

# Contribution to the theory of Rayleigh scattering of light in liquids

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It is shown that critical opalescence should be observed near the critical points for symmetrical (depolarized) scattering. The frequency dependence of the spectral intensity in the region of the closer Rayleigh-line wing is elucidated.

In the case of the Rayleigh scattering of light in liquids, a narrow "unshifted" line is produced as the result of fluctuations of the thermodynamic quantities

(pressure and entropy), with "wavelengths" on the order of the wavelength of the incident light, together with a broad background corresponding to scattering process-

es, which unlike the pure scalar scattering in the unshifted line are superpositions of a scalar and of a symmetrical (depolarization) scattering modes (see<sup>[1]</sup>). The unshifted line has been thoroughly investigated theoretically. No calculation of the background, on the other hand, is generally speaking possible without far-reaching model representations concerning the motion of the liquid particles, since the background is due usually to scattering by fluctuation rotation of the particles, and in general to scattering by changes, on an atomic scale, in the relative positions of the particles (see<sup>[2]</sup>).

1. The purpose of the present paper is to show that the part of the scattering corresponding to the region outside the unshifted line is due to fluctuations of thermodynamic quantities, whose "wavelengths" are large in comparison with the interatomic distance but are small in comparison with the wavelength of light, and that this part is decisive in certain important cases. More accurately speaking, we are dealing with fluctuations in the wave-vector distribution of the thermal fluctuations having the indicated wavelengths. The corresponding scattering contains a scalar part as well as the depolarized part. Indeed, consider a volume of liquid with dimensions that are small in comparison with the wavelength of the light, in which as a result of the fluctuation, the thermal fluctuations whose wavelengths are macroscopic but small in comparison with the volume dimensions have acquired predominantly the direction of the wave vector. It is clear that the mean value of the dielectric constant, which characterizes the considered volume, is in this case not a scalar quantity. In view of the macroscopic character of the problem, the indicated mean value can be easily calculated. We consider to this end some fluctuating thermodynamic quantity  $x$  (pressure, entropy, concentration) and write down its coordinate dependence in the form

$$x(\mathbf{r}) = \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} x_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}, \quad (1)$$

where  $V$  is the value of the considered volume. The dielectric constant differs from the equilibrium value by a small amount

$$\delta\epsilon(\mathbf{r}) = \frac{\partial\epsilon}{\partial x} \frac{1}{\sqrt{V}} \sum_{\mathbf{k}} x_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}}. \quad (2)$$

Since we are dealing of values of  $|\mathbf{k}|$  that greatly exceed the reciprocal wavelength of the light, the calculation of the averaged dielectric constant is perfectly analogous to the well-known derivation of the static dielectric constant of weakly inhomogeneous mixtures (see<sup>[1]</sup>, Sec. 9). The average deviation of the electric-induction vector from its value averaged over the volume is equal to  $\Delta\mathbf{D} = \delta\epsilon\delta\mathbf{E}$ , where the change  $\delta\mathbf{E}$  of the dielectric field is connected with  $\delta\epsilon$  by the equation  $\text{div } \delta\mathbf{D} = \text{div}(\delta\epsilon\mathbf{E} + \epsilon\delta\mathbf{E}) = (\mathbf{E} \cdot \nabla)\delta\epsilon + \epsilon \text{div } \delta\mathbf{E}$ . Expressing this in terms of Fourier components and recognizing that, by virtue of the potential character of  $\delta\mathbf{E}$ , the Fourier components  $\delta\mathbf{E}_{\mathbf{k}}$  is directed along  $\mathbf{k}$ , we obtain  $\delta\mathbf{E}_{\mathbf{k}} = -\delta\epsilon_{\mathbf{k}}(\mathbf{k} \cdot \mathbf{E})/\epsilon k^2$ , so that

$$\Delta D = -\frac{1}{V} \sum_{\mathbf{k}} \frac{\mathbf{k}(\mathbf{k}\mathbf{E})}{k^2} |\delta\epsilon_{\mathbf{k}}|^2 - \frac{1}{\epsilon V} \left( \frac{\partial\epsilon}{\partial x} \right)^2 \sum_{\mathbf{k}} \frac{\mathbf{k}(\mathbf{k}\mathbf{E})}{k^2} |x_{\mathbf{k}}|^2.$$

The effective dielectric constant is thus equal to

$$\epsilon_{ik} = \bar{\epsilon} \delta_{ik} - \frac{1}{\epsilon} \left( \frac{\partial\epsilon}{\partial x} \right)^2 \frac{1}{V} \sum_{\mathbf{k}} \frac{k_i k_k}{k^2} |x_{\mathbf{k}}|^2, \quad (3)$$

where  $\bar{\epsilon}$  is the result of the literal averaging of the dielectric constant over the considered volume, i. e., the result of integration over the volume followed by division by the volume.

Introducing the "distribution function"  $f_{\mathbf{k}} \equiv |x_{\mathbf{k}}|^2$  of the fluctuations, we write down the dielectric constant in the form

$$\epsilon_{ik} = \epsilon_0 \delta_{ik} - \frac{1}{\epsilon} \left( \frac{\partial\epsilon}{\partial x} \right)^2 \frac{1}{V} \sum_{\mathbf{k}} \frac{k_i k_k}{k^2} \Delta f_{\mathbf{k}}, \quad (4)$$

where  $\Delta f_{\mathbf{k}}$  is the fluctuation of the distribution function, i. e., its deviation from the equilibrium value  $|x_{\mathbf{k}}|^2$ . The difference between  $\epsilon_0$  and the dielectric constant of the equilibrium state is immaterial for our purposes, since it is due to fluctuations that contribute only to scattering corresponding to the unshifted line. The second term in (4) represents thus the fluctuation deviation of  $\epsilon_{ik}$  from the equilibrium value. We emphasize that the considered effect is due to dielectric-constant fluctuations that are proportional to the square of the deviations of the thermodynamic quantities from equilibrium value. The intensity of the scattering is in this case proportional to the fourth power of these deviations.

Since the fluctuations with values of  $k$  much smaller than the reciprocal interatomic distance have a small summary statistical weight, the considered scattering mechanism makes in general a contribution that is small in comparison with the total intensity of the background. We shall consider below, however, two cases in which it is precisely this mechanism which is decisive.

2. Let the liquid be in a state close to the critical point, where the so-called critical fluctuations increase abruptly, i. e., fluctuations of a certain parameter  $\eta$  (of the density for the liquid-gas critical point, of the concentration for the critical dissolution point, of the order parameter for a second-order phase transition), with small values of the wave vector  $\mathbf{k}$ . It is known that for scalar scattering this leads to critical opalescence. It is clear, however, that the mechanism considered above should cause critical opalescence also for depolarized scattering if the fluctuating quantity  $x$  is taken to be the critical parameter  $\eta$ . Let us calculate the scattering intensity, assuming that the critical point is described by the Landau theory (a generalization to the general case can be easily carried out with the aid of the well known scaling theory). The probability of the fluctuations is determined in this case by the formula (see<sup>[3]</sup>, Sec. 119)

$$w \sim \exp \left\{ - \sum_{\mathbf{k}} (a + b k^2) f_{\mathbf{k}} \right\},$$

where  $f_{\mathbf{k}} = |\eta_{\mathbf{k}}|^2$ ,  $b$  is a constant, and  $a$  is a function of the temperature  $T$  and vanishes in proportion to  $T - T_c$ .

at the point  $T_c$ . From this we obtain readily

$$\overline{\Delta f_{\mathbf{k}} \Delta f_{\mathbf{k}'}} = \frac{\delta_{\mathbf{k}\mathbf{k}'}}{(a+bk^2)^2} \quad (5)$$

With the aid of (4) and (5) we obtain ( $\mathbf{n} = \mathbf{k}/k$ ):

$$\overline{\Delta \epsilon_{i\mathbf{k}} \Delta \epsilon_{e\mathbf{m}}} = \frac{1}{V} \frac{1}{\epsilon^2} \left( \frac{\partial \epsilon}{\partial \eta} \right)^4 \int \frac{d^3 k}{(2\pi)^3} \frac{n_i n_k n_e n_m}{(a+bk^2)^2} \\ = \left\{ \frac{5}{3} \delta_{i\mathbf{k}} \delta_{e\mathbf{m}} + \left( \delta_{i\mathbf{e}} \delta_{k\mathbf{m}} + \delta_{i\mathbf{m}} \delta_{k\mathbf{e}} - \frac{2}{3} \delta_{i\mathbf{k}} \delta_{e\mathbf{m}} \right) \frac{(ab^3)^{-1/2}}{120\pi V \epsilon^2} \left( \frac{\partial \epsilon}{\partial \eta} \right)^4 \right\}$$

The first term in the curly brackets describes scalar scattering, and the remaining terms describe symmetrical scattering. Assuming that the wavelength of the light is large in comparison with the correlation radius  $(b/a)^{1/2}$ , we can use for the calculation of the corresponding extinction coefficients the customary formulas (see<sup>[1]</sup>, Sec. 95). We have

$$h_{\text{symm}} = 2h_{\text{scal}} = \frac{\Omega^4}{216\pi^2 c^4} \frac{(ab^3)^{-1/2}}{\epsilon^2} \left( \frac{\partial \epsilon}{\partial \eta} \right)^4 \quad (6)$$

where  $\Omega$  is the frequency of the scattered light and  $c$  is the velocity of the light in vacuum. Thus, the considered mechanism leads to scattering whose intensity increases like  $(T - T_c)^{1/2}$  as  $T \rightarrow T_c$ , whereas the intensity of the unshifted line increases, as is well known, in proportion to  $(T - T_c)^{-1}$ , i. e., much more rapidly. However, even the scalar part of (6) can be separated from the usual critical scattering, since the scattering (6) leads to a shift of the frequency of the light, on the order of the reciprocal time of attenuation of the critical fluctuations with wave vectors on the order of the reciprocal correlation radius, which is much larger than the width of the unshifted line.

3. Let us examine the frequency dependence of the spectral extinction coefficients  $h_{\text{scal}}(\omega)$  of the scalar scatterings, and  $h_{\text{symm}}(\omega)$  of symmetrical scattering, in the region of the near wing, i. e., frequency shifts  $\omega$  greatly exceeding the width of the unshifted line, but much smaller than the reciprocal characteristic relaxation times (Maxwellian time, Debye time, etc.) in the liquids. Choosing the pressure  $P$  and the entropy  $\sigma$  per unit mass as the independent variables describing the state of the liquid (single-component), and introducing the corresponding distribution functions  $f_{\mathbf{k}}(t) = |\delta P_{\mathbf{k}}|^2$  and  $g_{\mathbf{k}}(t) = |\delta \sigma_{\mathbf{k}}|^2$ , we obtain with the aid of standard fluctuation theory (see<sup>[3]</sup>, Sec. 121)

$$\overline{\Delta f_{\mathbf{k}}(\omega) \Delta f_{\mathbf{k}'}(\omega')} = 2\pi \delta(\omega + \omega') \delta_{\mathbf{k}\mathbf{k}'} \frac{2\rho^3 s^4 T^2 \gamma k^2}{\rho^2 \omega^2 + \gamma^2 k^4}$$

$$\overline{\Delta g_{\mathbf{k}}(\omega) \Delta g_{\mathbf{k}'}(\omega')} = 2\pi \delta(\omega + \omega') \delta_{\mathbf{k}\mathbf{k}'} \frac{c_p^2}{\rho^2} \frac{4\chi k^2}{\omega^2 + 4\chi^2 k^4} \quad (7)$$

where  $\rho$  is the density of the liquids,  $s$  is the speed of sound,  $\gamma = \frac{4}{3}\eta + \zeta + \chi(c_v^{-1} - c_p^{-1})$ ,  $\eta$  and  $\zeta$  are the first and second viscosity coefficients,  $\chi$  and  $\chi$  are the thermal conductivity and diffusivity coefficients, and  $c_p$  and  $c_v$  are the specific heats per unit mass. Since the fluctuations of the pressure and of the entropy are statistically independent, we obtain from (4) and (7)

$$\overline{\Delta \epsilon_{i\mathbf{k}}(\omega) \Delta \epsilon_{e\mathbf{m}}(\omega')} = 2\pi \delta(\omega + \omega') A_{i\mathbf{k}e\mathbf{m}}(\omega),$$

where

$$A_{i\mathbf{k}e\mathbf{m}}(\omega) = \frac{1}{V \epsilon^2} \int \frac{d^3 k}{(2\pi)^3} n_i n_k n_e n_m \left\{ \frac{2\rho^3 s^4 T^2 \gamma k^2}{\rho^2 \omega^2 + \gamma^2 k^4} \left( \frac{\partial \epsilon}{\partial P} \right) \right. \\ \left. + \frac{c_p^2}{\rho^2} \frac{4\chi k^2}{\omega^2 + 4\chi^2 k^4} \left( \frac{\partial \epsilon}{\partial \sigma} \right)^4 \right\} \quad (8)$$

The written integral diverges in the region of large  $k$ . This means that the main contribution to the wing intensity is made by fluctuations of atomic scale. However, if we calculate the derivative of (8) with respect to the frequency shift  $\omega$ , then we easily see that the main contribution to the derivative is made in the considered frequency region by fluctuations with microscopic wavelengths. This makes it possible to calculate the derivatives of the spectral extinction coefficients with respect to  $\omega$

$$\frac{\partial h_{\text{symm}}(\omega)}{\partial \omega} = 2 \frac{\partial h_{\text{scal}}(\omega)}{\partial \omega} = \frac{\Omega^4 |\omega|^{-1/2}}{216\pi^2 c^4 \epsilon^2} \frac{\omega}{|\omega|} \left[ \left( \frac{\partial \epsilon}{\partial P} \right)^4 s^4 T^2 \left( \frac{2\rho^7}{\gamma^3} \right)^{1/2} \right. \\ \left. + \left( \frac{\partial \epsilon}{\partial \sigma} \right)^4 \frac{c_p^2}{2\rho^2 \chi^{3/2}} \right] \quad (9)$$

referred to the frequency-shift interval  $d\omega/2\pi$ . The growth of the derivatives as  $\omega \rightarrow 0$  for the pressure fluctuations described in the first term in the square bracket of (9) stops when  $\omega$  is of the order of the width of the unshifted line. The second term of (9), on the other hand, retains its form down to much lower values of  $\omega$ , on the order of the width of the central component of the unshifted line.

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<sup>1</sup>L. D. Landau and E. M. Lifshitz, *Elektrodinamika sploshnykh sred* (Electrodynamics of Continuous media), Fizmatgiz, 1959 [Pergamon, 1957].

<sup>2</sup>I. L. Fabelinskii, *Molekulyarnoe rasseyanie sveta* (Molecular scattering of light), Nauka, 1965 [Cons. Bureau, 1968].

<sup>3</sup>L. D. Landau and E. M. Lifshitz, *Statisticheskaya fizika* (Statistical Physics), Nauka, 1964 [Pergamon, 1971].