PHYSICAL REVIEW A VOLUME 12, NUMBER 5 NOVEMBER 1975

# Effect of gravity on critical opalescence: The turbidity

H. K. Leung and Bruce N. Miller
*Physics Department, Texas Christian University, Fort Worth, Texas 76129*
(Received 20 February 1975; revised manuscript received 27 May 1975)

The effect of the earth's gravity on the total irradiance of light scattered from a simple fluid near its critical point is investigated. It is found that gravity modifies the results of the usual theories for the total scattering (turbidity) qualitatively in two ways. First, the total scattering at the critical point (in the Born approximation) does not diverge. Second, the turbidity does not achieve its maximum value at the critical temperature, but rather above it. For example, the turbidity of xenon with a sample height of 1 cm reaches its maximum value at about $10^{-2}$ K° above its critical temperature. By comparing these results with those of the modified Ornstein-Zernike theory (critical exponent $\eta \neq 0$) for a uniform fluid, an apparent gravity-induced $\eta$ is defined. This is a temperature- and sample-size–dependent quantity which, when substituted for $\eta$ in the modified Ornstein-Zernike theory for a uniform fluid, produces the same turbidity as the gravity-modified classical Ornstein-Zernike theory for a nonuniform fluid. It is surprising that the apparent $\eta$ increases rapidly, until it is of order unity, within a very short temperature range near the critical point, as the critical temperature is approached from above. It is more surprising that the sudden change in the apparent $\eta$ is quantitatively commensurate, through the scaling law $\gamma = \nu(2-\eta)$, with the rapid change in the exponent $\gamma$ observed by a number of experimenters.

## I. INTRODUCTION

Both the Smoluchowski-Einstein[1,2] and Ornstein-Zernike[3] (OZ) theories of light scattering from density fluctuations predict a divergence of the scattering at the critical point due to the singularity in isothermal compressibility $\kappa_T$. As the critical point is approached, the same divergent compressibility that is responsible for opalescence couples with gravity to produce a large density gradient in the fluid. Because the gradient is proportional to the compressibility, at the height in the fluid where the critical density occurs it too diverges as the critical temperature is approached. The importance of the effect of gravity on critical phenomena was recognized long ago.[4] However, it is only in recent years that its effect on light-scattering experiments has been considered.[5–12]

In a recent paper, Splittorff and Miller investigated the effect of gravity on the angular distribution of the scattered irradiance for a simple fluid near its critical point.[8] The results of that investigation are that gravity considerations modify the usual predictions in three ways. First, the scattering in the forward direction no longer diverges at the critical point. Second, the scattered irradiance in any other direction achieves its maximum value at a temperature greater than $T_c$, the critical temperature. Third, even with the OZ expression for the correlation function, Ornstein-Zernike-Debye (OZD) plots of the inverse scattered irradiance versus the square of the wave vector are not linear, but curve towards the origin for small scattering angles. This lack of linearity has heretofore been solely attributed to a nonzero value of the critical exponent $\eta$. Gravity effects here and, as we shall see, on the turbidity as well, demonstrate that deviations from OZ behavior are not solely due to the failure of classical theories. Besides gravity, it has recently been demonstrated that double-scattering effects are responsible for similar deviations from OZD behavior.[13]

A number of investigators operationally define $T_c$ as that temperature where the total light scattering (turbidity) is a maximum.[14] Others take $T_c$ to be the temperature where the transmitted beam vanishes.[15] In this article we study the influence of gravity on the total scattered irradiance from a simple fluid near its critical point. In contrast to the usual OZ theory for a uniform fluid, we find that including gravity removes the divergence in the total scattering at the critical point. Dramatically, the turbidity attains its maximum value not at $T_c$, but always at a temperature above $T_c$, say $T_m$, which depends on the geometry and critical parameters of the sample. For example, a xenon sample with a height of one centimeter has a temperature shift of about $10^{-2}$ K°, which is easily resolved with modern instruments. In general, larger samples produce larger shifts. Clearly the operational definitions of $T_c$ mentioned above fail.

The calculations upon which these conclusions rest employ the usual OZ theory of the pair correlation length, which assumes that the critical exponent $\eta$ is identically zero. Due to gravity, the results deviate from the OZ turbidity for a uniform fluid. If one now assumes that these deviations are not due to gravity, but rather to nonclassical critical behavior, we can deduce an apparent value of $\eta$, say $\eta_a$, which would yield the same deviation as gravity. As one would expect, we find that $\eta_a$ is small and varies little with temperature in the region $T \gg T_c$. However, as $T$ approaches $T_c$, there is a region where $\eta_a$ increases rapidly, until it attains values on the order of unity. This is reminiscent of the situation for the critical exponent $\gamma$. Experimenters have observed a rapid change in $\gamma$ over a small range in temperature for a number of fluids.[16] We find a remarkable quantitative relationship between the changes in $\eta_a$ and $\gamma$, namely, the apparent values of $\eta$ and $\gamma$ are correctly related by the scaling law $\gamma = \nu(2-\eta)$.

## II. TURBIDITY

The idealized experimental setup is the same as in our two earlier papers.[8,12] The sample fluid occupies a cylinder of height $2L$. The axis of the cylinder is aligned with the vertical, and the average density of the sample is its critical density $\rho_c$. Monochromatic plane-polarized light is incident on the bottom of the cylinder and propagates parallel to the axis. It is convenient to define a Cartesian coordinate system $(x, y, z)$ with origin located on the axis of the cylinder at the height where $\rho = \rho_c$, with $z$ directed upward along the axis of the cylinder, and with $x$ in the direction of polarization of the incident light.

When density varies little over changes in height in the sample on the order of a correlation length, $1/\kappa$, we may assume the usual asymptotic form of an OZ pair-correlation function,

$$G(r) = (a/r)e^{-\kappa r}. \tag{1}$$

Here, $a$ and $\kappa$ must be considered as functions of height $z$, through their dependence on the density for this isothermal situation. This argument of local equilibrium, which is discussed more fully in our previous papers,[8,12] is valid for all current experiments. It allows us to express the scattered irradiance in a given direction as the incoherent sum of the irradiance scattered from each small layer $dz$ in the fluid. Performing the sum quickly yields[8]

$$I = Q\sin^2(\psi)\int_{-L}^{L} dz \frac{1}{\kappa^2 + q^2}, \tag{2}$$

$$Q = I_0\left(\frac{v}{2L}\right)\frac{ak^4}{4\pi}\left(\rho\frac{\partial n^2}{\partial\rho}\right)_c^2, \tag{3}$$

$$q^2 = 2q_0^2\sin^2(\theta/2), \quad q_0^2 = 2k^2n_c^2, \tag{4}$$

for the scattered irradiance per unit solid angle. In the above, $I_0$ is the intensity of the incident beam, $V$ is the sample volume, $k$ is the wave number of the incident light, $n$ is the index of refraction, $\psi$ is the angle between the direction of the scattered radiation and the direction of polarization of the incident radiation, and $\theta$ is the scattering angle. The subscript $c$ indicates evaluation at the critical point.

Because $\kappa^2$ is inversely proportional to the isothermal compressibility, it varies rapidly with height in the critical region and must be retained in the integrand in Eq. (2). All other quantities are sensibly constant and are absorbed into the factor $Q$.

The turbidity is defined as the total power scattered through all directions. Integrating Eq. (2) over all angles, one finds

$$\tau = \frac{\pi Q}{q_0^2}\int_{-L}^{L} dz\, F(\sigma), \tag{5}$$

where

$$F(\sigma) = [1 + (1+\sigma)^2]\ln(1+2/\sigma) - 2(1+\sigma), \tag{6}$$

and a new height-dependent variable,

$$\sigma = \sigma(z) = \kappa^2/q_0^2 \tag{7}$$

is introduced. When gravity can be ignored, the fluid is uniform and the local density is the critical density. Under these circumstances $\sigma$ depends only on the temperature, and it is easy to see from the behavior of the function $F(\sigma)$ that the corresponding turbidity diverges as $T$ approaches $T_c$.

The explicit evaluation for $\tau$ for a particular fluid requires knowledge of the exact equation of state of the fluid in the critical region. Although there are many candidates,[17] no such equation is presently known. Here we require an approximate equation that is asymptotically valid for small and large values of $|\rho_r|$ and $\epsilon$,

$$\rho_r = (\rho_c - \rho)/\rho_c, \quad \epsilon = (T - T_c)/T_c, \tag{8}$$

and which is analytically tractable. An equation which satisfies these needs, and which Wilcox and Balzarini[18] have found to yield good density profiles for xenon, is

$$\left(\frac{\partial P}{\partial\rho}\right)_T = A\epsilon^\gamma + \delta B|\rho_r|^{\delta-1}, \tag{9}$$

where $A$ and $B$ are constants, and $\gamma$ and $\delta$ are the usual critical exponents.[16] This choice is discussed in some detail in our earlier effort.[8]

An application of the compressibility equation to the OZ correlation function yields[19]

$$b\kappa^2 = \frac{\partial P}{\partial\rho}, \quad b = \frac{l^2k_BT_c}{10m}, \tag{10}$$

where $k_B$ is the Boltzmann constant, $m$ is the molecular mass, and $l$ is a length characteristic of the short range of molecular interaction.

To evaluate $\tau$ analytically, the barometric equation is used to express the density and compressibility as a function of height. The explicit dependence of $\tau$ on the generalized temperature

$$x = A\epsilon^{\gamma}/bq_0^2 \tag{11}$$

and generalized sample height $h$ [See Eq. (A5)] is developed in Appendix A. Figure 1 gives plots of turbidity per unit height versus $x$ for several values of $h$. For comparison, the turbidity of the corresponding homogeneous system is also plotted with the same normalization.

The total scattered irradiance is reduced by this influence in such a manner that at the critical temperature the divergence of the turbidity is removed. Similar to the situation for the angular distribution of scattered irradiance (except in the forward direction), turbidity attains its maximum value at a temperature $T_m$, corresponding generalized temperature $x_m$, where $T_m > T_c$ ($x_m > 0$). Any interpretation of experimental data which assumes that the critical temperature occurs at maximum opalescence is suspect.[14,15]

The existence of $T_m > T_c$ has an intuitive as well as a computational basis. At a particular height, as $T_c$ is approached from above, a point is reached where the increase in scattering due to the decrease in $\epsilon$ is completely canceled by a decrease in scattering due to the increase in $|\rho_r|$. Averaging over the whole volume determines $T_m$ for the sample.

In order to calculate $T_m$ for a particular fluid, it is necessary to assign values to the parameters $A$ and $B$ characterizing the fluid. For xenon, $A$ and $B$ were found to be $8.7\times10^8$ cm$^2$/sec$^2$ and $1.9\times10^8$ cm$^2$/sec$^2$, respectively, by Wilcox and Balzarini.[18] For other fluids they may be estimated with the help of the principle of corresponding states.[20] The vacuum wavelength of the incident radiation and the short-range correlation length are approximated by setting $l/\lambda = 10^{-3}$. As is in the case of the angular distribution of scattered intensity,[8] the turbidity results are not sensitive to the variation of $\delta$ within the generally accepted range $4 \leq \delta \leq 5$. For convenience of computation, we set $\delta = 4$ and $\gamma = 1.22$. The estimated "positions" of maximum scattering for several fluids having a wide range of sample heights are listed in Table I.

Some of the values of $T_m - T_c$ are found to be experimentally accessible. To date, there are very few reports on turbidity measurements.[15,21,22] None of them observe a temperature shift for maximum turbidity.

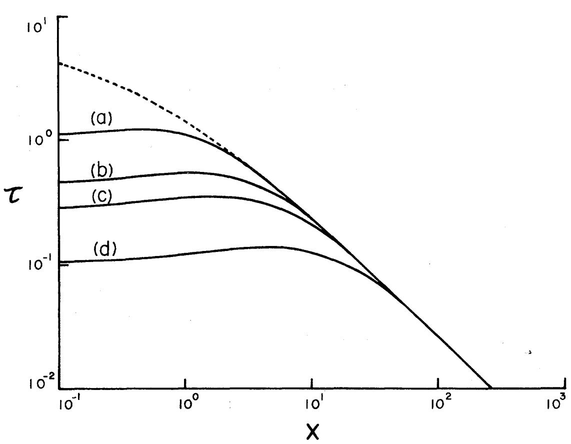


FIG. 1. Dimensionless turbidity per unit height vs the generalized temperature variable $x$ for four values of the sample-height parameter: (a) $h=1$, (b) $h=5$, (c) $h=10$, and (d) $h=50$. The dotted curve is the OZ result neglecting gravity.

## III. GRAVITY-INDUCED APPARENT CRITICAL EXPONENT $\eta_a$

Recently, Hohenberg and Barmatz found that including the influence of gravity in the interpretation of thermodynamic measurements in the critical region leads to important quantitative corrections of critical exponents.[23] Dobbs and Schmidt[7] also indicate that the neglect of gravity leads to an underestimation of the value of $\gamma$. In our last paper[8] we estimated the apparent $\eta$ one would compute from the gravity-induced curvature in OZD plots of the angular distribution. The values of $\eta$ so computed were significant in that they were of the order that one expects when gravity is neglected. Thus gravity alone is responsible for experimentally apparent values of $\eta$ as large as one expects for a uniform fluid.

The deviation of observations from the predictions of the classical OZ theory may be attributed to several unrelated factors, such as the gravity-induced density gradient,[8] the nonzero value of $\eta$ as proposed by Fisher,[24] and double and, in general, multiple scattering.[13] In this section we are

TABLE I. The "position" ($T - T_c$ in $10^{-3}$ °C) of maximum scattering for several fluids with sample heights $2L$ in cm.

| $2L$ | Xe | $CO_2$ | Ar | $SF_6$ | $O_2$ |
|---|---|---|---|---|---|
| 0.01 | 1.12 | 0.19 | 0.27 | 1.35 | 0.18 |
| 0.1 | 3.78 | 0.8 | 0.96 | 4.5 | 0.68 |
| 0.5 | 7.6 | 1.8 | 2.05 | 9.3 | 1.48 |
| 1.0 | 10.1 | 2.5 | 2.7 | 12.1 | 1.97 |
| 5.0 | 17.5 | 4.75 | 4.9 | 21.5 | 3.6 |

going to estimate the gravity-induced apparent $\eta$, $\eta_a$, by comparing two turbidity calculations, one for the system with a gravity-induced inhomogeneity using OZ theory ($\eta=0$) for the correlation function, and one for the homogeneous system using modified ($\eta \neq 0$) OZ theory.

The correlation function in the modified OZ theory may be expressed as[24]

$$G_1(r) = (a/r)^{1+\eta} e^{-\kappa_1 r} \tag{12}$$

for large $r$, where $\eta$ is expected to be small but nonvanishing, $0<\eta \lesssim 0.1$. When $\eta=0$, Eq. (12) reduces to the usual OZ theory given by Eq. (1). The inverse correlation length $\kappa_1$ depends differently on temperature and density than $\kappa$. As we have seen for $\kappa$, the explicit dependence requires an application of the compressibility equation and knowledge of the equation of state. Following this prescription we find that $\kappa$ and $\kappa_1$ are related by Eq. (B3) in Appendix B.

For a uniform system, the inverse correlation length is height independent. The angular distribution of the scattered irradiance for the case $\eta=0$ can be immediately found from Eqs. (2) and (3):

$$I_{\mathrm{OZ}} = 2LQ \sin^2\psi \frac{1}{\kappa^2+q^2}. \tag{13}$$

Similarly, for the case of nonzero $\eta$, a straightforward calculation yields

$$I_\eta = 2L \sin^2\psi \frac{Qa^\eta}{\kappa_1^{2-\eta}} \Gamma(1-\eta) \frac{1}{(1+\omega^2)^{1-\eta/2}} \times \left[\cos(\eta \tan^{-1}\omega) - \frac{1}{\omega}\sin(\eta\tan^{-1}\omega)\right], \tag{14}$$

where $\omega = q/\kappa_1$. The turbidity of the uniform fluid

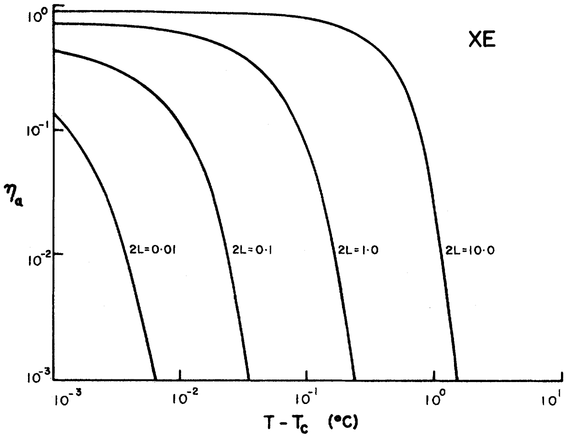


FIG. 3. Apparent critical exponent $\eta_a$ of xenon plotted as a function of $T-T_c$ for four different sample heights. The height of each sample, $2L$, is given in cm.

with $\eta\neq 0$, $\tau_\eta$, is calculated by integrating Eq. (14) over all angles. The complete expression is given in Appendix B. Numerical results are plotted in Fig. 2 for several values of $\eta$.

By comparing Fig. 2 with Fig. 1, we see that both the influence of gravity and the assumption of nonvanishing $\eta$ reduce the value of the turbidity from the classical OZ predictions. However, for all possible values of $\eta$ the modified OZ theory gives no analog of $T_m$ and predicts that the maximum turbidity occurs at the critical temperature. Moreover, as in the classical theory, $\tau_\eta/2L$ is independent of $L$.

The gravity-induced apparent exponent, $\eta_a$, is defined by equating $\tau$ with $\tau_\eta$ and solving for $\eta (=\eta_a)$. This procedure yields a temperature- and height-dependent $\eta_a$ which is plotted in Fig. 3 for xenon. Clearly negative values of $\eta_a$ are excluded.

When the temperature approaches $T_c$ from above, $\eta_a$ increases from zero to a maximum asymptote

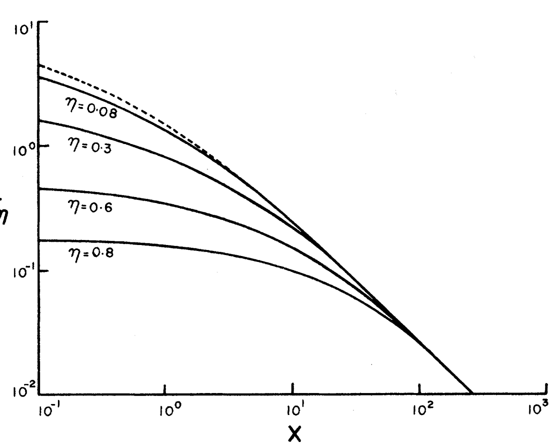


FIG. 2. Turbidity per unit height calculated from the modified OZ theory without the gravity effect. The dotted curve is the OZ result ($\eta$=0).

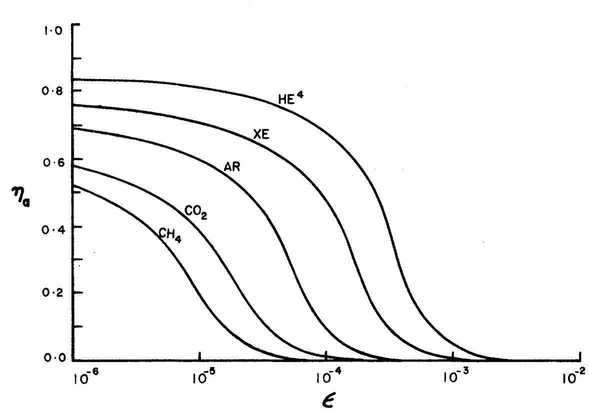


FIG. 4. Apparent critical exponent $\eta_a$ vs $\epsilon$ for several fluids, all having a sample height of 1.0 cm.

within a short temperature range. It is surprising that $\eta_a$ can assume such large values. This rapid increase and large magnitude may be useful to differentiate an apparent from a true exponent. Figure 4 gives $\eta_a(\epsilon)$ for several fluids with height $2L = 1$ cm. It also gives an indirect measure of the influence of gravity on critical scattering from these fluids. Hohenberg and Barmatz have calculated the characteristic temperature below which the influence of gravity becomes important.[23] We find that our results are in fair agreement with theirs.

The values of $\eta_a$ becomes unbelievably large when compared with expected values of $\eta$ as $T$ approaches $T_c$. However, if the scaling law relation $\gamma = \nu(2 - \eta)$ is considered, the sudden jump in $\eta_a$ (taken to be $\eta$ here) as a result of gravity must accompany a sudden drop in $\gamma$ if $\nu$ remains sensibly constant. This agrees with the observations that $\gamma$ changes "suddenly" from 1.44 to 0.97 when $\epsilon \simeq 10^{-3}$ for xenon,[16,18,25] and from 1.37 to 1.1 when $\epsilon \simeq 10^{-5}$ for carbon dioxide.[16,26] Thus, if the scaling law is a valid relation between apparent, gravity-induced exponents, then the observed drop in the apparent value of $\gamma$ is consistent with our computed jump in the apparent value of $\eta$.

## APPENDIX A

The evaluation of the right-hand side of Eq. (5) involves the integral

$$\int dx\, x^{ns} \ln(1 + bx^s) = \frac{1}{ns+1}\left(x^{ns+1}\ln(1+bx^s) + (-1)^n s b^{-(n+1/s)} L^{(s)}(b^{1/s}x) - s\sum_{l=0}^{n} (-1)^l \frac{1}{(n-l)s+1} b^{-l} x^{(n-l)s+1}\right), \tag{A1}$$

where $s = \delta - 1$; $n = 0, 1, 2, 3$, and

$$L^{(s)}(x) = \int \frac{dx}{1+x^s}.$$

When $s$ is an integer, $L^{(s)}$ may be evaluated with the method of integration by partial fractions.[8] By factoring out the temperature-independent constant multiplying $\tau$ in Eq. (5) and dividing by $2L$, we define $\mathcal{T}$, the dimensionless turbidity per unit height,

$$\mathcal{T} = \left(\frac{q_0^2}{2\pi Q L}\right)\tau = \frac{1}{2L}\int_{-L}^{L} dz\, F(\sigma). \tag{A2}$$

We find that

$$\mathcal{T} = \sum_{n=0}^{3} \frac{v_L^{ns+1}}{ns+1}\left(B_n + A_n \ln D_L - (-1)^n s \sum_{l=n+1}^{3} \frac{(-1)^l A_l}{ls+1}(\beta_1^{n-l} - \beta_2^{n-l})\right)$$
$$+ s\sum_{n=0}^{3} \frac{A_n}{ns+1}(-1)^n \left(\beta_1^{-(n+1/s)}[L^{(s)}(\beta_1^{1/s}v_L) - L^{(s)}(0)] - \beta_2^{-(n+1/s)}[L^{(s)}(\beta_2^{1/s}v_L) - L^{(s)}(0)]\right), \tag{A3}$$

where

$$x = \frac{A\epsilon^2}{bq_0^2}, \quad D_L = 1 + \frac{2}{x(1+\delta v_L^s)},$$

$$\beta_1 = \delta\frac{x}{x+2}, \quad \beta_2 = \delta,$$

$$A_0 = x(x^2 + 2x + 2), \quad A_1 = \delta x(3x^2 + 4x + 2),$$

$$A_2 = \delta^2 x^2 (3x + 2), \quad A_3 = \delta^3 x^3,$$

$$B_0 = -2x(x+1), \quad B_1 = -2\delta x(2x+1),$$

$$B_2 = -2\delta^2 x^2, \quad B_3 = 0.$$

To obtain numerical results, $v_L$ must be expressed in terms of $u_L$ in Eq. (A3) by inverting

$$u_L = v_L + v_L^{\delta}. \tag{A4}$$

A useful dimensionless height may be constructed by factoring out the dependence on generalized temperature from $u_L$:

$$h = x^{\delta/(\delta-1)} u_L = gL(B^{1/\delta}/bq_0^2)^{\delta/(\delta-1)}. \tag{A5}$$

## APPENDIX B

The functional relationship between the inverse correlation length and the generalized temperature parameter can be derived from the compressibility equation which relates the correlation function and the isothermal compressibility of the fluid. With $G(r)$ given by Eq. (1) and Eq. (12) for $\eta = 0$ and $\eta > 0$, respectively, we find that near the critical point,

$$\kappa^2 = 4\pi\rho a\beta\left(\frac{\partial P}{\partial \rho}\right), \quad \beta = \frac{1}{k_B T} \tag{B1}$$

$$\kappa_1^{2-\eta} = 4\pi\rho a^{1+\eta}(1-\eta)\Gamma(1-\eta)\beta\left(\frac{\partial P}{\partial \rho}\right), \tag{B2}$$

and thus

$$\kappa_1^{2-\eta} = a^{\eta}(1-\eta)\Gamma(1-\eta)\kappa^2 . \tag{B3}$$

At points not too close to the critical point the correlation length is much shorter than a light wavelength and $\omega = q/\kappa_1 \ll 1$, the angular distribution of scattered irradiance $I_\eta$ and the turbidity $\tau_\eta$ are then given respectively by Eqs. (1) and (2) of Ref. 15. For our purposes we compute the exact result without the small-$\omega$ approximation. We find

$$\tau_\eta = \frac{2x_1}{(1-\eta)x} \times \sum_{l=0}^{4} C_l \frac{1}{\eta + l}\{(1+2/x_1)^{(\eta+l)/2} \cos[(\eta+l)\tan^{-1}(2/x_1)^{1/2}] - 1\}, \tag{B4}$$

where

$$x_1 = [(aq_0)^{\eta}(1-\eta)\Gamma(1-\eta)x]^{2/(2-\eta)}, \tag{B5}$$

$$C_0 = x_1^2 + 2x_1 + 2, \quad C_1 = -4x_1(x_1+1), \quad C_2 = 2x_1(3x_1+1), \quad C_3 = -4x_1^2, \quad C_4 = x_1^2 . \tag{B6}$$

For the purposes of numerical computation we have taken

$$aq_0 = 10^{-2} .$$


[1]M. V. Smoluchowski, Ann. Phys. (Leipz.) 25, 205 (1908).
[2]A. Einstein, Ann. Phys. (Leipz.) 33, 1275 (1910).
[3]L. S. Ornstein and F. Zernike, Proc. K. Ned. Akad. Wet. 17, 763 (1914); F. Zernike, *ibid.* 18, 1520 (1916).
[4]A. Gouy, C. R. Acad. Sci. (Paris) 115, 720 (1892).
[5]F. E. Murray and S. G. Mason, Can. J. Chem. 30, 550 (1952); 33, 1399 (1955).
[6]A. V. Voronel', and M. Sh. Giterman, Zh. Eksp. Teor. Fiz. 39, 1162 (1960) [Sov. Phys.—JETP 12, 809 (1961)]; M. Sh. Giterman and S. P. Malyshenko, Zh. Eksp. Teor. Fiz. 53, 2077 (1967) [Sov. Phys.—JETP 26, 1176 (1968)].
[7]B. C. Dobbs and P. W. Schmidt, J. Chem. Phys. 56, 2421 (1972); also Phys. Rev. A 7, 741 (1973).
[8]O. Splittorff and B. Miller, Phys. Rev. A 9, 550 (1974).
[9]D. M. Kim, D. L. Henry and R. Kobayashi, Phys. Rev. A 10, 1808 (1974).
[10]J. A. White and B. S. Maccabee, Phys. Rev. A 11, 1706 (1975).
[11]B. Miller, J. Comput. Phys. 7, 576 (1971).
[12]B. Miller and O. Splittorff, J. Opt. Soc. Am. 62, 1291 (1972).
[13]D. W. Oxtoby and W. M. Gelbert, Phys. Rev. A 10, 738 (1974).
[14]A. V. Chalyi and A. D. Alekhin, Zh. Eksp. Teor. Fiz. 59, 337 (1970) [Sov. Phys.—JETP 32, 181 (1971)].
[15]P. Calmettes, I. Laguës and C. Laj, Phys. Rev. Lett. 28, 478 (1972).
[16]L. P. Kadonoff, W. Götze, D. Hamblen, R. Hecht, E. A. S. Lewis, V. V. Palciauskas, M. Rayl, F. Swift, D. Aspnes, and J. Kane, Rev. Mod. Phys. 39, 395 (1967).
[17]P. Schofield, J. D. Litster, and J. T. Ho, Phys. Rev. Lett. 23, 1098 (1969); M. Vicentini-Missoni, J. M. H. Levelt Sengers, and M. S. Green, Phys. Rev. Lett. 22, 389 (1969); M. Vicentini-Missoni, R. I. Joseph, M. S. Green, and J. M. H. Levelt Sengers, Phys. Rev. B 1, 2312 (1970).
[18]L. R. Wilcox and D. Balzarini, J. Chem. Phys. 48, 753 (1968).
[19]M. Fixman, J. Chem. Phys. 33, 1357 (1960).
[20]J. Hirschfelder, C. Curtiss, and R. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1967).
[21]V. G. Puglielli and N. C. Ford, Jr., Phys. Rev. Lett. 25, 143 (1970).
[22]J. H. Lunacek and D. S. Cannell, Phys. Rev. Lett. 27, 841 (1971).
[23]P. C. Hohenberg and M. Barmatz, Phys. Rev. A 6, 289 (1972).
[24]M. E. Fisher, J. Math. Phys. 5, 944 (1964).
[25]W. G. Schneider and H. W. Habgood, Can. J. Chem. 32, 98 (1954).
[26]H. L. Lorentzen, Acta Chem. Scand. 7, 1335 (1953).