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## Narrowing of a Rayleigh line wing in stratifying solutions of various concentrations

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Measurements were made of the half-width of a Rayleigh line wing as a function of the concentration of nitrobenzene-*n*-hexane, nitrobenzene-*n*-dodecane, and aniline-cyclohexane solutions at various temperatures. It was found that the wing became narrower on approach to the stratification point. A special feature of the experimental curves was a maximum at temperatures far from critical and a minimum at temperatures close to critical. An explanation of this property is proposed.

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Narrowing of a Rayleigh line wing on approach to the critical temperature was first observed in the homogeneous phase of stratifying binary nitrobenzene-*n*-hexane and aniline-cyclohexane solutions of critical concentration.<sup>1</sup> Further investigations of this effect<sup>2,3</sup> showed that the wing narrowing was nonmonotonic in most solutions: the half-width of the wing depended in a steplike manner on temperature. Moreover, it was later found that the depolarized Raman scattering lines, whose width (after subtraction of the temperature-independent terms) was governed by the same mechanism as the width of the Rayleigh line wing, also became narrower on approach to the critical temperature in solutions of critical concentration.<sup>3</sup> This observation was not only of independent interest but it also confirmed the existence of the narrowing of Rayleigh line wings.

Narrowing of various depolarized Raman lines was observed in various temperature ranges, indicating the existence of several anisotropy relaxation times and thus yielding information on the reason for the appearance of steps in the temperature dependences of the wing widths. These steps were attributed to the existence of several anisotropy relaxation times.<sup>4</sup> The narrowing of a wing was found to vary considerably from solution to solution. Moreover, according to several authors,<sup>5,6</sup> this effect was not observed at all in nitroethane-isooctane and nitroethane-3-methylpentene solutions. Consequently, Phillips *et al.*<sup>7</sup> compared and discussed the experimental methods and the methods of analysis of the results used in Refs. 5, 6, and 1-3.

One of us proposed earlier<sup>8</sup> an explanation of the narrowing of Rayleigh line wings in stratifying solutions of critical concentration based on allowance for the fact that the difference between the energies of interaction of two identical and two different molecules, which governs the critical temperature, is a function of the mutual orientation of these molecules, i.e., it is a function of the square of the anisotropy tensor. This dependence gives rise to a fourth-order term in the expression for the free energy and this term is proportional to the square of the anisotropy tensor and to the square of the concentration fluctuations. A special feature of the concentration fluctuations near the critical point of stratification is manifested as wing narrowing. This theory was used in Ref. 9 to discuss steps in the temperature dependence of a wing.

In all the cited investigations the narrowing of Rayleigh line wings was investigated in mixtures of critical concentration. The interpretation of the effect given in Ref. 8 also applies to such mixtures. However, additional information on the narrowing effect can be obtained also by investigating mixtures with concentrations other than critical. The present paper reports such an investigation of the narrowing of Rayleigh line wings of mixtures of different concentration on approach to the stratification point.

### 1. THEORY

In accordance with the overall aim of the present investigation, we shall generalize the theory of narrow-

ing of Rayleigh line wings in stratifying solutions of critical concentration<sup>8</sup> to the case of solutions of arbitrary concentration. We shall therefore express the stratification temperature of a solution  $T_{sol}$  in terms of the interaction energies of molecules. The critical temperature of stratification (on the absolute scale) can be described quite accurately by

$$T_c = k^{-1}z(\bar{v} - v), \quad (1)$$

where  $\bar{v}$  is the average energy of the interaction between two adjacent identical molecules;  $v$  is the average energy of the interaction between two adjacent different molecules;  $k$  is the Boltzmann constant;  $z$  is the number of nearest neighbors. A natural generalization of Eq. (1) is the following definition of the stratification temperature:

$$T_{sol} = k^{-1}z(\bar{v} - v_c), \quad (2)$$

where  $v_c$  is the average energy of the interaction of two adjacent molecules in a solution of concentration  $\bar{c}$  in the homogeneous phase;  $\bar{v}$  is the average energy of the interaction of two adjacent identical molecules in such a solution.

We shall use  $v_{11}$  and  $v_{22}$  for the energies of the interaction between two adjacent identical molecules of the component 1 and the component 2 of the solution, and  $v_{12}$  for the energy of the interaction between two adjacent different molecules. We can easily show that  $v_c$ , considered as a function of the molar concentration  $\bar{c}$  of the first component, has the following form:

$$v_c = \bar{c}^2 v_{11} + (1 - \bar{c})^2 v_{22} + 2\bar{c}(1 - \bar{c})v_{12}. \quad (3)$$

Using Eqs. (2) and (3) and assuming, for simplicity, that  $v_{11} = v_{22}$  we obtain

$$T_{sol} = 4k^{-1}z(v_{11} - v_{12}) \left[ \frac{1}{4} - (\bar{c} - 0.5)^2 \right]. \quad (4)$$

When  $\bar{c} = 0.5$ , this expression reduces to (1).

Equation (4) is the binodal of a solution. It is derived ignoring fluctuations of the concentration which are strong near the critical point of stratification. Therefore, our binodal is "simplified" to a parabola with its vertex at  $\bar{c} = 0.5$ . The critical concentrations of stratifying solutions are indeed close to 0.5 but are not exactly equal to 0.5. The form of a binodal of stratifying solutions is also close to a parabola but has a flattened vertex, which makes it closer to the cubic dependence. One could refine the above simplified binodal by allowing for the concentration fluctuations, but this is not required in the derivation of the expression for the width of a wing.

Assuming, as in Ref. 8, that  $v_{11}$  and  $v_{12}$  depend on the anisotropy tensor  $\xi_{mi}$ :

$$v_{11} = v_{11}^{(0)} - a_{11} \xi_{m1} \xi_{i1}, \quad v_{12} = v_{12}^{(0)} - a_{12} \xi_{m1} \xi_{i2} \quad (5)$$

( $v_{11}^{(0)}$ ,  $v_{12}^{(0)}$ ,  $a_{11}$ , and  $a_{12}$  are quantities independent of  $\xi_{mi}$ ) and substituting Eq. (5) in Eq. (4), we obtain

$$kT_{sol}/z = 4(v_{11}^{(0)} - v_{12}^{(0)}) \left[ \frac{1}{4} - (\bar{c} - 0.5)^2 \right] - 4(a_{11} - a_{12}) \left[ \frac{1}{4} - (\bar{c} - 0.5)^2 \right] \xi_{m1} \xi_{i1}. \quad (6)$$

Denoting, as in Ref. 8, by  $A$  the coefficient in front of  $\xi_{m1} \xi_{i1}$  in Eq. (6) with the opposite sign and performing calculations similar to those made in Ref. 8, we ob-

tain the following expression for the reciprocal of the anisotropy relaxation time divided by  $2\pi c$ :

$$\frac{1}{2\pi c \tau} = \frac{A}{L} + 4(a_{11} - a_{12}) \left[ \frac{1}{4} - (\bar{c} - 0.5)^2 \right] \left( \frac{T - T_{sol}}{T_{sol}} \right)^{3/2-1} \frac{z \gamma (b - \text{arc tg } b)}{4\pi^2 \xi_0^3 L}. \quad (7)$$

Here,  $A$ ,  $\gamma$ ,  $\xi_0$ ,  $b$ , and  $L$  have the same meaning as in Ref. 8:  $A$  is the coefficient in front of  $\xi_{m1} \xi_{i1}$  in the free-energy term which depends only on  $\xi_{m1} \xi_{i1}$ ;  $\gamma$  is the critical exponent ( $\gamma \approx 1.2$ );  $\xi_0$  is the coefficient in the expression for the correlation radius  $r_c$ :

$$r_c = \xi_0 [(T - T_{sol})/T_{sol}]^{-\nu/2},$$

$T$  is the absolute temperature;  $b$  is a constant ( $b \approx 5$ );  $L$  is the coefficient in front of  $\xi_{m1} \xi_{i1}$  in the dissipative function.

Among these quantities the only one which depends strongly on the concentration is the coefficient  $L$  which varies proportionally to the viscosity of the investigated solution  $\eta$ . The half-width of a wing  $\Delta\nu$  can be expressed in terms of  $\tau$  as follows:  $\Delta\nu = (2\pi c \tau)^{-1}$ , where  $c$  is the velocity of light. We can easily show that if  $v_{11} \neq v_{22}$ , the expressions (4), (6), and (7) should be transformed by the substitutions

$$v_{11} \rightarrow \frac{1}{2}(v_{11} + v_{22}), \quad a_{11} \rightarrow \frac{1}{2}(a_{11} + a_{22}).$$

As pointed out in Ref. 8, a wing should become narrower only if  $a > 0$ , which reduces to the following condition if  $v_{11} \neq v_{22}$ :

$$\frac{1}{2}(a_{11} + a_{22}) - a_{12} > 0. \quad (8)$$

If we use  $l_1$  and  $l_2$  to denote the lengths of the molecules of the components 1 and 2 and assume that  $\alpha_{11} \propto l_1^2$ ,  $\alpha_{22} \propto l_2^2$ ,  $\alpha_{12} \propto l_1 l_2$ , then for the same coefficients of proportionality in these expressions we find instead of Eq. (8) the condition  $(l_1 - l_2)^2 > 0$ , which is obeyed if the molecules are of different length.

In comparison with the experimental results, Eq. (7) can be conveniently rewritten in the form

$$\Delta\nu = \left\{ \frac{A_1}{\eta_1} + \frac{A_2}{\eta_1} \left[ \frac{1}{4} - (\bar{c} - 0.5)^2 \right] \left( \frac{T - T_{sol}}{T_{sol}} \right)^{3/2-1} \right\} \frac{\eta_1}{\eta}, \quad (9)$$

where  $A_1$  and  $A_2$  are constants,  $\eta_1$  is the shear viscosity corresponding to  $\bar{c} = \bar{c}_c$  and  $T - T_c = 0.1^\circ\text{C}$ .

## 2. MEASUREMENT METHOD AND DESCRIPTION OF THE INVESTIGATED SYSTEMS

The apparatus used to study the spectra of depolarized scattering was basically similar to that employed in Ref. 2. One should mention that we employed a double-pass Fabry-Perot interferometer, which increased considerably the precision of measurement of the line wing. The scattered light was excited by an He-Ne laser (632.8 nm, 20 mW). The laser radiation was polarized linearly in the scattering plane. Light scattered at an angle of  $90^\circ$ , polarized in the scattering plane and at right-angles to this plane, was investigated. The region in the vicinity of the Rayleigh line wing was investigated from the position of the undisplaced line to  $8 \text{ cm}^{-1}$  using the Fabry-Perot interferometer free spectral ranges of 0.3, 0.417, 0.714, 1, 2.5, 5, and  $16.7 \text{ cm}^{-1}$ . The half-widths of the Lorentzians representing the low-frequency part of a Rayleigh line

wing were determined by a method described in Ref. 2.

We investigated stratifying aniline-cyclohexane (AC), nitrobenzene-*n*-hexane (NH), and nitrobenzene-*n*-dodecane (ND) solutions. Figure 1 shows the coexistence curves of these solutions. Curves 1, 2, and 3 correspond to the NH, ND, and AC systems, respectively. In the case of the NH solutions measurements were made of the viscosity by a capillary viscometer in the range of temperatures exceeding the critical value by 20–1°C (Table I). In the case of the ND solutions the viscosity was measured only for a solution of critical concentration in the temperature range 50–28.5°C. The values of the viscosity were easily approximated [ $(t - t_c) \geq 1$ ] by the formula  $\eta_{ND} = \eta_D c + \eta_N(1 - c)$ , where  $c$  is the concentration of *n*-dodecane in molar fractions, whereas  $\eta_D$  and  $\eta_N$  are the shear viscosities of the components. Therefore, for the other concentrations the viscosity was calculated using the same formula, which should not result in significant errors because the viscosities of the components were similar. In the case of the AC solutions the viscosities were studied in a wide range of temperatures and concentrations in Ref. 10 and we used the results given there in an analysis of our data.

The AC and NH stratifying solutions were in many respects similar. At room temperature the shear viscosities of aniline and nitrobenzene were considerably greater than the viscosity of cyclohexane (by a factor of 3–4) and *n*-hexane (by a factor of 6–7). Our measurements indicated that the integrated intensity of the depolarized scattering in cyclohexane and *n*-hexane was more than order of magnitude less than in aniline and nitrobenzene. Bearing this point in mind, we could assume that in the case of the AC and NH solutions an instrument recorded mainly the light scattered by the aniline and nitrobenzene molecules.

The ND solutions differed from the AC and NH solutions. First of all, the viscosities of nitrobenzene and *n*-dodecane differed by just a factor of two at 20°C. In the low-frequency part of a wing of both components of the mixture there was a narrow region where the intensity distribution was Lorentzian.<sup>1)</sup> The half-widths of the Lorentzians of nitrobenzene and *n*-dodecane at 20°C were 0.12 and 0.05 cm<sup>-1</sup>, respectively. The integrated intensity of the spectrum of depolarized scattering in nitrobenzene was only ten times higher than in the case of *n*-dodecane, so that the spectrum of the solution

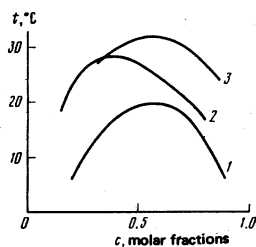


FIG. 1. Solution coexistence curves: 1) nitrobenzene-*n*-hexane ( $\bar{c}_c = 0.6$  molar fractions of *n*-hexane,  $T_c = 20^\circ\text{C}$ ); 2) nitrobenzene-*n*-dodecane ( $\bar{c}_c = 0.43$  molar fractions of *n*-dodecane,  $T_c = 28.2^\circ\text{C}$ ); 3) aniline-cyclohexane ( $\bar{c}_c = 0.56$  molar fractions of cyclohexane,  $T_c = 32^\circ\text{C}$ ).

TABLE I. Viscosity of NH solutions (cP).

Molar fraction of <i>n</i> -hexane	$t, ^\circ\text{C}$					Molar fraction of <i>n</i> -hexane	$t, ^\circ\text{C}$				
	50	40	30	22	21		50	40	30	22	21
0.2	0.87	0.966	1.1	1.235	1.25	0.7	0.345	0.355	0.4	0.44	0.45
0.4	0.82	0.87	0.755	0.92	0.935	0.8	0.3	0.31	0.35	0.38	0.397
0.6	0.4	0.49	0.56	0.67	0.7	0.9	0.24	0.26	0.3	0.32	0.325

should include light scattered by the nitrobenzene and *n*-dodecane molecules.

### 3. RESULTS OF MEASUREMENTS

Typical spectrograms (interferograms) obtained for an ND solution of critical concentration at temperatures 15°C and 1.3°C higher than the critical value are shown in Fig. 2. They were recorded using the free spectral range of the interferometer amounting to 5 cm<sup>-1</sup> (the instrumental function of the apparatus was then described by the Voigt distribution with the parameters  $\beta_1 = 0.0154$ ,  $\beta_2 = 0.056$ , and  $h = 0.11$ —Ref. 11). Figure 3 shows our dependences of the half-width of a Rayleigh line wing on the concentration of *n*-hexane, *n*-dodecane, and cyclohexane in the NH, ND, and AC mixtures at various temperatures.

In a stratifying ND solution in the low-frequency part of a Rayleigh line wing we found two Lorentzians with very different half-widths. The difference between these widths increased on approach of the solution concentration to the critical value.

Since in the case of the ND solutions the narrowing of a wing had not been investigated earlier in a mixture of critical concentration (this was in contrast to the NH and AC solutions), we reproduced in Fig. 4 the dependence of the logarithm of the anisotropy relaxation time  $\tau$  on  $-\ln \varepsilon$ , where  $\varepsilon = (T - T_c)/T_c$ , applicable to a wide Lorentzian. In the temperature interval from  $\Delta t = T - T_c = 20^\circ\text{C}$  to  $\Delta t = 2^\circ\text{C}$  this Lorentzian decreased in width by a factor of about 10. There was no change in the width in the temperature interval from  $\Delta t = 2^\circ\text{C}$  to  $\Delta t = 0.1^\circ\text{C}$ .

The behavior of the wing width in stratifying solutions was compared with the behavior in the case of pure

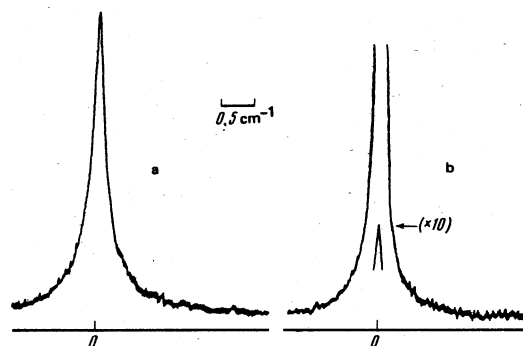


FIG. 2. Typical interferograms obtained for an ND solution when  $\Delta t = 15^\circ\text{C}$  (a) and  $\Delta t = 1.3^\circ\text{C}$  (b). The polarization of the scattered light was normal to the scattering plane and the free spectral range of the interferometer was 5 cm<sup>-1</sup>.

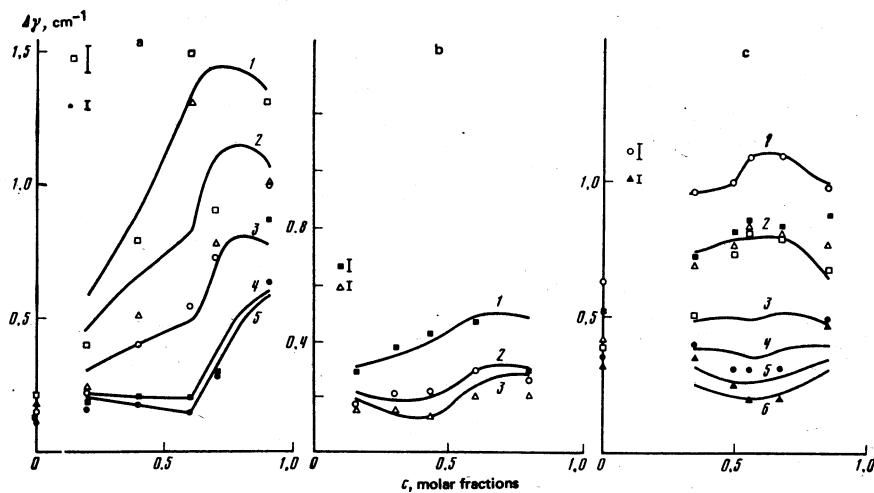


FIG. 3. Dependences of the half-width  $\Delta\nu$  of Rayleigh line wings at various temperatures ( $^{\circ}\text{C}$ ). a) Dependence on the concentration of *n*-hexane in an NH mixture: 1 (□) -50; 2 (Δ) -40; 3 (○) -30; 4 (■) -22; 5 (●) -21. b) Dependences on the concentration of *n*-dodecane in an ND mixture: 1 (■) -38.8; 2 (○) -31.2; 3 (Δ) -28.8. c) Dependences on the concentration of cyclohexane in an AC mixture: 1 (○) -61.8; 2 (■) -51; 3 (Δ) -42.4; 4 (□) -38.5; 5 (●) -35.3; 6 (▲) -33.2. The continuous curves are calculated using Eq. (9).

liquids and nonstratifying solutions by determining the temperature dependences of the anisotropy relaxation time of nitrobenzene, toluene, and aniline, and also solutions of these liquids in  $\text{CCl}_4$ . The open and black circles, squares, and triangles in Fig. 5 represent the values of  $\tau$  deduced from the half-width of the low-frequency part of a Rayleigh line wing in the case of aniline, toluene, and nitrobenzene, and of their solutions in  $\text{CCl}_4$  considered as a function of the viscosity. The results for the solutions of toluene in  $\text{CCl}_4$  were taken from the work of Alms *et al.*<sup>12</sup> The solvent ( $\text{CCl}_4$ ) for nitrobenzene and aniline was not chosen at random. The intensity of anisotropic scattering in  $\text{CCl}_4$ , cyclohexane, and *n*-hexane was approximately of the same order of magnitude so that nonstratifying nitrobenzene- $\text{CCl}_4$  and aniline- $\text{CCl}_4$  solutions were similar, in respect of the intensities of light scattered by the components of the solution, to the stratifying NH and AC solutions.

#### 4. DISCUSSION OF RESULTS

We can see from Fig. 5 that the anisotropy relaxation time of nonstratifying solutions and pure liquids varies with temperature in direct proportion to the viscosity. This proportionality is observed when the temperature of the solution is varied (dark circles in Fig. 5 corresponding to a solution of aniline and 0.6 molar fractions of  $\text{CCl}_4$  at various temperatures) or when the

concentration is altered (dark triangles in Fig. 5, corresponding to solutions of nitrobenzene in  $\text{CCl}_4$  at  $20^{\circ}\text{C}$  with concentrations of  $\text{CCl}_4$  from 0.1 to 0.8 molar fractions). It follows from Fig. 4 that in the case of stratifying solutions the value of  $\tau$  varies much more rapidly with temperature in the region  $T - T_c$  than does the viscosity.

It follows from Figs. 3 and 4 that the narrowing of a Rayleigh line wing occurs in the case of solutions of critical concentration and also in the case of solutions with concentrations other than critical when the point of stratification is approached. For example, in the case of the AC solutions (Fig. 3c) the greatest narrowing of the wing occurs at  $\bar{c} = \bar{c}_c$  (for this solution, we found that  $\bar{c}_c = 0.56$  molar fractions of cyclohexane). Similar narrowing is also observed at concentrations separated from  $\bar{c}_c$  by 0.1–0.2 molar fractions. Analogous behavior is exhibited also by the NH and ND solutions (Figs. 3a, 3b, and 4).

The nonmonotonic nature of the narrowing of a Rayleigh line wing observed earlier for solutions of criti-

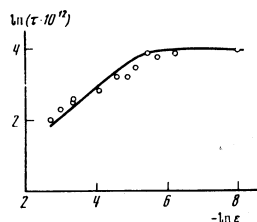


FIG. 4. Dependence of the logarithm of the anisotropy relaxation time  $\tau$  on  $-\ln \epsilon$  ( $\epsilon = \Delta T / T_c$ ) for an ND mixture of critical composition. The continuous curve is calculated using Eq. (9).

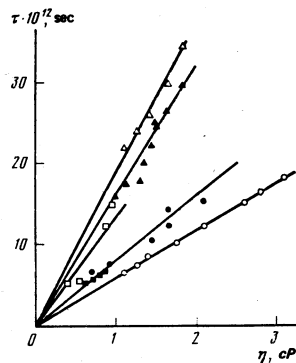


FIG. 5. Dependences of the anisotropy relaxation time  $\tau$  on the viscosity  $\eta$  of nitrobenzene (Δ), toluene (□), aniline (○) and their solutions in  $\text{CCl}_4$  (represented by ▲, ■, and ●, respectively).

cal concentration<sup>2-4</sup> occurs also in solutions of non-critical concentration. This is clearly seen in Fig. 3c, where the half-widths at 51, 42.4, and 38.5°C are similar for  $\bar{c} = \bar{c}_c$ , as well as for 0.49 and 0.65 molar fractions of cyclohexane. Such nonmonotonic narrowing of a Rayleigh line wing is not observed for the ND solutions (Figs. 3b and 4). As shown in Ref. 9, the existence of several anisotropy tensors, whose relaxation times vary in accordance with the theory of Ref. 8, may result in nonmonotonic narrowing of the wing since the method of analysis does not allow us to distinguish between Lorentzians with close half-widths. In the case of the ND solutions the low-frequency part of the wing is described, as pointed out earlier, by a sum of Lorentzians with very different (by an order of magnitude) half-widths, so that each Lorentzian can be easily separated from the spectrum. Clearly, this is why the narrowing of the wing is monotonic for the ND mixtures.

It readily follows from Fig. 3 that the narrowing of a Rayleigh line wing on variation of the solution concentration is characterized by the following features: the wing half-width considered as a function of the concentration has a maximum at temperatures far from  $T_c$  and a minimum at temperatures close to  $T_c$ . In the case of the AC and ND solutions this maximum and minimum are located near the critical concentration. However, in the case of the NH solutions the maximum is shifted toward higher *n*-hexane concentrations.

We shall now compare the results obtained with the formulas derived in Sec. 1. We shall begin with a qualitative comparison. Equations (7) and (9) predict a maximum in the concentration dependence of the wing half-width at temperatures far from  $T_c$  and a minimum at temperatures close to  $T_c$ , in agreement with the experimental results. If the viscosities of the solutions do not vary greatly with the concentration, as in the case for the AC and ND solutions, the maximum and minimum in Eqs. (7) and (9) are located near  $\bar{c} = \bar{c}_c \approx 0.5$ , which is again in agreement with the experimental results. When the viscosities depend strongly on the concentration, which is true of the NH solutions, in which case the viscosities of the components differ by a factor of 7 at 20°C, the maximum in the formulas (7) and (9) shifts toward lower viscosities, as indeed observed for an NH solution. At a fixed concentration the formulas (7) and (9) predict the observed narrowing of the wing on approach of  $T$  to  $T_{sol}$ .

A qualitative comparison of our experimental results with Eq. (9) is made in Fig. 3. The continuous curves are calculated using Eq. (9) selecting two constants  $A_1/\eta_1$  and  $A_2/\eta_1$ ; the points are the experimental values. The values of  $A_1/\eta_1$  and  $A_2/\eta_1$  and of  $\eta_1$  used in these calculations are listed in Table II. It is clear from Fig. 3 that the formula (9) describes reasonably the concen-

tration dependence of the half-width of a Rayleigh line wing in the case of the upper and lower curves. The disagreement for the intermediate curves is clearly associated with the steplike experimental dependences. The formula (7) predicts just one anisotropy relaxation time. The formula (9) applies also the average half-width of a Rayleigh line wing  $\overline{\Delta\nu} = (2\pi c\bar{c})^{-1}$  when there are several relaxation times  $\tau_1, \tau_2, \dots$  ( $\bar{c}^{-1} = \tau_1^{-1} + \tau_2^{-1} + \dots$ ), described by the formula (7). In the presence of steps in the experimental curves the formula (9) can describe only the behavior of the smoothed-out curve.

At  $\bar{c} = \bar{c}_c \approx 0.5$  the formula (9) reduces to the expression obtained in Ref. 8 for a solution of critical concentration:

$$(2\pi c\tau)^{-1} = \left[ \frac{A_1}{\eta_1} + \frac{A_2}{4\eta_1} \left( \frac{T-T_c}{T} \right)^{0.8} \right] \frac{\eta_1}{\eta} \quad (10)$$

We shall use this formula to compare our data on the temperature dependence of  $\tau$  of an ND solution of critical concentration. Since such a solution does not exhibit the steplike behavior, the formula (10) can be used without complications. Figure 4 shows a continuous curve plotted on the basis of Eq. (10) for  $A_1/\eta_1$  and  $A_2/\eta_1$  listed in Table II, whereas the points are the experimental values. It is clear from Fig. 4 that this equation describes well the experimental results so that the critical index for the wing half-width is indeed close to 0.8.

We shall conclude by considering a different explanation of the narrowing of a Rayleigh line wing. The alternative explanation in Ref. 4 is based on the Wilson<sup>13</sup> formula for the rotational diffusion coefficient:  $D_{rot} = kT/8\pi\eta r_c^3$ . This formula is obtained by replacing in the Debye expression the molecular radius with the correlation radius  $r_c$ . The Wilson formula is an analog of the experimentally tested expression for the translational diffusion coefficient  $D_{transl} = kT/6\pi\eta r_c$ , which is again obtained by replacing the molecular radius with the correlation radius but in the Stokes formula. We might mention that the Wilson formula might be valid near the transition from an isotropic liquid to a nematic liquid crystal, where a correlation is observed in the molecular orientation, but there is no justification to apply it at the critical point of stratification when there is no such correlation. Moreover, in the case of translational motion the displacement of molecules involves a change in the concentration and, therefore, a molecule tends to drag a region of volume  $r_c^3$  behind it; the rotational motion does not alter the concentration so that similar considerations are inapplicable. This raises doubts about the validity of the Wilson formula near the critical point of stratification.

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<sup>1)</sup>For brevity, we shall call this part a Lorentzian.

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TABLE II.

Solution	$A_1/\eta_1$	$A_2/\eta_1$	$\eta_1$
NH	0.1	15	0.78
ND	0.1	13	1.55
AC	0.15	13	1.95

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## Energy balance of charged particles multiply scattered in a randomly inhomogeneous magnetic field

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A consistent theory of energy exchange between high-energy charged particles and random magnetic-field inhomogeneities frozen in a moving plasma is developed. It is shown that the character of the change of the particle energy, given the plasma-velocity variation in space, is determined by the concrete form of the particle distribution function. An equation is obtained for the particle energy density, and the question of formation of the energy spectrum of the charged particles in the course of multiple scattering by random magnetic-field inhomogeneities is considered.

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### 1. INTRODUCTION

One of the vital problems of plasma physics, cosmic-ray physics, and plasma astrophysics is that of the motion of charged particles in a random magnetic field.<sup>1-5</sup> The first consistent kinetic approach to the problem of the motion of charged particles in a magnetic field with random inhomogeneities was developed by Dolginov and Toptygin.<sup>1</sup> They obtained a kinetic equation that describes the multiple scattering of charged particles by moving magnetic-field inhomogeneities, and established the correct form of the diffusion-approximation equations, namely the equation for the density of particles with a given momentum and the expression for the particle flux-density vector in space.

On the other hand, a phenomenological theory of propagation of charged particles in a random magnetic field was developed<sup>6-8</sup> in connection with problems of cosmic-ray physics. In this theory it became necessary to postulate an expression for the particle flux density in the space of the absolute values of the momentum due to the exchange of energy between the charged particles and the moving magnetic-field inhomogeneities. The dominant concept in the consideration of the process of energy dissipation in a system consisting of charged particles and magnetic inhomogeneities was the conviction that the energy-exchange mechanism is limited exclusively by the spatial char-

acter of the change of the velocity of the medium in which the random magnetic-field inhomogeneities are frozen-in. This point of view was formulated most clearly for the question of energy exchange between charged particles and magnetic inhomogeneities by Parker<sup>8</sup> and by Jokipii and Parker,<sup>9</sup> who used the hypothesis of adiabatic slowing down of the charged particles. The gist of this hypothesis is that high-energy charged particles scattered by radially moving magnetic field inhomogeneities lose energy systematically. We shall show that this is a restricted concept, since it takes no account of the character of the distribution of the charged particles, so that it is necessary to review the notions concerning energy dissipation in multiple scattering of charged particles by moving magnetic-field inhomogeneities. Actually, given the law that governs the variation of the velocity of the medium in space, the character of the change of the energy of the charged particles depends essentially on the form of the particle distribution function. If the system dimensions are large enough and the particles have time to become strongly scattered, so that their spatial distribution becomes close to isotropic, then the energy-exchange process is determined by the sign of the scalar product  $(\mathbf{u} \cdot \nabla)N$  [ $\mathbf{u}(\mathbf{r})$  is the velocity of the medium, and  $N(\mathbf{r}, p, t)$  is the density of the particles with given value of the momentum  $p$ ]<sup>10</sup> and at  $(\mathbf{u} \cdot \nabla)N > 0$  continuous energy transfer takes place from the moving magnetic-field inhomogeneities to the charged particles. In the