SESQUIALTERAL MOLECULAR LIGHT SCATTERING BY FLUIDS

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A new approach to the problem of the sesquialteral molecular light scattering by single-component fluids is reported, and the main results are reviewed. The scattering intensity is expressed in terms of the third thermodynamic moment of density fluctuations. The analysis of its relative magnitude and the temperature dependence with the Van der Waals model reveals that the sesquialteral scattering can be detected experimentally. It is shown that, with the sesquialteral scattering effects incorporated into the overall scattering pattern, the well-known features of the temperature behavior of the depolarization ratio in the vicinity of the critical point can be explained in a single way.

Spectroscopy of molecular light scattering is one of the most efficient methods for obtaining the information about the thermodynamic parameters and kinetic coefficients of a substance. The analysis of the scattering intensity in the non-critical temperature region enables one to directly study the asymptotic behavior of the pair correlation functions (CFs) for permittivity fluctuations $\delta\varepsilon$ which, in turn, are related to the thermal fluctuations of the concentration, temperature, and mutual orientation of molecules. As the liquid–vapor critical point (CP), the one under discussion below, is approached, the contribution from the long-wave density fluctuations becomes dominant. With their pair CF proportional to the isothermal compressibility β of the fluid, these fluctuations manifest themselves as an anomalous increase in scattering (the critical opalescence phenomenon).

The study of the critical opalescence and the interpretation of experimental data are complicated by a number of factors, one being the multiple scattering effects. In studies of them, the attention is typically centered on the the double scattering (see [2]). We recall that the concept of multiplicity comes into play whenever the iteration procedure is employed to solve the integral equation describing the wave propagation in a fluctuationally inhomogeneous medium. The field of the scattered wave is of the form $E_\alpha = E_\alpha^{(1)} + E_\alpha^{(2)} + E_\alpha^{(3)} + ...$, where $E_\alpha^{(n)}$ is the contribution to the α-component of the field from the nth step of the iteration procedure, and the scattering intensity is determined by the tensor $I_{\alpha\beta} = \sum_{n,m \geq 1} I_{\alpha\beta}^{nm}$, where the correlators $I_{\alpha\beta}^{nm} \propto < E_\alpha^{(n)} \times E_\beta^{(m)*} >$ represent the contributions of the multiplicity $(n + m)/2$ from the groups of n and m fluctuations. Here, the angle brackets denote the averaging over the permittivity fluctuations, the asterisk means taking the complex conjugation, and the subscripts specify a polarization state of the scattered field. The correlators $I_{\alpha\beta}^{nm}$ are expressed in terms of the convolutions of electromagnetic field propagators $T_{\alpha\beta}(r)$ and many-point CFs for the permittivity fluctuations; in fact, the latter are replaced by the corresponding CFs for the density fluctuations.

Customarily, the multiple scattering effects are treated as parasitic against the background of the single scattering, which is the result of a number of approximations usually made in calculating their intensities. Namely, the main contribution to the multiple scattering is believed to be made by successive re-emissions from the density fluctuations that are at the distances $r \gg \lambda > r_c$ apart, where λ is the wavelength of light in the medium, and r_c is the correlation radius. This allows one to replace the propagators $T_{\alpha\beta}(r)$ by their asymptotic wave-zone expressions and pass from the many-point CFs to the corresponding asymptotes. In fact, the factorization of the many-point CFs and the imposition of a quasi-Gaussian fluctuation model are made. As a result, any new information

of higher CFs, which is in principle hidden in the scattering effects of higher multiplicities, is completely lost. Moreover, the effects of fractional multiplicities, including the sesquialteral scattering (scattering effects of the multiplicity 3/2), are negligible in such a model [3, 4].

As a key experimental argument in support of this approach, the form of the temperature behavior of the depolarization ratio Δ in the critical region is considered. Since the intensity I_a of the depolarized scattering due to the anisotropy fluctuations is not practically changed as CP is approached, the intensity of the depolarized part of the double scattering increases as $I_{dd} \propto \beta^2$, and the intensity of the polarized scattering is determined mainly by the intensity of the single scattering due to the density fluctuations, $I_1 \propto \beta$, we get the relation

$$\Delta = \frac{I_a + I_{dd}}{I_1} \approx A\beta^{-1} + B\beta \tag{1}$$

for a single-component fluid, where A and B are constants. By estimates [3] for xenon placed into a spherical volume of radius $0.1 \, \mathrm{cm}$, the first term on the right-hand side of formula (1) is dominant in the temperature region $\tau \equiv |T - T_c|/T_c > 10^{-2}$ (where the double scattering can be ignored), and the the other term is dominant in the interval $10^{-4} < \tau < 10^{-2}$ (where the depolarization due to the double scattering is considered to be prevailing); the minimum of Δ occurs at $\tau \approx 1 \times 10^{-2}$.

Relation (1) is in good accord with the data of many experiments [2], though some deviations from law (1) have been reported. Of those, the main ones are: 1) a more rapid (than linear) increase of Δ with β in the temperature region $10^{-4} < \tau < 10^{-3}$[5]; it was interpreted as a manifestation of triple scattering effects which cause the appearance of an additional term proportional to β^2 on the right-hand side of (1); 2) a certain decrease in Δ in the temperature region $\tau \lesssim 1 \times 10^{-4}$ [6]; the authors, however, questioned the validity of this result.

The present work reports on a new approach to the problem of the sesquialteral molecular light scattering by fluids, which was offered by us in [7,8]. The intensity $I_{1.5}$ of the sesquialteral scattering is expressed in terms of the third thermodynamic moment of the density fluctuations. The estimates of its relative magnitude with the Van der Waals model reveal a possibility of experimental registration of the contribution of $I_{1.5}$. In this connection, the role of the sesquialteral scattering effects in the formation of Δ is scrutinized. It is shown that their presence in the overall scattering pattern may

cause the above peculiarities of the temperature behavior of Δ.

Our analysis is based upon the suggestion that the contribution $I_{1.5}$ is of the greatest relative magnitude at a certain distance from CP, where all the distances between the three contributing-to-scattering fluctuations satisfy the relation $r \lesssim r_c \ll \lambda$, and the use of asymptotic expressions for the three-point CFs is therefore impossible. This condition is surely satisfied for the temperature interval $\tau \gtrsim 1 \times 10^{-4}$ typical of the majority of light-scattering experiments. For instance, for xenon ($T_c \approx 290 \, \mathrm{K}$), the corresponding values of the correlation radius $r_c \lesssim 7 \times 10^{-6}$ cm, being almost an order of magnitude less than a typical light wavelength $\lambda \approx 5 \times 10^{-5}$ cm. In the case of four fluctuations, however, even for these values of temperature there exists such a configuration of their spatial locations that one pair of the fluctuations is at the distance $r \gg \lambda > r_c$ from the other; in other words, it is still possible to factorize the four-point CF and to pass to the above-mentioned quasi-Gaussian fluctuation model.

The computation of the intensity $I_{1.5}$ is carried out in several steps. At first, the contributions to the total scattering intensity from the so-called compact groups of fluctuations (all the distances, within which $|\mathbf{r}_i - \mathbf{r}_j| \ll \lambda$) are analyzed. These contributions are formed by those domains of the integration variables, where the internal propagators describing the re-emission processes within a compact group reveal a singular behavior. With the methods of the theory of generalized functions, the peculiarities of this behavior can be determined, and the desired contributions can be exerted from each iteration step. It turns out that, in the case of single-component fluids, the compact groups cause mainly the polarized scattering (the subscripts $\alpha = \beta$, which become equal to the corresponding subscript for the incident wave, are further omitted). At a distance R away from a system of volume V, the intensity of scattering by a pair of compact groups comprising n and m fluctuations is

$$I^{nm} = I_0 \frac{k_0^4 V \sin^2 \vartheta}{16\pi^2 R^2} \left(-\frac{1}{3\varepsilon_0}\right)^{n+m-2} \times$$

$$\times \int_V d\mathbf{r} < (\delta\varepsilon(\mathbf{r}))^n (\delta\varepsilon(\mathbf{0}))^m > \exp(-i\mathbf{q} \cdot \mathbf{r}), \tag{2}$$

where I_0 and $k_0 = 2\pi/\lambda_0$ are, respectively, the intensity and the wave vector of the incident wave (of length λ_0) in vacuum, $\mathbf{q}$ is the wave vector change in the medium due to the scattering, ϑ is the angle between the polarization unit vector and the direction toward

the point of observation, and ε_0 is the equilibrium value of the permittivity of the medium. In what follows, the factor in front of the parentheses is left out.

At the second stage, the contributions to intensities (2) from the short-range correlations between the compact groups separated by distances $r \lesssim r_c \ll \lambda$ are calculated. In this case, with the correlation between fluctuations being slightly non-local, these contributions can be expressed through the moments of order $(n+m)$ of the thermodynamic permittivity fluctuations $\Delta\varepsilon$. By defining the thermodynamic contributions to the nth power of the permittivity by

$$\Delta(\varepsilon^n) = \varepsilon^n - \overline{\varepsilon^n} = \frac{1}{\tilde{V}} \int\limits_V d\mathbf{r}\delta(\varepsilon^n(\mathbf{r})), \qquad (3)$$

where $\tilde{V}$ is some macroscopic volume, we obtain

$$I^{nm} \propto \left(-\frac{1}{3\varepsilon_0}\right)^{n+m-2} \tilde{V}\langle(\Delta\varepsilon)^{n+m}\rangle. \qquad (4)$$

The choice of $\tilde{V}$ is dependent of the temperature region under consideration and is discussed below.

In the opposite case where the long-ranging correlations between compact groups are of significance, formula (2) is in complete agreement with the hypothesis of the algebra of fluctuating quantities [9].

For a single-component fluid, the fluctuations $\Delta\varepsilon$ are reduced to the thermodynamic density fluctuations $\Delta\rho$: $\Delta\varepsilon \approx (\partial\varepsilon/\partial\rho)_T\Delta\rho$. The intensity $I_{1.5} = I^{12} + I^{21}$ is expressed through the third moment $\langle(\Delta\rho)^3\rangle$, the formal expression for which is found with the grand canonical ensemble. We have (k_B is the Boltzmann constant and P is the pressure):

$$I_{1.5} \propto -\frac{2}{3\varepsilon_0}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_T^3 \tilde{V}\langle(\Delta\rho)^3\rangle =$$

$$= -\frac{2}{3\varepsilon_0}\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)_T^3 \frac{k_{\mathrm{B}}^2 T^2}{\tilde{V}}\left[2\beta^2 + \left(\frac{\partial\beta}{\partial P}\right)_{TV}\right]. \qquad (5)$$

Thus, we reduce the problem to evaluating the thermodynamic derivative in formula (5). For the temperature region under consideration, its functional structure can be estimated with the help of the Van der Waals model. We find

$$I_{1.5} \propto -\frac{1}{\varepsilon_0}\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)_T^3 \frac{k_{\mathrm{B}}^2 T^2}{\tilde{V}} 6P_c\omega\beta^3, \qquad (6)$$

where P_c is the pressure value at CP, and the parameter $\omega \equiv \rho_c/\rho - 1$ describes deviations of the density from its critical value. In this model, as we see, the sesquialteral

scattering comes into play when a shift, planned or accidental (because of an experimental error), from the critical isochore occurs, and its contribution is negative for $\omega > 0$.

Note that, in the limiting case $\omega \to 0$, $\tau \to 0$, the equality $I_{1.5} = 0$ represents the orthogonality relation for the fluctuating scalar quantities with different scaling dimensions; according to the fluctuation theory of phase transitions (see [9]), it must hold for any system that possesses the symmetry with respect to conformal transformations. That fact that this relation occurs along the critical isochore $\omega = 0$ for arbitrary values of τ should be treated, in our view, as a specific feature of the Van der Waals model. Calculations, for instance with the use of the Dieterici equation of state, give $I_{1.5} \propto -\frac{2}{3\varepsilon_0}\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)_T^3 \frac{k_B^2 T^2}{\tilde{V}}(\beta^2 + 4P_c\omega\beta^3)$ for the region of slightly non-local fluctuations. We see that a negative sesquialteral scattering occurs in this model even if $\omega = 0$. Also, it is not difficult to verify that the intensity $I_{1.5}$ remains negative for any shifts into the region $\omega < 0$ as long as the inequality $\tau > 2|\omega|$ holds true. However, with the goal of obtaining the lower limit to $I_{1.5}$, we restrict our consideration to the Van der Waals model.

To further analyze the temperature behavior and the magnitude of $I_{1.5}$, we take advantage of a widely believed statement that the quantity $(\rho\partial\varepsilon/\partial\rho)_T$ slightly depends upon τ in the vicinity of CP (see review [2]) and also make certain assumptions as to the temperature behavior and a numerical value of the parameter $\tilde{V}$. In our opinion, in the above-mentioned (hydrodynamic) temperature region, two limiting cases can occur: 1) relatively far away from CP, the linear size $\tilde{V}^{1/3}$ is much greater than the range of action of intermolecular forces, yet remaining small as compared to λ [10]; if we additionally assume that $\tilde{V}$ is slightly dependent of temperature in this case, then the intensity $|I_{1.5}| \propto \beta^3$ as CP is approached (regime I); 2) as we move to a closer vicinity of CP, where r_c increases drastically, the volume $\tilde{V}$ becomes more definite [9]: $\tilde{V} \approx 4\pi r_c^3/3 \propto \beta^{3/2}$; correspondingly, $|I_{1.5}| \propto \beta^{3/2}$ (regime II).

Our quantitative estimates are consistent with the results of our treatment of the experimental data of work [11] for xenon, where the dependence of the ratio Δ on the quantity $D \equiv k_0^{-4}[(\varepsilon_0 - 1)(\varepsilon_0 + 1)/12\pi]^{-2}(k_{\mathrm{B}}T\beta)^{-1}$ was studied in detail, if we take the values $\tilde{V} \approx (0.25 \div 4.5) \times 10^{-17}$ cm^3 to be the upper limit, beyond which regime II develops. In other words, we expect regime II to be certainly underway for the values $r_c \gtrsim (0.85 \div 2.2) \times 10^{-6}$ cm (the temperatures $\tau \lesssim (0.65 \div 3.0) \times 10^{-3}$ in the case of xenon).

To make estimates within the Van der Waals model, let us set $r_c = r_0\tau^{-1/2}$, $\tilde{V} = 4\pi r_c^3/3$ and $\beta = (6P_c)^{-1}\tau^{-1}$. For regime II, with the formulas of work [8], for the relative magnitudes of the intensity $I_{1.5}$ in comparison with I_1, the polarized double scattering intensity I_d, and the intensity I_{dd}, we get

$$\frac{|I_{1,5}|}{I_1} = K_1|\omega|\tau^{-1/2}, \quad \frac{|I_{1,5}|}{I_d} = K_d|\omega|\tau^{1/2},$$

$$\frac{|I_{1,5}|}{I_{dd}} = K_{dd}|\omega|\tau^{1/2}, \tag{7}$$

where the proportionality coefficient $K_1 = \left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)_T k_B T/8\pi\varepsilon_0 r_0^3 P_c$ is determined only by the parameters of the substance of the system, and the coefficients $K_d = 45/4\varepsilon_0\left(\rho\frac{\partial\varepsilon}{\partial\rho}\right)_T L r_0^3 k_0^4$ and $K_{dd} \approx 8K_d$ additionally depend upon the characteristic linear size L of the system and the wavelength λ_0. Using data [11] for xenon, for a system with $L = 0.547$ cm and a light wave with $\lambda_0 = 4.88 \times 10^{-5}$ cm, we have: $K_1 \approx 0.65$, $K_d \approx 1.6 \times 10^4$, and $K_{dd} \approx 1.3 \times 10^5$. As τ decreases from 1×10^{-3} to 1×10^{-4} along the $\omega = 6.8 \times 10^{-3}$ isochore, the ratio $|I_{1.5}|/I_1$ increases from 0.14 to 0.44, and the ratios $|I_{1.5}|/I_d$ and $|I_{1.5}|/I_{dd}$ decrease, respectively, from 3.4 to 1.1 and from 28 to 8.8. At the same time, the relative fractions $I_d/I_1 = R_d\tau^{-1}$ ($R_d = K_1/K_d$) and $I_{dd}/I_1 = R_{dd}\tau^{-1}$ ($R_{dd} \approx \frac{1}{8}R_d$) of the polarized and depolarized double scatterings increase, as compared to I_1, from 0.041 to 0.41 and from 5.1×10^{-3} to 5.1×10^{-2}, respectively.

Thus, far enough from CP and off the critical isochore, the sesquialteral scattering can prevail over the double one. The negative sign of $I_{1.5}$ for $\omega > 0$ makes it possible to separate $I_{1.5}$ from the total scattering intensity. Indeed, with the sesquialteral scattering present, the relation

$$\Delta = \frac{I_a + I_{dd}}{I_1 + I_{1.5} + I_d} \tag{8}$$

should be used instead of formula (1) for the ratio Δ. Rewrite (8) as

$$\frac{I_{dd}}{I_1\Delta} = \frac{1 + I_{1.5}I_1^{-1} + I_dI_1^{-1}}{1 + I_aI_{dd}^{-1}} \tag{9}$$

and take into account that $I_a \approx const$ as CP is approached. We see that if $I_{1.5} = 0$, then the left-hand side of (9) proportional to the quantity $k_BT\beta/\Delta$ should be a monotonic function of the quantity $k_BT\beta$. As CP is approached, this function initially increases rapidly, because of the rapid decrease of the denominator

on the right-hand side of (9). Then it becomes linear and gradually flattens out in the close vicinity of CP, where the growth of the intensity I_d slows down. In the presence of the contribution $I_{1.5} < 0$, such a monotonic behavior may be violated: we expect that the above function will decrease after the initial increase, pass through a minimum, then increase again, and gradually flatten out. Moreover, if the temperature regime II is achieved on the interval of decrease and, in addition, the condition $I_{1.5} \gg I_d$ is met, then the quantity $k_BT\beta/\Delta$ is expected to decrease by the law $const - (k_BT\beta)^{1/2}$.

The results of the processing of experimental data [11], which is carried out in [8,12] for the non-critical isochore $\omega = 6.8 \times 10^{-3}$ of xenon, agree well with these conclusions. Namely: 1) the $(D\Delta)^{-1}$ versus D^{-1} dependence is non-monotonic indeed, the maximum and minimum being reached at $\tau \approx 4.1 \times 10^{-3}$ and $\tau \approx 1.8 \times 10^{-4}$, respectively; 2) the $(D\Delta)^{-1}$ versus $D^{-1/2}$ dependence seems to be linear as τ decreases from 6.5×10^{-4} to 1.8×10^{-4}.

Taking into account the above-listed properties of $I_{1.5}$, consider the effect of the sesquialteral scattering on the ratio Δ at $\omega > 0$ in more details. According to the foregoing estimates, this scattering can considerably exceed the double scattering contribution in the region $\tau > 10^{-3}$. If so, and if the temperature regime I is realized, then the sesquialteral scattering will cause a temperature dependence of the same type (1) as that typical of the double scattering:

$$\Delta \approx \frac{I_a}{I_1 - |I_{1.5}|} \approx \frac{I_a}{I_1} + \frac{I_a|I_{1.5}|}{I_1^2} \approx A\beta^{-1} + C\omega\beta, \tag{10}$$

C being a constant. The emergence of a noticeable depolarized double scattering in the region $\tau \lesssim 10^{-3}$ and the simultaneous presence of $I_{1.5} < 0$ can manifest themselves as the rate of the increase of Δ with β getting higher:

$$\Delta \approx \frac{I_a + I_{dd}}{I_1 - |I_{1.5}|} \approx \frac{I_a}{I_1} + \frac{I_{dd}}{I_1} + \frac{I_a|I_{1,5}|}{I_1^2} + \frac{I_{dd}|I_{1,5}|}{I_1^2} \approx$$

$$\approx A\beta^{-1} + B\beta + C\omega\beta^x + D\omega\beta^y, \tag{11}$$

where the exponents $x = 1$, $y = 3$ for regime I, $x = -1/2$, $y = 3/2$ for regime II, and D is a constant. Finally, with the rate of increase of $|I_{1.5}|$ reducing in regime II, and the rate of increase of I_d being higher than the preceding one, a fall in Δ may occur in the region $\tau \lesssim 10^{-4}$. In particular, if we extrapolate relations (7) to this temperature region, formula (8) takes the form $\Delta \approx R_{dd}/(\tau - K_1\omega\sqrt{\tau} + R_d)$. This function has a maximum

at $\tau^* = K_1^2 \omega^2 / 4$, whose location is determined, for a given isochore, by the coefficient K_1 alone and should depend on neither L nor λ_0. For xenon, $\tau^* \approx 0.1 \omega^2$; in the case of CO_2 ($K_1 \approx 1.1$), this maximum moves away from CP: $\tau^* \approx 0.3 \omega^2$.

Thus, the inclusion of sesquialteral scattering effects into the overall scattering pattern makes it possible to explain the well-known features of the temperature behavior of the depolarization ratio in the vicinity of CP in a single way. Under certain conditions, the sesquialteral scattering contribution can be separated from the total scattering intensity. This fact offers an opportunity of the direct experimental evaluation of the third thermodynamic moment of the density fluctuations and the associated thermodynamic parameters, such as the gap critical exponent related to the third derivative of the Gibbs potential with respect to pressure.

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ПОЛУТОРНЕ МОЛЕКУЛЯРНЕ РОЗСІЯННЯ СВІТЛА В РІДИНАХ

М.Я. Сушко

Р е з ю м е

Викладено новий підхід до проблеми полуторного молекулярного розсіяння світла в однокомпонентних рідинах та наведено огляд основних результатів. Інтенсивність розсіяння виражається через третій термодинамічний момент флуктуацій густини. Аналіз її відносної величини та температурної залежності за допомогою моделі Ван-дер-Ваальса вказує на можливість експериментальної реєстрації полуторного розсіяння. Показано, що врахування ефектів полуторного розсіяння в загальній картині розсіяння дозволяє єдиним чином пояснити відомі особливості температурної поведінки коефіцієнта деполяризації в околі критичної точки.