

Spectroscopy of depolarized molecular scattering of light by liquids near the critical point

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It is shown that the spectrum of depolarized scattered light near the critical point has a complex structure, with three lines whose widths are different and have different temperature dependences. The widths are analyzed by considering the frequency moments of the spectral density. The narrowing of the Rayleigh-line wing is determined by double scattering effects. It is shown that instrumental effects have an important influence on the observed narrowing.

§1. INTRODUCTION

The relation between the slowing down of the order-parameter relaxation in the neighborhood of the critical point and the parameters of the spectra of polarized light scattering has been well studied.^{1–3} The most direct and the clearest way of demonstrating this relation is to examine the increase in the integrated intensity and the reduction in the width of the central component. In contrast, the role of different processes in the evolution of depolarized-scattering spectra has not been elucidated to the same extent. The experimental confirmation of the narrowing of the wing of the Rayleigh line (WRL) and of the Raman lines near the separation critical point of binary solutions^{4,9} was therefore partly unexpected. Here, it is important to note that, in a sufficiently wide range of frequencies, the depolarized-scattering spectrum can be approximately represented by the sum of two Lorentzians of different width. As the separation critical point is approached, the wider component becomes appreciably narrower, whereas the second component remains practically unaltered. This narrowing was not observed in Refs. 10–14, since only the narrower Lorentzian was examined in detail.

The most characteristic features of the WRL variation as the critical point is approached are as follows: (1) the narrowing of the spectra is nonmonotonic in most cases and there are usually two or three regions with different temperatures dependence of the width; (2) the narrowing appears to cease in a relatively close proximity of the critical point [$\varepsilon = (T - T_c)/T_c \lesssim 10^{-3}$].

Theoretical ideas on the narrowing mechanism are few and far between, and cannot explain even the most essential features of the phenomenon. It is important to note that, in liquids consisting of anisotropic molecules, depolarization occurs as a result of scattering by fluctuations in the anisotropy tensor $\varphi_{\alpha\beta}(\mathbf{r}, t)$ and because of multiple (mostly double) scattering by fluctuations in the order parameter $\eta(\mathbf{r}, t)$. As $T \rightarrow T_c$, the spectrum of the contributions due to multiple scattering should undergo an appreciable alteration. Several of the corresponding spectra parameters were studied near T_c in Refs. 15–17. On the other hand, the narrowing of the WRL was interpreted in Refs. 18 and 9 as the result of an interaction between fluctuations in $\varphi_{\alpha\beta}$ and η . The specific character of the result turns out to be governed by the lar-

gest-scale fluctuations in the order parameter. However, this conclusion is not entirely correct because the anisotropy relaxation time and the time necessary for the damping of long-wave modes are very different, so that the effect of the one on the other cannot be considerable. Nor is it valid to use the expression $1/\tau = k_B T / 8\pi\xi r_c^3$ (r_c is the correlation length and ξ is the shear viscosity) to describe the spectral linewidth. Formal use of this expression reproduces the temperature dependence of the width only within $\Delta T \approx 1-2$ K.

In this paper, we examine the relative role and the characteristic properties of different contributions to the spectrum of depolarized scattered radiation near the critical point, due to double scattering and the interaction between anisotropy modes and the order parameter. It will be shown that the specific temperature dependence of the spectral linewidth is largely determined by the Andreev mechanism.¹⁵ In the immediate neighborhood of T_c , the narrow line due to "intrinsic" double scattering plays the dominant role. However, the true narrowing is distorted by the superposition of instrumental effects.

§2. FLUCTUATION SPECTRUM OF THE DISTRIBUTION OF THERMAL FLUCTUATIONS IN THE NEIGHBORHOOD OF THE CRITICAL POINT

It has been shown¹⁵ that one of the components of depolarization molecular-scattering spectrum is due to fluctuations in the distribution function of thermal fluctuations. This mechanism has a general model-free character and is particularly effective near the critical point. In this section, we shall investigate the temperature dependence of the width of this contribution to WRL.

The fluctuation part of the permittivity tensor is given by¹⁵

$$\delta\varepsilon_{\alpha\beta}' = \frac{1}{\varepsilon_0} \left(\frac{\partial \varepsilon}{\partial \eta} \right)^2 \frac{1}{U} \sum_{\mathbf{k}} \frac{k_\alpha k_\beta}{k^2} \delta f_{\mathbf{k}}, \quad (1)$$

$$\delta f_{\mathbf{k}} = |\eta_{\mathbf{k}}|^2 - \langle |\eta_{\mathbf{k}}|^2 \rangle,$$

where $\eta_{\mathbf{k}}$ is the Fourier component of the order parameter and ε_0 is the equilibrium permittivity. The values of \mathbf{k} over which the sum is taken satisfy the inequality $\lambda^{-1} \ll \kappa \ll k \ll \Lambda \ll a^{-1}$, where λ is the wavelength of the incident radiation, a is the separation between the particles, and $U \propto \kappa^{-3}$.

Let us suppose that the scattered spectrum is determined by the correlator

$$j(\omega, \mathbf{q}) \propto \langle \delta \varepsilon_{xy}(\mathbf{r}, t) \delta \varepsilon_{xy}(0, 0) \rangle_{\omega, \mathbf{q}}, \quad (2)$$

where $\mathbf{q} = \mathbf{k}_s - \mathbf{k}_0$, and $\mathbf{k}_0, \mathbf{k}_s$ are the wave vectors of the incident and scattered waves, respectively. We shall assume that \mathbf{k}_0 lies along the z axis and \mathbf{k}_s is in the xz plane. We shall investigate the spectrum I^{HV} .

We shall now determine the width of the spectral function $j(\omega, \mathbf{q})$, using the first two frequency moments:

$$\Gamma = \left(\frac{C_2(\mathbf{q})}{C_0(\mathbf{q})} \right)^{1/2},$$

$$C_{2n}(\mathbf{q}) = \int_{-\infty}^{+\infty} d\omega \omega^{2n} j(\omega, \mathbf{q}), \quad n=0, 1, 2, \dots \quad (3)$$

The odd moments C_{2n+1} are all zero because of the symmetry of the spectral intensity $j(\omega, \mathbf{q})$. The efficiency of this definition in the study of the critical properties of Γ is due to the fact that, as $T \rightarrow T_c$, the zero-order moment undergoes the greatest change. The definition (3) does not depend on the particular form of $j(\omega, \mathbf{q})$ and the widths of standard profiles calculated in accordance with (3) differ from full widths, at half-height by a factor of the order of unity.

Formula (3) has the further advantage that it does not presuppose the use of the kinetic equations. Near the critical point, it is difficult to construct these equations and to calculate the kinetic coefficients in them.

The following representation is valid:

$$C_0(\mathbf{q}) \propto \langle \delta \varepsilon_{xy}(\mathbf{r}, 0) \delta \varepsilon_{xy}(0, 0) \rangle_{\mathbf{q}},$$

$$C_2(\mathbf{q}) \propto \langle \delta \dot{\varepsilon}_{xy}(\mathbf{r}, 0) \delta \dot{\varepsilon}_{xy}(0, 0) \rangle_{\mathbf{q}},$$

$$\delta \dot{\varepsilon}_{xy}(\mathbf{r}, 0) = \left. \frac{\partial \delta \varepsilon_{xy}(\mathbf{r}, t)}{\partial t} \right|_{t=0}. \quad (4)$$

The determination of the temperature properties of the above width is thus reduced to the evaluation of static correlators.

Let us now consider the contribution to scattering due to fluctuations (1) in the permittivity tensor. Since fluctuations $\delta \varepsilon'_{\alpha\beta}$ in volumes V_1 and V_2 separated by a distance $l > \kappa^{-1}$ are statistically independent, the zero-order moment $m_0(q)$ of the correlator $\langle \delta \varepsilon'(\mathbf{r}, 0) \delta \varepsilon'(0, 0) \rangle_{\mathbf{q}}$ is isotropic. Proceeding by analogy with Ref. 15, we obtain

$$m_0 \propto \frac{1}{\varepsilon_0^2} \left(\frac{\partial \varepsilon}{\partial \eta} \right)^4 V \frac{r_c}{2} \left[\frac{\pi}{2} - \arctan \kappa r_c + \frac{\kappa r_c}{1 + \kappa^2 r_c^2} \right], \quad (5)$$

where V is the volume of the system. The second moment is

$$m_2(q) \propto \int d\mathbf{k} \langle \dot{\eta}(\mathbf{r}, 0) \dot{\eta}(0, 0) \rangle_{\mathbf{k}} \langle \dot{\eta}(\mathbf{r}, 0) \dot{\eta}(0, 0) \rangle_{\mathbf{q}-\mathbf{k}}.$$

Since the fluctuation correlator $\langle \dot{\eta}(\mathbf{r}, 0) \dot{\eta}(0, 0) \rangle$ is a short-range quantity ($\propto \delta(\mathbf{r})$), and the main contribution to the integral is due to large values of k ($\kappa r_c \gg 1$), the moment m_2 is insensitive to the proximity to the critical point. Bearing this in mind, and using (3) and (5), we obtain the following expression well away from the critical point ($\kappa r_c \ll 1$):

$$\Gamma_1 = \left(\frac{m_2}{m_0} \right)^{1/2} = \Gamma_{01} \left(\frac{r_c}{r_{c0}} \right)^{-1/2} = \Gamma_{01} \varepsilon^{\nu/2}, \quad (6)$$

$$I_1 \equiv m_0 = I_{10} \frac{r_c}{r_{c0}} = I_{10} \varepsilon^{-\nu},$$

whereas, in the immediate neighborhood of T_c ($\kappa r_c \gg 1$), we have

$$\Gamma_{1c} \gg \Gamma_{01} (\lambda/r_{c0})^{-1/2}, \quad I_{1c} \ll I_{10} (\lambda/r_{c0}), \quad (7)$$

where Γ_{01} and I_{01} are taken at a temperature T_0 that is sufficiently different from T_c , and $r_{c0} = r_c(T_0)$.

Thus, as the critical point is approached, the intensity I_1 of the contribution due to fluctuations in the distribution function of thermal fluctuations will increase, whereas the width will decrease. At the same time, the product $I_1 \Gamma_1^2$ remains invariant, which follows directly from the definition of Γ_1 . In the Landau theory $\nu = \frac{1}{2}$ and in similarity theory $\nu \simeq 0.63$, so that the critical exponent describing the narrowing of the line is close to 0.3. In the immediate neighborhood of the critical point ($\Delta T_c \equiv T - T_c \leq 0.1-0.3$ K), the intensity and width reach their limiting values. It may be expected that the intensity will increase by the factor $\lambda/r_{c0} \sim 10-100$ and the width will fall roughly by an order of magnitude.

The relative Andreev-scattering intensity is determined by the ratio I_1/I_φ , where I_φ is the intensity scattered by anisotropy fluctuations. The quantity I_φ can be estimated in a standard way, using the Cabannes factors. It is readily shown from published data^{1,19} that the situation is particularly favorable in the case of solutions. For liquids such as benzene and ethyl alcohol, $I_1/I_\varphi \sim 3 \times 10^6 - 6 \times 10^6 \text{ cm}^{-1} r_c$ (near the liquid-vapor critical point, the ratio I_1/I_φ is lower by an order of magnitude). It may be expected that the intensities I_1 and I_φ become comparable for ΔT_c of the order of a few degrees ($T_c \simeq 300$ K). Comparison of these conclusions with experimental data shows good quantitative and qualitative agreement for temperatures in the range $\Delta T_c = (1-5)-(30-40)$ K (Fig. 1). For temperatures in the range $\Delta T_c \leq 1$ K, other still unaccounted for factors begin to play an important role. This can be seen, on the other hand, in the increase in the role of narrowing before the limiting value Γ_{1c} is reached and, on the other hand, in the appear-

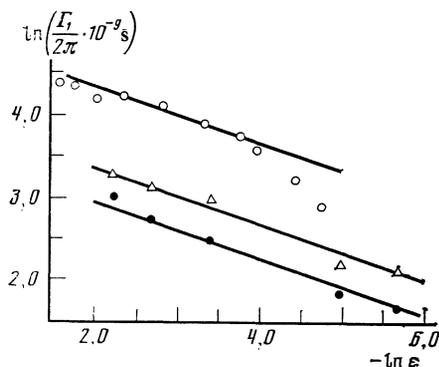


FIG. 1. Temperature dependence of Γ_1 . Points—experimental data: \circ — $\text{C}_2\text{H}_5\text{OH}-\text{CS}_2$, $c = 0.75$ molar fractions of CS_2 (Ref. 6); \bullet and \triangle —nitrobenzene- n -hexane, $c = 0.40$ and 0.75 molar fractions of n -hexane, respectively.⁹ The slope of these lines is numerically equal to $1/3$.

ance of an additional and rapidly rising component whose width decreases with a critical index $\simeq 0.6$.

These facts can be naturally explained by analyzing the overall picture of depolarized double scattering. The Andreev mechanism is an important component part of this. We now proceed to a presentation of our results.

§3. TEMPERATURE PROPERTIES OF THE DOUBLE-SCATTERED SPECTRUM

We shall write the doubly-scattered spectrum in the form

$$I(\omega) \propto \int d\mathbf{r}_1 \dots d\mathbf{r}_4 \exp[ik_0(\mathbf{r}_1 - \mathbf{r}_2) - ik_s(\mathbf{r}_3 - \mathbf{r}_4)] \\ \times T(\mathbf{r}_1 - \mathbf{r}_3) T^*(\mathbf{r}_2 - \mathbf{r}_4) \\ \times \langle \delta\eta(\mathbf{r}_1, t) \delta\eta(\mathbf{r}_2, 0) \delta\eta(\mathbf{r}_3, t) \delta\eta(\mathbf{r}_4, 0) \rangle_\omega, \\ T_{\alpha\beta}(\mathbf{r}) = (\nabla_\alpha \nabla_\beta + k_0^2 \delta_{\alpha\beta}) e^{ik_0 r} / r, \quad (8)$$

where $T(\mathbf{r})$ is the dipole propagator. The coefficient $(\partial\epsilon/\partial\eta)^4$ (and other standard factors) has no singularities as $T \rightarrow T_c$ and is omitted.

The integrated intensity is given by the zero-order moment C_0 of the spectrum (8):

$$C_0 \propto \int d\mathbf{r}_1 \dots d\mathbf{r}_4 \exp[ik_0(\mathbf{r}_1 - \mathbf{r}_2) - ik_s(\mathbf{r}_3 - \mathbf{r}_4)] \\ \times T(\mathbf{r}_1 - \mathbf{r}_3) T^*(\mathbf{r}_2 - \mathbf{r}_4) \\ \times \langle \delta\eta(\mathbf{r}_1, 0) \delta\eta(\mathbf{r}_2, 0) \delta\eta(\mathbf{r}_3, 0) \delta\eta(\mathbf{r}_4, 0) \rangle.$$

We now transform to the Fourier representation, using the formula

$$f(\mathbf{r}) = \frac{1}{V} \sum_{\mathbf{k}} e^{i\mathbf{k}\mathbf{r}} f(\mathbf{k}), \quad f = T, \delta\eta.$$

The dipole propagator and the four-point correlator for fluctuations in the order parameter have the following structure:

$$T_{\alpha\beta}(\mathbf{k}) \propto (k_\alpha k_\beta - k_0^2 \delta_{\alpha\beta}) / [k^2 - (k_0 + i\Delta)^2], \quad (10)$$

$$\langle \eta_{\mathbf{k}_1} \eta_{\mathbf{k}_2} \eta_{\mathbf{k}_3} \eta_{\mathbf{k}_4} \rangle = G(\mathbf{k}_1) G(\mathbf{k}_3) \delta_{\mathbf{k}_1, -\mathbf{k}_2} \delta_{\mathbf{k}_3, -\mathbf{k}_4} \\ + G(\mathbf{k}_1) G(\mathbf{k}_2) \delta_{\mathbf{k}_1, -\mathbf{k}_3} \delta_{\mathbf{k}_2, -\mathbf{k}_4} \\ + G(\mathbf{k}_1) G(\mathbf{k}_2) \delta_{\mathbf{k}_1, -\mathbf{k}_4} \delta_{\mathbf{k}_2, -\mathbf{k}_3} + G_4(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4), \\ G(\mathbf{k}_i) = \langle |\eta_{\mathbf{k}_i}|^2 \rangle. \quad (11)$$

After summation over \mathbf{k} , the quantity Δ in (10) tends to zero in an infinite system. In a spatially restricted system, Δ must be replaced in the final result by a small but finite quantity $\Delta \sim V^{-1/3}$ (Ref. 20). The last term in (11) describes irreducible four-point correlations. In the first order in the small parameter d , in the free energy

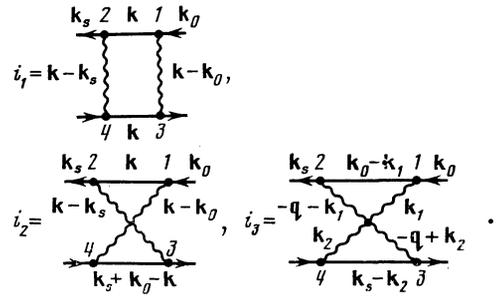
$$\Phi = \frac{1}{2} \int d\mathbf{r} \left[a\eta^2 + b(\nabla\eta)^2 + \frac{1}{2} d\eta^4 \right]$$

we have

$$G_4(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4) \\ = \frac{1}{2} d G(\mathbf{k}_1) G(\mathbf{k}_2) G(\mathbf{k}_3) G(\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3) \delta_{\mathbf{k}_4, \mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3}, \quad (12)$$

where $G(\mathbf{k}_i)$ is given by (11).

Structurally different contributions to C_0 are conveniently represented by the diagram technique used in the theory of multiple scattering of light.²⁰ We have $C_0 = i_1 + i_2 + i_3$, where



The upper line entering the vertex 1 corresponds to the incident wave whilst the outgoing line represents the scattered wave. The segment of the line between the two vertices corresponds to the propagator $T(\mathbf{k})$. For the lower line, the notation is the same except that we have to add the complex conjugation symbol. The star consisting of the four wavy lines, which have a common vertex and pass through the points 1, 2, 3, 4 in the third diagram, represents the irreducible part of the four-point correlator.

Integrals similar to i_1, i_2, i_3 are encountered in quantum electrodynamics.²¹ The first of these three diagrams is evaluated in Appendix A. The main results can be summarized as follows.

The zero-order moment can be written as the sum of two contributions of different physical origin:

$$C_0 = m_0 + p_0. \quad (13)$$

The term m_0 describes the contribution to scattering of short-wave fluctuations in the order parameter. It is characterized by a linear dependence on volume: $m_0 \propto V g_1(u)$, $u \equiv k_0 r_c$. When u is small, the function $g_1(u)$ is proportional to r_c whereas in the immediate neighborhood of T_c the function $g_1(u)$ is found to reach its limiting value for $u \gtrsim 1$. A detailed analysis of the parameters of the short-wave mechanism was given in the last section.

The term p_0 in (13) represents the contribution of distant dipole re-emission to the total doubly-scattered intensity. Strictly speaking, it is only scattering of this type (the second radiator lies in the wave zone of the first) that should be regarded as double scattering. It is characterized by a nonlinear dependence on volume: $p_0 \propto V^{4/3} g_2(u)$. For small u , we have $g_2(u) \propto u^4$ and, as can be seen from (A3), this leads to the isotropic scattering pattern. An appreciable dependence on the scattering angle becomes apparent as u increases. The quantity p_0 also reaches its limiting value in the neighborhood of T_c . This mechanism was investigated in Ref. 16, 17, 20, and 22–24 and elsewhere (see also Ref. 25).

It is important to note the following. In the zero-order approximation, the short-wave contributions of diagrams i_1 and i_2 are the same and the corresponding contribution of diagram i_3 is negligible. The former statement is obvious and the second is readily verified:

$$i_3 \propto \int d\mathbf{k}_1 \int d\mathbf{k}_2 T(\mathbf{k}_0 - \mathbf{k}_1) T^*(\mathbf{k}_s - \mathbf{k}_2) G_4(k_1, k_2, -\mathbf{q} - \mathbf{k}_1, -\mathbf{q} + \mathbf{k}_2).$$

The functions G_4 is given by (12). Since $q, k_0, k_s \ll k_1, k_2$, we can put $q = k_0 = k_s = 0$ in the zero-order approximation. It is readily seen from (12) that i_3 will be zero. In the long-wave region, the only dominant diagram will be diagram i_1 . Thus, according to Ref. 22, the ratio i_3/i_1 does not exceed $10^{-2}e^{2\nu}$. From the physical point of view, the small value of the ratio i_2/i_3 is explained by the rapid attenuation of correlation with increasing separation between the scattering centers.

The contribution to the second moment due to diagram i_1 is

$$C_2^{(1)} \propto V \int d\mathbf{k} |T(\mathbf{k})|^2 [G(\mathbf{k} - \mathbf{k}_0) \check{G}(\mathbf{k} - \mathbf{k}_s) + \check{G}(\mathbf{k} - \mathbf{k}_0) G(\mathbf{k} - \mathbf{k}_s)], \quad (14)$$

$$\check{G}(\mathbf{k}) = \langle |\dot{\eta}_{\mathbf{k}}|^2 \rangle, \quad \dot{\eta}_{\mathbf{k}} = -D(k) k^2 \eta_{\mathbf{k}}.$$

It is shown in Appendix B that the spatial dispersion of the mutual diffusion coefficient of the solutions is described by

$$D(k) = (k_B T / 6\pi\xi) (B^{-1} G(\mathbf{k}))^{-1/2},$$

so that

$$\check{G}(\mathbf{k}) = B (k_B T / 6\pi\xi)^2 k^4.$$

The principal contribution to (14) is due to small-scale fluctuations:

$$m_2 \propto {}^8/_{75}\pi V B^2 (k_B T / 6\pi\xi)^2 \Lambda^5 [1 + O(k_0^2/\Lambda^2)], \quad (15)$$

where Λ is the cutoff parameter ($\Lambda \ll 1/a$). The principal contributions to $\check{G}(\mathbf{k})$ and $C_2^{(1)}$ are practically insensitive to the critical point. The contribution of the poles of the propagator in (14) does not have a simple structure. When $u \ll 1$, we have

$$p_2^{(1)} \propto {}^8/_{15}\pi^2 V^{4/3} B^2 (D_0 r_0)^2 k_0^8 r_c^2 [1 + {}^{1/7}(1 + \sin^2 \theta)], \quad (16)$$

where $D_0 = k_B T / 6\pi\xi r_0$ is the diffusion coefficient well away from T_c and θ is the scattering angle. When $u \gtrsim 1$, the explicit form of $p_2^{(1)}$ for arbitrary θ is complicated and inconvenient for analysis. We shall now exploit the fact that, usually, $\theta = 90^\circ$, in which case the contribution of the poles in $C_2^{(1)}$ is given by

$$p_2^{(1)}(\theta=90^\circ) \propto \frac{\pi^2}{8} V^{4/3} B^2 (D_0 r_0)^2 k_0^8 F \left\{ -\frac{13}{15} + \frac{20}{3} F^2 - F^4 + \frac{1}{2} \left[F^5 - 7F^3 + 3F + \frac{3}{F} \right] \ln \frac{F+1}{F-1} \right\}, \quad (17)$$

where $F \equiv 1 + 1/2u^2$ and we have used the approximate results

$$(\mathbf{k} - \mathbf{k}_i)^4 \approx 4k_0^4 (1 - \mathbf{n}\mathbf{n}_i)^2, \quad \mathbf{n} = \mathbf{k}/k, \quad \mathbf{n}_i = \mathbf{k}_i/k_0 \quad (i=0, s),$$

which will also improve the convergence of the corresponding integrals.

When $u \ll 1$, expression (17) becomes identical with (16) for $\theta = 90^\circ$. In the neighborhood of the critical point, $p_2^{(1)}$ reaches the limiting value

$$p_{2c}^{(1)}(\theta=90^\circ) \propto {}^3/_{5}\pi^2 V^{4/3} B^2 (D_0 r_0)^2 k_0^6. \quad (18)$$

We now note the following points in relation to the contribution of diagrams i_2 and i_3 to the first moment. The magnitudes of the short-wave contributions generated by i_2 are the same in the zero-order approximation as those for diagram i_1 . On the other hand, since the contribution of the propagator poles of diagram i_2 and the resultant contribution of diagram i_3 to the zero-order moment are negligible, there is no need to calculate the other spectral parameters. We thus have $m_2 \approx 2m_2^{(1)}$, $p_2 \approx p_2^{(1)}$.

The fact that the short-wave and long-wave contributions to the moments of the doubly-scattered spectral intensity can be separated is a reflection of the fact that they describe different processes. The long-wave contribution is characterized by a different temperature dependence and different response to a change in the dimensions of the system. This is confirmed by the fact that the doubly-scattered spectrum is the sum of two profiles with different widths and different integrated intensities. It is clear from (A3) that m_0 and p_0 are of the same order of magnitude when $r_c(\varepsilon^*) \approx k_0^{-4/3} V^{-1/9}$ which means that, when $V \approx 1 \text{ cm}^3$ and $k_0 \approx 10^5 \text{ cm}^{-1}$, we have $\varepsilon^* \approx 0.02-0.03$ or $\Delta T_c^* \approx 7 \text{ K}$. When $\Delta T_c > \Delta T_c^*$, the Andreev mechanism predominates, whereas for $\Delta T_c < \Delta T_c^*$ the double re-emission mechanism is predominant. According to (A3) and (15), the width $\Gamma_1 = (m_2/m_0)^{1/2}$ varies in accordance with

$$\Gamma_1 = \frac{k_B T}{6\pi\xi} \left(\frac{8}{5\pi} \Lambda^5 \right)^{1/2} r_c^{-1/2} \quad (u \ll 1). \quad (19)$$

The temperature dependence of Γ_1 is determined by the correlation length and shear viscosity. The influence of the latter may be reduced by ensuring that the experiments are performed under isochoric conditions. The reduction in the Andreev contribution ceases for $u \gtrsim 1$. Assuming that $\Lambda \approx 5 \times 10^7 - 7 \times 10^7 \text{ cm}^{-1}$, $\xi \approx 0.005 \text{ Pa}$, and $r_0 \approx 2.5 \times 10^{-8} \text{ cm}$, we find from (19) that $\Gamma_{01}/2\pi \approx 10^{10} \text{ s}^{-1}$ for $\Delta T_c \approx 30 \text{ K}$ and then decreases to $\Gamma_1/2\pi \approx 3 \times 10^9 \text{ s}^{-1}$ for $\Delta T_c \approx 1 \text{ K}$.

In contrast to the Andreev-type scattering, the intrinsic double-scattering linewidth is very small. It follows from (A3) and (16) that the width $\Gamma_2 = (p_2/p_0)^{1/2}$ for small u is given by

$$\Gamma_2 = 2^{1/2} D_0 r_0 k_0^2 r_c^{-1} [1 + {}^{1/7}(1 + \sin^2 \theta)]^{1/2}. \quad (20)$$

The maximum value of Γ_2 is reached well away from the critical point: $\Gamma_{20}/2\pi \lesssim 10^5 \text{ s}^{-1}$. When the scattering angle is fixed, the temperature variation of Γ_2 is the same as that of the width Γ_0 of the central component of polarized singly-scattered spectrum. However, in contrast to Γ_0 , the angular dependence of Γ_2 is not well defined. It follows from (20) that their ratio is

$$\Gamma_2(\theta)/\Gamma_0(\theta) = 2^{-1/2} [1 + {}^{1/7}(1 + \sin^2 \theta)]^{1/2} / \sin^2(\theta/2).$$

In the immediate neighborhood of T_c , the width Γ_2 assumes its minimum value Γ_{2c} which, according to (18) and (A4), is given by

$$\Gamma_{2c}(\theta=90^\circ) = 2[6/5(2 \ln 2 - 1)]^{1/2} D_0 r_0 k_0^3. \quad (21)$$

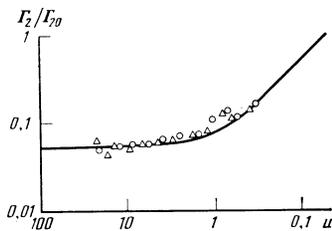


FIG. 2. The ratio Γ_2/Γ_{20} as a function of u . Points—experimental data for the methanol-cyclohexane solution.²⁶ The value of Γ_{20} is taken at $u = 0.05$ and is: \circ — $\Gamma_{20}/2\pi = 6.87 \times 10^3 \text{ s}^{-1}$ ($\lambda = 5145 \text{ \AA}$); \triangle — $\Gamma_{20}/2\pi = 9.74 \times 10^3 \text{ s}^{-1}$ ($\lambda = 4579 \text{ \AA}$). Solid line—theoretical.

The order-of-magnitude estimate is $\Gamma_{2c}/2\pi \approx k_0 r_0 \Gamma_{20}/2\pi \approx 5 \cdot 10^2 \text{ s}^{-1}$. Lines of this width are usually examined in detail by correlation spectroscopy. Comparison with experimental data²⁶ shows that all the most characteristic features of the temperature behavior of Γ_2 can be satisfactorily reproduced (Fig. 2). We note that the analysis of the linewidth by the method of moments provides a painless way of proceeding from the hydrodynamic region ($u \ll 1$) to the fluctuation region ($u \gg 1$).

§4. INSTRUMENTAL EFFECTS

The essential point here is that, in the usual experiments on WRL structure, the parameters of a doubly-scattered line are highly distorted by instrumental effects. Instead of the expected line $I(\omega)$, the system will record $\tilde{I}(\omega)$, which is related to $I(\omega)$ and the instrumental function $A(\omega)$ by¹

$$\tilde{I}(\omega) = \int_{-\infty}^{+\infty} d\omega' I(\omega') A(\omega - \omega').$$

The instrumental function can be satisfactorily approximated by the Lorentzian $A(\omega) \propto \Gamma_A/(\omega^2 + \Gamma_A^2)$ provided the frequency interval is not too wide. The wide Γ_A of the Lorentzian turns out to be^{6,8} smaller than Γ_{01} by roughly an order of magnitude and, essentially, the intrinsic doubly-scattered line may be regarded as a delta-function, in which case,

$$\tilde{I}_2(\omega) \propto p_0 \Gamma_A/(\omega^2 + \Gamma_A^2).$$

Let $\Gamma_{01} = 11\Gamma_A$. The observed doubly-scattered spectrum is then the sum of two lines:

$$\tilde{I}(\omega) \propto \frac{1}{1 + \varepsilon^{-\nu} x^2} + \frac{R(\varepsilon)}{1 + 121x^2}, \quad x \equiv \frac{\omega}{\Gamma_{01}}, \quad (22)$$

$$R(\varepsilon) = R_0 \varepsilon^{-5\nu/2}, \quad R_0 = 11k_0^4 r_0^3 V^{1/2}.$$

Apart from (22), the spectrum will also contain a component due to the scattering of light by anisotropy fluctuations. However, this will have no effect on our subsequent conclusions.

The procedure used to determine the width of the Lorentzians that together describe the experimental data $I_e(\omega)$ is as follows. The first step is to plot $I_e^{-1}(\omega)$ as a function of ω^2 . Straight-line segments are then identified (this is possible when the linewidths are essentially different). These segments are then extrapolated until they cut the I_e^{-1} axis. The

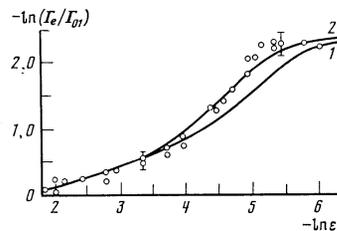


FIG. 3. Temperature dependence of Γ_e . Points—experimental data for the $\text{C}_2\text{H}_5\text{OH}-\text{CS}_2$ solution.⁶ The value of Γ_{01} is taken for $-\ln \varepsilon = 1.65$ and is $\Gamma_{01}/2\pi = 2.97 \text{ cm}^{-1}$. Curves 1 and 2 show the results of a theoretical calculation based on (22) with $R_0 = 0.1$ and $R_0 = 0.3$, respectively.

values of ω^* for which $I_e^{-1}(\omega^*) = 2I_e^{-1}(0)$ then give the values of the corresponding widths.

Let us apply this procedure to the function $\tilde{I}(\omega)$. So long as $\Delta T_c > \Delta T_c^*$, the second term in (22) can be neglected. The condition $\tilde{I}^{-1}(\omega) = 2\tilde{I}^{-1}(0)$ will determine the width of the Andreev line. However, because of the rapid rise in $R(\varepsilon)$ even for $\Delta T_c \approx 1 \text{ K}$, the width of the observed line will be determined by the width of the instrumental function. In fact, the width Γ_e of the resultant line falls by a factor of between nine and seven in the range 3–5 K. Assuming that $\Gamma_e \sim \varepsilon^\nu$, we find that for $R_0 = 0.1$ the exponent ν is close to 0.8. For $R_0 = 0.3$, the index approaches 0.95 (the values of R_0 are somewhat different for different media). All these facts are in good agreement with the experimental data (Fig. 3).

Thus, the rapid narrowing of the WRL in the immediate ($\Delta T_c < \Delta T_c^*$) neighborhood of T_c is most likely to be due to the rapid rise in the intensity of intrinsic double scattering and the distortions introduced by the instrumental function.

§5. RELAXATION OF THE ANISOTROPY TENSOR

Let us now examine the other mechanisms that can give rise to the narrowing of the molecular scattering spectrum produced by the solutions of liquids consisting of anisotropic molecules. For simplicity and greater clarity, let us consider the solution of anisotropic molecules in a solvent consisting of isotropic molecules. The depolarized molecular-scattering spectrum is then determined by the correlator of fluctuations in anisotropy $\varphi_{\alpha\beta}$:

$$I_\varphi(\omega, q) \propto \langle \varphi_{xy}(\mathbf{q}, t) \varphi_{xy}(-\mathbf{q}, 0) \rangle_\omega. \quad (23)$$

If we neglect the mutual effect of the molecules, we have

$$\begin{aligned} \varphi_{\alpha\beta}(\mathbf{r}, t) &= \sum_i J_{\alpha\beta}^i(t) \delta(\mathbf{r} - \mathbf{r}_i(t)), \\ \varphi_{\alpha\beta}(\mathbf{q}, t) &= \sum_i J_{\alpha\beta}^i(t) \exp[i\mathbf{q}\mathbf{r}_i(t)], \end{aligned} \quad (24)$$

where J^i is the polarizability tensor of the i th molecule. In particular, it may be due to the mechanical anisotropy of the molecules. It is usually assumed (see Ref. 27) that, for $\omega > \nu q^2 \sim 10^8$, the anisotropy tensor satisfies the following simple relaxation law:

$$\dot{\varphi}_{\alpha\beta}(\mathbf{q}, t) = -\varphi_{\alpha\beta}(\mathbf{q}, t)/\tau,$$

so that

$$I_q(\omega, q) \propto \gamma_0 / (\gamma_0^2 + \omega^2), \quad \gamma_0 = 1/\tau.$$

The time τ can be estimated with the aid of some particular hydrodynamic model and, for solutions, it can be a function of concentration: $\tau = \tau(c)$. The essential point is that the rotational motion of the molecules is not the only mechanism responsible for the variation in $\varphi_{\alpha\beta}(\mathbf{r}, t)$.

The density of the anisotropy tensor (24) will also vary as a result of fluctuations in the concentration of impurity molecules:

$$\dot{c}(\mathbf{k}, t) = -D(k) k^2 c(\mathbf{k}, t).$$

The effect is particularly noticeable in small volumes (large k). Accordingly, $\varphi_{\alpha\beta}$ satisfies the equation

$$\dot{\varphi}_{\alpha\beta} = -\gamma(c) \varphi_{\alpha\beta} - \text{div}(\varphi_{\alpha\beta} \mathbf{u}), \quad (25)$$

where $\mathbf{u}(\mathbf{r}, t)$ is the hydrodynamic velocity in the diffusion equation $c\mathbf{u} = -D\nabla c$. It is assumed that, in general, the mutual diffusion coefficient is nonlocal. The appearance of the contribution $\text{div}(\varphi_{\alpha\beta} \mathbf{u})$ is not unexpected if we interpret $\varphi_{\alpha\beta}$ as the polarization density. This density is an extensive quantity in the molecular system. Equation (25) can also be looked upon as the equation for the density of the moments of inertia of the molecule. To take into account the effect of fluctuations in concentration on the nonconserved part of $\varphi_{\alpha\beta}$, we expand the coefficient $\gamma(c)$ into a series:

$$\gamma(c) = \gamma_0 + \gamma_1 c + \gamma_2 c^2 + \dots, \quad \gamma_i = \gamma_i(\bar{c}), \quad (26)$$

where \bar{c} is the equilibrium concentration and c is the deviation from \bar{c} . This expansion corresponds to the deviation

$$\delta\Phi = 1/2 \alpha_1 \varphi_{\alpha\beta}^2 + 1/2 \alpha_2 \varphi_{\alpha\beta}^2 c^2$$

of the thermodynamic potential Φ from its equilibrium value and to the expansion of the coefficient λ in the equation $\dot{\varphi}_{\alpha\beta} = -\lambda \delta\Phi / \delta\varphi_{\alpha\beta}$ in powers of c :

$$\lambda = \lambda_0 + \lambda_1 c + \lambda_2 c^2 + \dots$$

In the last case, the existence of linear terms is not forbidden by stability considerations. Expansion (26) is meaningful so long as the correction terms are small in comparison with γ_0 .

We must also take into account the fact that the angular correlation between the anisotropic molecules is quite weak. Accordingly, the terms $\mathbf{u} \nabla \varphi_{\alpha\beta}$ in (25) can be neglected. In the approximation that is quadratic in the fluctuations, we have

$$\dot{\varphi}_{\alpha\beta} = -(\gamma_0 + \gamma_1 c + \gamma_2 c^2) \varphi_{\alpha\beta} - \varphi_{\alpha\beta} \text{div} \mathbf{u}. \quad (27)$$

The term $\varphi \text{div} \mathbf{u}$ describes the variation in φ due to the loss of particles by diffusion from the neighborhood of the point \mathbf{r} . An interaction between φ and c should lead to strong frequency dispersion of the width function because an anomalous rise in large-scale concentration fluctuations near the critical point cannot radically alter the character of small-scale rotational motion of the molecules.

Equation (27) may be looked upon as a relaxation equation with a random force:

$$\dot{\varphi}_{\alpha\beta} = -\gamma_0 \varphi_{\alpha\beta} - \varphi_{\alpha\beta} \psi(\mathbf{r}, t), \quad \psi(\mathbf{r}, t) = \gamma_1 c + \gamma_2 c^2 + \text{div} \mathbf{u}. \quad (28)$$

This has the obvious solution

$$\varphi_{\alpha\beta}(t) = K \exp \left\{ -\gamma_0 t - \int_0^t dt' \psi(t') \right\} \varphi_{\alpha\beta}(0) \quad (K = \text{const}). \quad (29)$$

Substituting this in (28) and averaging over all the possible realizations of the field ψ , we obtain the equations for the smoothly-varying variable $\bar{\varphi}$:

$$\begin{aligned} \dot{\bar{\varphi}}_{\alpha\beta} &= -\bar{\gamma}_{\alpha\beta} \bar{\varphi}_{\alpha\beta}, \quad \bar{\gamma}_{\alpha\beta}(t) = -\gamma_0 \bar{\varphi}_{\alpha\beta}(t) \\ &- \left\langle \psi(t) \exp \left\{ -\int_0^t dt' \psi(t') \right\} \right\rangle K \exp(-\gamma_0 t) \bar{\varphi}_{\alpha\beta}(0). \end{aligned} \quad (30)$$

The average in this equation can be determined by the Furutsu-Novikov method.^{28,29} Here, we take into account the fact that the correlation properties of the field $\psi(t)$ can be described with good precision by the Gaussian approximation. We then have^{28,29}

$$\begin{aligned} &\left\langle \psi(t) \exp \left\{ -\int_0^t dt' \psi(t') \right\} \right\rangle \\ &= -\int_0^t dt' \langle \psi(t) \psi(t') \rangle \left\langle \exp \left\{ -\int_0^{t'} dt'' \psi(t'') \right\} \right\rangle, \end{aligned}$$

which, together with (30), leads to

$$\dot{\bar{\varphi}}_{\alpha\beta} = -\gamma_0 \bar{\varphi}_{\alpha\beta} + \int_0^t dt' \langle \psi(t) \psi(t') \rangle \bar{\varphi}_{\alpha\beta}(t'). \quad (31)$$

After the Fourier transformation of (31) with respect to time, and the application of the fluctuation-dissipation theorem, we obtain

$$\begin{aligned} &\langle \bar{\varphi}_{xy}(t) \bar{\varphi}_{xy}(0) \rangle_{\omega} \\ &= \langle \bar{\varphi}_{xy}^2(0) \rangle \cdot 2 \text{Re} \left([-i\omega + \gamma_0 - \langle \psi(t) \psi(0) \rangle_{\omega}]^{-1} \right). \end{aligned} \quad (32)$$

The diffusion equation $\dot{c} = -\text{div} \bar{c} \mathbf{u}$, where $\bar{c} \mathbf{u} = -D\nabla c$, leads to

$$\langle \text{div} \mathbf{u} \text{div} \mathbf{u} \rangle_{\omega} = (\omega^2 / \bar{c}^2) \langle c(\mathbf{r}, t) c(\mathbf{r}, 0) \rangle_{\omega}.$$

Finally, the contribution of fluctuations in anisotropy to the spectrum of depolarized scattered radiation is given by

$$\begin{aligned} I_q(\omega) &\propto \text{Re} \left(\left[-i\omega + \gamma_0 - \left(\frac{\omega^2}{\bar{c}^2} + \gamma_1^2 \right) \langle c(\mathbf{r}, t) c(\mathbf{r}, 0) \rangle_{\omega} \right. \right. \\ &\left. \left. - \gamma_2^2 \langle c^2(\mathbf{r}, t) c^2(\mathbf{r}, 0) \rangle_{\omega} \right]^{-1} \right). \end{aligned} \quad (33)$$

In contrast to the contributions proportional to γ_1^2 and γ_2^2 , which are small in comparison with γ_0 , the diffusion contribution $(\omega^2 / \bar{c}^2) \langle c(\mathbf{r}, t) c(\mathbf{r}, 0) \rangle_{\omega}$ is comparable with γ_0 for $\omega \sim \gamma_0$. It follows directly from the diffusion that

$$\langle c(\mathbf{r}, t) c(\mathbf{r}, 0) \rangle_{\omega} = B r_c^2 \sum_k \frac{1}{-i\omega + D(k) k^2} \frac{1}{1 + k^2 r_c^2}.$$

If we neglect the dispersion of the diffusion coefficient, the above sum can be evaluated very simply:

$$\langle c(\mathbf{r}, t) c(\mathbf{r}, 0) \rangle_\omega = \frac{\sqrt{2} Br_c^2}{8\pi D_0 r_0 (1 + \Omega^2)} \{ (\sqrt{2} - \Omega^{1/2} + \Omega^{3/2}) + i\Omega^{1/2} (1 - \sqrt{2} \Omega^{1/2} + \Omega) \}, \quad \Omega \equiv \omega \frac{r_c^3}{D_0 r_0}.$$

When the spatial dispersion of $D(k)$ is taken account (see Appendix B), the result becomes very unwidely. The first few terms of the asymptotic expressions are as follows:

$$\langle c(\mathbf{r}, t) c(\mathbf{r}, 0) \rangle_\omega = \frac{Br_c^2}{2\pi^2 D_0 r_0} \begin{cases} 1 - \left(2 + \frac{\pi\sqrt{2}}{4}\right) \Omega^{1/2} + 2\Omega + \dots \\ + i \frac{\pi\sqrt{2}}{4} \Omega^{1/2} (1 - \sqrt{2} \Omega^{1/2} + \Omega + \dots), & \Omega \ll 1, \\ \frac{\pi\sqrt{3}}{9\Omega^{3/2}} \left(1 - \frac{1}{2\Omega^{3/2}} + \frac{5}{16\Omega^2} + \dots\right) \\ + i \frac{\pi}{3\Omega^{3/2}} \left(1 - \frac{3}{2\Omega^{3/2}} + \frac{1}{\Omega^{3/2}} + \dots\right), & \Omega \gg 1. \end{cases} \quad (34)$$

It is clear from (33) and (34) that, for $0 < \omega < D_0 r_0 / r_c^3$, the width of the profile is reduced by the amount

$$\Delta\gamma \sim Br_c^2 \gamma_1^2 / 2\pi^2 D_0 r_0 \sim 10^{-18} (\gamma_1^2 / b) \varepsilon^{-2\nu}.$$

Moreover, $D_0 r_0 / r_c^3 \sim \gamma_0$ only at sufficient distance from the critical point ($\Delta T_c > 20$ K). Correspondingly, the intensity at zero frequency increases by the factor $1 + \Delta\gamma / \gamma_0$. The validity of these estimates is restricted by the condition $\Delta\gamma / \gamma_0 < 1$. The contribution $\gamma_2^2 \langle c^2(\mathbf{r}, t) c^2(\mathbf{r}, 0) \rangle_\omega$ has an analogous behavior, but its magnitude is much smaller.

There is, however, a more important point that, perhaps, should be brought out here. The diffusion contribution to the width function leads to a departure of the line shape from the Lorentz shape and to the corresponding slowing down in the reduction in intensity $I_\varphi(\omega)$ for $\omega > \gamma_0$: $I_\varphi(\omega) \propto \omega^{-4/3}$. The approximation of this profile by a set of Lorentzians is then physically incorrect and may lead to spurious effects. The essential point is that the integrated intensity of this contribution remains practically the same as T_c is approached.

Thus, we may conclude that it is only well away from the critical point that anisotropy fluctuations can lead to observable effects, i.e., a reduction in the linewidth and an increase in intensity at zero frequencies.

§6. DISCUSSION

We have shown that the narrowing of the WRL in solutions near the critical point is largely determined by double scattering effects. For temperatures in the range $T_c + \Delta T_c^* < T < T_c + (30-40)$ K, we have $\Gamma_1 \propto \varepsilon^{\nu/2} / \xi$ and the narrowing is determined by the Andreev mechanism. The contribution of this mechanism is an appreciable fraction of the intensity scattered by anisotropy fluctuations, which increases as the critical point is approached.

The accelerated narrowing of the WRL near the critical point is not actually due to any particular mechanism but is

the result of the influence of the instrumental function. This can be readily verified by varying its width and form. We draw attention to the fact that it will be essential to increase the precision of experimental data. It can be directly verified that an error of a few percent in the measured $I_e^{-1}(\omega)$ in the region in which there is a rapid narrowing leads to an appreciable change in the temperature behavior of Γ_e . In particular, this may lead to the appearance of "steps." We note that the influence of double-scattering effects can violate the condition $\Delta_h = I^{HH} / I^{HV} = 1$ in the region of rapid narrowing.

The spectrum of anisotropy fluctuations undergoes a definite change only well away from the critical point. The more important result here is that the line profile is not analytic and cannot be represented approximately by a finite set of Lorentzians.

We are indebted to A. F. Andreev, I. L. Fabelinskiĭ, and V. S. Starunov for discussions of these results.

APPENDIX A

Evaluation of the diagram i_1

The diagram i_1 corresponds to the following analytic expression:

$$i_1 \propto V \int d\mathbf{k} |T_{xy}(\mathbf{k})|^2 G(\mathbf{k} - \mathbf{k}_0) G(\mathbf{k} - \mathbf{k}_*),$$

$$G(\mathbf{k}) = B \frac{r_c^2}{1 + k^2 r_c^2}, \quad B = \frac{k_B T}{b}.$$

Using Feynman's formula

$$\frac{1}{a_1 a_2} = \int_0^1 dt [a_1 t + a_2 (1-t)]^{-2}$$

and transforming to the dimensionless variables $\mathbf{z} = \mathbf{k} r_c$, $\Delta^* = \Delta r_c$, $\mathbf{u} = \mathbf{k}_0 r_c$, we find that

$$i_1 \propto B^2 V r_c \left[\int d\mathbf{z} z^4 n_x^2 n_y^2 / \prod_{i=1}^4 (z - z_i) \right]$$

$$\int_0^1 dt [1 + u^2 + z^2 - 2\mathbf{z}\boldsymbol{\mu}(t)\mathbf{u}]^{-2},$$

where $\boldsymbol{\mu}(t) = (t\mathbf{q} + \mathbf{k}_0) / k_0$, $\mathbf{n} = \mathbf{z} / z$, $z_i = \pm u \pm i\Delta^*$ are the poles of the propagator $T(\mathbf{k})$. Since the integral with respect to z converges satisfactorily, the limits of integration can be removed to infinity. We now rotate the coordinate frame around the y -axis through the angle α , so that the vector $\boldsymbol{\mu}(t)$ in the new frame lies along the polar axis. It is readily verified that

$$\sin^2 \alpha = t^2 \sin^2 \theta [1 - 4t \sin^2(\theta/2) + 4t^2 \sin^2(\theta/2)]^{-1},$$

where θ is the angle between \mathbf{k}_0 and \mathbf{k}_* . Integration with respect to the aximuthal coordinate yields

$$i_1 \propto \frac{\pi B^2 V r_c}{16u^2} \left[\int_{-\infty}^{+\infty} dz z^4 / \prod_{i=1}^4 (z - z_i) \right]$$

$$\times \int_0^1 \frac{dt}{\mu^2} \int_0^1 dx \frac{x^2 + P^2}{(x^2 - P^2)^2} [f_1(x) + f_2(x) \sin^2 \alpha], \quad (A1)$$

where

$$P \equiv (1+u^2+z^2)/2\mu uz, \quad f_1(x) = (1-x^2)^2,$$

$$f_2(x) = (1-x^2)(5x^2+1).$$

All the integrals in (A1) can be evaluated explicitly. The final result can be conveniently written in the form of the following series:

$$\begin{aligned} i_4 \propto 2\pi B^2 V r_c \sum_{n=0}^{\infty} \frac{4^n I_n u^{2n}}{(2n+3)(2n+5)} \Phi_{2n}(3,1) \\ + 16\pi B^2 V r_c u^2 \cos^2 \frac{\theta}{2} \sum_{n=0}^{\infty} \frac{4^n (n+1) u^{2n}}{(2n+3)(2n+5)(2n+7)} \\ \times \left\{ 1 - \left[1 - (2n+4) \sin^2 \frac{\theta}{2} \right] I_n \right\} \Phi_{2n}(4,2), \quad (\text{A2}) \end{aligned}$$

where

$$I_n = \frac{(n!)^2}{(2n+1)!} \sum_{k=0}^n 4^{n-k} C_{2k}^k \left(\cos^2 \frac{\theta}{2} \right)^{n-k},$$

$$\Phi_{2n}(p,s) = \Phi_{2n}'(p,s) + \Phi_{2n}''(p,s).$$

The function

$$\Phi_{2n}'(p,s) = \frac{2\pi i}{(2s+2n-1)!} \frac{d^{2(n+s)-1}}{dz^{2(n+s)-1}} \frac{z^{2(p+n)}}{(z^2-u^2)^2} \frac{1}{(z+z_0)^{2(s+n)}} \Big|_{z_0=i(1+u^2)^{1/2}}$$

describes scattering by small-scale fluctuations in the order parameter. The second function

$$\Phi_{2n}''(p,s) = \frac{\pi}{2\Delta r_c} \frac{u^{2(p+n-1)}}{(1+2u^2)^{2(n+s)}}$$

describes the contribution of distant dipole re-emissions. The series in (A2) converge absolutely. The first few terms of (A2) are:

$$\begin{aligned} i_4 \propto \pi^2 B^2 V r_c \left\{ \frac{1}{15} \frac{(1+u^2)^{3/2} (1+6u^2)}{(1+2u^2)^3} + \dots \right\} + \pi^2 B^2 V^{3/2} \\ \times \left\{ \frac{1}{15} \frac{u^4}{(1+2u^2)^2} \right. \\ \left. + \frac{4}{105} \left(1+2 \cos^2 \frac{\theta}{2} + 2 \sin^2 \theta \right) \frac{u^8}{(1+2u^2)^4} + \dots \right\}. \quad (\text{A3}) \end{aligned}$$

In the special case where $\theta = 90^\circ$, the limiting value of the contribution of the propagator poles for $u \rightarrow \infty$ is

$$p_{0c}(\theta=90^\circ) \propto {}_1/8 \pi^2 B^2 V^{3/2} (2 \ln 2 - 1).$$

APPENDIX B

Spatial dispersion of the mutual diffusion coefficient of solutions

Various methods^{30,31} are available for determination of the properties of kinetic coefficients in the neighborhood of the critical point. They rely on various assumptions and lead to differential functional expressions for the mutual diffusion coefficient D .

We shall show that it is possible to use a direct method, based on the determination of the width of the spectral function $\langle c(\mathbf{r},t)c(0,0) \rangle_{\omega,\mathbf{q}}$ with the aid of the frequency moments [see formula (3)], to establish the behavior of D .

Fick's law $\dot{c}_q(t) = -q^2 D(q) c_q(t)$ shows that the spectrum of the correlator

$$\langle c(\mathbf{r},t)c(0,0) \rangle_{\omega,\mathbf{q}} \propto \frac{Dq^2}{\omega^2 + (Dq^2)^2}$$

has the width

$$\gamma = D(q) q^2. \quad (\text{B1})$$

When $qr_c \gtrsim 1$, the diffusion coefficient becomes essentially nonlocal. Comparison of (3) with (B1) leads to the following definition:

$$D(q) = q^{-2} [\langle \dot{c}(\mathbf{r},0) \dot{c}(0,0) \rangle_{\mathbf{q}} / \langle c(\mathbf{r},0)c(0,0) \rangle_{\mathbf{q}}]^{1/2}. \quad (\text{B2})$$

The zero-order moment $S(q) = \langle c(\mathbf{r},0)c(0,0) \rangle_{\mathbf{q}}$ is the usual structure factor of the system. In the Landau theory, $S(q) = Br_c^2 / (1 + q^2 r_c^2)$. We note that the second moment and the higher-order moments are regular at the critical point for all q . For the second-order moment, this follows directly from the definition of concentration:

$$c = \frac{n_1}{n_1 + n_2}, \quad n_i(\mathbf{r},t) = \sum_l^{N_l} \delta(\mathbf{r} - \mathbf{r}_l^i(t)).$$

This means that the critical properties of $D(q)$ are largely due to the structure factor of the system: $D(q) \propto S^{-1/2}(q)$.

The additional weak temperature dependence introduced by the second moment can be estimated as follows. It follows from (B2) that, well away from the critical point,

$$\langle \dot{c}(\mathbf{r},0) \dot{c}(0,0) \rangle_{\mathbf{q}} \approx Br_0^2 D_0^2(T) q^4. \quad (\text{B3})$$

where we have used the estimate $S(q) \approx Br_0^2$, $r_0 \sim 10^{-8}$ cm. The coefficient $D_0(T) \sim T/\xi$, where ξ is the shear viscosity, but otherwise $D_0(T)$ depends only on the molecular parameters. Since the second moment is regular, its structure (B3) must be preserved in the neighborhood of the critical point. The regular parts of $D_0(T)$ and ξ must be taken in this procedure.

Thus, in accordance with (B2) and (B3), in the region of highly developed fluctuations, we have

$$D(q) = D_0(T) (r_0/r_c) (1+q^2 r_c^2)^{1/2}.$$

If we use the Einstein formula $D_0(T) = k_B T / 6\pi \xi r_0$ and take into account the deviation from the Landau theory, we obtain

$$D(q) = \frac{k_B T}{6\pi \xi r_c} \left(\frac{r_c}{r_0} \right)^{\eta/2} (1+q^2 r_c^2)^{1/2(1-\eta/2)}, \quad (\text{B4})$$

where η is the anomalous dimensionality. The structure of this formula is essentially different from the results in Refs. 30 and 31 although it becomes identical with them in limiting cases. According to Ref. 3, the formula $\Gamma_0 = D(q) q^2$ with $D(q)$ given by (B4) provides the best approximation to experimental data on the width of the central component of

the spectrum of polarized scattered intensity for qr_c in the range 0.1–10.

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