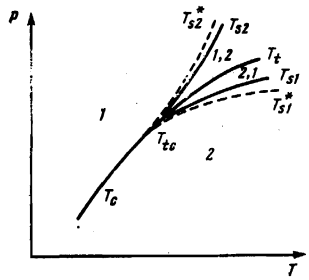
The distinctive features of the loss of stability of metastable phases in solids

A. P. Levanyuk

Institute of Crystallography, USSR Academy of Sciences
(Submitted January 10, 1974)
Zh. Eksp. Teor. Fiz. **66**, 2255–2261 (June 1974)

The fluctuations near the spinodes of first-order transitions that are accompanied by crystal-symmetry changes and that allow the introduction of a characteristic transition parameter η are considered. It is shown that in the low-symmetry phase the mean square of the spatially homogeneous fluctuations in η differs by a finite value from the mean square of the extremely long wavelength spatially inhomgeneous fluctuations. The corresponding "gap" vanishes at the second-order phase transition point, and is finite at the spinode of the low-symmetry phase, in which, in contrast to the critical points, the long-wavelength η fluctuations remain finite. The existence of the gap is explained by the relation between the η and density fluctuations, which, in a solid, are accompanied by the appearance of shear deformations if the fluctuations are spatially inhomogeneous. The singularities of the frequency spectrum of the fluctuations near the spinodal are investigated. The question of the nature of the light-scattering anomaly observed in the $\alpha \rightleftarrows \beta$ transition in quartz is briefly discussed.

A system undergoing a first-order phase transition can, as is well known, be in a metastable phase, owing to supercooling or superheating. In the P-T diagram there exist lines (spinodals) separating the region of metastable states from the regions where one or another phase is absolutely unstable (see the figure). It is natural to expect that the anomalies in the properties of a substance near a spinodal are the same as the anomalies in the properties near the critical points of the substance (in particular, near its second-order phase transition points). Indeed, the latter also lie on the boundary of the region of absolute instability of the phase, and it is precisely this circumstance that underlies the high fluctuation level, which, in its turn, is the cause of the major "critical anomalies" (see, for example, [1]). The idea that critical points and spinodes are similar is used in the analysis [2] of experimental data on the "tails" of the critical anomalies observed in many first-order phase transitions [2-4].



Phase diagram for a substance undergoing first- and second-order transitions: 1) the low-symmetry phase, 2) high-symmetry phase; T_c is the second-order-transition temperature, T_t the thermodynamic temperature of the first-order transition, T_{s1} and T_{s2} are respectively the temperatures at the spinodes of the low- and high-symmetry phases, T_{tc} is the temperature corresponding to the tricritical point, and $T_{s1}*$ and $T_{s2}*$ are the temperatures at which stability against inhomogeneous fluctuations is lost (see Sec. 3).

The object of the present paper is to draw attention to the fact that in the case of solids such an analogy is incomplete, and that the fluctuations near spinodes can be significantly different in nature from the fluctuations near critical points. As will be shown below, the mean squares of only the spatially homogeneous fluctuations diverge at the spinodes, whereas the spatially inhomogeneous fluctuations (no matter how long their wavelengths) remain finite. In other words, the magnitudes of the fluctuations expressed as functions of the wave vector k have "gaps" at $k=0$. As is well known, such gaps do not exist at critical points.

1. Let us first carry out a qualitative analysis. We shall be interested in first-order transitions for which a transition parameter η can be introduced in the same manner as is done in the Landau theory [5]. The spatially homogeneous fluctuations in η diverge at the spinodes of the high- and low-symmetry phases. Let us first verify that the spatially inhomogeneous fluctuations at the spinodes of the low-symmetry phase are finite, i.e., there is a gap in the fluctuation spectrum. The symmetry of the low-symmetry phase does not change when η is varied. Consequently, η should vary in proportion to the other quantities whose variation also does not change the symmetry. Of these quantities we shall be interested in only the density ρ.

There is always a gap in the density-fluctuation spectrum of a solid. The point is that, in contrast to the homogeneous fluctuations, the inhomogeneous ρ fluctuations are accompanied by shear deformations, and, consequently, the magnitudes of these fluctuations are determined by different elastic moduli: by the coefficient of hydrostatic compression in the first case and the coefficient of uniaxial compression that does not change the transverse dimensions of the body in the second. In fact, the inhomogeneous density fluctuations in a solid are longitudinal acoustic Debye waves, the square of whose velocity is proportional precisely to the coefficient of uniaxial compression. It is clear that owing to the linear coupling between $\Delta\eta$ and $\Delta\rho$, the η-fluctuation spectrum also contains a gap. The magnitude of this gap depends on the coefficient of proportionality between $\Delta\eta$ and $\Delta\rho$. The latter is proportional to the equilibrium value η_0 of the transition parameter (in the symmetric phase, where $\eta_0=0$, the linear coupling does not exist). It is clear, therefore, that the gap vanishes at a second-order phase transition point, but has a finite value at the point where the low-symmetry phase loses its stability in the first-order transition ($\eta_0 \neq 0$).

Let us now derive in the framework of the Landau theory explicit expressions for the fluctuations in the characteristic transition parameter and the strains in the

low-symmetry phase. We shall, for simplicity, restrict ourselves to the case of a one-component parameter η, and we shall not consider explicitly the anisotropy of the crystal. The expression for the thermodynamic potential then has the form

$$\Phi=\Phi_0+\frac{\alpha}{2}\eta^2+\frac{\beta}{4}\eta^4+\frac{\gamma}{6}\eta^6+r\eta^2u_{ll}+\frac{K}{2}u_{ll}^2+\mu\left(u_{ik}-\frac{\delta_{ik}}{3}u_{ll}\right)^2, \quad (1)$$

where K is the coefficient of hydrostatic compression, μ is the shear modulus, r is the coefficient attached to the mixed term, which reflects the coupling between η and u_{ik}. Let us compute, on the basis of (1), the second derivatives of Φ with respect to η at constant stresses σ_{ik} and constant T, i.e., $\Phi_{\eta\eta}^{\sigma T}$, and with respect to u_{ll} at constant T and constant generalized force conjugate to the quantity η, i.e., Φ_{uu}^{fT}:

$$\Phi_{\eta\eta}^{\sigma T}=2\eta_0^2(\beta_1^2-4\alpha\gamma)^{1/2}, \quad \Phi_{uu}=K(\beta_1^2-4\alpha\gamma)^{1/2}\left[(\beta_1^2-4\alpha\gamma)^{1/2}+\frac{2r^2}{K}\right]^{-1}; \quad (2)$$

the equilibrium value η_0 of the transition parameter is equal to

$$\eta_0=\frac{-\beta_1+(\beta_1^2-4\alpha\gamma)^{1/2}}{2\gamma}, \quad \beta_1=\beta-\frac{2r^2}{K}. \quad (3)$$

The expression under the radical sign in (3) vanishes at the spinode ($T=T_{S1}$) of the low-symmetry phase. As can be seen from (2), this leads to the vanishing of the second derivatives of Φ: $\Phi_{\eta\eta}^{\sigma T}$ and Φ_{uu}^{fT} (the isothermal modulus of hydrostatic compression); both of these quantities are proportional to $(T_{S1}-T)^{1/2}$. The specific heat and the coefficient of thermal expansion have a temperature dependence similar to that of the isothermal compressibility, i.e., they increase in proportion to $(T_{S1}-T)^{-1/2}$. With the quantities (2) are related the mean squares of the fluctuations in η and u_{ll}:

$$\langle(\Delta\eta)^2\rangle=TV^{-1}\Phi_{\eta\eta}^{\sigma T}, \quad \langle(\Delta u_{ll})^2\rangle=TV^{-1}\Phi_{uu}^{fT} \quad (4)$$

(V is the volume of the system), from which it follows that these fluctuations diverge at $T\to T_{S1}$.

Let us now consider the spatially inhomogeneous fluctuations. In computing them, we should bear in mind that the independent variables are not the components of the strain tensor, but the components of the displacement vector. Adding, moreover, the term $\frac{1}{2}\delta(\text{grad }\eta)^{1/2}$ to the expression (1), and proceeding further in the usual manner [5], we find

$$\langle\eta(\mathbf{k})\eta(-\mathbf{k})\rangle=TV^{-1}(\Phi_{\eta\eta}^{\sigma T}+16\mu r^2\eta_0^2/3K\tilde{K}+\delta k^2)^{-1}, \quad (5)$$

$$k^2\langle u_k(\mathbf{k})u_k(-\mathbf{k})\rangle=TV^{-1}(\Phi_{uu}^{fT}+{}^4/_3\mu)^{-1}, \quad (6)$$

$$k\langle iu_k(\mathbf{k})\eta(-\mathbf{k})+\text{к.с.}\rangle=2r\eta_0\tilde{K}^{-1}\langle\eta(\mathbf{k})\eta(-\mathbf{k})\rangle, \quad (7)$$

where $\tilde{K}=K+{}^4/_3\mu$, $\eta(\mathbf{k})$ and $\mathbf{u}(\mathbf{k})$ are the Fourier transforms of the functions $\eta(\mathbf{r})$ and $\mathbf{u}(\mathbf{r})$, and $u_{\mathbf{k}}$ is the component of the vector $\mathbf{u}(\mathbf{k})$ in the direction of the vector $\mathbf{k}$; the quantity δk^2 has been neglected in the expression (6), since we shall henceforth be interested in only long-wavelength fluctuations. It is evident that as $k\to 0$ the expressions (5) and (6) do not go over into the expressions (4). Thus, a gap exists in the fluctuation spectrum of not only ρ, but of η as well. The magnitude of this gap for η is, as can be seen from (5), proportional to η_0^2 and μ. It is therefore different from zero at the point where the low-symmetry phase loses its stability only for first-order phase transitions ($\eta_0\neq 0$) and only in solids ($\mu\neq 0$).

Let us estimate quantitatively the influence of the gap on the η-fluctuations for the ferroelectric transition in $BaTiO_3$ [6]. Let us assume the following values for the coefficients [6] (in esu; $\eta\equiv P$): $d\alpha/dT=7.4\times10^{-5}$, $\beta=10^{-12}$, $\gamma=2\times10^{-21}$, $r\approx 1$, $K=1.4\times10^{12}$, $\mu=0.4\times10^{12}$, $\tilde{K}=1.9\times10^{12}$, and $T_{S1}-T_t=5$ °K (T_t is the thermodynamic transition temperature). As estimates show, the second term in the expression (5) is comparable to the first term when $T_{S1}-T\approx 2-3°$, and is roughly 1.5 times less than it at $T=T_t$. Notice, however, the tentative nature of the estimates: the anisotropy of the elastic and striction constants of $BaTiO_3$ are not taken into account in them.

2. Let us now consider the temporal characteristics of the η and ρ fluctuations near the spinode of the low-symmetry phase. Let us compute the spectral densities [5] $\langle\eta(\mathbf{k},\omega)\eta(-\mathbf{k},-\omega)\rangle$ and $\langle\rho(\mathbf{k},\omega)\rho(-\mathbf{k},-\omega)\rangle$. The spectral intensity of scattering of any radiation by the η and ρ fluctuations is, as is well known, proportional to these spectral fluctuation densities. For light scattering, which is the only one to be considered below, the vector $\mathbf{k}$ can, as a rule, be assumed to be small [1)], which is taken into consideration in writing down the expressions given below. Since in the asymmetric phase the η and ρ fluctuations are coupled, the spectral density $\langle\eta(\mathbf{k},\omega)\rho(-\mathbf{k},-\omega)\rangle$ should, generally speaking, also be taken into account in the analysis of the spectrum of the scattered light. Such a refinement does not, however, alter the final results, and will not be carried out here. The functions $\langle\eta(\mathbf{k},\omega)\eta(-\mathbf{k},-\omega)\rangle$ and $\langle\rho(\mathbf{k},\omega)\rho(-\mathbf{k},-\omega)\rangle$ are, as is well known [5], proportional to the generalized susceptibilities, which are determinable from the corresponding equations of motion. The equation for η has the form

$$(-m\omega^2+i\gamma\omega+\Phi_{\eta\eta}^{uT})\eta(\mathbf{k},\omega)+2r\eta_0 iku_{\mathbf{k}}(\mathbf{k},\omega)+\alpha'\eta_0T'(\mathbf{k},\omega)=f_\eta(\mathbf{k},\omega), \quad (8)$$

where $\Phi_{\eta\eta}^{uT}$ is the second derivative of Φ, (1), with respect to η at constant u_{ik} and constant T; $T'(\mathbf{r},t)$ is the deviation of the local temperature from its equilibrium value; $\alpha'=d\alpha/dT$. Here we have allowed for terms of up to second order in ω; this is quite sufficient in the region of not too high frequencies, which is the most interesting region. Equation (8) should be supplemented by the equation of motion for the elastic strains u_{ik} and the entropy-balance equation. Choosing the x axis along the direction of the vector $\mathbf{k}$, we have

$$\rho\ddot{u}_x=\frac{\partial\sigma_{xx}}{\partial x}, \quad \sigma_{xx}=\tilde{K}u_{xx}+r\eta^2, \quad (9)$$

$$T\frac{\partial S}{\partial T}=C_{\eta u}\frac{\partial T}{\partial t}-T\alpha'\eta_0\frac{\partial\eta}{\partial t}=\varkappa\frac{\partial^2T}{\partial x^2}, \quad (10)$$

where $\varkappa$ is the thermal conductivity coefficient. In writing down (9) and (10) we assumed the coefficient of thermal expansion of the high-symmetry phase to be equal to zero; this assumption has practically no effect on the results. From (8)–(10) we find an expression for the inverse susceptibility $\alpha^{-1}(\mathbf{k},\omega)$ corresponding to η ($\eta(\mathbf{k},\omega)=\alpha(\mathbf{k},\omega)f(\mathbf{k},\omega)$):

$$\alpha^{-1}(\mathbf{k},\omega)=-m\omega^2+i\gamma\omega+\Phi_{\eta\eta}^{uT}-\frac{4r^2\eta_0^2k^2}{-\rho\omega^2+\tilde{K}k^2}+T\frac{\alpha'^2\eta_0^2i\omega}{i\omega C_{\eta u}+\varkappa k^2}. \quad (11)$$

Let us introduce the characteristic frequencies:

$$m\omega_0^2=\Phi_{\eta\eta}^{uT}+\frac{T\alpha'\eta_0^2}{C_\eta}=\Phi_{\eta\eta}^{us}, \qquad \rho\omega_1^2=\tilde{K}k^2, \quad \omega_2C_\eta=\varkappa k^2. \quad (12)$$

If the damping constant is sufficiently small, then the fluctuations are oscillations, and, what is more, since in real cases $\omega_1, \omega_2\ll\omega_0$, the frequency of these oscillations are close to ω_0. The quantity ω_0 is thus what is generally called the "soft-mode" frequency. The tem-

perature dependence of ω_0 is determined by the quantity $\Phi_{\eta\eta}^{uS}$ (see (12)), which is finite at $T = T_{S1}$. Consequently, the "soft-mode" frequency remains finite at the spinode of the low-symmetry phase. This conclusion applies equally well to phase transitions in solids as in liquids, since in deriving the expression (12) we took into consideration the fact that the elastic deformations do not have time to follow the oscillations in η. Let us recall that the oscillation frequency vanishes at a second-order phase transition point (see, for example, [7])

For low frequencies ($\omega < \omega_1, \omega_2$) the expression (11) gets simplified:

$$\alpha^{-1}(k, \omega) = -m\omega^2 + i\gamma\omega + \Phi_{\eta\eta}^{\sigma T} + 16\mu r^2\eta_0^2/3\bar{K}K. \quad (13)$$

Since [5]

$$\langle \eta(k,\omega)\eta(-k,-\omega)\rangle = \frac{T}{\pi\omega}\operatorname{Im}\alpha(k,\omega),$$

when $m\gamma^2/4$ exceeds the sum of the last three terms in (13), the function $\langle\eta(k, \omega)\eta(-k, -\omega)\rangle$ has a maximum at $\omega = 0$. If $\mu = 0$, then the magnitude of this maximum increases as $T \to T_{S1}$ like $(T - T_{S1})^{-1}$, while the width decreases as $(T - T_{S1})^{1/2}$. Consequently, the total intensity of scattering of light by the η fluctuations increases in proportion to $(T - T_{S1})^{-1/2}$.

Thus, if the shear modulus is sufficiently small, then there is enhanced scattering of light near the spinode, this enhancement occurring largely on account of the increase in the intensity of the unshifted component. At the same time the side maxima corresponding to the frequency ω_0 exist right up to the spinode. This differs significantly from what obtains near second-order phase transition points, where the Raman components connected with the η fluctuations merge as $T \to T_c$ [8].

A similar result is valid for the spectral composition of the light scattered by the density fluctuations. The Raman frequency in this case is given by

$$\omega_\rho^2 = \rho^{-1/3}(\Phi_{uu}^{fS} + {}^4/_3\mu), \quad \Phi_{uu}^{fS} = \Phi_{uu}^{fT} C_{f\sigma}/C_{\eta\sigma}. \quad (14)$$

Since $\Phi_{uu}^{fT} \propto (T - T_{S1})^{1/2}$ and $C_{f\sigma} - C_{\eta\sigma} \propto (T - T_{S1})^{-1/2}$, the modulus remains finite at $T = T_{S1}$. At $\mu = 0$, there is an enhancement of the scattered-light intensity $I_\rho \propto (T - T_{S1})^{-1/2}$, an enhancement which, near the spinodal, occurs owing to an increase in the unshifted component.

The system (8)–(10) can also be used to analyze the η-relaxation-induced anomalies in the velocity and coefficient of absorption of sound [9]. Eliminating $\eta(k, \omega)$, we find from Eq. (9) that

$$k^2 = \frac{\rho\omega^2}{\bar{K}} \frac{i\gamma\omega + \Phi_{\eta\eta}^{uS}}{i\gamma\omega + \Phi_{\eta\eta}^{\sigma S} + 16\mu r^2\eta_0^2/3K\bar{K}}. \quad (15)$$

The quantities

$$\tau^{uS} = \gamma(\Phi_{\eta\eta}^{uS})^{-1}, \quad \tau^{\sigma S} = \gamma(\Phi_{\eta\eta}^{\sigma S} + 16\mu r^2\eta_0^2/3K\bar{K})^{-1} \quad (16)$$

have the meaning of the corresponding η-relaxation times in the inhomogeneous case. For second-order transitions, $\tau_1^{\sigma S} \to \infty$ as $T \to T_c$. The anomaly in the so-called relaxation absorption of sound [9] is connected precisely with this circumstance. On the other hand, as $T \to T_{S1}$ not only do the quantities $\tau_1^{\sigma S}$ remain finite, but so also does the quantity $\Phi_{\eta\eta}^{\sigma S}$.

3. Let us discuss the results. The finiteness of the long-wavelength fluctuations of the characteristic parameter (and, consequently, the finiteness of the correlation length) at the spinode indicates that the fluctuations do not cause the thermodynamic quantities (e.g., the specific heat) to diverge at this point, i.e., it indicates the finiteness of the so-called fluctuation or correlation corrections [10,11]. Nevertheless, in the low-symmetry phase, the specific heat and the quantities similar to it do diverge as $T \to T_{S1}$, this being due to the temperature dependence of η_0 (the Landau theory considers only the contribution that such a dependence makes to the anomalies). It is not difficult to verify, using the expression (1), that the specific heat varies like $(T_{S1} - T)^{-1/2}$ as $T \to T_{S1}$.

It must follow from the above arguments, if we carry them over to the high-symmetry phase, that there is no gap for the η fluctuations in the high-symmetry phase. Nevertheless, the spatially inhomogeneous fluctuations also remain finite at the spinode of this phase, i.e., a gap nonetheless exists, this being due to the influence of the critical fluctuations on the temperature dependence of the thermodynamic quantities. Allowance for such influence (this requires the consideration of the interaction between the η and ρ fluctuations – an interaction which, in the high-symmetry phase, can only be nonlinear) leads to the conclusion that the loss by the high-symmetry phase of its stability occurs not as a result of the growth of the η fluctuations, but as a result of the vanishing of the modulus of hydrostatic compression at a higher temperature [12,13]. Naturally, the η fluctuations are finite at this temperature. Also finite are the ρ fluctuations, owing to the existence of the above-indicated gap.

Thus, loss of stability in a solid occurs at the spinodes only for one and two degrees of freedom of the system: loss of stability against the homogeneous ρ fluctuations in the high-symmetry phase and against the homogeneous η and ρ fluctuations in the low-symmetry phase. We can attain the points at which the inhomogeneous long-wavelength fluctuations diverge by "clamping" the crystal. In the figure the temperatures of these points for the low- and high-symmetry phases are denoted by T_{S1}^* and T_{S2}^*. Let us emphasize, however, that the values of these temperatures depend on the "clamping" conditions, e.g., on precisely which value of the density ρ is fixed. Using the results of [13], we can verify that the long-wavelength ρ fluctuations diverge at $T = T_{S2}^*$ (in the high-symmetry phase), since the modulus of uniaxial compression vanishes at this point, while the η fluctuations still remain finite. The situation is, apparently similar to that obtaining at $T = T_{S1}^*$.

Let us discuss the possibility of attaining the spinodes in an experiment. A general method of preparing metastable phases consists, as is well known, in eliminating as many of the nucleation centers of the stable phase as possible. This in a solid may just require the prevention of the nucleation of the new phase on the surface of the sample. Indeed, the appearance of a nucleating center of a new phase inside the old one leads to the deformation of the crystal, the energy connected with this deformation being proportional to the volume of the nucleating center [14]. This circumstance inhibits the growth of even an arbitrarily large nucleating center inside the sample, making supercooling or superheating inevitable. If the first-order transition is near enough to being of second order (i.e., if it is sufficiently close to the critical point), then a nucleating center of the new phase does not grow even at the spinode. Nucleation on the surface can be eliminated by creating in the crystal

a nonuniform temperature field in such a way that the temperature at the center of the crystal is lower (or higher) than the temperature at its periphery. Furthermore, such a temperature distribution, which has already been experimentally realized [15], effects (if the crystal is sufficiently large) a partial "clamping" of the internal region of the crystal, the "clamping" being complete in the case of an infinitely large shear modulus. Thus, there arises the possibility of getting near to the temperatures T^*_{S1} and T^*_{S2}.

Let us again touch upon the distinctive features of light scattering near the tricritical point determined by the conditions $\alpha = 0$ and $\beta_1 = 0$ (see the figure). Here we actually assume that the influence of the critical fluctuations on the temperature dependence of the coefficients of the thermodynamic potential is negligible. Under conditions when this influence is substantial the presence of the shear modulus leads to the conversion of the second-order transition into a first-order transition [13], and the concept of a tricritical point itself loses meaning. As follows from (2) and (3), for the transition corresponding to this point, $\eta^2 \propto (T_{tc} - T)^{1/2}$ and $\Phi^{\sigma T}_{\eta\eta} \propto T_{tc} - T$. Consequently (see (5)), $\langle \eta(\mathbf{k})\eta(-\mathbf{k})\rangle \propto (T_{tc} - T)^{-1/2}$ if k is sufficiently small, which, as has already been noted, is practically always the case. Of the same form is the temperature dependence of the intensity of scattering of light for the cases when the coefficient of proportionality between the change Δn in the refractive index and $\Delta\eta$ does not vary with temperature. This is the case if the symmetry of the crystal admits of a linear dependence on η of the permittivity tensor ϵ_{ik}, which describes the optical properties of the medium. A more typical case is the one in which the dependence of ϵ_{ik} on η can only be quadratic. In this case [16] $\Delta n = \eta_0 \Delta\eta$ and

$$I \sim \langle (\Delta n)^2 \rangle \sim \eta_0^2 \langle \eta(\mathbf{k})\eta(-\mathbf{k})\rangle. \qquad (17)$$

Taking into account the above-given temperature dependences of η_0^2 and $\langle \eta(\mathbf{k})\eta(-\mathbf{k})\rangle$, we can verify that the intensity of scattering of light remains finite as $T \to T_{tc}$. This does not agree with the results obtained in [16,7], where the presence of the shear modulus is not taken into account. The conclusion is reached in these papers that the intensity of scattering of light increases in proportion to $(T_{tc} - T)^{-1/2}$, and attempts are made to explain on this basis the sharp increase (by roughly a factor of 10^4) in the intensity of scattering of light in the region of the $\alpha \rightleftharpoons \beta$ transition in quartz [17]. Such an explanation is evidently incorrect. To solve the problem of the nature of the strong anomalous scattering near the $\alpha \rightleftharpoons \beta$ transition in quartz, it is necessary to take into account the contribution of the scattering by the static inhomogeneities to the total scattering intensity, as well as the fact that the true temperature dependence of the coefficients of the thermodynamic potential is different from the dependence given by the Landau theory.

The author is grateful to V. L. Ginzburg, D. G. Sannikov, and A. A. Sobyanin for a discussion of the present paper.

[1)] This assertion ceases to be valid when the correlation length of the fluctuations becomes comparable to the wavelength of the light, i.e., in the immediate neighborhood of the points where the system loses its stability against inhomogeneous fluctuations—the critical points, for example (for other examples, see Sec. 3).

[1] M. Fisher, The Nature of the Critical State (Russ. transl.), Mir, 1968.
[2] A. V. Voronel', ZhETF Pis. Red. 14, 263 (1971) [JETP Lett. 14, 174 (1971)].
[3] A. V. Voronel' and S. R. Garber, Zh. Eksp. Teor. Fiz. 52, 1464 (1967) [Sov. Phys.-JETP 25, 970 (1967)].
[4] B. A. Strukov and K. S. Ivanov-Shitz, Kristallografiya 18, 866 (1973) [Sov. Phys.-Crystallogr. 18, 548 (1974)].
[5] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1964 (Eng. Trans., Addison-Wesley Publishing Co., Reading, Mass., 1969).
[6] W. Känzig, Ferroelectrics and Antiferroelectrics, Academic Press, New York, 1957 (Russ. Transl., IIL, 1960).
[7] V. L. Ginzburg, Usp. Fiz. Nauk 77, 662 (1962) [Sov. Phys.-Uspekhi 5, 649 (1963)].
[8] V. L. Ginzburg and A. P. Levanyuk, Zh. Eksp. Teor. Fiz. 39, 192 (1960) [Sov. Phys.-JETP 12, 138 (1961)].
[9] L. D. Landau and I. M. Khalatnikov, Dokl. Akad. Nauk SSSR 96, 469 (1954).
[10] A. P. Levanyuk, Fiz. Tverd. Tela 5, 1776 (1963) [Sov. Phys.-Solid State 5, 1294 (1964)].
[11] V. G. Vaks, A. I. Larkin, and S. A. Pikin, Zh. Eksp. Teor. Fiz. 51, 361 (1966) [Sov. Phys.-JETP 24, 240 (1967)].
[12] O. K. Rice, J. Chem. Phys. 22, 1535 (1954).
[13] A. I. Larkin and S. A. Pikin, Zh. Eksp. Teor. Fiz. 56, 1664 (1969) [Sov. Phys.-JETP 29, 891 (1969)].
[14] B. Ya. Lyubov and A. L. Roĭtburd, Dokl. Akad. Nauk SSSR 131, 552 (1960) [Sov. Phys.-Dokl. 5, 382 (1960)]; B. Ya. Lyubov, Kineticheskaya teoriya fazovykh prevrashcheniĭ (The Kinetic Theory of Phase Transitions), Metallurgiya, 1969.
[15] S. É. Khaĭkin and N. P. Bene, Dokl. Akad. Nauk SSSR 23, 31 (1939).
[16] V. L. Ginzburg and A. P. Levanyuk, Issledovaniya po éksperimental'noĭ i teoreticheskoĭ fizike (Investigations in Experimental and Theoretical Physics (Collection of Papers in Memory of G. S. Landsberg)), AN SSSR, 1959, p. 107; J. Phys. Chem. Solids 6, 51 (1958); L. P. Levanyuk and A. A. Sobyanin, Zh. Eksp. Teor. Fiz. 53, 1024 (1967) [Sov. Phys.-JETP 26, 612 (1968)].
[17] I. A. Yakovlev, T. S. Velichkina, and L. F. Mikheeva, Dokl. Akad. Nauk SSSR 107, 675 (1956) [Sov. Phys.-Dokl. 1, 215 (1956)]; Kristallografiya 1, 123 (1956) [Sov. Phys.-Crystallogr. 1, 91 (1956)]; I. A. Yakovlev and T. S. Velichkina, Usp. Fiz. Nauk 63, 411 (1957).

Translated by A. K. Agyei
230