_0 = \hat{p}_1 \cdot \hat{k}_0/\sin\Phi'$$
$$= -\cos\Phi \cos\theta/\sin\Phi \sin\Phi' = \frac{y}{(y^2+z^2)^{1/2}} , \tag{4.15}$$

where we have used $\hat{k}_0 \cdot \hat{k}_2 = \hat{k}_0 \cdot \hat{p}_0 = 0$. Hence the intensities polarized horizontally and vertically are

$$I_{HH} = 8\sigma_0^2 \int_0^{r_0} dy \int_0^{r_0} dx \int_0^{h/2} dz \, \frac{x^2 y^2}{(x^2+y^2+z^2)^3} ,$$
$$I_{HV} = 8\sigma_0^2 \int_0^{r_0} dy \int_0^{r_0} dx \int_0^{h/2} dz \, \frac{x^2 z^2}{(x^2+y^2+z^2)^3}$$
$$= I_{VH} \tag{4.16}$$

where the last equality only holds when, as in the present case, the range of the integral in the x and y directions is the same. Integrating over z and $r = (x^2+y^2)^{1/2}$ yields I_{HV}/I_{HH} as a ratio of single integrals:

$$\frac{I_{HV}}{I_{HH}} = \int_0^{\pi/4} d\theta I_{HV}(\theta) \Big/ \int_0^{\pi/4} d\theta I_{HH}(\theta) , \tag{4.17}$$

where

$$I_{HV}(\theta) = \frac{1}{2}\left[\frac{1}{\cos\theta} \tan^{-1}\left(\frac{1}{\gamma}\cos\theta\right) + \frac{\gamma}{\gamma^2+\cos^2\theta}\right] ,$$

$$I_{HH}(\theta) = \sin^2\theta\cos^2\theta\left[\frac{3}{\cos\theta}\tan^{-1}\left(\frac{1}{\gamma}\cos\theta\right) + \frac{4}{\gamma}\ln\left(1+\frac{\gamma^2}{\cos^2\theta}\right) - \frac{\gamma}{\gamma^2+\cos^2\theta}\right]. \tag{4.18}$$

The ratio I_{HV}/I_{HH} is plotted versus γ in Fig. 8. For large γ (small h) the asymptotic form is

$$I_{HV}/I_{HH} = [\ln\gamma + 0.428 + O(\gamma^{-2})]^{-1} \tag{4.19}$$

(where $0.428 = 1/\pi + \ln 2 - (2/\pi)G$, G being Catalan's constant), while for small γ (large h) the ratio saturates to a value

$$\lim_{\gamma \to 0} \frac{I_{HV}}{I_{HH}} = \sqrt{2}\ln(1+\sqrt{2}) \simeq 1.25 . \tag{4.20}$$

V. SUMMARY

We have calculated the double-scattering contributions to the measured scattering intensity in a binary liquid. Although the results of this paper are equally valid for a simple fluid, their greatest usefulness will be in the analysis and interpretation of scattering intensity data for binary liquids with

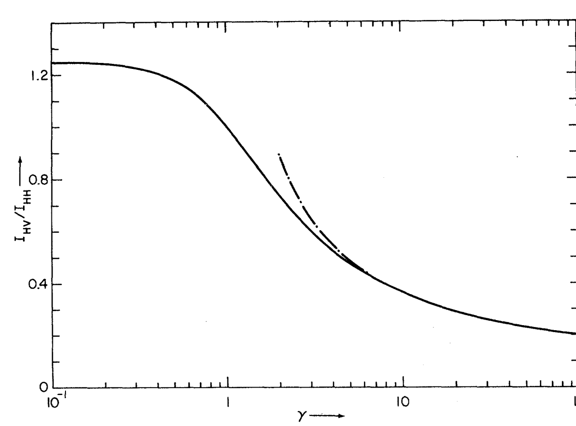

FIG. 8. Ratio I_{HV}/I_{HH} vs γ according to Eqs. (4.17) and (4.18). Dash-dot curve is the asymptotic form for large γ, Eq. (4.19).

approximately matched refractive indices. For such systems there can be a range of temperatures near the critical point where the double-scattering correction is sufficiently large that its inclusion is essential for correct interpretation of the data, yet not so large that still higher-order effects have to be included.

The calculations cover a family of experimental geometries, in which the scattering volume is a cylinder, or a cuboid with square cross section, of arbitrary dimensions and in which the scattering angle is fixed at 90°, with the direction of scattering perpendicular to the polarization vector of the incident beam. This type of geometry is a typical one in many experiments.

The results show that a simple turbidity correction is in general a poor approximation, especially near the critical point when the logarithmic divergence in the scattering "out" term due to turbidity is cancelled by scattering "in" contributions due to double scattering.

We have exploited throughout the fact that the width of the sample seen by the detector is a small fraction of the total sample width illuminated by the incident beam. Using this simplification we have also computed the depolarization due to double scattering. In the hydrodynamic regime $k\xi \ll 1$, we have derived a simple expression (as a single integral) for the function g introduced by Reith and Swinney, and computed g for all values of the sample height, obtaining explicit analytic expressions in the limit of small and large h. For the case in which the polarization of the incident beam is parallel to the direction of scattering, double scattering dominates since single scattering is forbidden. The ratio of intensities polarized perpendicular and parallel to the plane of scattering is a pure number which depends only on the sample geometry.

ACKNOWLEDGMENTS

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APPENDIX: CORRECTIONS FOR FINITE BEAM WIDTH

We wish to take into account the finite width w_B of the incident beam, which we have so far regarded as small compared to the sample height h. We will compute the effect of finite w_B on the function $g(h/2r_0)$ associated with the depolarization ratio (Sec. IV) and on the total intensity due to double scattering ϵ_{in} (Sec. III). Assuming always that $w_B/(2r_0) \ll 1$, we will find that in the former case the effect of finite w_B is completely negligible, while in the latter case the effect is small but calculable.

For simplicity we consider a rectangular incident beam, with height w_B and uniform intensity, centered on the y axis, though the calculation can be extended to any intensity distribution. The cross-polarized scattered intensity due to the element of beam between the planes $y=\frac{1}{2}u$ and $y=\frac{1}{2}(u+du)$ is [see Eq. (4.5)]

$$dI_{\text{VH}} = \frac{du}{2w_B}\,\sigma_0^2 \times \int_{-r_0}^{r_0} dy \int_{-r_0}^{r_0} dx \int_{-(h/2+u/2)}^{h/2-u/2} dz\, \frac{y^2 z^2}{(x^2+y^2+z^2)^3}, \tag{A1}$$

$$dI_{\text{VH}} = \frac{du}{2w_B}\,\sigma_0^2 r_0 \left[\left(\frac{h-u}{2r_0}\right) g\left(\frac{h-u}{2r_0}\right) + \left(\frac{h+u}{2r_0}\right) g\left(\frac{h+u}{2r_0}\right)\right], \tag{A2}$$

where $g(x)$ is defined by Eq. (4.7), and we have specialized as in Sec. IV to the hydrodynamic limit $k\xi \ll 1$. Hence

$$I_{\text{VH}} = \sigma_0^2 \frac{r_0}{w_B} \int_{-w_B}^{w_B} du \left(\frac{h+u}{2r_0}\right) g\left(\frac{h+u}{2r_0}\right). \tag{A3}$$

Now the finite beam width only becomes significant when h is comparable with w_B. Since both h and w_B are then small compared to $2r_0$, we may use the asymptotic form Eq. (4.8) for $g(x)$ in Eq. (A3):

$$I_{\text{VH}} = \sigma_0^2 \frac{r_0}{w_B} \int_{-w_B}^{w_B} du \left(\frac{h+u}{2r_0}\right) \times \left(\tfrac{1}{4}\pi - \tfrac{1}{6}\left(1+\tfrac{1}{2}\pi\right)\frac{(h+u)^2}{(2r_0)^2} + \cdots\right), \tag{A4}$$

$$I_{\text{VH}} = \sigma_0^2 h\left\{\tfrac{1}{4}\pi - \tfrac{1}{6}\left(1+\tfrac{1}{2}\pi\right)\left[(h/2r_0)^2 + (w_B/2r_0)^2\right] + \cdots\right\} \tag{A5}$$

The expression in the curly brackets is the corrected g. The term in $(w_B/2r_0)^2$ represents the effect of finite beam width. Since $w_B/(2r_0) \ll 1$ (typically $w_B/(2r_0) \sim 10^{-2}$), this term is completely negligible compared to the leading term $\frac{1}{4}\pi$. Only when h is reduced below w_B does the finite beam width take effect, for then the effective incident intensity is reduced by a factor h/w_B, giving

$$I_{\text{VH}} \simeq \tfrac{1}{4}\pi\sigma_0^2 h^2/w_B, \quad h \leq w_B \tag{A6}$$

To compute the total double-scattered intensity ϵ_{in}, Eq. (A3) has to be replaced by

$$\epsilon_{in} = \frac{\pi r_0 B^2}{(2\beta-1)(1-1/\beta)^{1/2}} \frac{1}{w_B} \times \int_{-w_B}^{w_B} du \frac{(h+u)}{2r_0} \left[\ln\left(\frac{2r_0}{h+u}\right) + D(\alpha) \right], \quad \text{(A7)}$$

where we have used the small h form [Eq. (3.25)], for the contribution to ϵ_{in} from an element of incident beam since it is only for small h that the finite beam width becomes important. The integral is elementary and yields:

$$\epsilon_{in} = \frac{2\pi r_0 B^2}{(2\beta-1)(1-1/\beta)^{1/2}} \frac{1}{\gamma} \left[\ln\gamma + D(\alpha) + f(w_B/h) \right], \quad \text{(A8)}$$

where

$$f(x) = \tfrac{1}{2} - [(1+x)^2/4x] \ln(1+x) + [(1-x)^2/4x] \ln(1-x) \quad \text{(A9)}$$

represents the finite beam width correction. For small x, $f(x) \simeq -\frac{1}{6}x^2$, decreasing to $(\frac{1}{2} - \ln 2) \simeq -0.193$ for $x = 1$.

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[1]See, for example, P. A. Fleury and J. P. Boon, in *Advances in Chemical Physics*, edited by I. Prigogine and S. A. Rice (Wiley, New York, 1973), and references cited therein.

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[10]Results for general temperatures will be presented in a forthcoming publication.