Critical opalescence in fluids: 1.5-Scattering effects and the Landau–Placzek ratio

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Abstract

We adduce new arguments for the significance of so-called 1.5- (or sesquialteral) molecular light scattering in one-component fluids. For this purpose, we analyze its effect on the Landau–Placzek ratio for the critical opalescence ratio. The results obtained are used to reveal experimental data which can be interpreted as evidence for its existence and to evaluate both the relative magnitude and the sign of the 1.5-scattering contribution.

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I. INTRODUCTION

The accuracy of experimental data obtained with the method of molecular spectroscopy for the thermodynamic and kinetic parameters of fluids depends heavily on the validity of theoretical views of the physical mechanisms responsible for the formation of the spectra under one or other circumstances. In particular, it is widely believed that the critical opalescence spectra from one-component fluids are formed only by single and true multiple scattering effects [6–12]. The latter are treated as successive single scatterings by distant (satisfying the wave-zone condition $r >> \lambda$, where $\lambda$ is the wavelength of probing radiation in the fluid) pairs of density fluctuations.

Recently, we suggested [13–15] that besides the above mechanisms, a so-called 1.5- (or sesquialteral) scattering can become of significance near the critical point. This scattering is formed by those three-point configurations of density fluctuations in which the fluctuations are spaced by distances $r << r_c < \lambda$, $r_c$ being the correlation radius. Groups of fluctuations satisfying this condition are termed further as compact.

Based on theory [13–15], we have managed to estimate the intensity and the sign of 1.5-scattering, identify the thermodynamic paths most favorable for its observation, and analyze its effect on the depolarization ratio and the Rayleigh line halfwidth of the critical opalescence spectra. The 1.5-scattering contribution proves to be most pronounced at a certain distance from the critical point. Asymptotically close to the critical point, it is expected to vanish, in line with Polyakov’s hypothesis [16, 17] of conformal symmetry of critical fluctuations.

Here, we give a brief account of our analysis of the 1.5-scattering effect on the Landau–Placzek ratio for the critical opalescence spectra. The results obtained enable us to quote new experimental data in support of the existence of the 1.5-scattering contribution and to make new independent estimates of its relative magnitude and sign.

II. GENERAL STRUCTURE OF THE SINGLE-SCATTERING SPECTRUM

According to Refs. [13, 15], the spectrum of polarized single-scattering is given by

$$I(q, \omega) = \sum_{n,m=1} I_{nm}(q, \Omega),$$

where the term

$$I_{nm}(q, \Omega) \propto \left(-\frac{1}{\varepsilon_0}\right)^{n+m-2}$$

$$\times \frac{1}{\pi} \text{Re} \int_0^{+\infty} dt \int d\mathbf{r} \langle (\delta \varepsilon(\mathbf{r}, t))_n (\delta \varepsilon(0, 0))_m \rangle e^{i\Omega t - i\mathbf{q} \cdot \mathbf{r}},$$

represents the contribution from a pair of compact groups of $n$ and $m$ permittivity fluctuations, and $\Omega$ and $\mathbf{q}$ are the changes in the frequency and wavevector of the wave due to scattering. Expression (2) is the frequency transform of the function

$$I_{nm}(q, t) \propto \left(-\frac{1}{\varepsilon_0}\right)^{n+m-2}$$

$$\times \int d\mathbf{r} \langle (\delta \varepsilon(\mathbf{r}, t))_n (\delta \varepsilon(0, 0))_m \rangle e^{-i\mathbf{q} \cdot \mathbf{r}},$$

whose value at $t = 0$ is equal to the integrated intensity of scattering by the above pair.

We accept further that for one-component fluids, the permittivity fluctuations are mainly due to the density ($\rho$) fluctuations $\delta \rho(\mathbf{r}, t)$: $\delta \varepsilon(\mathbf{r}, t) \approx (\partial \varepsilon / \partial \rho) \delta \rho(\mathbf{r}, t)$. 

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III. SPECTRUM OF THE “STANDARD” SINGLE SCATTERING

It is only the term $I_{11}(q, \Omega)$ in Eq. (1) that is customarily believed to form (besides the true multiple scattering) the critical opalescence spectra. With sufficient accuracy, it can be analyzed under the assumptions that both the linearized hydrodynamic equations and the concept of local thermodynamic equilibrium are valid. For the case where the transverse part of the velocity is not coupled with $\delta \rho(r, t)$, the lowest-order term of the Fourier component $\rho_k(t)$ of $\delta \rho(r, t)$ evolves in time by the law [3]

$$\rho_k(t) = \rho_k(0) \left[ \frac{c_p - c_v}{c_p} e^{-\Gamma_h(k)t} + \frac{c_v}{c_p} e^{-\Gamma_h(k)t} \cos(\omega_st) \right],$$

where

$$G_R(k) = \frac{\kappa}{\rho c_p} k^2, \quad \Gamma_B(k) = \frac{1}{\rho c_p} \left[ \frac{4}{3} \eta + \zeta \left( \frac{1}{c_v} - \frac{1}{c_p} \right) \right] k^2,$$

$c_p$ and $c_v$ are the specific heats at constant pressure and volume ($c_p/c_v \equiv \gamma$), $\kappa$ is the thermal conductivity, $\eta$ and $\zeta$ are the shear and bulk viscosities, and $u_S$ is the adiabatic speed of sound. Correspondingly,

$$I_{11}(q, t) \propto \left( \frac{\partial \varepsilon}{\partial \rho} \right)^2 G(q) \left[ A e^{-\Gamma_h(q)t} + B e^{-\Gamma_h(q)t} \cos(u_Sqt) \right],$$

where $G(q) = \langle \rho_q(0) \rho_q(0) \rangle$, $A \equiv (c_p - c_v)/c_p$, and $B \equiv c_v/c_p$.

The two addends in the brackets signify that both thermal and mechanical processes contribute to the evolution of $\delta \rho(r, t)$. They lead to the formation of three lines in the spectrum of the “standard” single scattering, with total integrated intensity $I_{11}(q) \propto (\partial \varepsilon/\partial \rho)^2 G(q)$. One of these, not shifted in frequency, is the Rayleigh line, with halfwidth $\Gamma_{1R} = \Gamma_B(q)$ and integrated intensity $I_{1R} = A I_{11}(q)$, and the others, shifted, are the Brillouin lines, with halfwidth $\Gamma_{1B} = \Gamma_B(q)$ each and total integrated intensity $I_{1B} = BI_{11}(q)$. The quotient

$$R = \frac{I_{1R}}{I_{1B}} = \frac{A}{B} = \gamma - 1,$$

is known as the Landau–Placzek ratio.

As the critical point is approached, long-range density correlations become of crucial importance and, strictly speaking, the applicability of the above approach becomes questionable. Yet the structure of Eq. (4) is usually preserved by suggesting that the kinetic coefficients can be treated as functions of temperature, wave vector and, in general, frequency. Some of the approaches offered to recover the explicit forms of these functions are reviewed in Refs. [5, 12].

IV. SPECTRUM OF THE 1.5-SCATTERING

The 1.5-scattering spectrum is represented in Eq. (1) by the terms with $n = 1, m = 2$ and $n = 2, m = 1$. For one-component fluids, its inverse Fourier transform is

$$I_{1.5}(q, t) \propto -\frac{1}{3 \varepsilon_0} \left( \frac{\partial \varepsilon}{\partial \rho} \right)^3 \int \frac{d \mathbf{r} e^{i \mathbf{q} \cdot \mathbf{r}}}{V} \times \left[ (\delta \rho(r, t)(\delta \rho(0, 0))^2 + (\delta \rho(r, t)\delta \rho(0, 0)) \right].$$

To evaluate the effect of 1.5–scattering on the overall spectrum, we follow the following procedure. First, we assume in the standard way [1, 2] that the time evolution of $\rho_k(t)$ is given by Eq. (1). Then we change to the wave-vector space to represent the fluctuation $\delta \rho(r, t)$ as

$$\delta \rho(r, t) = \sum_k \rho_k(0) \left[ A e^{-\Gamma_h(k)t} + B e^{-\Gamma_h(k)t} \cos(u_Sqt) \right] e^{i \mathbf{k} \cdot \mathbf{r}},$$

where we consider the quantities $A$ and $B$ as $k$–independent. With representation (8), the statistical averaging in Eq. (7) is equivalent to averaging over all realizations of the initial values $\rho_k(0) = \rho_k$. In doing so, we take advantage of the approximation [15] ($c'$ is a parameter)

$$\langle \rho_{k_1} \rho_{k_2} \rho_{k_3} \rangle \approx -\frac{2c'}{k_B T \sqrt{V}} G(k_1)G(k_2)G(k_3) \delta_{k_3, -k_1 - k_2},$$

for the three-point correlation function of density fluctuations. This gives:

$$I_{1.5}(q, t) = \sum_{k} I_{1.5}^{(i)}(q, t),$$

$$I_{1.5}^{(1)}(q, t) \propto A e^{-\Gamma_h(q)t} KG(q) \int d \mathbf{k} G(k) G(|\mathbf{q} - \mathbf{k}|),$$

$$I_{1.5}^{(2)}(q, t) \propto B e^{-\Gamma_h(q)t} \cos(u_Sqt)KG(q) \int d \mathbf{k} G(k) G(|\mathbf{q} - \mathbf{k}|).$$
It follows that combining spectroscopic (of the functions (11)–(15), and its integrated intensity is
the sum of the frequency transforms where
Rayleigh and Brillouin lines in the overall spectrum.
Finally, we analyze the frequency distributions of
terms (11)–(15) and estimate their combined contribu-
tions
\[ I_{1.5}(q, t) \propto B^2 K G(q) \int dk G(k) G(|q - k|) e^{-\Gamma_n(k)t - \Gamma_n(|q-k|)t} \cos(u_S|q - k|t), \]
\[ I_{1.5}(q, t) \propto 2AB K G(q) \int dk G(k) G(|q - k|) e^{-\Gamma_n(k)t - \Gamma_n(|q-k|)t} \cos(u_S|q - k|t), \]
\[ I_{1.5}(q, t) \propto 2AK G(q) \int dk G(k) G(|q - k|) e^{-\Gamma_n(k)t - \Gamma_n(|q-k|)t} \cos(u_S|q - k|t), \]
\[ I_{1.5}(q, t) \propto 2AK G(q) \int dk G(k) G(|q - k|) e^{-\Gamma_n(k)t - \Gamma_n(|q-k|)t} \cos(u_S|q - k|t), \]

where \( K \equiv \frac{2}{3\epsilon(2\pi)^3} \frac{c^3}{k_B T} \left( \frac{\partial \epsilon}{\partial \rho} \right)^3 \). The 1.5–scattering spec-
trum is given by the sum of the frequency transforms of the functions (11)–(15), and its integrated intensity is
(A + B = 1)
\[ I_{1.5}(q) \propto 2K G(q) \int dk G(k) G(|q - k|). \]

Finally, we analyze the frequency distributions of terms (11)–(15) and estimate their combined contribu-
tions \( I_{1.5R} \) and \( I_{1.5B} \) to the integrated intensities of the Rayleigh and Brillouin lines in the overall spectrum. Since the term (15) contributes (in a proportion \( x \) to 1 – \( x \)) to both, we obtain:
\[ I_{1.5R} \approx I_{1.5}^{(1)}(q, 0) + I_{1.5}^{(3)}(q, 0) + xI_{1.5}^{(5)}(q, 0) = aAI_{1.5}(q), \]
\[ I_{1.5B} \approx I_{1.5}^{(2)}(q, 0) + I_{1.5}^{(4)}(q, 0) + (1-x)I_{1.5}^{(5)}(q, 0) = bBI_{1.5}(q), \]
\[ a = \frac{1}{2} \left( 1 + A + x \frac{B^3}{A} \right), \quad b = \frac{1}{2} \left[ 1 + 2A + (1 - x)B \right]. \]

VI. EFFECT OF 1.5–SCATTERING ON THE LANDAU–PLACZEK RATIO

With 1.5–scattering effects present and in view of Eqs. 6 and 17–19, the Landau–Placzek ratio takes the form
\[ R_{\text{exp}} = \frac{I_{1R} + I_{1.5R}}{I_{1B} + I_{1.5B}} = R \frac{1 + af}{1 + bf}, \]
where the quantity \( f \equiv I_{1.5}(q)/I_{11}(q) \) has the meaning of the relative magnitude of the 1.5-scattering intensity as compared to that of the “standard” single scattering. From Eq. 20,
\[ f = \frac{R - R_{\text{exp}}}{bR_{\text{exp}} - aR}. \]
It follows that combining spectroscopic (\( R_{\text{exp}} \)) and caloric (\( c_P \) and \( c_V \)) data opens, in principle, an opportunity for
direct experimental estimation of the 1.5-scattering contribution.

VI. SITUATION WITH EXPERIMENT

We have found in the literature only a few measurement of the Landau–Placzek ratio for pure fluids near the
the critical point. In Refs. 18, 19, \( R \) was studied for CO2 along the critical isochore above \( T_c \) (the temperature
range was about \( 3 \cdot 10^{-4} < \tau < 3 \cdot 10^{-2} \)). In both works, the \( \tau \)-dependence of \( R \) was approximated by a single exponent (0.95 \( \pm \) 0.15 and 1.02 \( \pm \) 0.03 respectively). In Ref. 20, \( R \) was measured for saturated \( n \)-butane along the vapor (\( 2.2 \cdot 10^{-3} < \tau < 0.08 \)) and liquid (\( 3.3 \cdot 10^{-3} < \tau < 0.3 \)) branches of the coexistence curve. For \( \tau < 0.1 \), the experimental data were also approximated by straight lines for both branches, while the values of \( \gamma - 1 \), calculated with data 21, exhibited a small curvature. However, for the vapor the deviations were within the limits of error, and for the liquid there was a small deviation just outside the limit of error for \( \tau < 3.5 \cdot 10^{-3} \).

According to our estimates 13, 15, the conditions in the above experiments were unfavorable for observation of 1.5–scattering. In contrast, of great interest are the results of Ref. 22 for liquid He close to the \( \lambda \)-line, where the measurements of \( R \) were carried out over the temperature range \( 0.01 \text{mK} < |\Delta T| < 10 \text{mK} \) both below and above the \( \lambda \)-transition. Most of the measurements were made for a pressure of 18.24 bars and some for 26 bars. Provided \( |\Delta T| > 0.3 \text{mK} \), the observed values of \( R \) were in good agreement with the values of \( \gamma - 1 \), calculated with data 23, but for smaller \( |\Delta T| \) they were observed to fall below \( \gamma - 1 \).

Consider the case of He above the \( \lambda \)-line, where it behaves as an ordinary liquid. According to data 22, 23, for \( 0.04 \text{mK} \) and a pressure of 18.24 bars \( R_{\text{exp}} \approx 0.16 \) and \( \gamma \approx 1.21 \). Taking \( x \approx 0.5 \), we find \( f \approx -0.26 \). This new result agrees well with our earlier estimates 14, 15, obtained by processing the depolarization ratio data for Xe.

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