THE EFFECT OF DOUBLE SCATTERING ON CRITICAL FLUID RAYLEIGH LINEWIDTH MEASUREMENTS *

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We apply recent work on the intensity correlation function of light double scattered from a system of brownian diffusing balls to the case of a fluid near the critical point. We evaluate the relative intensities and intensity correlation times of the polarized and depolarized components of the double scattered light as a function of $k_0\xi$. We compare these correlation times to those found for single scattering and find that the more intense polarized component of the double scattered light has a correlation time nearly equal to the singly scattered light in the critical region where $k_0\xi \gtrsim 8$.

Laser light scattering has proved to be a useful probe of the microscopic dynamics of fluids near a critical point. In analyzing the data from such experiments, one assumes the light is singly scattered. However, due to strong critical opalescence very near the critical point, the single scattering assumption may break down. While some experimentalists have tried to observe possible effects of multiple scattering [1,2], most have ignored the problem. We feel the latter approach is unjustified. For example, work by Oxtoby and Gelbart [3,4] and Bray and Chang [5] has shown that an erroneous value of the critical exponent η may result from an analysis of intensity data that contains double scattered light.

In this note we examine theoretically the effects of double scattering on the correlation function of light scattered from a fluid system near its critical point. Recently, we presented a theory for the correlation function of light double scattered from a system of particles undergoing brownian diffusion [6] (hereafter referred to as I). Because of the success of this work, we propose to apply it to a critical fluid system.

In evaluating the double scattered correlation function in I, we made several assumptions concerning the nature of the brownian particle suspension and the scattered light. We assumed that the individual brownian particles did not interact, thus their motion was uncorrelated. Similarly, we assume for light double scattered from a critical fluid that the first and second scattering *regions* are uncorrelated. For a critical fluid the Ornstein–Zernike correlation length ξ gives a measure of the distance over which regions of the fluid are correlated. In general $\xi \lesssim 1$ μm. Since a typical illuminated scattering volume may measure at least 100 μm on a side, in general we expect any two first and second scattering regions to be uncorrelated. We assumed the particles were separated by a distance r such that $k_0 r \gg 1$. Here k_0 is the incident light wavevector, $k_0 = 2\pi/\lambda_m$, λ_m being the wavelength of the light in the medium. By the reasoning above we have $r > 1$ μm so that $k_0 r > 1$ will hold for a typical scattering volume. We also made an assumption concerning the experimental scattering geometry. Our theoretical results applied to a situation in which the second scatterer was surrounded by a spherically symmetric region of first scatterers. This "spherical scattering geometry" assumption was satisfied by allowing our detector to observe light scattered from a small region near the axis of a comparatively large (diameter $\simeq 5$ mm) incident beam. In this work we shall use the spherical scattering geometry assumption and indicate any corrections such an

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assumption will require.

Lastly, we derived the field correlation function in I, whereas in most experiments, as for example in the case of homodyne detection, the intensity correlation function is measured. These two correlation functions are simply related by the Siegert relation if the scattered field is gaussian [7]. As discussed in I and references cited therein, for a large enough scattering volume there will be many double scattering events and so the double scattered field will be gaussian.

We will take the lowest order contribution to the multiple scattered light correlation function for a system of moderate optical density to be $\langle \boldsymbol{E}_2^* \cdot \boldsymbol{E}_2 \rangle$, the double scattered term. Because we assumed different scattering regions are uncorrelated, terms of the form $\langle \boldsymbol{E}_1^* \cdot \boldsymbol{E}_m \rangle$ where $m \neq 1$ are zero.

Under the assumptions given above we were able in I to show that this double scattered correlation function has the form one would expect from two *independent* single scattering events in succession. Thus we need to consider the single scattered field correlation of light scattered from a critical fluid [8],

$$\langle \boldsymbol{E}_1^*(t) \cdot \boldsymbol{E}_1(0) \rangle = A[\hat{\boldsymbol{r}}' \times (\hat{\boldsymbol{\varepsilon}} \times \hat{\boldsymbol{r}}')] \frac{\mathrm{e}^{-Dq^2(1+\xi^2 q^2)^{1/2} t}}{q^2 + \xi^{-2}}, \quad (1)$$

where $D = k_B T/6\pi\eta\xi$, and $\boldsymbol{q} = \boldsymbol{k}_0 - \boldsymbol{k}'$. Here, ξ is the Ornstein–Zernike correlation length, η is a shear viscosity, k_B is Boltzmann's constant, T the temperature, and $\boldsymbol{k}'$ is the wavevector of the scattered light. The incident field has polarization $\hat{\boldsymbol{\varepsilon}}$ and $\hat{\boldsymbol{r}}$ is a unit vector in the $\boldsymbol{k}'$ direction, the direction from the scatterer to the detector. A is a constant which includes factors not pertinent to our development, and the critical exponent η is taken to be zero.

By the results of I, the double scattered field correlation can be shown to be

$$\langle \boldsymbol{E}_2^*(t) \cdot \boldsymbol{E}_2(0) \rangle = A^2 [\hat{\boldsymbol{r}} \times (\hat{\boldsymbol{\varepsilon}} \times \hat{\boldsymbol{r}})] \times \frac{\mathrm{e}^{-Dq_1^2(1+\xi^2 q_1^2)^{1/2} t}}{q_1^2 + \xi^{-2}} \frac{\mathrm{e}^{-Dq_2^2(1+\xi^2 q_2^2)^{1/2} t}}{q_2^2 + \xi^{-2}}, \quad (2)$$

where $\boldsymbol{q}_1 = \boldsymbol{k}_0 - \boldsymbol{k}''$, $\boldsymbol{q}_2 = \boldsymbol{k}'' - \boldsymbol{k}'$, and $\hat{\boldsymbol{\varepsilon}} = \hat{\boldsymbol{r}}'' \times (\hat{\boldsymbol{\varepsilon}} \times \hat{\boldsymbol{r}}'')$. Here $\boldsymbol{k}''$ is the intermediate scattering wavevector describing the scattering from the first to the second scatterer, and now $\boldsymbol{k}'$ is the wavevector describing the scattering from the second scatterer to the detector; $\hat{\boldsymbol{r}}'' = \hat{\boldsymbol{k}}''$, and $\hat{\boldsymbol{r}}' = \hat{\boldsymbol{k}}'$.

The vector $\boldsymbol{r}''$ gives the position of the first scatterer relative to the second. In a real experiment, $\boldsymbol{r}''$ could assume any direction or length, thus we find the average $\langle \boldsymbol{E}_2^* \cdot \boldsymbol{E}_2 \rangle$ by integrating over $\boldsymbol{r}''$ in a spherical region.

The resulting correlation function will be a sum of exponentials and thus will be nonexponential itself. Thus to characterize the correlation function we evaluated its first cumulant, K_1, in the usual manner [9], where τ_2 the characteristic decay time is given by $1/K_1$ [6].

This proved satisfactory for the case of Brownian particles studied in I. The integral over $\boldsymbol{r}''$ was performed numerically. The results for the polarized and depolarized components of the double scattered correlation function are given in the accompanying figures.

If there is only single scattering from a system, the depolarized scattered intensity will be zero. Experimentally, one may consider the ratio of the depolarized to polarized scattered intensities, the depolarization ratio, as a measure of the degree of multiple scattering. For our case in which we consider only double scattering corrections, the depolarization ratio may be written as

$$R = I_{2\perp}/(I_1 + I_{2\parallel}), \quad (3)$$

where $I_{2\perp}$ and $I_{2\parallel}$ are the depolarized and polarized intensities of the double scattered light, respectively. If we write $I_{2\perp} = R_2 I_{2\parallel}$ we find

$$I_{2\parallel}/I_1 = R/(R_2 - R). \quad (4)$$

Eq. (4), with a knowledge of R_2, may be used to evaluate the relative intensities of the double and single scattered light. To evaluate R_2 we have used eq. (2) and performed the integration over $\boldsymbol{r}''$ for each component at $t = 0$. The results for scattering angles of 30° and 90° are given in fig. 1. We point out that for

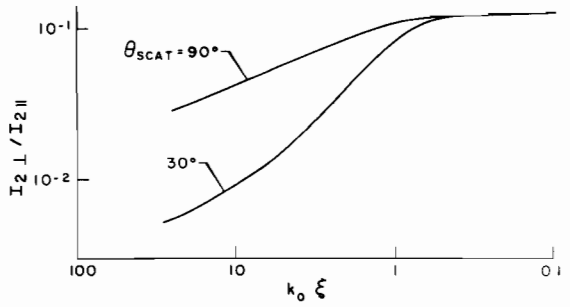

Fig. 1. The ratio of the depolarized to polarized intensity of the double scattered light from a critical fluid as a function of $k_0\xi$.

$k_0\xi \ll 1$ the ratio $R_2 = \frac{1}{8}$. This is the ratio found for point like particles in I. However, as $k_0\xi$ grows, R_2 decreases. Thus the polarized part of the double scattered light is the more intense component. Failure to account for this with eqs. (3) and (4) would lead to erroneously small estimates of the double scattered to single scattered light ratio.

In figs. (2) and (3) we plot the ratio τ_2/τ_1 versus

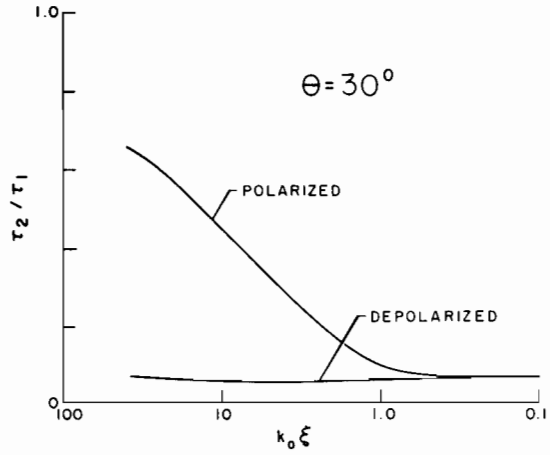

Fig. 2. The ratio of the double scattered to single scattered correlation time of light scattered from a critical fluid for both the polarized and depolarized components of the double scattered light as a function of $k_0\xi$ for a scattering angle of $\theta_{scat} = 30°$.

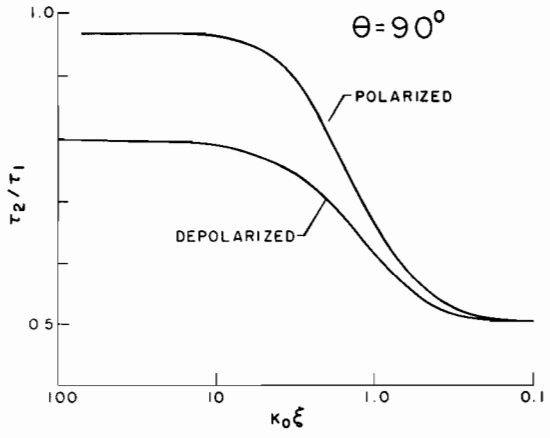

Fig. 3. The ratio of the double scattered to single scattered correlation time of light scattered from a critical fluid for both the polarized and depolarized components of the double scattered light as a function of $k_0\xi$ for a scattering angle of $\theta_{scat} = 90°$.

$k_0\xi$ for scattering angles of 30° and 90°, respectively. Here τ_1 is the decay time of the single scattered correlation function determined from eq. (1) and τ_2 is the decay time of the double scattered correlation function determined from the integration over r'' of eq. (2). We notice that the polarized and depolarized components of the double scattered light have different decay times, especially for $k_0\xi > 1$. The most remarkable result is that the much more intense polarized component has a correlation time almost equal to the single scattered correlation time at large $k_0\xi$. Large $k_0\xi$ is the region in which one expects significant effects from double scattering. Thus for a system of moderate optical density, one for which double scattering is not large until $k_0\xi \gtrsim 8$, we expect only minor effects on the measured correlation time, especially at $\theta_{scat} = 90°$. This conclusion helps explain why so many experimenters have been successful while neglecting the effects of double scattering very near the critical point.

However, a problem still remains for dense systems in the region $k_0\xi \lesssim 8$. In this region we might expect that the mixing of the shorter double scattered correlation function with the single scattered correlation function will result in a measured decay time that is shorter than that predicted by eq. (1). It is possible that this effect has been observed but unidentified in previous linewidth measurements. As discussed by Swinney and Henry [8], many linewidth measurements deviate by as much as 20% from the predictions of the mode theories in this region. This deviation could be explained in terms of double scattering effects.

The results above apply to the spherical scattering geometry. From our work in I, we expect that as the beam is narrowed to the more conventional geometry, the double scattered correlation decay time may increase by 20%. Such a change does not alter our qualitative conclusions given above, in fact in the case of $\theta_{scat} = 30°$ it tends to strengthen them.

From our experience we feel that to truly determine the effects of double scattering on Rayleigh linewidth measurements one should use the expanded beam technique because of the ease of calculating the double scattered decay time.

Finally we point out that we have considered only the double scattered correction. We expect higher order scattering to have correlation times shorter than the double scattered correlation time. While these calcula-

tions are a straightforward extension of our techniques here and in I, the necessary integrations appear prohibitively difficult.

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