Narrowing of the Rayleigh line wing near the critical stratification point

I. A. Chaban

Acoustics Institute

(Submitted February 18, 1975)
Zh. Eksp. Teor. Fiz. **69**, 1550–1557 (November 1975)

An explanation is proposed for the recently observed narrowing of the Rayleigh line wing as the critical stratification point in a binary liquid mixture in the single-phase state is approached. It is shown that the dependence of the molecular interaction energy on their mutual orientation, which is described by the anisotropy tensor, is proportional to the product of the square of the anisotropy tensor and the square of the concentration fluctuation in the thermodynamic potential. This term gives the dependence of the anisotropy tensor relaxation time, which determines the width of the wing, on the concentration fluctuations. It is the peculiarity of these fluctuations which is manifested in the narrowing of the wing. This term also leads to the appearance of a new scattering line due to scattering by the sum (difference) modes of the concentration and anisotropy "waves." The spectrum of this line is calculated and its intensity is estimated.

PACS numbers: 78.30.Ly, 64.80.Cz

Narrowing of the Rayleigh line wing as the temperature T approaches the critical temperature T_c in critical-composition mixtures of nitrobenzene-n-hexane and aniline-cyclohexane in the single-phase state was recently observed experimentally.[1] In the present work, a mechanism of this narrowing is proposed.

In the mixtures studied in[1], as in most pure liquids, the wing consisted of two contours—a narrow part and a broad part. Similar narrowing of both contours was observed. Assuming independence of the scattering mechanisms responsible for these parts, we limit ourselves to the consideration of the narrow part of the wing only.

The presence of an intense wing in the components of the mixtures studied in[1] means that their molecules do not possess spherical symmetry. The energy of the interaction of such molecules should depend on their mutual orientation, which is described by the anisotropy tensors.[2,3] In mixtures of these components, the orientation part of the energy of the interaction of the molecules with the nearest neighbors will depend on the concentration of the components in their vicinity. This should lead to a dependence of the anisotropy relaxation time, which determines the width of the wing, on the concentration fluctuations. Thanks to this dependence, the singularity of concentration fluctuations near the critical stratification point manifests itself in the narrowing of the wing. This constitutes the physical picture of the proposed explanation. We now proceed to the calculation.

We find that term of the thermodynamic potential which describes the sought-for link between the concentration fluctuations and the anisotropy tensor. Inasmuch as the mixtures studied in[1] have an upper critical point, we limit our consideration for definiteness only to mixtures with an upper critical point. As is well known, the critical stratification temperature is determined with sufficient accuracy by the relation

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

where z is the number of nearest neighbors, $\tilde{v}$ is the average energy of interaction of two neighboring, identical molecules (we assume it to be the same for both components), v is the average energy of interaction of two neighboring, different molecules, k is the Boltzmann constant. (This relation, in particular, can be obtained by the method of the self-consistent field[4].) Simplifying the situation somewhat, we shall assume that the mutual orientation of the like and unlike molecules is described by the same anisotropy tensor[1)] ξ_{ml}. Taking into account the dependence of $\tilde{v}$ and v on ξ_{ml}, we can write the expression for T_c in the following fashion:

$$T_c = k^{-1} z (\tilde{v}^{(0)} - v^{(0)} - a \langle \xi_{ml} \xi_{lm} \rangle), \tag{1}$$

where $\tilde{v}^{(0)}$ and $v^{(0)}$ are the parts of $\tilde{v}$ and v which are independent of ξ_{ml}, a is some coefficient, and the angle brackets denote the average over the volume. Using (1), we expand the part of the thermodynamic potential which depends on the concentration fluctuations in a series in $-k^{-1} z a \langle \xi_{ml} \xi_{lm} \rangle$, limiting ourselves to the first terms. This part of the thermodynamic potential has the following form in the region that is not too close to the critical point:

$$\Delta \Phi = \frac{VB}{(2\pi)^3} \int_{(\infty)} |c_{\mathbf{q}}|^2 \frac{1}{\chi(q\rho)} d\mathbf{q}, \tag{2}$$

where $|c_q|^2$ is the spectral intensity of the concentration fluctuations with the wave number **q**, B is a quantity proportional to the derivative of the chemical potential with respect to the concentration: $B = B_1(T - T_c)^\gamma$, $\gamma \approx 1.2$; B_1 is a constant quantity in the critical region; ρ is the correlation radius of the concentration fluctuations; $\chi(q\rho)$ are functions which take into account the nonlocal character of the concentration fluctuations; in correspondence with the similarity hypothesis, it depends only on the combination $q\rho$; $\chi(q\rho)$ is assumed to be normalized so that $\chi(0) = 1$; V is the volume of the considered system; the integration is carried out over the entire space of the wave vectors. The cited form of the thermodynamic potential is justified by the fact that the expression that comes from it for the total intensity of the central component of the polarized light scattered by the concentration fluctuations

$$I = GM^2 \frac{kT}{2B} \chi(q\rho)$$

is identical with that which was observed in numerous experiments[5,6]. In this expression, M is the derivative of the dielectric constant with respect to the concentration, G is a known factor which depends on the characteristics of the incident light, on the distance from the scattering region to the point of observation, and on the size of the scattering volume. Expanding $\Delta\Phi$ in a series at fixed $|c_q|^2$, we get

$$\Delta\Phi=\frac{V}{(2\pi)^3}\int\limits_{(\infty)}\left[\frac{B}{\chi(q\rho)}\right]_{\xi_{ml}=0}|c_{\mathbf{q}}|^2\,d\mathbf{q}+\frac{az}{(2\pi)^3k}\int\limits_{V}\xi_{ml}\xi_{lm}\,dV\int\limits_{(\infty)}\frac{\partial}{\partial T}\left[\frac{B}{\chi(q\rho)}\right]|c_{\mathbf{q}}|^2\,d\mathbf{q}. \tag{3}$$

The second component in (3) is the sought component, which describes the connection between the concentration fluctuations and the anisotropy tensor. Conversely, if we start out from the thermodynamic potential (3), then, in addition to other effects, the last component leads to a small shift in the critical temperature.

We now proceed to the calculation of the relaxation time of the anisotropy tensor, which determines the width of the wing. For this purpose, we consider the part of the thermodynamic potential which depends on the concentration fluctuations and the anisotropy tensor. It is obtained by the addition to (3) of a term which depends only on the fluctuations of the anisotropy tensor, and takes the following form:

$$\Phi=\Delta\Phi+A\int\limits_{V}\xi_{ml}\xi_{lm}\,dV. \tag{4}$$

(In order not to complicate the picture, the connection of the fluctuations of the anisotropy tensor with the deformation fluctuations was not taken into account.) For the anisotropy tensor indicated in footnote 1), the coefficient A is of the order of η/τ', where τ' is the relaxation time of the anisotropy in the mixture at the critical temperature, η is the viscosity of the mixture at the considered temperature.[2] The dissipation function, which is connected with the anisotropy tensor, is of the following form:

$$R=L\int\limits_{V}\dot{\xi}_{ml}\dot{\xi}_{lm}\,dV,$$

where L is practically a constant in the critical region (the weak singularity of the viscosity near the critical stratification point is neglected). Equating the derivative of R with respect to ξ_{ml} to the derivative of Φ with respect to ξ_{ml} with opposite sign, and averaging over the ensemble, we obtain the following equation of motion for ξ_{lm}:

$$\dot{\xi}_{lm}=-\frac{1}{\tau}\xi_{lm},$$

where

$$\frac{1}{\tau}=\frac{1}{L}\left[A+\frac{az}{(2\pi)^3k}\int\limits_{(\infty)}\frac{\partial}{\partial T}\left[\frac{B}{\chi(q\rho)}\right]\langle|c_{\mathbf{q}}|^2\rangle d\mathbf{q}\right]. \tag{5}$$

This expression also represents the half-width of the wing of interest to us.

We now consider the last component in (5) in more detail. For $q\rho \ll 1$, the function $\chi(q\rho)$ has the Orenstein-Zernike form

$$\chi(q\rho)=\frac{1}{1+(q\rho)^2}.$$

For $q\rho \gg 1$ the exact form of $\chi(q\rho)$ is not known. We shall assume

$$\chi(q\rho)=1/(q\rho)^2 \quad \text{if} \quad q\rho\gg1.$$

This assumption is in agreement with the data on light scattering and x-ray scattering from concentration fluctuations, and is close to that given in[7]. It is indirectly confirmed by the agreement of the results of the present calculation with experiment.[1] Since, according to the experimental data, $B\rho^2$ is practically independent of the temperature in the critical region, this assumption leads to the result that

$$\frac{\partial}{\partial T}\left[\frac{B}{\chi(q\rho)}\right]=0 \quad \text{if} \quad q\rho\gg1.$$

We now assume that this quantity vanishes at $q\rho > b$, where b is a number of the order of several units. Here the integral in (5) turns out to be cut off at a value of q equal to $q_{\max} = b/\rho$:

$$\int\limits_{(\infty)}\frac{\partial}{\partial T}\left[\frac{B}{\chi(q\rho)}\right]\langle|c_{\mathbf{q}}|^2\rangle\,d\mathbf{q}=4\pi\frac{\partial B}{\partial T}\int\limits_0^{b/\rho}\langle|c_{\mathbf{q}}|^2\rangle q^2\,dq. \tag{6}$$

This expression can also be represented in the form $(\partial B/\partial T)\langle\tilde{c}^2\rangle$, where $\tilde{c}$ is the concentration fluctuation, averaged over the spherical regions with radius of the order of $\pi\rho/b$. Substituting the expression (6) in (3) with averaging omitted, we see that the fluctuations of the anisotropy tensor turn out to be coupled only with the fluctuations of the concentration c averaged in the form described above. Substituting in (6),

$$\langle|c_{\mathbf{q}}|^2\rangle=kT/2B[1+(q\rho)^2], \quad \rho=\xi_0(T/T_c-1)^{-\gamma/2},$$

where ξ_0 is constant in the critical region, and also the expression B, we obtain the following final expression for $1/\tau$:

$$\frac{1}{\tau}=\frac{1}{L}\left[A+\frac{az\gamma}{4\pi^2\xi_0^3}\left(\frac{T}{T_c}-1\right)^{3\gamma/2-1}(b-\operatorname{arctg}b)\right]. \tag{7}$$

We first note that the narrowing takes place only for $a > 0$. Moreover, for its existence, it is necessary that the ratio σ of the second component to the first was of the order of or greater than unity in the range of temperatures studied in[1]. We estimate σ, assuming

$$\xi_0=2\text{ Å}, \quad \gamma=1.2, \quad b=5, \quad z(\tilde{v}^{(0)}-v^{(0)})\approx kT_c.$$

We shall set $a = d(\tilde{v}^{(0)} - v^{(0)})$, where d characterizes the fraction of molecules in the interaction which depend on their relative orientation (for the estimate, we shall assume $d = 1/4$). According to the latest data, as kindly communicated to me by the authors of[1], $\tau' > 10^{-9}$ sec, for the narrow part of the wing. Since $\eta \approx 10^{-2}$ poise for the mixtures studied in[1], it follows that $A < 10^7$ erg/cm^3. Using the given values, we obtain $\sigma > 13(T/T_c - 1)^{0.8}$. For $T/T_c - 1 = 4\times10^{-2}$, we have $\sigma > 1$. For large values of $T/T_c - 1$, we can neglect the first component in (7) and assume, approximately, that

$$1/\tau\sim(T/T_c-1)^{0.8}.$$

The critical exponent 0.8 that has been found is practically identical, in the limits of experimental error (10–30%), with the critical exponents of 0.62 and 0.66 observed in[1] for the narrow and broad parts of the wing.

The term which is proportional to $\xi_{ml}\xi_{lm}\tilde{c}^2$ in the thermodynamic potential (the last component in (3)), in addition to the considered effect of narrowing of the spectrum of light scattered by the anisotropy fluctuations, should lead also to another effect—the appearance of a new scattering line. Actually, the mean square of the fluctuations of the dielectric constant, generally speaking, should contain terms of this same type, as also Φ. Therefore, the general expression for the fluctuations of the dielectric constant $\delta\epsilon_{ml}$ should itself have a component proportional to $\xi_{ml}c$, in addition to the components proportional to ξ_{ml}:

$$\delta\varepsilon_{ml}=N_0\xi_{ml}+N\xi_{ml}\tilde{c}+Mc\delta_{ml},$$

where

$$N_0=\frac{\partial\varepsilon_{ml}}{\partial\xi_{ml}},\qquad N=\frac{\partial^2\varepsilon_{ml}}{\partial\xi_{ml}\partial\tilde{c}},\qquad M=\frac{1}{3}\frac{\partial\varepsilon_{mm}}{\partial c}.$$

In the depolarized scattering considered below, only the first two terms make a contribution. The scattering by the fluctuations of the dielectric constant, which are proportional to ξ_{ml}, is given by the formulas of the work of Leontovich and Rytov,[2,3] in which $1/\tau$ should be expressed by Eq. (7). A new line appears as a result of scattering from the fluctuations, proportional to $\xi_{ml}\tilde{c}$, and which are described by the second term.[2] We now find the intensity spectrum of this line.

Since only scattering in the mode $\delta\varepsilon_{ml}$ with wave number $\mathbf{p}=\mathbf{q}_s-\mathbf{q}_i$ is recorded at a fixed angle of observation ($\mathbf{q}_i$ is the wave number of the incident light, $\mathbf{q}_s$ the wave number of the scattered light), the contribution to the considered scattering will be given by all the modes ξ_{ml} with wave number $\mathbf{q}$ and all modes $\tilde{c}$ with wave number $\mathbf{q}'$, for which $\mathbf{q}+\mathbf{q}'=\mathbf{p}$. Thus, the considered scattering is the scattering from the sum and difference modes of the anisotropy and concentration "waves." The time during which the sum (difference) mode will exist is equal to the smaller of the two times: the relaxation time of the anisotropy and the time of diffusion dissipation of the concentration fluctuations. This time also determines the width of the line under consideration. In different temperature intervals, first one, then the other of these times turns out to be the minimum. Denoting the mean spectral intensity of the fluctuations of $\tilde{c}$ with wave number $\mathbf{q}$ and frequency ω by $\langle|\tilde{c}_{\mathbf{q},\omega}|^2\rangle$ and the corresponding spectral intensity of the anisotropy fluctuations by $\langle|(\xi_{ml})_{\mathbf{q},\omega}|^2\rangle$, we can write the intensity of the light with frequency ω scattered through an angle of 90° by the fluctuations proportional to $\xi_{ml}\tilde{c}$ in the following form:

$$I_{ml}(\omega,\mathbf{p})=GN^2\iint\langle|(\xi_{ml})_{-\mathbf{q}+\mathbf{p},\omega-\omega'}|^2\rangle\langle|\tilde{c}_{\mathbf{q},\omega'}|^2\rangle d\mathbf{q}\,d\omega',\tag{8}$$

where l and m are the directions of polarization of the incident and scattered light. In view of the previously assumed smallness of the expansion parameter $-k^{-1}za\langle\xi_{ml}\xi_{lm}\rangle$, the concentration fluctuations were assumed to be independent of the fluctuations of the anisotropy tensor in writing down this expression. The spectral intensities entering into this expression have the form

$$\langle|(\xi_{ml})_{-\mathbf{q}+\mathbf{p},\omega-\omega'}|^2\rangle=\frac{kT\tau^2}{L\pi}\frac{1}{1+(\omega-\omega')^2\tau^2},$$

where τ is determined from the expression (7):

$$\langle|\tilde{c}_{\mathbf{q},\omega'}|^2\rangle=\frac{kT}{2B\pi}\frac{Dq^2\varphi(q\rho)\chi(q\rho)}{(\omega')^2+(Dq^2\varphi(q\rho))^2}$$

where D is the diffusion coefficient, $\varphi(q\rho)$ the Kawasaki function:[8,9]

$$\varphi(q\rho)=\frac{3}{4}\left[\frac{1}{(q\rho)^2}+1+\left(q\rho-\frac{1}{(q\rho)^3}\right)\operatorname{arctg} q\rho\right].$$

Since the integral in (8) falls off rapidly at large q, we can make the following simplification: the integration is carried out not up to $q_{\max}=b/\rho$ but up to ∞, and we set $\varphi(q\rho)=1$. We then obtain

$$I_{ml}(\omega,\mathbf{p})=GN^2\frac{(kT)^2\tau\pi\sqrt{\beta}}{2BL\rho D}F(x,\beta),\tag{9}$$

where

$$F(x,\beta)=\frac{1}{(1+x^2-{}^1\!/_4\beta^2)^2+x^2\beta^2}$$

$$\{(1+x^2-{}^1\!/_4\beta^2)[(\sqrt{1+x^2}+{}^1\!/_2\beta)\sqrt{(1+x^2)^{1/2}+1}-\sqrt{\beta}-{}^1\!/_2\beta\sqrt{\beta}]$$
$$+x\beta[x\sqrt{\beta}-(\sqrt{1+x^2}-{}^1\!/_2\beta)\sqrt{(1+x^2)^{1/2}-1}]\},\tag{10}$$
$$x=\omega\tau,\quad \beta=\tau/\tilde{\tau},\quad \tilde{\tau}=\rho^2/2D.$$

In view of these simplifications, the resultant expression ceases to be valid for $x>b^2\beta$. For $\beta\ll1$,

$$F(x,\beta)=\sqrt{2},\quad x\ll1;\qquad F(x,\beta)=1/\sqrt{x},\quad x\gg1.$$

For $\beta\gg1$,

$$F(x,\beta)=2/\sqrt{\beta},\quad x\ll1;\qquad F(x,\beta)=1/\sqrt{x},\quad x\gg\beta.$$

Thus the shape of the considered line is not Lorentzian; for large $\omega\tau$ the intensity falls off very slowly, as $1/\sqrt{\omega\tau}$. For $\beta\ll1$, the halfwidth of this line is determined by the time τ and for $\beta\gg1$, by the time $\tilde{\tau}$.

Far from the critical point, $\tilde{\tau}\approx10^{-11}$ sec, $\tau\approx10^{-10}$ sec for the narrow part of the wing, so that $\beta\gg1$ and the half-width of the line is determined by $\tilde{\tau}$. As the critical point is approached, D decreases as $1/\rho$ and consequently $\tilde{\tau}$ increases, as ρ^3, i.e., more rapidly than τ. Therefore, for this case, β decreases, reaching the range $\beta\ll1$, where the half-width of the line is determined by the time τ. Graphs of the function $F(x,\beta)$ for different β are shown in Fig. 1.

The total intensity of the depolarized light, consisting of the intensity of the light scattered by the fluctuations of the anisotropy and by the fluctuations of $\xi_{ml}\tilde{c}$ take the following form:

$$I_{ml}(\omega,\mathbf{p})=\frac{GN_0{}^2kT\tau^2}{L\pi}\left[\frac{1}{1+x^2}+SF(x,\beta)\right],\tag{11}$$

where

$$S=\frac{N^2\pi^2kT}{N_0{}^2B_1\rho_1{}^2\rho\sqrt{\beta}}=\frac{\pi N^2}{2N_0{}^2\sqrt{\beta}(b-\operatorname{arctg} b)}\langle\tilde{c}^2\rangle,$$

ρ_1 is the correlation radius for $T-T_c=1$°K. In this temperature range, where we can assume $\tau\propto(T/T_c-1)^{-0.8}$, S depends weakly on $T-T_c$.

We estimate the value of S in this temperature range. We begin with the quantity N_0/N. As is well known, for the anisotropy tensor indicated in footnote 1, we have

$$N_0=4\pi n[c_0(\alpha_1^{(1)}-\alpha_2^{(1)})+(1-c_0)(\alpha_1^{(2)}-\alpha_2^{(2)})],$$

where $\alpha_1^{(1)}$ and $\alpha_2^{(1)}$ are the principal polarizabilities of the molecules of the first component, $\alpha_1^{(2)}$ and $\alpha_2^{(2)}$ are the corresponding quantities for the second component, n is the number of molecules per unit volume, and c_0 is the mean concentration of the first component in the

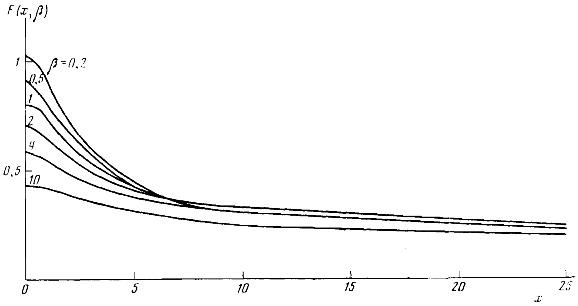

FIG. 1

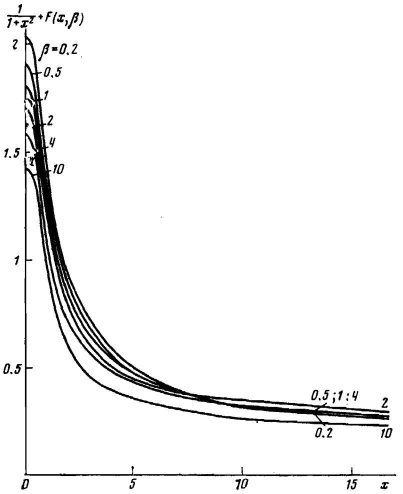

FIG. 2

mixture. Using this expression for the ratio $N_0/N = N_0(\partial N/\partial c_0)^{-1}$, we obtain $N_0/N = [c_0(\alpha_1^{(1)} - \alpha_2^{(1)}) + (1 - c_0)(\alpha_1^{(2)} - \alpha_2^{(2)})]/(\alpha_1^{(1)} - \alpha_2^{(1)} - \alpha_1^{(2)} + \alpha_2^{(2)})$. For a mixture of nitrobenzene—n-hexane at the critical temperature, we get $N_0/N \approx 1/2$, since the principal polarizabilities of the n-hexane molecules are much smaller than the corresponding quantities for the nitrobenzene molecules. Further, assuming N_0 and N to be quantities of the same order, we get as an estimate of S,

$$S \approx \langle \tilde{c}^2 \rangle \frac{1}{\sqrt{\beta}} = \langle \tilde{c}_f{}^2 \rangle \frac{\rho_f}{\rho} \frac{1}{\sqrt{\beta}},$$

where the index "f" indicates "far from the critical point." Using the estimates

$$\beta \approx 10(\rho_f/\rho)^2, \quad \langle \tilde{c}_f{}^2 \rangle \approx 1,$$

we find that $S \sim 1$ to 0.1. Thus, the new line that has been considered should be observable. Graphs of the function $1/(1 + x^2) + F(x, \beta)$ are shown in Fig. 2 for various β.

A line of the type considered appears also as a result of double scattering of light by terms in $\delta\epsilon_{ml}$ that are linear in the fluctuations, when one scattering act takes place from anisotropy fluctuations and the other from concentration fluctuations.[10] The intensity of this scattering will be referred to the intensity of scattering from that sum (difference) modes of concentration and anisotropy fluctuations as $N_0^2M^2/N^2$. This quantity is less than unity for the mixture of nitrobenzene and n-hexane.

We note that, in addition to the mechanisms considered, an important contribution to the depolarized light scattering near the critical stratification point is also made by double scattering from concentration fluctuations.[11,12]

I take this opportunity to express my thanks to V. S. Starunov and I. L. Fabelinskiĭ for valuable comments in a discussion of the present research.

---

[1] In the case of elongated molecules that are symmetric relative to the "long" axis, their mutual orientation can be characterized by the tensor $\xi_{ml} = (3/2)(\langle n_m n_l \rangle - (1/3)\,\delta_{ml})$, where n_m and n_l are the projections of the unit vector in the direction of the long axis of the molecule on the m and l axes of the laboratory system of coordinates; the averaging is carried out over the nearest neighbors of the central molecule.

[2] The cross term from the first and second terms in the intensity of depolarized scattered light is equal to zero.

[1] A. K. Atakhodzhaev, L. M. Kashaev, L. M. Sabirov, V. S. Starunov, T. M. Utarova, and I. L. Fabelinskiĭ, ZhETF Pis. Red. **17**, 95 (1973) [JETP Lett. **17**, 65 (1973)].

[2] M. Leontovich, J. of Phys. **4**, 499 (1941).

[3] S. M. Rytov, Zh. Eksp. Teor. Fiz. **58**, 2154 (1970) [Sov. Phys.-JETP **31**, 1163 (1970)].

[4] R. Brout, Phase Transitions (Russian translation), Mir, 1967.

[5] P. Debye, J. Bashaw, B. Chu, and D. M. Tan Greti, J. Chem. Phys. **44**, 4302 (1966).

[6] A. F. Chang, P. H. Keyes, Y. V. Sengers, and C. O. Alley, Phys. Rev. Lett. **27**, 1705 (1971).

[7] A. Z. Patashinskiĭ and V. L. Pokrovskiĭ, Zh. Eksp. Teor. Fiz. **50**, 439 (1966) [Sov. Phys.-JETP **23**, 292 (1966)].

[8] K. Kawasaki, Phys. Lett. **30A**, 325 (1969).

[9] R. A. Ferrell, Phys. Rev. Lett. **24**, 1169 (1970).

[10] A. Poulet, J.-P. Mathieu, Vibrational Spectra and the Symmetry of Crystals (Russian translation), Mir, 1973, ch. 10.

[11] A. F. Andreev, ZhETF Pis. Red. **19**, 713 (1974) [JETP Lett. **19**, 368 (1974)].

[12] D. W. Oxtoby and W. M. Gelbart, J. Chem. Phys. **60**, 3359 (1974).

Translated by R. T. Beyer
166