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Weak crystallization theory

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Abstract:

We discuss the weak crystallization of a liquid or a liquid crystal which is a first-order phase transition close to a continuous one. Such a phase transition is accompanied by the softening of the order parameter, describing the short-wavelength density modulation. The softening occurring in the vicinity of certain lines or surfaces in the reciprocal space induces a number of characteristic peculiarities of the transition. Quantitatively the softening may be characterized by the value of the gap, figuring in the expression for the pair correlator of fluctuations of the order parameter. The value of the gap is small near the phase transition temperature and possesses a complex behaviour. A peculiarity of the weak crystallization is the important role of fluctuations of the order parameter accounted for by a large phase volume of the fluctuations. We investigate the behaviour of the gap both in the framework of mean field approximation and with the effects of fluctuations taken into account. The theory enables us to construct the phase diagram of the system which appears to be rather reach for all the considered cases. In this diagram there arise (depending on the strength of the anisotropy and fluctuations) both crystalline phases of different symmetry and smectic, columnar and quasicrystalline phases. The dynamics of the order parameter is pure relaxational and the respective kinetic coefficient proves to be insensitive to the phase transition, therefore the relaxation time is inversely proportional to the gap. All physical characteristics of the system in some degree depend on the proximity to the transition point. For example the heat capacity and the compressibility of the system have singular contributions which may be expressed explicitly through the value of the gap. The most singular behaviour near the phase transition is inherent in the bulk viscosity coefficients determining the sound attenuation.

WEAK CRYSTALLIZATION THEORY

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1. Introduction

It was Landau [1937] who made the first attempt to study the crystallization of a liquid in the framework of his phase transition theory. At the crystallization there emerges a short-wavelength density modulation which should be regarded as the order parameter of this phase transition. Since in the expansion of the free energy there is a term, cubic with respect to the introduced parameter, the crystallization must be a first-order phase transition. This conclusion is in agreement with the experimental situation.

However, the description of the crystallization in the framework of the Landau phase transition theory is possible if the mentioned cubic term is anomalously small. In this case the crystallization will be close to a continuous transition. This circumstance, in particular, implies that a jump of entropy at this transition will be small, i.e., much smaller than it usually is at the crystallization of liquids. Besides, the amplitude of the short-wavelength density modulation at such a transition will be small in comparison with the density of the liquid. This phase transition will be termed weak crystallization.

The development of the weak crystallization theory was stimulated by considerable achievements in the theory of second-order phase transitions where the long-wavelength fluctuations of the order parameter play a key role. Although the order parameter of the weak crystallization theory is short-wavelength, its fluctuations also play an essential role in the theory. The problem is that the fluctuations "soften" in the vicinity of the weak crystallization phase transition as fluctuations of the order parameter near the second-order phase transition.

The softening of fluctuations of the density modulation should lead to the singular behaviour of the structural factor, which may be directly measured by neutron scattering or by X-ray scattering. This softening also manifests itself in the anomalous behaviour of such characteristics as compressibility or heat capacity of the sample. As was noted in our paper [Kats, Lebedev and Muratov 1988], most sensitive to the influence of fluctuations are viscosity coefficients, determining the attenuation of sound.

A peculiarity of the weak crystallization theory in comparison with the conventional second-order (or weak first-order) phase transitions is that the softening of the order parameter takes place in the vicinity of some sphere in the reciprocal space. Therefore the phase transition gives rise to condensation of several Fourier components of the order parameter with wave vectors near the sphere. There can be a few of such phases due to different possible structures of the short-wavelength order parameter. As a result, there may occur crystalline and quasicrystalline phases, possessing different symmetries, between which phase transitions can also take place. Therefore the phase diagram of the system may prove to be fairly rich. The richness of the phase diagram distinguishes weak crystallization from usual phase transitions with the conventional long-wavelength order parameter.

Apparently, the first attempt to construct the phase diagram of certain systems with weak crystallization was made by Kirzhnits and Nepomnyaschiy [1970]. They have formulated the possibility of existence of two types of crystals – conventional crystals where atoms are localized in sites of a regular lattice and coherent crystals characterized by a smooth periodic density modulation. They have attributed solid helium to the second class. Kirzhnits and Nepomnyaschiy have considered some structures of coherent crystals (body-centered cubic, face-centered cubic,

hexagonal and rhombic) and computed their energies in the mean field approximation.

The possibitity of existence of cubic structures in neutron stars was discussed in the framework of mean field weak crystallization theory in the work by Baym, Bethe and Pethic [1971]. Then the conclusions they had arrived at were specified by other authors [e.g., Alexander and McTague 1978, Liebler 1980, Fredrickson and Helfand 1987, Kendrick, Sluckin and Grimson 1988]. A brief review of results obtained for weak crystallization in the mean field approximation can be found in the monograph [Toledano and Toledano 1987].

Besides the crystalline phases in the theory of the weak crystallization there appear quasicrystalline phases. Experimentally such phases were firstly observed by Shechtman [1984] and Bancel [1985] who, studying fastly cooled alloys by means of X-ray scattering, obtained a system of reflexes whose analysis testifies for the presence of an icosahedrical quasi-crystalline ordering in the alloy. It is interesting to note that already Alexander and MacTague [1978] noted the possibility of existence of icosahedral structures. Recently there appeared a number of works where quasi-crystalline phases are studied in terms of the weak crystallization theory [see Kalugin, Kitaev and Levitov 1985, Back 1985, Troian and Mermin 1985, Jaric 1986, Toner 1986]. All these studies were performed in the framework of the mean field approximation.

The following important comment was made by Brazovsky [1975]. He has shown that in the weak crystallization theory an essential role is allotted to thermal fluctuations, concentrated in the vicinity of the above mentioned sphere in the reciprocal space. The strength of the order parameter fluctuations is so large that due to fluctuation effects the crystallization becomes a first-order transition even in the absence of terms, odd in the order parameter, in the expansion of the free energy. Let us stress that fluctuations of the order parameter are strong both in the high-temperature isotropic phase and in the low-temperature crystalline phase since the disturbance of the structural factor associated with the appearance of the density modulation is weak due to smallness of the modulation.

In our survey we will mainly pay attention to fluctuation effects since they are characteristic of weak crystallization and determine the majority of peculiarities of a system near a weak crystallization phase transition. Note that if though fluctuations are quantitatively small, they bring about some qualitative effects. For example, they stabilize the high-temperature (high-symmetry) phase and make it metastable at all temperatures.

We would like to note that the approach elaborated in the framework of the weak crystallization theory is used in the theory of instabilities. Namely, a variety of structures appearing as a result of the instability process near the point of absolute instability may be studied by weak crystallization theory methods. We refer a reader interested in the subject to the monograph by Gershuni and Zhukhovitsky [1976] and refs. [Malomed 1983, Malomed and Tribelsky 1987, Malomed, Nepomnyaschiy and Tribelsky 1989]. Practically all results presented in our survey are applicable for the description of structures arising at convective instabilities. Note, however, that for such transitions fluctuation contributions (the most part of our survey is devoted to) are irrelevant due to the macroscopic value (of the order of the thickness of the sample) of the period of the structures which arise.

Weak crystallization theory was also successfully applied to investigation of the structure of the so-called "blue phase" of cholesteric liquid crystals. Among the works devoted to this problem one should mention the works by Brazovsky and Dmitriev [1975], Brazovsky and Filev [1979], Kleinert and Maki [1981], Grebel, Hornreich and Shtrikman [1983]. It is interesting that Kleinert and Maki have argued that the icosahedral phase can be realized as a metastable one in cholesterics.

In this review we are not going to study this range of problems, first, because the formation of "blue phases" is associated with "condensation" of a fairly specific orientation order parameter, and, second, because these problems have already been rather extensively described in the literature (see,

e.g., the survey by Belyakov and Dmitrienko [1985]). So to keep our review within bounds we will consider only those cases of weak crystallization where the short-wavelength density modulation φ is the order parameter. There is another circumstance. In our review we will pay much attention to fluctuation effects at weak crystallization phase transitions. Fluctuations almost undoubtedly are irrelevant at phase transitions of weak crystallization into "blue phases", which is accounted for by a large value of the period of these structures.

The most comprehensive description, known to us, of the weak crystallization theory of an isotropic liquid can be found in the work by Brazovsky, Dzyaloshinsky and Muratov [1987]. In this paper both the mean field theory and the fluctuation effects are discussed. The results of Brazovsky et al. are in agreement with the conclusions made by Dyugaev [1982], who using the microscopic approach investigated the π-meson condensation. The weak crystallization theory, with the order parameter fluctuations taken into account, was also discussed in the paper by Fredrickson and Helfand [1987].

Unfortunately, for known simple liquids the crystallization is a strong first-order transition, therefore the theory under study is not applicable to such materials. Nevertheless, there is a broad class of substances experiencing phase transitions, which could be regarded as weak crystallization. We mean the substances, possessing liquid-crystalline phases. The review of properties of liquid crystals may be found in monographs by de Gennes [1974], Chandrasekhar [1977] and Pikin [1981], and in the survey by Stephen and Straley [1974].

As is well known, in the liquid-crystalline state one can observe diverse phase transitions, as a rule, associated with partial or complete crystallization. Firstly, transitions from the nematic (which is an anisotropic liquid) into smectic state (which possesses one-dimensional translational order) can be termed crystallization. These transitions are usually close to continuous phase transitions. Partial (two-dimensional) crystallization is also the nematic–columnar phase transition observed often in discotic liquid crystals. Besides, complete crystallization of smectics is also weak crystallization. The latter statement requires some clarification.

Different smectic phases are traditionally labelled by the letters A–I. Not all of these phases are genuinely smectic (genuine smectics are characterized by the one-dimensional density modulation). Namely, genuine smectics are smectics-A, C and part of smectics-B. To avoid confusion, in conformity with the conventional practice, genuine smectics-B will be called hexatic smectics-B or simply hexatics (the title is accounted for by the most typical case where there is a sixth-order axis in the symmetry group of this phase). A considerable part of smectics-B and practically all smectics D–I are, strictly speaking, genuine crystals, therefore we will call these phases crystalline smectics.

The mentioned crystalline phases are called smectics because of their layered structure in virtue of which they are in experiment hardly distinguishable from genuine smectics. In particular, in crystalline smectics the shear module is anomalously small, which testifies for a weak density modulation in a smectic layer. It means that genuine smectic–crystalline smectic transitions can be studied in the framework of weak crystallization theory. Small values of latent heats of these transitions also confirm it.

In this connection we would like to say some words about the comparison of the theory with experiment. The experimental data concerning crystallization transitions in liquid crystales may be found in the reviews by Chandrasekhar [1982], Gramsbergen, Longa and de Jeu [1986] and in the monograph by de Jeu [1980]. As usual, the phase diagram contains many different phases. Therefore it is impossible to describe the behaviour of any substance in the overall region of existence of the liquid-crystalline state on the basis of a simple model, since a great number of parameters characterizing anisotropy, fluctuations, mutual influence of neighboring phase transitions and so on must be taken into account.

Nevertheless, the proposed theory may be used for a quantitative description of a substance in some particular regions of the phase diagram. The theory predicts singular contributions to different physical properties of the substance. Besides, the weak crystallization theory enables us to explain qualitatively the diversity and the structure of observable phase diagrams and the general character of the behaviour of observable quantities.

Peculiarities of crystallization phase transitions in the liquid-crystalline state are due to the anisotropy of the state, which ordinary liquids do not possess. This anisotropy leads to a nonuniform angular distribution of the regions in the reciprocal space where density fluctuations soften. Besides, in a number of cases fluctuations of the orientational order parameter are also relevant. This complicates the consideration of crystallization of liquid crystals in comparison with the weak crystallization of an isotropic liquid. Nevertheless, the problem is not hopeless.

For weakly anisotropic nematics the weak crystallization theory may be constructed by analogy with the weak crystallization theory of liquids [Kats and Muratov 1988]. For a strong anisotropy the character of crystallization is essentially different. The density fluctuations in this case soften either in the vicinity of a circle or in the vicinity of certain points in the reciprocal space. The first case is realized for the nematic–smectic-C, nematic–columnar phase, smectic-A–crystalline smectic transitions; the second case is realized for the nematic–smectic-A, nematic–smectic-C or hexatic–crystalline smectic transitions.

If density fluctuations soften in the vicinity of a circle (or two circles) in the reciprocal space, then, like in the isotropic case, fluctuation effects are very strong. In the most explicit way the role of fluctuations manifests itself in the nematic–smectic-C transition, which in the mean field theory is a second-order phase transition. Fluctuations transform this transition into a first-order transition [Swift 1976]. The theory of the smectic-A–crystalline smectic and nematic–columnar phase transitions was studied in our work [Kats, Lebedev and Muratov 1989].

If density fluctuations soften down only in the vicinity of isolated points in the reciprocal space, the description of such crystallization reduces to the description of a standard phase transition with the long-wavelength order parameter. In the mean field theory the hexatic–crystalline smectic transition is a first-order transition, the nematic–smectic-A and smectic-C–crystalline smectic transitions are second-order transitions. However, the analysis of the latter transitions is complicated by fluctuations of the director. These fluctuations may lead to transformation of a second-order transition into a first-order transition [Halperin, Lubensky and Ma 1974, Wiegmann and Filev 1975].

We would like to note that besides the conventional (thermotropic) liquid crystals there also exist the so-called lyotropic liquid crystal phases observing in water solutions of different organic molecules. The lyotropic state possesses the same variety of phases as the thermotropic one. The basic experimental data concerning lyotropic liquid crystals may be found in the books by Blumstein [1978] and by Brown and Wolken [1979]. But we should stress that crystallization transitions in lyotropic systems cannot be examined in the framework of the weak crystallization theory. The problem is that the density modulation emerging at the crystallization in lyotropic systems has several Fourier harmonics of the same order. This leads to the conclusion that for lyotropic systems higher-order terms in the Landau expansion describing the self-interaction of the order parameter play an important role, and therefore we cannot limit ourselves only to the first terms of the expansion.

Some words about notations of different phases in our survey. We shall use the notations, known from the solid state physics such as body-centered cubic (BCC) or face-centered cubic (FCC) structures. These notations are prompted by the concept of a crystal as a system of atoms, localized in sites of a regular lattice. This description can be applied to conventional crystals, where the mean atom displacement is small in comparison with the interatomic distance. But in the phases emerging

as a result of weak crystallization transitions the mean displacement of atoms is of the order of interatomic distance, and therefore the above mentioned scheme is not adequate for describing such structures. Nevertheless we will utilize these designations, having in mind that the symmetry of the density modulation function in the appropriate phases has the same symmetry as in conventional crystalline phases.

The structure of our review is the following. In section 2 we consider the weak crystallization of an isotropic liquid and in sections 3 and 4 we consider the weak crystallization theory in the anisotropic state, namely in liquid crystals. A short description of liquid-crystalline phases is presented at the beginning of section 3. Section 2 is mainly methodical, since known conventional liquids crystallize by strong first-order transitions. Therefore we will not consider softening of the order parameter near two or more spheres in the reciprocal space. This possibility, actually realized in smectic phases of substances consisting of polar molecules, is studied in section 3 where these substances are considered. The theory of crystallization of weakly anisotropic liquid crystals presented in section 4 is close to the theory of an isotropic liquid. Since the majority of liquid-crystalline phases are strongly anisotropic, the theory of such systems described in section 3 is mainly related to experiment.

2. Weak crystallization theory of liquids

We are now starting our survey with the theory of weak crystallization of an isotropic liquid. Despite the fact that so far we are ignorant of any simple liquids crystallizing by a weak first-order phase transition (note that there is probably one alloy experiencing weak first-order crystallization [Voronel, Steinberg and Sverbilova 1980]), we believe it stands to reason to study this theory in detail. By presenting this simple example, we can describe a method also applicable to more sophisticated cases.

The theory of weak crystallization is constructed in terms of the Landau phase transition theory. Therefore, in the first place, one should introduce the order parameter, associated with the transition. For this purpose, define the quantity

$$\varphi = \rho_{\text{short}}/\rho\,. \tag{2.1}$$

Here ρ is a long-wavelength component of the density and ρ_{short} is a short-wavelength component of the density. In virtue of the definition, the field φ contains Fourier components with wave vectors of the order of the inverse molecular size. In the liquid phase the average $\langle\varphi\rangle = 0$, in the crystalline phase there emerges a non-zero average $\langle\varphi\rangle$. Thus, the field φ can be regarded as the crystallization order parameter so this is how φ will be termed hereafter.

As follows from the definition (2.1), the condensate of the field φ (i.e., $\langle\varphi\rangle$) characterizes the amplitude of the short-wavelength density modulation of the crystalline phase. In practically all known crystals $\langle\varphi\rangle \sim 1$, whereas at the weak crystallization there should appear a condensate, satisfying the condition

$$\langle\varphi\rangle \ll 1\,. \tag{2.2}$$

This inequality means that in particular in the crystalline phase in the vicinity of the phase transition point, the shear modules will be anomalously small.

2.1. Landau functional

Weak crystallization can be described phenomenologically by means of the thermodynamic potential Ω, which is the functional of the chemical potential ζ, temperature T and field h, thermodynamically conjugated to the order parameter φ. The physical state of the system corresponds to the value $h = 0$. However, it is convenient to formally retain the dependence of the thermodynamic potential on h. This is because the coefficients of the expansion of Ω in h are just the correlation functions of the order parameter.

The differential of the thermodynamic potential is

$$d\Omega = -\int dr\, (\langle\rho\rangle\, d\zeta + \langle s\rangle\, dT + \langle\varphi\rangle\, dh)\,. \tag{2.3}$$

Here $\langle\rho\rangle$ and $\langle s\rangle$ are densities of the mass and entropy, averaged over fluctuations. Let us perform the Legendre transformation

$$\Omega' = \Omega + \int dr\, \langle\varphi\rangle h\,. \tag{2.4}$$

For the new function Ω', which we will also call the thermodynamic potential, from (2.3) follows the relation

$$\delta\Omega'/\delta\langle\varphi(r)\rangle = h(r)\,. \tag{2.5}$$

Since for the physical state of the system $h = 0$, this state, in virtue of (2.5), corresponds to the extremum of $\Omega'(\langle\varphi\rangle)$. The ground state of the system corresponds to the absolute minimum of Ω'.

The thermodynamic potential Ω or Ω' possesses total rotational and translational invariance. The same invariance is also inherent in the liquid state, where $\langle\varphi\rangle = 0$. However in the case when the minimum of Ω' is reached at $\langle\varphi\rangle \neq 0$, the ground state will no longer possess translational and rotational invariance. This phenomenon is spoken of as spontaneously breaking of the symmetry at a phase transition.

2.1.1. Structure of the condensate

A few words are in order about the structure of the condensate of the field φ, resulting under the crystallization. Generally speaking, the average $\langle\varphi\rangle$ is a sum of an infinite number of spatial Fourier harmonics. Yet, under the condition (2.1), out of these harmonics one can single out principal harmonics, whose number is finite. The remaining harmonics will have amplitudes much smaller than the amplitudes of the principal harmonics.

Thus, in the leading approximation the average $\langle\varphi\rangle$ could be represented as

$$\langle\varphi(r)\rangle = 2\,\mathrm{Re}\sum_{n=0}^{N} a_n \exp(i\boldsymbol{q}_n\cdot\boldsymbol{r}) = \tilde{\sum_n} a_n \exp(i\boldsymbol{q}_n\cdot\boldsymbol{r})\,. \tag{2.6}$$

Here N is the number of the principal harmonics, a_n are their amplitudes. The tilde over the summation sign in (2.6) means that the summation is carried out over the positive (from 1 to N) and over the negative (from $-N$ to -1) values of n. Then

$$a_{-n} = a_n^*, \quad \boldsymbol{q}_{-n} = -\boldsymbol{q}_n\,. \tag{2.7}$$

The asterisk in (2.7) denotes complex conjugation. The summation procedure, denoted by the tilde, will be used by us hereafter.

From the condition (2.1) results the inequality

$$|a_n| \ll 1 . \tag{2.8}$$

Since $\langle\varphi(\boldsymbol{r})\rangle$ is determined by the extremum of the thermodynamic potential (2.4), one can formulate the iteration procedure for calculating higher-order harmonics via the principal harmonics (2.6). Then there arise harmonics with wave vectors, which are linear combinations of the wave vectors of the principal harmonics. Amplitudes of higher-order harmonics will have the order $|a|^2$, $|a|^3$ and so on, depending on the step of the iteration procedure where they emerge. From the inequality (2.8) the amplitudes of higher-order harmonics prove to be much smaller than the amplitudes of the principal harmonics, which in fact justifies the above assertion.

Note that the average of the form (2.6) may belong both to the crystalline and quasicrystalline states. The latter is realized if among the wave vectors entering in (2.6), there are some incommensurate vectors. The number of crystalline and quasicrystalline structures of different symmetries is rather large. The question which of the states is actually realized, cannot be solved in a general form; the reply to this question should be sought for by minimizing the functional $\Omega'(\langle\varphi\rangle)$ for each individual case.

To calculate the value of the thermodynamic potential Ω', we will, as $\langle\varphi\rangle$, employ the sum of the principal harmonics (2.6). This procedure implies that the calculation of Ω' is performed in the main approximation over the small parameter $\langle\varphi\rangle$. Then we will deal with the symmetry of the sum (2.6) but not with the symmetry of the total average $\langle\varphi(\boldsymbol{r})\rangle$. Yet, one can assert that these symmetries coincide. Because of the total rotational and translational invariance of Ω' in the iteration procedure (as a result of which from the sum (2.6) one can obtain the total average $\langle\varphi(\boldsymbol{r})\rangle$), the symmetry of the condensate cannot alter. Thus, the symmetry of the sum (2.6) straightforwardly determines the symmetry of the respective phase.

To find the minimum of Ω' it is necessary to consider averages $\langle\varphi\rangle$ of different forms. Of course, it is not possible to check all possible structures. Then, in principle, the ground state of the system may be missing. Having this in mind, we will nevertheless confine ourselves to a minimally possible amount of structures to be studied, trying to make the choice sufficiently reasonable from the physical point of view so as to annul the possibility to miss the ground state.

2.1.2. Landau expansion

To find the form of the functional $\Omega'(\langle\varphi\rangle)$, it is necessary to start with the Landau functional F_L

$$F_L = F_L(\varphi) . \tag{2.9}$$

The quantity F_L denotes the energy, associated with the order parameter φ. Note that the the functional F_L can be introduced since the order parameter softens near the phase transition point. Quantitatively, in the weak crystallization theory this "softness" is ensured by the small value of the average φ emerging at the phase transition.

Let us stress the distinction between the functionals F_L and Ω'. The former determines the energy, associated with the order parameter fluctuations, whereas the latter is the quantity averaged over fluctuations. The quantities Ω' and F_L coincide only if fluctuations are neglected.

Here we will, as usual, confine ourselves to the first few terms of the expansion of the Landau functional in the order parameter. For the case of weak crystallization we are studying, this expansion

is justified by the inequality (2.2). The first terms of the expansion of F_L in φ can be written as

$$\int d\boldsymbol{r}\ (\tau'\varphi^2/2 - \mu\varphi^3/6 + \lambda\varphi^4/24)\,. \tag{2.10}$$

Here, there is no linear term in φ since φ is a short-wavelength field and, consequently, does not involve a zero Fourier harmonics. By analogy with quantum field theory we will call the quantities μ, λ vertices. The higher-order terms of the Landau expansion in φ can be omitted if the vertex λ is positive and not anomalously small, which will be assumed below.

The phase transition, associated with the emergence of the average $\langle\varphi\rangle$, occurs when the parameter τ' in (2.10) diminishes. Due to the presence of the cubic term in the expansion (2.10) this transition is a first-order transition and could become continuous only in a certain isolated point on the phase transition line [Landau 1937]. The weak crystallization theory holds actually in the vicinity of this isolated point. Thus, for this theory to hold, it is necessary that the additional condition*) of the small value of the coefficient μ in the expansion (2.10) should be fulfilled. This condition could be expressed via the inequality

$$\mu/\lambda \ll 1\,. \tag{2.11}$$

Note that the crystallization might be described by a more sophisticated order parameter than the density modulation (e.g. it may be related to many-point correlation functions of the density modulation). In this case it is possible to imagine the situation of all odd terms in the Landau expansion being forbidden by the symmetry [Marchenko 1991]. This case can be formally described as well in the framework of our consideration if we assume $\mu = 0$.

As has already been mentioned, the field φ is of short-wavelength character and therefore the dependence of the coefficients of the expansion of the Landau functional F_L in φ on the wave vectors of the field φ is rather important. Thus, the coefficient τ' in (2.10) is a function of module of the wave vector $\boldsymbol{q}$. We will have in mind the situation of $\tau'(\boldsymbol{q})$ reaching the minimum on a certain sphere of radius q_0 in the reciprocal space. We will be interested in the fluctuations of the Fourier harmonics of the field φ with the wave vectors in the vicinity of this sphere. Expanding τ' near the $|\boldsymbol{q}| = q_0$, we find with the necessary accuracy

$$\tau'(\boldsymbol{q}) = \tau + \alpha(|\boldsymbol{q}| - q_0)^2\,. \tag{2.12}$$

Here, the coefficients τ and α no longer contain the dependence on $\boldsymbol{q}$. Note that $\tau = \tau'(q_0)$.

The parameter τ in (2.12) changes its sign in the vicinity of the transition point. Therefore, in the case when the phase transition takes place at a variation of the temperature, for the parameter τ one can use the standard expression

$$\tau = \varpi\,(T - T^*)\,. \tag{2.13}$$

Here ϖ is a constant and T^* is the temperature at which τ becomes zero. Since the phase transition under consideration is a first-order transition, the temperature T^* does not coincide with the crystallization temperature, although it is close to it as long as the average $\langle\varphi\rangle$, emerging at the crystallization, is small. If the phase transition takes place at a variation of concentration, then the

*) In this sense there is a similarity with the tricritical behaviour, which is observed if a certain additional constraint on the constants of the Landau expansion is obeyed.

concentration will play the role of the temperature in (2.13). For the constants α, ϖ, figuring in (2.12), (2.13), one can expect the following natural estimates:

$$\alpha \sim \lambda/q_0^2, \quad \varpi \sim \lambda/T^*. \tag{2.14}$$

These estimates, in conjunction with the inequality (2.11), guarantee the consistency of our approach in the framework of the weak crystallization theory. Note that these estimates are sufficient but not obligatory.

The condition for eq. (2.12) to be applicable is the inequality

$$|q - q_0| \ll q_0. \tag{2.15}$$

In the same approximation, the second-order term of the expansion of the Landau functional in φ can be respresented as

$$F_L^{(2)} = \int d\boldsymbol{r}\, \{\tau\varphi^2/2 + \alpha[(\nabla^2 + q_0^2)\varphi]^2/8q_0^2\}. \tag{2.16}$$

This expression is handy since it is easily written in a local form.

The third- and fourth-order terms of the expansion of the Landau functional can, in general form, be represented as

$$F^{(3)} = -\tfrac{1}{6}V\sum_{q}\mu(\boldsymbol{q}_1,\boldsymbol{q}_2,\boldsymbol{q}_3)\varphi(\boldsymbol{q}_1)\varphi(\boldsymbol{q}_2)\varphi(\boldsymbol{q}_3), \tag{2.17}$$

$$F^{(4)} = \tfrac{1}{24}V\sum_{q}\lambda(\boldsymbol{q}_1,\boldsymbol{q}_2,\boldsymbol{q}_3,\boldsymbol{q}_4)\varphi(\boldsymbol{q}_1)\varphi(\boldsymbol{q}_2)\varphi(\boldsymbol{q}_3)\varphi(\boldsymbol{q}_4). \tag{2.18}$$

Here V is the volume of the system and $\varphi(\boldsymbol{q})$ is the Fourier component of the field φ:

$$\varphi(\boldsymbol{r}) = \sum_{q}\varphi(\boldsymbol{q})\exp(i\boldsymbol{q}\cdot\boldsymbol{r}). \tag{2.19}$$

The summation in (2.17) is performed over the wave vectors, obeying the condition

$$\boldsymbol{q}_1 + \boldsymbol{q}_2 + \boldsymbol{q}_3 = 0, \tag{2.20}$$

and in (2.18) the summation is performed over the wave vectors, obeying the condition

$$\boldsymbol{q}_1 + \boldsymbol{q}_2 + \boldsymbol{q}_3 + \boldsymbol{q}_4 = 0. \tag{2.21}$$

We will assume the vertex λ to be positive at all wave vectors.

2.1.3. Dependence of vertices on wave vectors

In the weak crystallization theory an important role is played only by Fourier components of the field φ with the wave vectors, obeying the inequality (2.15). In this case, the condition (2.20) determines the triplet of wave vectors forming a closed, almost regular triangle and the vertex μ in (2.17) can be regarded as constant.

The latter assertion requires some clarification. It is correct if the natural estimate

$$\partial\mu/\partial q \sim \mu/q_0 \tag{2.22}$$

is correct. On the other hand, in the vicinity of an isolated point on the phase transition line (where μ is zero), one should expect the estimate

$$\partial\mu/\partial q \sim \lambda/q_0 . \tag{2.23}$$

In this case the dependence of μ on the wave vectors can be relevant in the weak crystallization theory. Yet, for the real phase transitions in liquid crystals we have in mind, rather the estimate (2.21) is valid. Therefore, we will henceforth take μ = const.

Since we assume that the coefficient λ in (2.18) is not small, for the derivative $\partial\lambda/\partial q$ one should expect the natural estimate

$$\partial\lambda/\partial q \sim \lambda/q_0 . \tag{2.24}$$

In this case, the dependence of λ on the modules of the wave vectors $\boldsymbol{q}_1$, $\boldsymbol{q}_2$, $\boldsymbol{q}_3$, $\boldsymbol{q}_4$, can be discarded, and we may assume these modules to be equal to q_0. Then, from the condition (2.21), the dependence of λ on the wave vectors $\boldsymbol{q}$ reduces to a dependence on two angles. As these angles one can choose the angle between the vectors $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$ (equal to the angle between $\boldsymbol{q}_3$ and $\boldsymbol{q}_4$) and the angle between the vectors $\boldsymbol{q}_1 - \boldsymbol{q}_2$ and $\boldsymbol{q}_3 - \boldsymbol{q}_4$. The fact that λ should be symmetric with respect to the permutation of $\boldsymbol{q}_1$, $\boldsymbol{q}_2$, $\boldsymbol{q}_3$, $\boldsymbol{q}_4$ imposes certain evident constraints on the form of this angular dependence.

Naturally, it is impossible to analyse quantitatively the model with an arbitrary angular dependence of λ on the angles. Henceforth we will mainly consider the case λ = const., since the general peculiarities of the theory may be demonstrated by this example. Certain concrete results will be obtained for an angular dependence of the coefficient λ of the form

$$\lambda(\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3, \boldsymbol{q}_4) = \lambda\{(1 + \lambda'[(\boldsymbol{e}_1\boldsymbol{e}_2)(\boldsymbol{e}_3\boldsymbol{e}_4) + (\boldsymbol{e}_1\boldsymbol{e}_3)(\boldsymbol{e}_2\boldsymbol{e}_4) + (\boldsymbol{e}_1\boldsymbol{e}_4)(\boldsymbol{e}_2\boldsymbol{e}_3)]/3\} . \tag{2.25}$$

Here λ, λ' are constants, $\boldsymbol{e}_i$ are unit vectors in the directions of the wave vectors $\boldsymbol{q}_i$ *). The interaction term (2.18) with the function (2.25) can be written down within the necessary accuracy as

$$F^{(4)} = \frac{\lambda}{24}\int \mathrm{d}\boldsymbol{r}\,[\varphi^4 + \lambda'(\nabla\varphi\nabla\varphi)^2 q_0^{-4}] . \tag{2.26}$$

This expression is convenient since it is written in local form. For more complicated cases we will discuss the consequences of the angular dependence of λ only qualitatively.

2.1.4. Interaction with the long-wavelength degrees of freedom

So far, we have dealt only with fluctuations of the order parameter φ. Fluctuations associated with long-wavelength degrees of freedom are not important in the weak crystallization theory. Nevertheless, the interaction between "soft" short-wavelength field φ and long-wavelength degrees of freedom must be incorporated in the calculation of the anomalous contribution to such quantities as the heat capacity or compressibility.

Having in mind these problems as well as dynamic effects, introduce the functional

$$H = H(\rho, s, \varphi) , \tag{2.27}$$

denoting the energy of the system. Since fluctuations of the mass density ρ and entropy density s are irrelevant in studying fluctuations of φ, one can treat the conditions

$$\delta H/\delta\rho = \zeta(\boldsymbol{r}) = \text{ const.}, \quad \delta H/\delta s = T(\boldsymbol{r}) = \text{ const.} \tag{2.28}$$

*) Expression (2.25) exhausts all possible scalar combinations up to the fourth order in $\boldsymbol{e}$.

as fulfilled. These conditions imply that in the system there is a thermodynamic equilibrium with respect to the variables ρ, s. Note that the conditions (2.28) do not imply that ρ, s are homogeneous because they may vary in space in the presence of a dependence of φ on $\boldsymbol{r}$.

The conditions (2.28) indicate that fluctuations of φ should be described not by means of the functional (2.27) but by means of the functional, dependent on ζ, T. This is the Landau functional $F_L(\zeta, T, \varphi)$. Thus, all coefficients τ, α, μ, λ of the expansion of F_L in φ are also functions of ζ, T. The relation between the functionals F_L and H is given by the Legendre transformation:

$$H = F_L + \int d\boldsymbol{r}\, (\zeta\rho + Ts). \tag{2.29}$$

As a result of (2.29), we find the expression

$$\rho = -\delta F_L/\delta\zeta, \quad s = -\delta F_L/\delta T, \tag{2.30}$$

which yields local values of the mass and entropy densities with fluctuation of φ taken into account.

2.2. Mean field theory

The mean field approximation implies that fluctuations of the field φ should be neglected. This is justified when the distribution function over φ has a sharp maximum in the vicinity of $\varphi = \langle\varphi\rangle$. In this case the thermodynamic potential Ω' can be found if the simple substitution

$$\Omega' = F_L(\langle\varphi\rangle) \tag{2.31}$$

is performed.

In our approximation, F_L is determined by the sum of the terms (2.16), (2.17), (2.18) and as $\langle\varphi\rangle$ one should use the sum (2.6). After the insertion of this sum into (2.16), (2.17), (2.18), the thermodynamic potential is expressed via a_n, $\boldsymbol{q}_n$. Minimizing Ω' over these parameters, one can find the values of these quantities. This is also the way of constructing the phase diagram of the system since stable phases correspond to an absolute minimum of the thermodynamic potential.

2.2.1. Comparison with conventional phase transitions

The study of weak crystallization in the framework of the mean field theory considerably repeats the study of usual first-order phase transitions, close to continuous transitions. For convenience of comparison with the results of fluctuation theory, here we will quote the main issues of mean field theory (see for details the monographs by Landau and Lifshits [1980] and Anisimov [1991], and the reviews by Stephen and Straley [1974] and Gramsbergen, Longa and de Jeu [1986]).

Quantitatively, the traditional mean field theory of first-order phase transitions with a one-component order parameter is based on the same expansion (2.10) of the thermodynamic potential as the theory of weak crystallization. The only but very important distinction is the character of this order parameter. For usual phase transitions the order parameter is a long-wavelength field, and therefore the dependence of the Landau expansion coefficients on wave vectors is always irrelevant.

In the model considered (with long-wavelength order parameter), upon the variation of τ one phase transition is observed which is of first order. The phase transition occurs at the value $\tau_c = \frac{1}{3}\mu^2/\lambda$, obtained from the condition of the equality of the thermodynamic potentials of the ordered (low-temperature) and disordered (high-temperature) phases. For $\mu = 0$ we obtain the continuous phase transition occurring at $\tau_c = 0$.

Remember that in the vicinity of a weak first-order phase transition we may assume $\tau = \varpi(T - T^*)$, where ϖ is a constant and T^* is a temperature close to the transition temperature T_c but not equal to it. The physical meaning of the temperature T^* is that at this temperature the thermodynamic potential minimum corresponding to the disordered phase vanishes. Thus, T^* is the boundary of absolute instability of the overcooled high-temperature phase.

Similarly, one can find the boundary of stability of the overheated low-temperature phase T^{**} which is the temperature at which the minimum corresponding to the ordered phase vanishes. The corresponding value of τ appears to be

$$\tau^{**} = \tfrac{8}{3}\mu^2/\lambda.$$

For second-order phase transitions (i.e., at $\mu = 0$), the temperatures T^*, T^{**} coincide with the critical temperature. The closeness of these temperatures or of the corresponding values of the parameters τ_c, τ^*, τ^{**} is accounted for by the small value of the Landau expansion coefficient μ, which justifies the form of the Landau expansion (2.10).

It is well known that at a second-order phase transition there occurs a universal jump of heat capacity,

$$\Delta C_P = 3\varpi^2/\lambda.$$

At a first-order phase transition, to this jump is added the contribution associated with the singular temperature dependence of φ in the ordered phase. Due to this contribution, the heat capacity jump at the transition point $T = T_c$ proves to be equal to $12\varpi^2/\lambda$, i.e., irrespective of the value of μ it increases four times as much in comparison with the second-order phase transition. As long as the coefficient μ diminishes, the width of the temperature range where the characteristic behaviour of φ leading to this jump occurs also diminishes, and at $\mu = 0$ we go back to the well-known Landau result for second-order phase transitions.

The behaviour of a system near the weak crystallization transition point in the framework of mean field theory is qualitatively the same as near the conventional weak first-order phase transitions. However, there are some distinctions we want to stress. Firstly, in a system there occur several phase transitions between different phases. Secondly, in the weak crystallization theory (as we have seen above) the coefficient λ can be considerably dependent on wave vectors. The character of the dependence essentially affects both the structure of the phase diagram and the temperature behaviour of all observable quantities.

The closest to the traditional Landau theory is the weak crystallization theory with $\lambda = \text{const}$. In this case universal formulae for jumps of heat capacity of the above written type may be derived for each phase transition occurring in the system. But the numerical coefficients in these expressions of course will not coincide with the coefficient appearing in the conventional theory. In the general case, the coefficients will be determined by an integral over the angles of the function λ.

As we will see in what follows, fluctuations qualitatively affect the character of the temperature dependence of all thermodynamic quantities, even if the corresponding corrections are quantitatively small. It is to the study of these effects that the main part of our survey is devoted to.

2.2.2. Estimates

Prior to a quantitative investigation of the problem, let us give a number of estimates. A phase transition occurs at

$$\tau \sim \mu^2/\lambda. \tag{2.32}$$

Hence it follows that on the plane τ, μ the phase transition lines are parabolas. At the transition there emerges an average $\langle\varphi\rangle$ where amplitudes of the principal harmonics have the order of magnitude

$$a_n \sim \mu/\lambda. \tag{2.33}$$

Thus the inequality (2.11) guarantees fulfillment of the condition (2.8). The latent heat of the transition has the order of magnitude

$$Q \sim \mu^4/\lambda^3. \tag{2.34}$$

The given estimates can be obtained if

$$|\boldsymbol{q}_n| = q_0, \tag{2.35}$$

which makes it possible to ignore the gradient term in (2.16). Now we will estimate deviations of the wave vector modules from q_0. Upon a variation of the wave vectors by $\delta\boldsymbol{q}$, the loss of the gradient energy amounts to a value of the order

$$\alpha a^2(\delta\boldsymbol{q})^2 V, \tag{2.36}$$

where V is the volume of the system. The gain in the energy is related to the dependence of λ on $\boldsymbol{q}$ and can be estimated as

$$(\partial\lambda/\partial q)\delta q a^4 V. \tag{2.37}$$

Comparing the quantities (2.36) and (2.37), we get

$$\delta q \sim \alpha^{-1} a^2 \partial\lambda/\partial q. \tag{2.38}$$

This value is small in virtue of the inequality (2.8). Using the natural estimates (2.14), (2.24), we find

$$\delta q/q_0 \sim a^2 \ll 1.$$

The dependence of μ on $\boldsymbol{q}$ does not affect the results if the estimate (2.22) is correct.

The change of the energy at a shift of the wave vectors by the value (2.38) can be estimated by substituting this value into (2.36) or (2.37), which produces a gain in the energy of the order of magnitude

$$V\alpha^{-1}(\partial\lambda/\partial q)^2 a^6 \sim V\lambda a^6. \tag{2.39}$$

This contribution can be neglected as compared to the leading term $\sim \lambda a^4$. As will be shown in subsection 2.3, all statements, devoted to $\delta\boldsymbol{q}$, are valid also, with fluctuations taken into account. Thus, the presence of the difference of the modules of the wave vectors $\boldsymbol{q}_n$ from q_0 does not produce any important effects. Therefore, we will henceforth regard the condition (2.35) as fulfilled.

2.2.3. Minimization of the thermodynamic potential

Due to what is said above, the gradient term in (2.16) drops out from our further study (but only in the mean field approximation). Recall that the vertex μ in (2.7) can be regarded as constant. Also assume that the condition

$$\lambda = \text{const}. \tag{2.40}$$

is fulfilled. Thus, we return to eq. (2.10) for the free energy, where the coefficients $\tau' = \tau, \mu, \lambda$ are constants and, consequently, the free energy is defined as an integral of the local expression. This largely simplifies calculations.

Inserting eq. (2.6), as $\langle\varphi\rangle$, into (2.10), and performing integration, we get

$$\Omega'/V = \tau A + \lambda A^2/2 + f\,. \tag{2.41}$$

Here the following designations are introduced:

$$A = \sum_{n=1}^{N} |a_n|^2, \tag{2.42}$$

$$f = -\lambda \sum_{n=1}^{N} |a_n|^4/4 - \mu \tilde{\sum_{nml}} a_n a_m a_l/6 + \lambda \tilde{\sum_{nmlk}} a_n a_m a_l a_k/24\,. \tag{2.43}$$

The meaning of the tilde at the summation sign has been clarified above, under eq. (2.6); in the sums denoted with the tilde only terms are taken into account for which the conditions

$$\boldsymbol{q}_n + \boldsymbol{q}_m + \boldsymbol{q}_l = 0, \tag{2.44}$$

$$\boldsymbol{q}_n + \boldsymbol{q}_m + \boldsymbol{q}_l + \boldsymbol{q}_k = 0, \tag{2.45}$$

respectively, are fulfilled.

Let us explain the additional restriction imposed on the summation in the last sum in the right-hand side of (2.43). If all four wave vectors of a term in the sum lie in one plane, they form a rhombus and therefore may be represented as pairs of parallel vectors. The contributions to Ω' corresponding to such configurations of wave vectors are taken into account by the the second term in the right-hand side of (2.41) and by the the first term in the right-hand side of (2.43). Hence there should be no terms of which the four wave vectors contain collinear vectors. We will call the quartets of vectors figuring in the last sum of (2.43) (satisfying (2.45) and not lying in the same plane) nontrivial quartets of vectors.

The dependence of the termodynamic potential (2.41) on the wave vectors $\boldsymbol{q}_n$ reveals itself only in the structure of the second and third terms in (2.43). Therefore the free energy minimum should be sought for in the following way. Firstly, we set a certain configuration of wave vectors $\boldsymbol{q}_n$, reflecting the assumed symmetry of the phase under study, which determines the form of the term (2.43). Then it is necessary to minimize (2.41) over a_n. The latter operation can be conveniently carried out in two stages: first, find the minimum of the function f (2.43) over a_n under the condition (2.42), and then perform a minimization of (2.41) over A.

Let us illustrate the above on the simplest example, assuming that in the set $\boldsymbol{q}_n$ there are no triplets of vectors obeying (2.44), and no nontrivial quartets of vectors. In this case, in eq. (2.43), for the function f one should incorporate only the first term. Its minimization over a_n under the condition (2.42) yields the result

$$|a_1| = \sqrt{A}, \quad a_2 = \cdots = a_N = 0, \tag{2.46}$$

$$f = -\lambda A^2/4. \tag{2.47}$$

Thus we arrive at a one-dimensional modulation of the density with the condensate,

$$\langle\varphi\rangle = 2A^{1/2}\cos(q_1 z + \Phi)\,. \tag{2.48}$$

Here Φ is an arbitrary phase, the Z-axis is directed along the vector $\boldsymbol{q}_1$. The condensate of the form of (2.48) corresponds to the smectic-A phase, which we will call SA.

The insertion of (2.47) into (2.41) leads to an expression for the thermodynamic potential which has a minimum at a non-zero value of A at $\tau < 0$. Thus, the phase with the one-dimensional density modulation proves to be metastable at least at $\tau < 0$. The minimum of the thermodynamic potential (2.41) is reached at

$$A = -2\tau/\lambda. \tag{2.49}$$

The value of the potential in this minimum is

$$\Omega_{SA}/V = -\tau^2/\lambda. \tag{2.50}$$

The expression (2.49) determines the density modulation amplitude in (2.48).

Now consider a configuration $\boldsymbol{q}_n$ consisting of the four wave vectors, obeying the condition (2.45) and not lying in the same plane. In this case the last term in (2.43) becomes involved, and the function f becomes

$$f = -\lambda \sum_{n=1}^{4} |a_n|^4/4 + 2\lambda |a_1 a_2 a_3 a_4| \cos(\Phi_1 + \Phi_2 + \Phi_3 + \Phi_4). \tag{2.51}$$

Here

$$\Phi_n = \arg(a_n). \tag{2.52}$$

The minimization of (2.51) over the phases Φ_n yields the condition

$$\Phi_1 + \Phi_2 + \Phi_3 + \Phi_4 = \pi. \tag{2.53}$$

Inserting this value into (2.51) and minimizing the result over $|a_n|$ under the condition (2.42), we get

$$|a_1| = |a_2| = |a_3| = |a_4| = A^{1/2}/2, \quad f = -3\lambda A^2/16. \tag{2.54}$$

The resulting configuration $\langle\varphi\rangle$ in terms of the symmetry belongs to an orthorhombic crystal R. The insertion of the quantities of (2.54) into (2.41) brings about the conclusion that this local minimum of the free energy occurs at $\tau < 0$ and is characterized by the parameters

$$A = -8\tau/5\lambda, \quad \Omega_R/V = -4\tau^2/5\lambda. \tag{2.55}$$

We now study the configuration of three vectors $\boldsymbol{q}_n$, forming a regular triangle. In this case the second term in (2.43) becomes involved and the function f reads

$$f = -\lambda \sum_{n=1}^{3} |a_n|^4/4 - 2\mu |a_1 a_2 a_3| \cos(\Phi_1 + \Phi_2 + \Phi_3). \tag{2.56}$$

Minimizing this expression over the phases and amplitudes, under the condition (2.42), we find

$$|a_1| = |a_2| = |a_3| = (A/3)^{1/2}, \quad f = -\lambda A^2/12 - 2|\mu|(A/3)^{3/2}. \tag{2.57}$$

The resulting configuration $\langle\varphi\rangle$ in terms of the symmetry belongs to a hexagonal columnar phase D_h. The local minimum of the free energy for this structure arises at

$$\tau = 4\mu^2/45\lambda \tag{2.58}$$

and is characterized by the quantity

$$A^{1/2} = (3)^{1/2}|\mu|(1 + (1 - 10\tau\lambda/\mu^2)^{1/2})/5\lambda. \tag{2.59}$$

The energy of this phase now may be found using eqs. (2.41) and (2.57).

2.2.4. More sophisticated structures

Here we will consider more sophisticated structures having symmetries of known crystals (or quasicrystals). In the general case, for a crystal of the given symmetry the set $\{\boldsymbol{q}_n, a_n\}$ falls into subsets inside which $\{\boldsymbol{q}_n, a_n\}$ transform into each other under the action of elements of the point symmetry group of a crystal (or quasicrystal). The state of the crystal (or quasicrystal) under these operations cannot change. This means that the amplitudes a_n inside the subset have the same modules but can have different phases. Below we will study the structures, defined by only one subset of this kind.

The procedure for determining the structure of a stable or a metastable phase is as follows. Take a certain point symmetry group and chose a set $\{\boldsymbol{q}_n\}$, invariant with respect to this symmetry group. The modules of a_n are equal and therefore they are expressed via the quantity A, introduced in (2.42). The insertion of (2.6) into (2.43) yields an expression for the thermodynamic potential in terms of A and the arguments Φ_n, introduced in (2.52). The minimization of Ω' over Φ_n, A produces the energy of the respective phase. Note that the crystalline or quasicrystalline character of the obtained state is determined already by the point symmetry group taken in the described procedure.

Let us consider phases, possessing the cubic symmetry. We will confine ourselves to the structures determined by a set of six vectors $\boldsymbol{q}_n$, which are diagonals of the cube facets. It is not difficult to make sure that the set of vectors generates a body-centered cubic structure. Out of the six vectors one can form four different triplets of vectors obeying the condition (2.44) as well as three nontrivial quartets. This dictates the structure of two last terms in (2.43).

In the search for the minimum of the thermodynamic potential it is convenient to arrange the terms in the combinations

$$\theta_1 = \Phi_1 + \Phi_2 + \Phi_3, \quad \theta_2 = -\Phi_1 + \Phi_4 - \Phi_6,$$
$$\theta_3 = -\Phi_2 - \Phi_4 + \Phi_5, \quad \theta_4 = -(\theta_1 + \theta_2 + \theta_3) = -\Phi_3 - \Phi_5 + \Phi_6. \tag{2.60}$$

For the model with $\lambda = \text{const.}$ the function f in this notation acquires the form

$$f = -\lambda A^2/24 - \mu(\cos\theta_1 + \cos\theta_2 + \cos\theta_3 + \cos\theta_4)(A/3)^{3/2}2^{-1/2}$$
$$+\lambda A^2[\cos(\theta_1 + \theta_2) + \cos(\theta_1 + \theta_3) + \cos(\theta_2 + \theta_3)]/18. \tag{2.61}$$

Let us take the extremum, having the symmetry of a cube when all phases Φ are equal. Then $\theta_1 = 3\Phi$, $\theta_2 = \theta_3 = \theta_4 = -\Phi$ and the condition that the function f should be minimal with respect to the phase Φ yields

$$\mu(\sin\Phi + \sin 3\Phi)/6^{1/2} + \lambda A^{1/2}\sin(2\Phi/3) = 0. \tag{2.62}$$

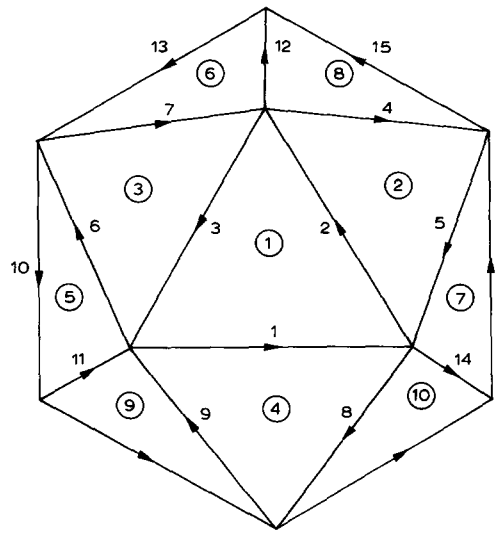

Fig. 1. Form of the icosahedron along the third-order symmetry axis.

Equation (2.62) has two solutions, corresponding to the minimum of f. One of them ensures the smallest contribution of the terms with the coefficient μ, the second ensures the smallest contribution, coming from the nontrivial quartets. Let us label these solutions as BCC_1 and BCC_2, respectively. The functions f for these phases equal

$$f_1 = -4 \cdot 2^{-1/2}|\mu|(A/3)^{3/2} + \lambda A^2/8, \quad f_2 = -5\lambda A^2/24. \tag{2.63}$$

From a comparison of the second formula in (2.63) with (2.47) it becomes clear that BCC_2 is a metastable phase. For BCC_1 it is not difficult to find that the local minimum of the energy (arising at $\tau = 16\mu^2/135\lambda$) is characterized by the following values of the quantity A and of the thermodynamic potential Ω:

$$A^{1/2} = 4 \cdot 6^{-1/2}|\mu|[1 + (1 - 15\tau\lambda/2\mu^2)^{1/2}]/5\lambda,$$

$$\Omega_{BCC_1}/V = -|\mu|(2A/3)^{3/2} + 5\lambda A^2/8 + A\tau. \tag{2.64}$$

Let us consider the possibility of the appearance of quasicrystalline icosahedric ordering in the weak crystallization theory. We will examine the structure where principal wave vectors of the reciprocal lattice can be arranged as the edges of an icosahedron. An icosahedron is a regular polyhedron, having twenty triangular faces, thirty edges and twelve vertices. The form of the icosahedron along the third-order axis is shown in fig. 1. It possesses six fifth-order axes, ten third-order symmetry axes and fifteen second-order axes. In this figure we have indicated by numbers (1–15) edges of the icosahedron and by numbers 1–10 (in circles) – its faces. Note that we have enumerated a half of the edges and faces of the icosahedron. In the energy of such structure there are contributions from the triangles (e.g. a triangle formed by wave vectors directed along the edges 1–2–3) and from nontrivial quartets (e.g. 1–2–7–6).

Like for the BCC structure, for an icosahedral quasicrystal there are two extrema for one of which (Y_1) the contribution of the triangles is minimal and for the other (Y_2) the contribution from the

nontrivial quartets is minimal. The function f for Y_1 is

$$f = -4 \cdot 5^{-1/2}\mu(A/3)^{3/2} + 7\lambda A^2/60. \tag{2.65}$$

It can be shown that for Y_2

$$f > -3\lambda A^2/20. \tag{2.66}$$

A comparison of eqs. (2.65) and (2.66) with (2.47) and (2.57) shows that for the model with λ = const. icosahedral phases can be metastable only because the energy of the SA or D_h phase is lower than the energy in both icosahedral phases for any value of τ and μ.

2.2.5. Cascade of transitions

A comparison of the energies, given by formulas (2.47)–(2.66) shows that only phases SA, D_h and BCC_1 can be absolutely stable under the condition λ = const. At increasing temperature the following cascade of phases is realized in the model:

$$SA\text{–}D_h\text{–}BCC_1\text{–}I,$$

where I denotes the isotropic liquid. The transitions between these phases take place at the following values of the parameter τ:

$$\tau(SA\text{–}D_h) = -(7 + 3 \cdot 6^{1/2})\mu^2/5\lambda, \quad \tau(D_h\text{–}BCC_1) \cong -0.073\mu^2/\lambda,$$

$$\tau(BCC_1\text{–}I) = 16\mu^2/135\lambda. \tag{2.67}$$

In conformity with the fundamental statements of the Landau theory, the described structural transformations are first-order phase transitions.

The above obtained sequence of transitions was first predicted by Kleinert and Maki in their study of the theory of the "blue phase" of cholesteric liquid crystals [Kleinert and Maki 1981]. Note also the paper by Leibler [1980] wherein, for a particular example, he studied the mean field model of weak crystallization with λ = const. Such sequences of phase transformations are observed in experiments with solutions and melts of block-copolymers [Tiddy 1980, Fredrickson and Helfand 1987].

2.2.6. Angular dependence of λ

We now discuss the situation when the quartic vertex λ in the Landau expansion depends nontrivially on the momenta $\boldsymbol{q}$. Firstly, we study the simplest dependence (2.25). It can be rewritten as

$$\lambda(\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3, \boldsymbol{q}_4) = \lambda(1 + \lambda' X), \tag{2.68}$$

where $\boldsymbol{q}_i = q_0 \boldsymbol{e}_i$, and

$$X = [(\boldsymbol{e}_1\boldsymbol{e}_2)(\boldsymbol{e}_3\boldsymbol{e}_4) + (\boldsymbol{e}_1\boldsymbol{e}_3)(\boldsymbol{e}_2\boldsymbol{e}_4) + (\boldsymbol{e}_1\boldsymbol{e}_4)(\boldsymbol{e}_2\boldsymbol{e}_3)]/3.$$

For the λ to be positive we should assume $\lambda' > -1$. The energy of the system in this case can be conveniently represented as

$$\Omega/V = A\tau + \lambda(1 + \lambda')A^2/4 + f', \tag{2.69}$$

The function f' is defined by

$$f' = \lambda \sum_{n>m} \{1 + \lambda'/3[4(\boldsymbol{e}_n\boldsymbol{e}_m)^2 - 1]\}|a_n|^2|a_m|^2 - \mu \tilde{\sum_{nml}} a_n a_m a_l/6$$

$$+ \tilde{\sum_{nmlk}} (1 + \lambda' X) a_n a_m a_l a_k/24. \tag{2.70}$$

With this definition the value of f' is zero for the one-dimensional ordering. Therefore, the analysis of the smectic-A phase will be the same as previously. The parameters of the phase are set by the formula

$$A = -2\tau/\lambda(1 + \lambda'), \quad \Omega_{SA}/V = -\tau^2/\lambda(1 + \lambda'). \tag{2.71}$$

If there are no nontrivial quartets in the set $\boldsymbol{q}_n$, then from symmetry considerations it is evident that one should above all study a simple cubic phase SC. It is characterized by a set of three mutually orthogonal wave vectors $\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3$. For this phase

$$f' = \lambda A^2(1 - \lambda'/3)/6, \quad A = 3a^2. \tag{2.72}$$

The respective local minimum appears for $\tau < 0$. The parameters of the phase are determined by the relations

$$A = -18\tau/\lambda(15 + 7\lambda'), \quad \Omega_{SC}/V = -9\tau^2/\lambda(15 + 7\lambda'). \tag{2.73}$$

Now take the case when there are nontrivial configurations of wave vectors. The simplest of them is a structure of four vectors $\boldsymbol{q}_n = q_0\boldsymbol{e}_n$ satisfying (2.45) and not lying in the same plane. The function f' then acquires the form

$$f' = \lambda a^4(3 - \lambda' + 4\lambda' X) + 2\lambda a^4(1 + \lambda' X)\cos(\Phi_1 + \Phi_2 + \Phi_3 + \Phi_4).$$

The minimization of f' over the phases yields

$$f' = \lambda A^2(1 - \lambda' + 2\lambda' X)/16, \quad A = 4a^2.$$

The quantity X, defined by eq. (2.68), can be determined as a function of the two angles α and γ between the wave vectors in the form

$$X = [(\cos^2(2\alpha) + 2(\cos^4\alpha + \sin^4\alpha\cos^2\gamma)]/3.$$

The minimal value of the quantity X, equal to 1/9, is achieved when all the angles between the vectors $\boldsymbol{e}_1, \boldsymbol{e}_2, \boldsymbol{e}_3, \boldsymbol{e}_4$ are equal to each other and then $(\boldsymbol{e}_1\boldsymbol{e}_2) = -1/3$. This set of vectors can be arranged along the spatial diagonals of a cube. This set determines the face-centered cubic lattice (FCC). The function f' is then

$$f' = \lambda A^2(9 - 7\lambda')/144. \tag{2.74}$$

The parameters of the FCC phase are set by the expressions

$$A = -72\tau/\lambda(45 + 29\lambda'), \quad \Omega_{FCC}/V = A\tau/2. \tag{2.75}$$

The simplest structure with a non-zero contribution of the triplet of wave vectors satisfying (2.34) is still D_h. The function f' for it equals

$$f' = -2|\mu|(A/3)^{3/2} + \lambda A^2/6. \tag{2.76}$$

As is seen from (2.76), the energy of this columnar phase is independent of the parameter λ' and is, as previously, determined by eq. (2.59).

Let us pass over to the BCC phases. The function f' for the BCC_1 phase equals

$$f' = -|\mu|(2A/3)^{3/2} + \lambda A^2(27 + \lambda')/72, \tag{2.77}$$

and the total energy is determined by

$$\Omega_{BCC_1}/V = -|\mu|(2A/3)^{3/2} + \lambda A^2(45 + 19\lambda')/72 + A\tau. \tag{2.78}$$

For the BCC_2 phase we similarly get

$$f' = \lambda A^2(1 - \lambda')/24, \tag{2.79}$$

$$A = -12\tau/(7 + 5\lambda'), \quad \Omega_{BCC_2}/V = A\tau/2. \tag{2.80}$$

An analysis of eqs. (2.71)–(2.80) leads us to the following conclusions: For negative values of the parameter λ' there are no qualitative changes in the phase diagram in comparison with the case $\lambda = \text{const.}$, though the temperature of phase transitions naturally can change. At $\lambda' > 1$, in the diagram, instead of the one-dimensional smectic-A phase, there occur new phases, namely BCC_2 for $1 < \lambda' < 3$, FCC for $3 < \lambda' < 15$, SC for $15 < \lambda'$. The other phases remain the same as for $\lambda = \text{const}$.

Apart from the simplest dependence of λ on the directions of the wave vectors, without any difficulty one can study also other cases. So, for instance, if the anisotropy of λ is such that its minimum (sufficiently deep) can be achieved at a certain non-zero angle γ between the vectors $\boldsymbol{q}_n$ and $\boldsymbol{q}_m$, then instead of the one-dimensional smectic-A structure, absolutely stable can be a rhombic crystal with three basis vectors at a most favourable angle γ to each other.

The icosahedral quasicrystal Y is still metastable for the simplest anisotropy of λ of the form of (2.54). At the same time it is not difficult to imagine the anisotropy of λ, rendering the icosahedral phase absolutely stable. For this purpose it is necessary that the vertex λ should have sufficiently deep minima for the angles between the basis vectors of 36° and 72°.

Thus, the nontrivial dependence of the vertex λ on the angles between the wave vectors may essentially modify the phase diagram obtained at the weak crystallization. For a weakly inhomogeneous function λ the sequence of phase transformations has the same form as at $\lambda = \text{const}$. Yet, as long as the inhomogeneity of λ is growing, the situation is getting more complicated. Some examples of this nonuniversal behaviour have been considered above.

2.3. *Fluctuation effects*

The Landau functional F_L determines the energy, related to fluctuations of the order parameter $\varphi(\boldsymbol{r})$. Therefore, in conformity with the Gibbs distribution, the probability of emergence of such fluctuations is proportional to

$$\exp(-F_L/T).$$

If we also introduce the field h, thermodynamically conjugated to the order parameter φ, the distribution function of the order parameter fluctuations becomes

$$\exp\left[T^{-1}\left(\Omega - F_{\mathrm{L}} + \int \mathrm{d}r\, h\varphi\right)\right]. \tag{2.81}$$

The averages, denoted below with angular brackets, are taken over the distribution function (2.81).

The φ-independent constant Ω is introduced in the distribution function (2.81) for the purpose of normalization. This quantity coincides with the thermodynamic potential Ω [Landau and Lifshits 1976], discussed in subsection 2.1. The normalization condition for the distribution function (2.81) yields the representation for the thermodynamic potential

$$\exp(-\Omega/T) = \int \mathrm{D}\varphi\, \exp\left[T^{-1}\left(-F_{\mathrm{L}} + \int \mathrm{d}r\, h\varphi\right)\right]. \tag{2.82}$$

The r.h.s. of (2.81) involves the functional integral over fluctuations of the order parameter φ.

2.3.1. Correlation functions

Recall that the physical state of the system corresponds to $h = 0$. Yet, it is convenient to retain the dependence of the thermodynamic potential Ω on the field h, thermodynamically conjugated to φ. Note that, by eq. (2.82), the coefficients of the expansion of Ω in series in h coincide (with the accuracy up to numerical factors) with the irreducible correlation functions of the order parameter φ, calculated for the physical state (i.e., at $h = 0$).

Differentiating the relation (2.82) over h, we get the expression for the irreducible correlation functions

$$\langle\varphi(r)\rangle = -\delta\Omega/\delta h(r), \quad \langle\varphi(r_1)\varphi(r_2)\rangle - \langle\varphi(r_1)\rangle\langle\varphi(r_2)\rangle = -T\delta^2\Omega/\delta h(r_1)\delta h(r_2) \tag{2.83}$$

and so on. Here the brackets denote averaging over fluctuations of φ with the distribution function (2.81) at $h \neq 0$. The physical values of the quantities may be found by substituting $h = 0$. The first relation in (2.83) follows, as it should, from the identity (2.3). The second relation in (2.83) yields an expression for the irreducible pair correlation function for which we will use the special notation

$$D(r_1, r_2) = \langle\varphi(r_1)\varphi(r_2)\rangle - \langle\varphi(r_1)\rangle\langle\varphi(r_2)\rangle. \tag{2.84}$$

If, in accordance with the definition (2.4), we pass over to the function $\Omega'(\langle\varphi\rangle)$, we obtain the dependence of the thermodynamic potential on $\langle\varphi\rangle$. The physical state of the system is determined by the minimum of Ω'. Variational derivatives of Ω' over $\langle\varphi\rangle$ are "dressed" vertex functions. The derivative

$$h(r) = \delta\Omega'/\delta\langle\varphi(r)\rangle \tag{2.85}$$

has the meaning of the field, thermodynamically conjugated to φ. We will also introduce the so-called self-energy function Σ in conformity with the definition

$$\Sigma(r_1, r_2) = -\delta^2\Omega'_{\mathrm{fl}}/\delta\langle\varphi(r_1)\rangle\delta\langle\varphi(r_2)\rangle. \tag{2.86}$$

Here Ω'_{fl} labels the fluctuation contribution into the thermodynamic potential Ω'.

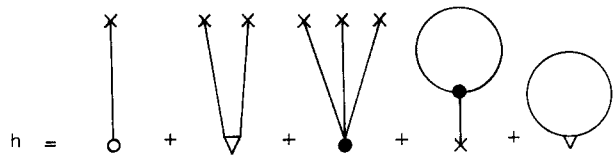

Fig. 2. One-loop corrections for the field h, conjugated to the order parameter φ.

For the correlation function (2.84) there is a standard relation [see Popov 1983],

$$\hat{\tau}D(\boldsymbol{r},\boldsymbol{r}_1) - \int \mathrm{d}\boldsymbol{r}_2\, \Sigma(\boldsymbol{r},\boldsymbol{r}_2)D(\boldsymbol{r}_2,\boldsymbol{r}_1) = T\delta(\boldsymbol{r}-\boldsymbol{r}_1)\,. \tag{2.87}$$

Here the operator

$$\hat{\tau} = \tau + \alpha(\nabla^2 + q_0^2)^2/4q_0^2 \tag{2.88}$$

acts upon the argument $\boldsymbol{r}$. The bare value D_0 of the correlation function (2.84) is deduced if we substitute in (2.87) $\Sigma = 0$. It is clear that D_0 will depend only on the difference $\boldsymbol{r} - \boldsymbol{r}_1$. In the Fourier representation the expression for the bare value D_0 will read

$$D_0(\boldsymbol{q}) = \int \mathrm{d}\boldsymbol{r}\, \exp(-\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r})D_0(\boldsymbol{r},0) = T/[\tau + \alpha(q-q_0)^2]\,. \tag{2.89}$$

Here we have used the inequality (2.15).

To calculate the correlation functions of the field φ with fluctuations taken into account, one can make use of the diagram technique where the bare Green's function is determined by eq. (2.89) and the bare vertices are determined by the interaction terms (2.17) and (2.18). The perturbation series for such quantities as D and Σ may be constructed started from the representation (2.81) by conventional methods [see Popov 1983].

2.3.2. One-loop approximation

It proves that in the weak crystallization theory the one-loop approximation is the main one, which will be demonstrated below. In this approximation the expressions for h and Σ are determined by the diagrams, given respectively in figs. 2 and 3. In these figures the open circle denotes the operator (2.88), the triangle denotes the triple vertex μ and the black circle is the quartic vertex λ. The solid line in loops is the Green's function (2.84) and the line with a cross at the edge is the average $\langle\varphi\rangle$.

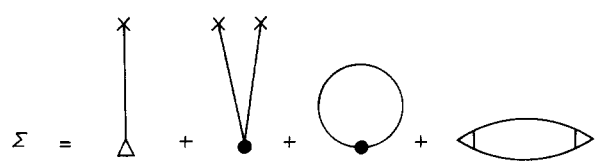

Fig. 3. One-loop corrections for the self-energy function Σ.

The diagram representations given in figs. 2 and 3, can be easily written out analytically if to assume that λ = const. Bearing in mind that also μ = const., we find from eqs. (2.16), (2.17) and (2.18)

$$h(\boldsymbol{r}) = \hat{\tau}\langle\varphi(\boldsymbol{r})\rangle - \mu\langle\varphi(\boldsymbol{r})\rangle^2/2 + \lambda\langle\varphi(\boldsymbol{r})\rangle^3/6 + \lambda\langle\varphi(\boldsymbol{r})\rangle D(\boldsymbol{r},\boldsymbol{r}) - \mu D(\boldsymbol{r},\boldsymbol{r})/2, \tag{2.90}$$

$$\Sigma(\boldsymbol{r},\boldsymbol{r}_1) = [(\mu\langle\varphi(\boldsymbol{r})\rangle - \lambda\langle\varphi(\boldsymbol{r})\rangle^2/2 - \lambda D(\boldsymbol{r},\boldsymbol{r})/2]\delta(\boldsymbol{r}-\boldsymbol{r}_1). \tag{2.91}$$

Recall that the operator $\hat{\tau}$ is defined by eq. (2.88). In eq. (2.91), for Σ the term determined by the last diagram in fig. 3 is dropped, the reasons for this will be given below.

Introduce the notation

$$\Delta = \tau + \lambda\overline{\langle\varphi(\boldsymbol{r})\rangle^2}/2 + \lambda\overline{D(\boldsymbol{r},\boldsymbol{r})}/2. \tag{2.92}$$

Here and in the following, the overbar above a function denotes spatial averaging, namely

$$\overline{D(\boldsymbol{r},\boldsymbol{r})} = \int \mathrm{d}\boldsymbol{r}\, D(\boldsymbol{r},\boldsymbol{r})/V. \tag{2.93}$$

In other words, the overbar on a function implies that one should retain only the zero Fourier harmonics in it. Now eq. (2.87) can be written as

$$[(\Delta + \alpha(\nabla^2 + q_0^2)^2/4q_0^2 - \boldsymbol{\Theta}(\boldsymbol{r})]D(\boldsymbol{r},\boldsymbol{r}_1) = T\delta(\boldsymbol{r}-\boldsymbol{r}_1). \tag{2.94}$$

Here the function $\boldsymbol{\Theta}$ satisfies the condition

$$\overline{\boldsymbol{\Theta}(\boldsymbol{r})} = 0. \tag{2.95}$$

It means that $\boldsymbol{\Theta}(\boldsymbol{r})$ involves Fourier components only with non-zero wave vectors of the order of q_0.

2.3.3. Equation for the gap

Let us seek for the solution of eq. (2.94) in the form of a series in $\boldsymbol{\Theta}$:

$$D = D_1 + T^{-1}D_1\boldsymbol{\Theta}D_1 + T^{-2}D_1\boldsymbol{\Theta}D_1\boldsymbol{\Theta}D_1 + \cdots$$

The function D_1 here is dependent only on the difference of the coordinates $\boldsymbol{r}-\boldsymbol{r}_1$. In the Fourier representation, introduced similarly to eq. (2.89), we get

$$D_1(\boldsymbol{q}) = T/[\Delta + \alpha(q-q_0)^2]. \tag{2.96}$$

This expression differs from the bare expression (2.89) by the replacement $\tau \to \Delta$. Henceforth we will refer to the quantity Δ as the gap, which is justified by the form of the function (2.96).

Now calculate the single-point correlator $D(\boldsymbol{r},\boldsymbol{r})$ figuring in eqs. (2.90) and (2.91). As we will see later in this calculation we can employ eq. (2.96) as D. As a result we find

$$D(\boldsymbol{r},\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{q}\, D_1(\boldsymbol{q})/(2\pi)^3 = Tq_0^2/2\pi(\alpha\Delta)^{1/2}. \tag{2.97}$$

Here we have used the inequality (2.15) and confined ourselves to the vicinity of the sphere $|\boldsymbol{q}| = q_0$ in the reciprocal space. For characteristic vectors, determining the integral (2.97), from eq. (2.96) we have the estimate

$$|q-q_0| \sim (\Delta/\alpha)^{1/2}. \tag{2.98}$$

Therefore, for the constraint (2.15) to hold it is necessary that the inequality

$$\Delta \ll \alpha q_0^2 \tag{2.99}$$

should be fulfilled. Thus, if the estimate (2.14) holds, then $\Delta \ll \lambda$.

Now, estimate the contribution into $D(\boldsymbol{r},\boldsymbol{r})$ due to higher-order terms of the expansion of D in $\boldsymbol{\Theta}$. Then one should remember the estimate

$$\boldsymbol{\Theta} \sim \Delta. \tag{2.100}$$

Firstly, consider in D the term $D_2 = T^{-1}D_1\boldsymbol{\Theta}D_1$, linear in $\boldsymbol{\Theta}$. The quantity $D_2(\boldsymbol{r},\boldsymbol{r})$ is set by the integral over the reciprocal space from the two functions D_1 with the arguments $\boldsymbol{q}$ and $\boldsymbol{q}+\boldsymbol{k}$, where $\boldsymbol{k}$ is a wave vector of one of the Fourier components of $\boldsymbol{\Theta}$; it is of the order of q_0. A simple analysis shows that in this situation the main contribution to the integral is determined by a region near the intersection of the respective spheres in the reciprocal space. The value of this integral, with the estimate (2.100) taken into account, is small in comparison with eq. (2.97), namely of the order $(\Delta/\alpha q_0^2)^{1/2}$. A similar analysis shows that, in virtue of the inequality (2.99), one can neglect the contributions to $D(\boldsymbol{r},\boldsymbol{r})$ from higher-order terms of the expansion of D in $\boldsymbol{\Theta}$, as compared with eq. (2.97).

Employing this expression, from eq. (2.91) we get an equation for the gap Δ,

$$\Delta = \tau + \lambda\overline{\langle\varphi(\boldsymbol{r})\rangle^2}/2 + \beta\Delta^{-1/2}, \tag{2.101}$$

where

$$\beta = \lambda T q_0^2/4\pi\alpha^{1/2}. \tag{2.102}$$

The first two terms in the r.h.s. of (2.101) are the mean field terms and the last term emerges due to fluctuations. Note that for the liquid phase, i.e., at $\langle\varphi\rangle = 0$, eq. (2.101) has a solution for Δ at an arbitrary value of τ. In other words, fluctuation effects in the model under study prove to be so strong that they stabilise the liquid phase (i.e., render this phase metastable) even at $\tau < 0$.

2.3.4. Estimates of fluctuation contributions

The last fluctuation term in the r.h.s. of eq. (2.101) becomes important in comparison with the first term at

$$|\tau|^3 \leq \lambda^2 T^2 q_0^4/\alpha. \tag{2.103}$$

In the derivation of (2.103) we have made use of the estimate $\Delta \sim \tau$. Since in the mean field theory the transition occurs at $\tau \sim \mu^2/\lambda$, the fluctuation term in eq. (2.101) should be important at

$$|\mu|^3 \leq \lambda^{5/2} T q_0^2/\alpha^{1/2}. \tag{2.104}$$

The conditions (2.103) and (2.104) determine on the plane (τ,μ) a region near the origin where fluctuation effects play an essential role. If the estimate (2.14) holds, this region is described by the inequalities

$$|\tau|^3 \leq \lambda T^2 q_0^6, \quad |\mu|^3 \leq \lambda^2 T q_0^3. \tag{2.105}$$

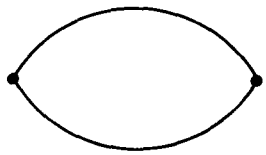

Fig. 4. Main fluctuation correction to the quartic vertex λ.

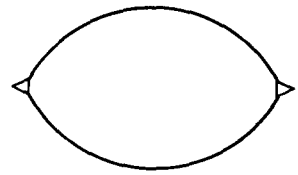

Fig. 5. Main self-energy correction, defined by the triple vertex μ.

An amazing property of eq. (2.101) is that at $\tau \to 0$ the gap Δ does not tend to zero but remains a constant of the order of

$$\Delta \sim (\lambda^2 T^2 q_0^4/\alpha)^{1/3}, \tag{2.106}$$

which becomes particularly evident for the liquid phase, where $\langle\varphi\rangle = 0$. This property testifies to a large strength for the fluctuations of φ in the weak crystallization theory, which is accounted for by a large phase volume of fluctuations, distributed near the sphere in the reciprocal space. For comparison note that at a conventional second-order transition, fluctuations are concentrated in the vicinity of one or several points in the reciprocal space.

The applicability condition for the weak crystallization theory is the inequality (2.15) and the relation (2.99), following from it. Equation (2.106) yields an estimate of Δ from below. Since for this value the relation (2.99) should be fulfilled, we arrive at the inequality

$$\lambda T/\alpha^2 q_0 \ll 1. \tag{2.107}$$

If the estimate (2.14) holds, the conditions (2.107) bring about the inequalities

$$\tau \ll \lambda, \quad \mu \ll \lambda,$$

valid on the boundary of the fluctuation region, defined for this case by the inequalities (2.105).

Comparing the term in the l.h.s. of (2.101) and the term in the r.h.s. of (2.101), we get the estimate

$$\langle\varphi\rangle \sim (\Delta/\lambda)^{1/2}. \tag{2.108}$$

Now using eq. (2.106), we find that, with fluctuations taken into account, at a phase transition there emerges an average (condensate),

$$\langle\varphi\rangle \sim (T^2 q_0^4/\alpha\lambda)^{1/6}. \tag{2.109}$$

If the estimate (2.14) holds, then due to eqs. (2.107) and (2.109) there is the inequality $\langle\varphi\rangle \ll 1$. Thus, the inequality (2.107) makes the weak crystallization theory self-consistent.

Now consider the fluctuation correction to the vertex λ, given by the diagram of fig. 4. The summary wave vector in the loop will be assumed to have the order q_0. In this case for the correction to the vertex we have the estimate:

$$\delta\lambda \sim T q_0 \lambda^2/\alpha\Delta. \tag{2.110}$$

Employing eq. (2.106), we get for $\delta\lambda$ an estimate from above. Thus

$$\delta\lambda/\lambda \leq (\lambda T/\alpha^2 q_0)^{1/3} \ll 1. \tag{2.111}$$

This inequality is a consequence of the condition (2.107).

Similarly, we can obtain an estimate for the contribution to Δ, due to the diagram, given in fig. 5:

$$\delta\Delta \sim Tq_0\mu^2/\alpha\Delta\,. \tag{2.112}$$

Having in mind the constraint (2.104) and the estimate (2.106), we get

$$\delta\Delta/\Delta \leq (\lambda T/\alpha^2 q_0)^{1/3} \ll 1\,. \tag{2.113}$$

This inequality is a consequence of the condition (2.107). Thus we justify the neglect of the contribution into Δ, made in the derivation of eq. (2.89).

The estimates, analogous to the ones, given above, show that as long as the parameter (2.107) is small, under the condition (2.104) higher-order fluctuation corrections to μ, λ are also small. This justifies all estimates given in subsection 2.2 for the difference of wave vectors modules of the main harmonics of the condensate from q_0. Correct is also the conclusion made in subsection 2.2 that the effects, associated with this circumstance, are irrelevant. Therefore below we, like in subsection 2.2, will believe that $|\boldsymbol{q}_n| = q_0$. This, in particular, means that in eq. (2.90) (but not in eq. (2.87)!) $\hat{\tau}$ could be replaced with τ.

Estimates of the many-loop diagrams bring us to the conclusion that many-loop corrections to the one-loop expressions for h, Σ written out in eqs. (2.90) and (2.91), are small in the parameter (2.107). Then it should be borne in mind that fluctuation effects are important only at values of μ, determined by (2.104). It means that this consideration is self-consistent. Thus, the inequality (2.82) not only ensures the applicability of the weak crystallization theory (at sufficiently small values of μ, of course) but also ensures the validity of relatively simple equations for h, Σ. This permits to achieve progress in analysing the role of fluctuations in the weak crystallization theory.

2.3.5. Thermodynamic analysis

In virtue of eq. (2.85), the variation of the thermodynamic potential Ω' at the change of the condensate by $\mathrm{d}\langle\varphi(\boldsymbol{r})\rangle$, could be written out as

$$\mathrm{d}\Omega' = V\overline{h(\boldsymbol{r})\,\mathrm{d}\langle\varphi(\boldsymbol{r})\rangle}\,. \tag{2.114}$$

Inserting here eq. (2.90), we get

$$\mathrm{d}\Omega'/V = \tau\overline{\langle\varphi(\boldsymbol{r})\rangle\,\mathrm{d}\langle\varphi(\boldsymbol{r})\rangle} - \tfrac{1}{2}\mu\overline{\langle\varphi(\boldsymbol{r})\rangle^2\,\mathrm{d}\langle\varphi(\boldsymbol{r})\rangle} + \tfrac{1}{6}\lambda\overline{\langle\varphi(\boldsymbol{r})\rangle^3\,\mathrm{d}\langle\varphi(\boldsymbol{r})\rangle}$$
$$+ \tfrac{1}{2}\lambda\overline{\langle\varphi(\boldsymbol{r})\rangle\,\mathrm{d}\langle\varphi(\boldsymbol{r})\rangle D(\boldsymbol{r},\boldsymbol{r})}\,. \tag{2.115}$$

The last term in the r.h.s. of eq. (2.90) gives a contribution to $\mathrm{d}\Omega'$ equal to zero, due to homogeneity of the function $D(\boldsymbol{r},\boldsymbol{r})$ defined in eq. (2.97), and due to the condition $\overline{\mathrm{d}\langle\varphi(\boldsymbol{r})\rangle} = 0$. Now employing eq. (2.92), we get

$$\mathrm{d}\Omega'/V = \Delta\overline{\langle\varphi\rangle\,\mathrm{d}\langle\varphi\rangle} - \tfrac{1}{2}\mu\overline{\langle\varphi\rangle^2\,\mathrm{d}\langle\varphi\rangle} + \tfrac{1}{6}\lambda\overline{\langle\varphi\rangle^3\,\mathrm{d}\langle\varphi\rangle} - \tfrac{1}{2}\lambda\overline{\langle\varphi\rangle^2\langle\varphi\rangle\,\mathrm{d}\langle\varphi\rangle}\,. \tag{2.116}$$

The equilibrium or metastable state corresponds to a local minimum of Ω'. That is why eq. (2.116) could be used to determine the explicit form of the condensate; for this purpose it is necessary to solve the equation $\mathrm{d}\Omega' = 0$, which is the condition of the extremum of Ω'. Equation (2.116) could also be used to find the difference of values of the thermodynamic potential for

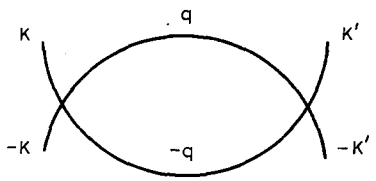

Fig. 6. One-loop correction to the quartic vertex λ.

Fig. 7. "Ladder" diagrams determing relevant corrections to the quartic vertex λ.

various metastable states. To do this one should continuously transform $\langle\varphi\rangle$ from one state to another and calculate the integral

$$\Omega_2' - \Omega_1' = \int_1^2 d\Omega' \tag{2.117}$$

along the trajectory of the transformation of $\langle\varphi\rangle$. Here the gap Δ is assumed to be expressed via $\langle\varphi\rangle$ by means of eq. (2.101). It is particularly convenient to choose as the initial state in (2.117) a liquid phase, where $\langle\varphi\rangle = 0$.

2.3.6. Renormalization of the vertex λ

The assertion that fluctuation corrections to the scattering vertex λ are small, concerns scattering processes with a not small summary wave vector, whereas corrections to the scattering vertex with a small summary wave vector prove to be not small at all.

For instance, consider the correction, given by the diagram of fig. 6. The anomalously large value of this diagram at a small summary wave vector is accounted for by the overlapping of the spheres in whose vicinity the functions D achieve their maxima in the reciprocal space. A straightforward calculation of the contribution to $\lambda(\boldsymbol{k}, -\boldsymbol{k}, \boldsymbol{k}', -\boldsymbol{k}')$, determed by this diagram, yields

$$\lambda^{(1)} = -\frac{\lambda}{2T(2\pi)^3}\int d\boldsymbol{q}\ (D(\boldsymbol{q}))^2 = -\frac{\lambda^2 T q_0^2}{8\pi\alpha^{1/2}\Delta^{3/2}}. \tag{2.118}$$

Here we have used the approximation (2.96) for the function D. From the estimate (2.106), the correction $\lambda^{(1)}$ proves to be of the order of λ. The same holds also for some higher-order corrections to the scattering vertex by the zero angle. It is not difficult to understand that all these corrections have a "ladder" structure, given in fig. 7. Summing up the "ladder" sequence of the diagrams, we find

$$\lambda(\boldsymbol{k}, -\boldsymbol{k}, \boldsymbol{k}', -\boldsymbol{k}') = Z\lambda,$$

where

$$Z = (1 + \beta/2\Delta^{3/2})^{-1}. \tag{2.119}$$

Thus, the scattering vertex with the zero summary wave vector is smaller than the bare vertex but of the same order of magnitude.

These corrections to λ are important for angles θ between the wave vectors satisfying the estimate

$$|\pi - \theta| \leq (\Delta/\alpha q_0^2)^{1/2}. \tag{2.120}$$

From the inequality (2.100), the region of angles (2.120) is narrow. Therefore, even a considerable variation of the vertex λ in this region does not affect integral characteristics. This justifies the above made assumptions.

2.3.7. Fluctuation contribution to the long-wavelength characteristics

In virtue of the identity (2.3) the densities of the mass and of entropy equal

$$\langle\rho\rangle = -\delta\Omega/\delta\zeta, \quad \langle s\rangle = -\delta\Omega/\delta T. \tag{2.121}$$

The fluctuation contribution into these quantities could be found using the representation (2.82) for the thermodynamic potential. Differentiating the relation (2.82) over ζ, T we get

$$\langle\rho\rangle = -\langle\delta F_L/\delta\zeta\rangle, \quad \langle s\rangle = -\langle\delta F_L/\delta T\rangle, \tag{2.122}$$

where the angular brackets imply the averaging over fluctuations of φ with the distribution function (2.81). Remember that all coefficients in the expansion of the Landau functional F_L in φ are functions of ζ, T.

Virtually, in the expansion of F_L in φ one should incorporate the ζ, T-dependence of only the coefficient τ. Unlike τ, the derivatives $\partial\tau/\partial\zeta$, $\partial\tau/\partial T$ do not contain any special smallness in the vicinity of the phase transition point. Therefore it is these derivatives that the main terms in eq. (2.122) are related to, thus we arrive at the result

$$\langle\rho\rangle = \rho_0(\zeta, T) - (\partial\tau/\partial\zeta)\overline{\langle\varphi^2\rangle}/2, \quad \langle s\rangle = s_0(\zeta, T) - (\partial\tau/\partial T)\overline{\langle\varphi^2\rangle}/2. \tag{2.123}$$

Here the functions ρ_0, s_0 determine the regular behavior of the density and entropy and the second terms in the r.h.s. of (2.123) determine the anomalous contributions into $\langle\rho\rangle, \langle s\rangle$ due to the order parameter. Note that these anomalous contributions are proportional to $\langle\varphi^2\rangle$ and are small since $\langle\varphi\rangle \ll 1$.

The r.h.s. of (2.123) contains the quantity

$$\overline{\langle\varphi^2\rangle} = \overline{\langle\varphi\rangle}^2 + \overline{D(\boldsymbol{r}, \boldsymbol{r})}. \tag{2.124}$$

The quantity $\overline{D}$ is determined here by eq. (2.97). With fluctuations φ neglected, we come back to the mean field result.

Now consider the derivatives

$$\partial\langle s\rangle/\partial T, \quad \partial\langle s\rangle/\partial\zeta = \partial\langle\rho\rangle/\partial T, \quad \partial\langle\rho\rangle/\partial\zeta, \tag{2.125}$$

via which such quantities as heat capacity or compressibility are expressed. So, for instance,

$$C_P = T\left(\frac{\partial\langle s\rangle}{\partial T} - \frac{\langle s\rangle}{\langle\rho\rangle}\frac{\partial\langle\rho\rangle}{\partial T}\right).$$

To calculate the derivatives (2.125) one must use eq. (2.123), keeping in mind that the angular brackets denote the averaging over fluctuations of φ with the distribution function (2.81) and taking into account the relation (2.121). As a result, in the same approximation as has been employed for the derivation of (2.123), we find

$$\partial\langle s\rangle/\partial T = \partial s_0/\partial T + (\partial\tau/\partial T)^2 \int d\boldsymbol{r}_1 \langle\langle\varphi^2(\boldsymbol{r})\varphi^2(\boldsymbol{r}_1)\rangle\rangle. \tag{2.126}$$

The double brackets denote the irreducible correlation function

$$\langle\langle\varphi^2(\boldsymbol{r})\varphi^2(\boldsymbol{r}_1)\rangle\rangle \equiv \langle\varphi^2(\boldsymbol{r})\varphi^2(\boldsymbol{r}_1)\rangle - \langle\varphi^2(\boldsymbol{r})\rangle\langle\varphi^2(\boldsymbol{r}_1)\rangle . \tag{2.127}$$

Formulas, analogous to (2.126) are derived for the other derivatives in eq. (2.125).

The r.h.s. of eq. (2.126) involves a zero Fourier component of the correlation function (2.127). For this quantity all arguments used in the calculation of $\lambda(\boldsymbol{k}, -\boldsymbol{k}, \boldsymbol{k}', -\boldsymbol{k}')$ are valid. In other words, the zero Fourier component (2.127) is represented as a series of ladder diagrams of the type given in fig. 7, the first term being the diagram with one loop. Summing up the ladder sequence, we get

$$\int d\boldsymbol{r}_1 \langle\langle\varphi^2(\boldsymbol{r})\varphi^2(\boldsymbol{r}_1)\rangle\rangle = Zq_0^2T^2/2\pi\alpha^{1/2}\Delta^{3/2}, \tag{2.128}$$

where Z is defined by eq. (2.119).

It ensues from eq. (2.102) that this expression has the order of T/λ, i.e., it does not contain any factors related to the small value of Δ. It apparently means that the singular contribution into the compressibility or heat capacity near the transition point will be of the order of the regular contribution. Let us stress that the latter assertion holds only in the region determined by the conditions (2.103) and (2.104), where fluctuation effects are strong. Beyond this region the fluctuation contribution into the heat capacity or compressibility is small in comparison with the regular contribution.

2.3.8. Account of the angular dependence of λ

Now we generalize the proposed scheme for the case of an arbitrary dependence of the vertex λ on wave vectors.

In this case the self-energy function Σ will no longer have a simple form (2.91). Instead of eq. (2.92), we introduce

$$\Delta(\boldsymbol{e}) = \int d\boldsymbol{r}_1\, d\boldsymbol{r}_2\, \exp(iq_0\boldsymbol{e}\cdot(\boldsymbol{r}_1 - \boldsymbol{r}_2))\Sigma(\boldsymbol{r}_1, \boldsymbol{r}_2)/V , \tag{2.129}$$

where $\boldsymbol{e}$ is a unit vector. For the function (2.91), corresponding to $\lambda = \text{const.}$, eq. (2.129) does not contain the dependence on $\boldsymbol{e}$ and apparently coincides with (2.92). Equation (2.87) for the angle-dependent vertex λ is now written as

$$[\hat{\Delta} + \alpha(\nabla^2 + q_0^2)^2/4q_0^2 - \hat{\Theta}]D(\boldsymbol{r}, \boldsymbol{r}_1) = T\delta(\boldsymbol{r} - \boldsymbol{r}_1) , \tag{2.130}$$

where $\hat{\Delta}$, $\hat{\Theta}$ are linear operators. In the Fourier representation, $\hat{\Theta}$ is a nondiagonal operator, and $\hat{\Delta}$ is a diagonal operator whose action reduces to the multiplication by $\Delta(\boldsymbol{q}/q)$. Equation (2.130) is the generalization of eq. (2.94).

When the term with $\hat{\Theta}$ in (2.130) is neglected, we find the function D_1, dependent only on the difference $\boldsymbol{r} - \boldsymbol{r}_1$. In the Fourier representation, introduced similarly to (2.87) for D_1 we have eq. (2.96), where now $\Delta = \Delta(\boldsymbol{q}/q)$. At the calculation of $D(\boldsymbol{r}, \boldsymbol{r})$ the matrix elements of the operator $\hat{\Theta}$ for the wave vectors of the order of q_0 are relenant. Therefore all above given arguments concerning the calculation of functions $D(\boldsymbol{r}, \boldsymbol{r})$ are valid, i.e., in calculating this function, it is sufficient to confine oneself to the approximation $D = D_1$.

Thus, with all said above taken into account, instead of eq. (2.42) we get for the gap the equation

$$\Delta(\boldsymbol{e}) = \tau + \sum_n \lambda(q_0\boldsymbol{e}, -q_0\boldsymbol{e}, \boldsymbol{q}_n, -\boldsymbol{q}_n)|a_n|^2 + \int d\boldsymbol{q}\, \lambda(q_0\boldsymbol{e}, -q_0\boldsymbol{e}, \boldsymbol{q}, -\boldsymbol{q})D_1(\boldsymbol{q})/16\pi^3 . \tag{2.131}$$

This equation is the generalization of (2.92) and transforms into it in the case $\lambda = \text{const}$. Let us also give the generalization of eq. (2.116):

$$d\Omega'/V = -\mu\tilde{\sum_{nm}} a_n a_m \, da_l/2 + \sum_m \Delta(q_m/q_m)(a_m^* \, da_m + a_m \, da_m^*)$$

$$+\tilde{\sum_{nml}} \lambda(q_n, q_m, q_l, q_j) a_n a_m a_l \, da_j$$

$$-\sum_{nm} a_m^* a_m \lambda(-q_m, q_m, -q_n, q_n)(a_n^* \, da_n + a_n \, da_n^*). \tag{2.132}$$

The definition of the sum labelled by the tilde has been introduced in eq. (2.6); in such sums the summation in performed under the conditions (2.20) and (2.21).

2.3.9. Concrete examples

To illustrate how the formulated procedure works, let us consider the problem of the crystallization of liquids with fluctuations of the order parameter taken into account, in the simplest case when the vertex λ is independent of the angles between wave vectors. The solution of this problem in the framework of the mean field theory has been obtained in subsection 2.2. It follows that in the case under discussion absolutely stable can be four phases: the initial isotropic liquid I, a one-dimensional lattice of liquid layers SA, a two-dimensional hexagonal lattice of liquid columns D_h and a body-centered cubic crystal BCC_1. The transitions between these phases at $\mu \neq 0$ are first order transitions and occur at the values of the parameter τ, determined by eqs. (2.67).

In the given case, taking the fluctuations into account does not lead to the emergence of new absolutely stable phases. Therefore, to solve the problem with fluctuations taken into account, suffice it to analyse the equations of state for the three mentioned inhomogeneous phases.

Rewrite eq. (2.101) as

$$\Delta = \tau + \lambda A + \beta \Delta^{-1/2}. \tag{2.133}$$

Here the designation

$$\beta = \lambda T q_0^2 / 4\pi\alpha^{1/2}$$

is employed, and the parameter A, defined by eq. (2.42), for the three phases equals

$$A_{SA} = a^2, \quad A_{D_h} = 3a^2, \quad A_{BCC_1} = 6a^2.$$

The parameter a is the module of the density wave amplitude in inhomogeneous phases (2.6). To get from eq. (2.133) a closed equation for the value of the gap in an inhomogeneous phase, it is necessary to use the condition of the minimum of the potential Ω'

$$d\Omega' = 0. \tag{2.134}$$

Like in subsection 2.2, it is convenient to represent the potential as a sum of the two terms

$$\Omega'/V = F + f, \tag{2.135}$$

where the function f is defined by eq. (2.43). With the relation (2.116) incorporated, eq. (2.134) can be written out as

$$\frac{2\,\mathrm{d}\Omega'}{V\,\mathrm{d}\overline{\langle\varphi\rangle}^2} = \frac{\mathrm{d}F}{\mathrm{d}A} + \frac{\mathrm{d}f}{\mathrm{d}A} = \Delta + \frac{\mathrm{d}f}{\mathrm{d}A} = 0. \tag{2.136}$$

Inserting the expressions for the functions f from eqs. (2.47), (2.57) and (2.63) into eq. (2.136), we get

$$\Delta_{\mathrm{SA}} = \lambda A/2, \tag{2.137}$$

$$\Delta_{\mathrm{D_h}} = \lambda A/6 + |\mu|\sqrt{A/3}, \tag{2.138}$$

$$\Delta_{\mathrm{BCC_1}} = -\lambda A/4 + |\mu|\sqrt{2A/3}. \tag{2.139}$$

To determine the dependence $A(\Delta)$ from the two solutions of eqs. (2.138) and (2.139), one should choose the largest one since it corresponds to the energy minimum. Solving eqs. (2.137)–(2.139) with respect to A and inserting the result into eq. (2.133), we get closed equations for the gap,

$$\tau + \Delta_{\mathrm{SA}} + \beta\Delta_{\mathrm{SA}}^{-1/2} = 0, \tag{2.140}$$

$$\tau - \Delta_{\mathrm{D_h}} + 3\mu^2(\sqrt{1 - 2\lambda\Delta/\mu^2} - 1)^2/\lambda + \beta\Delta_{\mathrm{D_h}}^{-1/2} = 0, \tag{2.141}$$

$$\tau - \Delta_{\mathrm{BCC_1}} + 4\mu^2(\sqrt{1 - 3\lambda\Delta/2\mu^2} + 1)^2/\lambda + \beta\Delta_{\mathrm{BCC_1}}^{-1/2} = 0. \tag{2.142}$$

To calculate the phase diagram, we must calculate the energies of inhomogeneous phases. For this purpose, integrate the equation

$$\mathrm{d}F/\mathrm{d}A = \Delta$$

over the parameter A from zero up to the equilibrium value, determined from eqs. (2.137)–(2.139). In calculating the integral, it is convenient to pass from the integration over A to the integration over Δ, using the relation (2.133),

$$F(A) - F(0) = \int_0^A \frac{\mathrm{d}F}{\mathrm{d}A'}\,dA' = \int_{\Delta_0}^{\Delta} \mathrm{d}\Delta\,\frac{\Delta + \beta\Delta^{-1/2}}{\lambda}$$

$$= \frac{\Delta^2/2 - \Delta_0^2/2 + \beta(\sqrt{\Delta} - \sqrt{\Delta_0})}{\lambda}. \tag{2.143}$$

In eq. (2.143) the parameter Δ for the inhomogeneous phase has to be found from eqs. (2.140)–(2.142), and Δ_0 from the solution of eq. (2.133) for the gap in the original liquid phase, where the parameter A is, naturally, zero. The equation for the gap Δ_0 in the liquid phase has a solution at any τ, therefore the liquid phase is metastable at any τ and its energy also may be defined for any τ. From eq. (2.143) one can then calculate the energy of the inhomogeneous phase for arbitrary values of τ.

To complete the calculation of the phase diagram one must numerically solve eqs. (2.140)–(2.142) and find the energy of the inhomogeneous phases in conformity with eq. (2.135), where

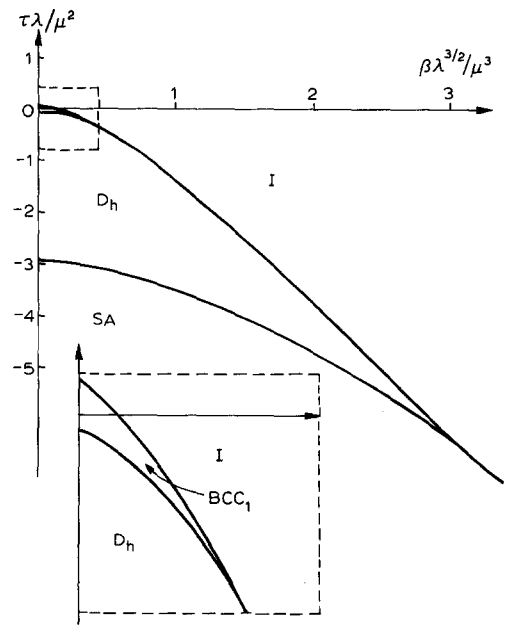

Fig. 8. Phase diagram of weak crystallization of a liquid, obtained with fluctuations taken into account.

$F(A)$ is determined by eq. (2.143), and the function f is defined by one of the formulas (2.47), (2.57) and (2.63), depending on the structure of the phases. Recall that the values of A, Δ are connected by relations (2.137)–(2.139). The phase realized at given τ, μ will be determined by the absolute minimum of Ω' given by eq. (2.135).

2.3.10. Results

The results of the calculation are presented in fig. 8. For values

$$\mu \gg (\lambda^5 T^2 q_0^4/\alpha)^{1/6},$$

the diagram of state is close to the one, as predicted in the mean field theory. In the region

$$\mu \leq (\lambda^5 T^2 q_0^4/\alpha)^{1/6},$$

fluctuations considerably affect the structure of the phase diagram. At decreasing parameter μ the cubic and columnar phases vanish from the phase diagram. In conformity with the result obtained by Brazovsky [1975], then there remains only one SA–I transition occurring at the value of τ

$$\tau(\text{SA–I}) \cong -2.03\beta^{2/3}.$$

In the mean field theory this transition should be continuous, however, fluctuations render this transition a first-order transition.

The performed analysis permits to make general conclusions about the influence of thermal fluctuations on the phase diagram of the system under the weak crystallizations valid also in the case when λ is dependent on the angles between the wave vectors. As has been demonstrated in

subsection 2.2, inhomogeneous phases fall into two categories: some of them ensure the minimal contribution of the interaction term $\lambda\varphi^4$ into the total energy, these, for instance, are SA, FCC, BCC_2, R phases, whereas the others can be absolutely stable due to the minimal contribution of the term $\mu\varphi^3$ (such as D, BCC_1, Y phases). Out of the phase belonging to the first category at the certain anisotropy of the coefficient λ in the mean field theory only one is realized (which does not actually change when fluctuations are taken into account). This phase occupies in the diagram of state a region lying at large negative τ. The phases belonging to the second category occupy a sector between the low-temperature phase and the original liquid phase; as a rule here the columnar and BCC_1 phases are realized.

In the mean field theory the interphase equilibrium lines are parabolas $\tau \sim \mu^2/\lambda$ with a common origin in the point $(\tau, \mu) = (0, 0)$. The influence of the order parameter fluctuations on the described phase diagram reduces to the fact that in a region near the origin in the plane (τ, μ) all intermediate phases of the second category vanish and at a decrease of τ a direct transition from the liquid phase into the low-temperature phase occurs. Fluctuations stabilize the original isotropic phase, therefore this transition is a first-order transition at negative values of τ. For sufficiently large values of the parameter μ the diagram of states is very close to the one of the mean field theory.

These results for the case when the vertex λ depends on the directions of the wave vectors are only qualitative. In the general case, the integral equation for the gap (2.131), for a three-dimensional system at the angle-dependent function λ, can be solved only numerically. For this reason a detailed analysis of the simultaneous influence of the fluctuations and the angular dependence of the function λ in a three-dimensional system is quite a problem. At the same time, a similar problem in a two-dimensional system in some cases allows for an analytical solution (see section 3).

2.4. Dynamic phenomena

In this subsection we investigate theoretically dynamic phenomena near the weak crystallization transition point. One may expect that the dynamic phenomena will be to some degree analogous to the phenomena observed near a second-order phase transition. Therefore we can address the reader to the theory of critical dynamics. The main results of the theory are presented in the review [Halperin and Hohenberg 1977].

All physical quantities have singular contributions near the second-order transition point. In dynamics the singular behaviour of such quantities as sound velocities is related to the static critical behaviour of the elasticity modules. But the critical behaviour of such purely dynamic quantities as kinetic coefficients is not related to the behaviour of any static quantity and needs a separate investigation. The same situation occurs near the weak crystallization transition point. Particularly, we may expect an increase of viscosity coefficients near the transition point.

Since the quantity φ near the phase transition point is a "soft" field (which is actually the applicability condition for the weak crystallization theory), the time, characterizing the relaxation of the quantity to the equilibrium increases near the transition point. Therefore the dynamics of the quantity φ should be considered in the framework of a macroscopic equation of the hydrodynamic type. A favourable circumstance simplifying the problem is that the dynamics of φ is purely relaxational.

In dynamics, like in statics, fluctuations of the order parameter play an essential role. To study the effects connected with these fluctuations one can construct a perturbation theory over nonlinearities in the dynamic equation. As a result of the summation of the principal series of diagrams, the dynamic correlation functions of the order parameter may be found. The renormalization of the

correlation functions reduces (like it was in statics) to a redefinition of the gap Δ in the bare expressions.

In order to study the influence of fluctuations of the soft parameter φ on the macroscopic dynamic properties of the system, we have to incorporate the interaction between the critical and the long-wavelength degrees of freedom. The interaction is described by nonlinear terms in the overall system of dynamic equations. Therefore our first goal will be to incorporate the field φ alongside with the conventional macroscopic variables (mass density, momentum density, etc.) into the system of nonlinear hydrodynamic equations.

2.4.1. Derivation of the dynamic equation for φ

It is simpler to construct the non-dissipative part of this system of equations by means of the Poisson brackets method in terms of which the dynamic equation for φ reads

$$\partial\varphi/\partial t = \{H, \varphi\}, \tag{2.144}$$

where H is the Hamiltonian of the system. The non-dissipative dynamic equations have a similar structure for other hydrodynamic variables. A systematic description of the Poisson brackets method for hydrodynamic systems can be found in the review [Dzyaloshinsky and Volovik 1980], this method is also formulated in the monograph [Kats and Lebedev 1988].

To write out equations of the type of (2.144) one should know the dependence of the Hamiltonian on the hydrodynamic variables as well as the explicit expressions of Poisson brackets for all pairs of these variables. Alongside with φ, it is convenient to use also the following set: the mass density ρ, entropy density s and momentum density $\boldsymbol{j}$. The Poisson brackets for the quantities $\rho, s, \boldsymbol{j}$ are well-known [Dzyaloshinsky and Volovik 1980, Kats and Lebedev 1988] and we will not present them here.

We now derive the expression of Poisson brackets for φ. The non-dissipative equations must be invariant to time reversal. Hence, it follows that in the main approximation only the bracket $\{\boldsymbol{j}, \varphi\}$ is non-zero and the brackets for the other hydrodynamic variables with φ are zero. The structure of this non-zero bracket is found from the momentum conservation law; in the general case this bracket can be written as

$$\{j_i(\boldsymbol{r}_1), \varphi(\boldsymbol{r}_2)\} = -\nabla_i \varphi \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2) + \nabla_k \delta(\boldsymbol{r}_1 - \boldsymbol{r}_2) f_{ik}(\boldsymbol{r}_2). \tag{2.145}$$

Here f_{ik} is some function of φ, s, ρ, symmetric with respect to the subscripts i, k. It, however, should be borne in mind that $\boldsymbol{j}$ is a long-wavelength field, whereas φ is a short-wavelength field. Therefore the function f_{ik} should also be of short-wavelength character.

Henceforth we will take the case when the Hamiltonian (energy) can be represented as the integral of the local function:

$$H = \int \mathrm{d}\boldsymbol{r}\, [(\boldsymbol{j}^2/2\rho + E(\varphi, \nabla\varphi, \nabla\nabla\varphi)]. \tag{2.146}$$

Here E has the meaning of the energy density, the character of its dependence on φ is determined by the terms of the expansion (2.16), (2.26). The respective terms of the expansion of E can be obtained in conformity with the recipe (2.29), with (2.30) taken into account. The generalization of this procedure for the case when E depends on higher-order derivatives of φ is not difficult, although it makes the formulas more complicated. The results are not practically affected by this generalization.

Employing eqs. (2.145) and (2.146), we can now, in accordance with the recipe (2.144), obtain for φ the non-dissipative equation

$$d\varphi/dt = 0, \quad \text{where} \quad d\varphi/dt \equiv \partial\varphi/\partial t + \boldsymbol{v}\nabla\varphi + f_{ik}\nabla_i v_k . \tag{2.147}$$

Here $\boldsymbol{v} = \boldsymbol{j}/\rho$ is the local velocity of the medium.

With the dissipation taken into account, the equation for the field φ becomes

$$\Gamma\, d\varphi/dt + \delta H/\delta\varphi = 0. \tag{2.148}$$

Here Γ is a positive kinetic coefficient and $d\varphi/dt$ is defined by eq. (2.147).

2.4.2. Hydrodynamic equations for conventional variables

Now we formulate the equations for the conventional hydrodynamical variables including terms induced by the field φ. The equation for the mass density ρ is well-known,

$$\partial\rho/\partial t = -\nabla\boldsymbol{j}. \tag{2.149}$$

From the Galilean invariance, this equation is exact and therefore there are no corrections to the equation connected with dissipation or with the field φ.

The equation for the momentum density $\boldsymbol{j}$ has the form of a local conservation law,

$$\partial j_i/\partial t + \nabla_k(T_{ik}^{(r)} + T_{ik}^{(d)}) = 0. \tag{2.150}$$

Here $T_{ik}^{(r)}$ is the non-dissipative (reactive) part of the stress tensor, and $T_{ik}^{(d)}$ is its dissipative part. The latter is determined by viscosity. The non-dissipative term $T_{ik}^{(r)}$ is determined by the form of the Hamiltonian (2.146) and by the structure of the Poisson brackets, involving $\boldsymbol{j}$. Explicit expressions for these brackets can be found in the survey [Dzyaloshinsky and Volovik 1980] and in the monograph [Kats and Lebedev 1988].

We will not derive here the expressions for $T_{ik}^{(r)}$ and give only the final result,

$$T_{ik}^{(r)} = P\delta_{ik} + \rho v_i v_k + \frac{\partial E}{\partial\nabla_k\varphi}\nabla_i\varphi - \nabla_n\frac{\partial E}{\partial\nabla_k\nabla_n\varphi}\nabla_i\varphi + \frac{\partial E}{\partial\nabla_k\nabla_n\varphi}\nabla_n\nabla_i\varphi + f_{ik}\frac{\delta H}{\delta\varphi}. \tag{2.151}$$

Here the pressure P is

$$P = \rho\,\partial E/\partial\rho + s\,\partial E/\partial s - E. \tag{2.152}$$

Note that in the absence of the dependence of E on φ eq. (2.151) reduces to a well-known expression for the non-dissipative stress tensor of a conventional liquid, which should be expected.

The tensor (2.151) is not symmetric. Yet, the divergence of this tensor, figuring in eq. (2.150), could be reduced to the divergence of the symmetric tensor, namely

$$\nabla_k T_{ik}^{(r)} = \nabla_k T_{ik}^{(s)},$$

where

$$T_{ik}^{(s)} = P\delta_{ik} + \rho v_i v_k + f_{ik}\frac{\delta H}{\delta \varphi} - \nabla_n\left(\frac{\partial E}{\partial \nabla_k \nabla_n \varphi}\nabla_i\varphi + \frac{\partial E}{\partial \nabla_i \nabla_n \varphi}\nabla_k\varphi - \frac{\partial E}{\partial \nabla_i \nabla_k \varphi}\nabla_n\varphi\right)$$

$$+\frac{\partial E}{\partial \nabla_k \varphi}\nabla_i\varphi + 2\frac{\partial E}{\partial \nabla_k \nabla_n \varphi}\nabla_n\nabla_i\varphi\,.$$

The combination

$$\delta\theta_j \epsilon_{jik} T_{ik}^{(s)} = \delta\theta_j \epsilon_{jik}\left(\frac{\partial E}{\partial \nabla_k \varphi}\nabla_i\varphi + \frac{\partial E}{\partial \nabla_k \nabla_n \varphi}\nabla_n\nabla_i\varphi\right)$$

determines the infinitesimal variation of the energy density E at a rotation of coordinates by the angle $\delta\theta_j$. From the rotational invariance, this variation is zero. Hence it follows that the antisymmetric part of $T_{ik}^{(s)}$ is zero, i.e., $T_{ik}^{(s)}$ is a symmetric tensor. Thus, $\partial \boldsymbol{j}/\partial t$ reduces to the divergence of the symmetric stress tensor, which permits us to formulate the conventional angular momentum conservation law.

The dissipative stress tensor is written as

$$T_{ik}^{(d)} = -\eta_1(\nabla_k v_i + \nabla_i v_k - \tfrac{2}{3}\delta_{ik}\nabla \boldsymbol{v}) - \eta_2 \delta_{ik}(\nabla \boldsymbol{v})\,. \tag{2.153}$$

Here η_1, η_2 are coefficients of the first and second viscosities.

In studying the dynamics of the order parameter, we can neglect in the main approximation the non-dissipative terms (associated with the velocity $\boldsymbol{v}$) in eq. (2.148). Besides, we can assume that the conditions (2.28) are fulfilled. Then eq. (2.148) becomes

$$\Gamma\, \partial\varphi/\partial t + \delta F_L/\delta\varphi = 0\,. \tag{2.154}$$

Thus, the dynamics of the order parameter proves to be purely relaxational.

Generally speaking, the kinetic coefficient Γ in eq. (2.154) is a function of the wave vector $\boldsymbol{q}$ of the field φ. This dependence could have been fairly important since the field φ is a short-wavelength field. However, we are interested only in Fourier harmonics with the wave vectors of the values close to q_0. In this case one can assume Γ = const., which will be implied henceforth.

2.4.3. Dynamic diagram technique

To investigate fluctuation effects we will make use of the diagram technique, especially adapted for hydrodynamic systems. Such a diagram technique was constructed firstly by Wyld [1961] who studied velocity fluctuations in a turbulent liquid. The next step was made in the work [Martin, Siggia and Rose 1973], where the Wyld technique was generalized to a broad class of hydrodynamic systems. The description of the Wyld diagram technique can be found in the book by Ma [1976].

The diagram technique may be formulated in terms of functional integration as it was firstly suggested by De Dominicis [1976] and Janssen [1976]. We will use such a functional integration representation in our review. A textbook description of functional integration methods closely related to the present problem may be found in the book by Popov [1983].

Following the work by de Dominicis and Peliti [1978], we may assert that the correlation functions of hydrodynamical variables may be found by using the generating functional constructed on the basis of nonlinear hydrodynamical equations. Note that in the expression given in this work there appears a functional determinant which may be represented in the form of an integral over

auxiliary Fermi fields [Feigelman and Tsvelik 1982, Lebedev, Sukhorukov and Khalatnikov 1983]. It can be demonstrated that in our case the determinant is equal to unity because of the causality properties of the Green's functions. Therefore we will omit the determinant. For details see the monograph by Kats and Lebedev [1988], which we will follow in our description.

Fluctuation effects, associated with the degree of freedom, obeying eq. (2.154) can be studied by means of the effective action

$$I_\varphi = \int \mathrm{d}t\, \mathrm{d}\boldsymbol{r}\, (\Gamma p\, \partial\varphi/\partial t + p\, \delta F_{\mathrm{L}}/\delta\varphi + \mathrm{i}T\Gamma p^2)\,. \tag{2.155}$$

Here p is an auxiliary field. Like φ, p is a short-wavelength field; then the Fourier components of this field with the wave vectors having values close to q_0, are important. Dynamic correlation functions can be calculated by means of averaging over the fields φ, p with the distribution function $\exp(\mathrm{i}I)$. So, for instance,

$$\langle\varphi(t,\boldsymbol{r})\rangle = \int \mathrm{D}\varphi\, \mathrm{D}p\, \varphi(t,\boldsymbol{r}) \exp\left(\mathrm{i}I_\varphi - \mathrm{i}\int \mathrm{d}t\, \mathrm{d}\boldsymbol{r}\, hp\right)\,. \tag{2.156}$$

In the definition (2.156) there is a term with the field h, thermodynamically conjugated to φ. The reasons for its introduction have been discussed above.

Higher-order correlation functions of the fields φ, p are defined similarly to eq. (2.156). We will introduce special notations for pair correlation functions,

$$D(t_1 - t_2, \boldsymbol{r}_1, \boldsymbol{r}_2) = \langle\langle\varphi(t_1,\boldsymbol{r}_1)\varphi(t_2,\boldsymbol{r}_2)\rangle\rangle \equiv \langle\varphi(t_1,\boldsymbol{r}_1)\varphi(t_2,\boldsymbol{r}_2)\rangle - \langle\varphi(t_1,\boldsymbol{r}_1)\rangle\langle\varphi(t_2,\boldsymbol{r}_2)\rangle\,, \tag{2.157}$$

$$G(t_1 - t_2, \boldsymbol{r}_1, \boldsymbol{r}_2) = \langle\varphi(t_1,\boldsymbol{r}_1)p(t_2,\boldsymbol{r}_2)\rangle\,. \tag{2.158}$$

The averages $\langle p\rangle$, $\langle pp\rangle$ are zero; the proof of this fact can be found in ref. [Khalatnikov, Lebedev and Sukhorukov 1984]. Since $\langle p\rangle = 0$, the reducible part of the correlation function (2.158) is zero, therefore we have used in (2.158) the designation of the conventional average but not the designation of the irreducible average, figuring in eq. (2.157).

At the variation of the field h by $\mathrm{d}h$, the mean value of the order parameter changes by the value

$$\mathrm{d}\langle\varphi(t,\boldsymbol{r})\rangle = -\mathrm{i}\int \mathrm{d}t\, \mathrm{d}\boldsymbol{r}_1\, G(t - t_1, \boldsymbol{r}, \boldsymbol{r}_1)\, \mathrm{d}h(t_1,\boldsymbol{r}_1)\,. \tag{2.159}$$

This relation directly entails from the definition (2.156) and from eq. (2.158). Thus, G is the susceptibility of the system with respect to the field h. Therefore, from the causality principle,

$$G(t < 0) = 0\,. \tag{2.160}$$

For correlation functions determined by the effective action (2.155), at $h = 0$ we have the relation

$$\mathrm{i}\partial D(t,\boldsymbol{r}_1,\boldsymbol{r}_2)/\partial t = T[-G(t,\boldsymbol{r}_1,\boldsymbol{r}_2) + G(-t,\boldsymbol{r}_1,\boldsymbol{r}_2)]\,. \tag{2.161}$$

This equality is in fact the fluctuation–dissipation theorem, relating the pair correlation function D to the generalized susceptibility. In the Fourier representation eq. (2.161) acquires the more habitual form

$$D(\omega) = -T[G(\omega) - G(-\omega)]/\omega\,. \tag{2.162}$$

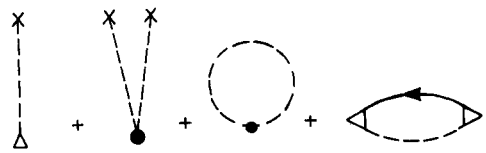

Fig. 9. One-loop corrections to the dynamic self-energy function Σ.

Integrating the relation (2.161) over t, from $-\infty$ to 0, with (2.160) taken into account, we get

$$iD(t = 0)/T = G(\omega = 0). \tag{2.163}$$

The expression in the r.h.s. of (2.163) is the zero Fourier harmonic of the correlation function $G(t)$. The l.h.s. of eq. (2.163) contains the one-time correlation function, discussed in subsection 2.3. Thus, from the fluctuation–dissipation theorem, $G(\omega = 0)$ is expressed via static characteristics of the system.

Inserting into eq. (2.155) the terms (2.16)–(2.18) of the Landau expansion, at μ = const., λ = const. we find

$$I = \int dt\, d\boldsymbol{r}\, (\Gamma p\, \partial\varphi/\partial t + p\hat{\tau}\varphi + iT\Gamma p^2 - \mu p\varphi^2/2 + \lambda p\varphi^3/6). \tag{2.164}$$

Here the operator $\hat{\tau}$ is determined by eq. (2.88). Bare values of the correlation functions (2.157) and (2.158) are determined by the quadratic part of the action (2.164), the fluctuation interaction is set by the third- and fourth-order terms in eq. (2.164). Thus we arrive at the conclusion that the dynamic diagram technique involves the same vertices μ and λ as the static technique does.

Singling out self-energy blocks in the diagram series for the correlation function (2.158), we come to the standard relation

$$(\Gamma\, \partial/\partial t + \hat{\tau})G(t - t_1, \boldsymbol{r}, \boldsymbol{r}_1) - \int dt_2\, d\boldsymbol{r}_2\, \Sigma(t - t_2, \boldsymbol{r}, \boldsymbol{r}_2)G(t_2 - t_1, \boldsymbol{r}_2, \boldsymbol{r}_1)$$

$$= i\delta(\boldsymbol{r} - \boldsymbol{r}_1)\delta(t - t_1). \tag{2.165}$$

Here Σ is a self-energy function, determined by the sum of a series of self-energy diagrams. It follows from the relation (2.163) and eq. (2.87) that the quantity $\Sigma(\omega = 0)$ coincides with the static self-energy function, introduced in subsection 2.3.

2.4.4. One-loop approximation

In the one-loop approximation the self-energy function Σ is determined by the sum of diagrams, given in fig. 9. In this figure the dashed line stands for the correlation function (2.157), the solid line for the correlation function (2.158), the dashed line with a cross on its edge for the average (2.156), the white triangle denotes the vertex μ and the black circle denotes the vertex λ. Note the formal similarity of the diagrams of fig. 9 with the static diagrams for the self-energy function depicted in fig. 3.

The one-loop approximation for Σ in the framework of the weak crystallization theory is the main approximation. Besides, the contribution into Σ, associated with the last diagram of fig. 9, can be disregarded. The argumentation of these statements is analogous to the argumentation of subsection 2.3, where the static case has been touched on.

The other diagrams of fig. 9 give a contribution into $\Sigma(\omega)$, identically coinciding with the static expression for Δ since this contribution does not involve the dependence on the frequency ω and at $\omega = 0$ the function $\Sigma(\omega)$ must necessarily coincide with the static function in virtue of the fluctuation–dissipation theorem. Actually, μ, λ in these diagrams coincide with the static vertices and the average (2.156) is time-independent, therefore the closed line in fig. 9 stands for the one-time correlation function $D(t = 0, \boldsymbol{r}, \boldsymbol{r})$ coinciding with the static correlation function.

Like in subsection 2.3, retaining only the homogeneous part of Σ we find from (2.165) for the function G in the Fourier representation the expression

$$G_1(\omega, \boldsymbol{q}) = -[\Gamma\omega + \mathrm{i}\Delta + \mathrm{i}\alpha(q - q_0)^2]^{-1}. \tag{2.166}$$

Here $\boldsymbol{q}$ is the wave vector and Δ is the gap introduced in eq. (2.92). Equation (2.166) corresponds to the static correlation function (2.96). The dynamic pair correlation function D can be obtained from eq. (2.165) by means of the relation (2.162), which just the fluctuation–dissipation theorem.

In our approximation, the expression for the dressed Green function G can now be derived from eq. (2.165) as a series in the inhomogeneous part of the self-energy function Θ,

$$G = G_1 - \mathrm{i}G_1\Theta G_1 - G_1\Theta G_1\Theta G_1 + \cdots$$

This series is analogous to the series for the function $D(t = 0)$, derived in subsection 2.3.

The generalization of eq. (2.166) to the case of the vertex λ, dependent on wave vectors, is self-evident. Since in our approximation corrections to the coefficient Γ are absent, the correlation function (2.166) conserves its form and only the gap Δ will be the function of a direction of the wave vector determined by eq. (2.131). The form of this function has been discussed in subsection 2.3.

Since, in conformity with (2.159), the function G is the generalized susceptibility, singularities of $G(\omega)$ determine the dispersion law for the eigenmode, associated with the relaxation φ. The function (2.166) has a pole at

$$\omega = -\mathrm{i}[\Delta + \alpha(q - q_0)^2]\Gamma. \tag{2.167}$$

It is not difficult to make sure that corrections to the dispersion law (2.167) due to the presence of Θ are small in the parameter $\Delta/\alpha q_0^2$. Thus, the mode, associated with the parameter φ, is a purely relaxational mode. Note that in the dispersion law near the transition point only the gap Δ possesses a singular behaviour.

Let us stress that all the above is valid both for the disordered (liquid) phase and for the low-temperature ordered phases.

2.4.5. Long-wavelength degrees of freedom

Our next objective is to study the influence of fluctuations of the field φ on macroscopic dynamic characteristics of the system. Then it is necessary to employ the diagram technique, incorporating long-wavelength degrees of freedom. Recall that in the case of liquids, these degrees of freedom can be set by means of the mass density ρ, entropy density s and momentum density $\boldsymbol{j}$.

It is convenient to develop the dynamic diagram technique, starting with an expression for the effective action, analogous to (2.155). With the long-wavelength degrees of freedom taken into account, the effective action acquires the form

$$I = \int \mathrm{d}t\, \mathrm{d}\boldsymbol{r}\, [\Gamma p\, \partial\varphi/\partial t + p\, \delta H/\delta\varphi + \mathrm{i}T\Gamma p^2 + \boldsymbol{p}\, \partial\boldsymbol{j}/\partial t + p_i \nabla_k T_{ik}^{(\mathrm{r})}$$

$$+\eta_1(\nabla_k p_i + \nabla_i p_k)(\nabla_i v_k + \mathrm{i}T\nabla_i p_k) + (\eta_2 - 2\eta_1/3)\nabla\boldsymbol{p}(\nabla\boldsymbol{v} + \mathrm{i}T\nabla\boldsymbol{p}) + \cdots]. \tag{2.168}$$

Here $\boldsymbol{p}$ is an auxiliary field, conjugated to $\boldsymbol{j}$, the dots label the terms associated with the mass density ρ and entropy density s. The terms, entering eq. (2.168), are constructed in such a way that the extremals of the functional I will be the nonlinear dynamic equations (2.148) and (2.150) (the details can be found in the monograph [Kats and Lebedev 1988]). In writing out eq. (2.168), we have taken into account the explicit form (2.153) of the dissipative stress tensor.

Like for the fields φ, p, the dynamic correlation functions of the long-wavelength fields are calculated by means of the distribution function $\exp(\mathrm{i}I)$. We are interested in the correlation function

$$G_{ik}(t_1 - t_2, \boldsymbol{r}_1, \boldsymbol{r}_2) = \langle j_i(t_1, \boldsymbol{r}_1) p_k(t_2, \boldsymbol{r}_2) \rangle . \tag{2.169}$$

As follows from eq. (2.168), this correlation function defines the response of the system to the force density $f_j(t, \boldsymbol{r})$, applied to the system

$$\langle j_i(t, \boldsymbol{r}) \rangle = -\mathrm{i} \int \mathrm{d}t_1 \, \mathrm{d}\boldsymbol{r}_1 \, G_{ij}(t - t_1, \boldsymbol{r}, \boldsymbol{r}_1) f_j(t_1, \boldsymbol{r}_1) .$$

Thus, G_{ij} is the susceptibility of the system to the external force. Due to this, the poles of $G_{ij}(\omega)$ determine dispersion laws of the modes, emerging due to excitation of the hydrodynamic motion.

The bare value of the correlation function (2.169), which we will denote as G_{0ik}, can be calculated by means of the quadratic part of the effective action (2.168). The function, obtained in the result of this calculation, depends only on the difference $\boldsymbol{r}_1 - \boldsymbol{r}_2$. It is convenient to write this function, performing Fourier transformation over $t - t_1$, $\boldsymbol{r} - \boldsymbol{r}_1$. As a result, we get

$$G_{0ik}^{-1}(\omega, \boldsymbol{q}) = -\omega \delta_{ik} + c_0^2 q_i q_k / \omega - \mathrm{i}\eta_2 q_i q_k - \mathrm{i}\eta_1 (q^2 \delta_{ik} + q_i q_k / 3) . \tag{2.170}$$

Here

$$c_0^2 = (\partial P_0 / \partial \rho)_\sigma ,$$

where P_0 is the bare pressure and $\sigma = s/\rho$ is the specific entropy. The quantity c_0 has the meaning of the bare value of the velocity of sound.

Let us now show how one can from the overall action (2.168) derive the effective action (2.155) for the field φ. Then it is necessary to make use of the relation

$$\exp(\mathrm{i}I_\varphi) = \int \mathrm{D}\boldsymbol{j} \, \mathrm{D}\boldsymbol{p} \, \mathrm{D}\rho \, \mathrm{D}s \, \mathrm{D}p_s \, \mathrm{D}p_\rho \, \exp(\mathrm{i}I) . \tag{2.171}$$

This functional integral involves the auxiliary fields p_ρ, p_s, conjugated to ρ and s. The relation (2.171) means that the correlation functions of the fields φ, p, which are by definition set by integrals over all degrees of freedom, can be calculated according to the recipe (2.156).

Fluctuations of the variables, describing the long-wavelength degrees of freedom over which the integration is performed in eq. (2.171), can be neglected. This means that the integral (2.171) can be calculated in the Gaussian approximation, then it is sufficient to retain in the effective action I the second-order terms with respect to fluctuations of $\boldsymbol{j}$, $\boldsymbol{p}$, ρ, s, p_s, p_ρ. As is known, Gaussian integrals are calculated exactly. The explicit calculation of the integral (2.171) in the main approximation yields eq. (2.155).

Let us now clarify how in the result of the described calculation in the effective action there emerges a Landau functional of which all expansion terms are functions of the temperature T and

the chemical potential ζ. Write out one of the terms of the interaction of long-wavelength degrees of freedom and the fields φ, p,

$$I_{\text{int}} = \int \mathrm{d}t\, \mathrm{d}\mathbf{r}\, (\tau_\rho p\varphi\delta\rho/\rho + \nabla_i p_i \tau_\rho \varphi^2/2)\,. \tag{2.172}$$

Here

$$\tau_\rho = \rho(\partial\tau/\partial\rho)_\sigma \tag{2.173}$$

and the derivative in eq. (2.173) is taken at a constant specific entropy σ. For the constant (2.173) we have the estimate

$$\tau_\rho \sim \lambda\,. \tag{2.174}$$

The first term in (2.172) emerges from the term $p\delta H/\delta\varphi$ in (2.168), and the second term in (2.172) emerges from the term $p_i\nabla_i P$ in (2.168), which is generated by the term with the pressure in the non-dissipative stress tensor (2.151).

At the Gaussian integration due to the interaction term (2.172) in the effective action there emerges an additional term, which can be written as

$$\mathrm{i}\tau_\rho^2 p\varphi\langle\delta\rho\nabla_i p_i\rangle_0\varphi^2/2\,, \tag{2.175}$$

where the subscript 0 labels the bare value. The emergence of the term (2.175) implies redefinition of the quartic vertex $\lambda(\rho, s)$, resulting from the expansion of H. Employing the fluctuation–dissipation theorem it is possible to show that the redefinition of the vertex λ determined by the term (2.175) implies the Legendre transformation (2.29) from the variables s, ρ to the variables T, ζ.

2.4.6. Correlation functions of the long-wavelength degrees of freedom

Now it is necessary to find an expression for the correlation function (2.169) with the contribution due to the interaction of long-wavelength degrees of freedom with the field φ, described by the terms of the type of (2.172). The analysis of the diagrams, giving the main contributions into G_{ik}, is identical to the analysis, performed in the work [Gurovich, Kats and Lebedev 1988] for the case of critical dynamics. A detailed formulation of the selection rule for diagrams for G_{ik} as well as the method of their summation can be found in the work [Gurovich, Kats and Lebedev 1991]. Therefore, omitting the intermediate calculations, we will give the result for the renormalization, generated by the interaction term of the type of (2.172).

The renormalized value of $G_{ik}(\omega, \boldsymbol{q})$ differs from the bare value $G_{0ik}(\omega, \boldsymbol{q})$ by the replacement of the bare elasticity modules with renormalized modules. In this case replacing c_0^2 by the renormalized value $\tilde{\beta}$, we find

$$G_{ik}^{-1}(\omega, \boldsymbol{q}) = -\omega\delta_{ik} + \tilde{\beta}q_i q_k/\omega - \mathrm{i}\eta_2 q_i q_k - \mathrm{i}\eta_1(q^2\delta_{ik} + q_i q_k/3)\,. \tag{2.176}$$

The expression for $\tilde{\beta}$ reads

$$\tilde{\beta}(\omega) = c_0^2 - \rho^{-1}\tau_\rho^2 F(\omega)/[1 + F(\omega)Y]\,. \tag{2.177}$$

Here

$$Y = (\partial\tau/\partial\zeta)_T(\partial\tau/\partial\rho)_s + (\partial\tau/\partial T)_\zeta(\partial\tau/\partial s)_\rho, \tag{2.178}$$

$$F(\omega) = \int \mathrm{d}t\, \mathrm{d}\boldsymbol{r}_1\, \exp(\mathrm{i}\omega t)\overline{\langle\varphi^2(t,\boldsymbol{r}_1)p(0,\boldsymbol{r}_2)\varphi(0,\boldsymbol{r}_2)\rangle}\,. \tag{2.179}$$

The averaging here is performed over $\boldsymbol{r}_2$.

Equation (2.177) holds as long as the condensate $\langle\varphi\rangle$ is small, which is satisfied in the framework of weak crystallization theory. Note that in the isotropic (liquid) phase the correlation function $\langle\varphi^2 p\varphi\rangle$ depends only on the difference $r_1 - r_2$. In the crystalline phase in this correlation function there occur terms, dependent on the both arguments, which is accounted for by the emergence of the condensate $\langle\varphi\rangle$. However, the amplitude of these terms is small as long as $\langle\varphi\rangle$ is small, therefore we will discard them. In this approximation it is possible to perform explicitly the averaging over $\boldsymbol{r}_2$ in eq. (2.179).

We will be interested in the long-wavelength limit, characterized by large scales and low frequencies. This region is determined by the inequalities

$$R \gg \sqrt{\alpha/\Delta}\,, \quad \omega \ll \Delta/\Gamma\,. \tag{2.180}$$

Here R is a characteristic length scale, ω is a characteristic frequency.

Having in mind eq. (2.180) we retain in eq. (2.179) only a zero Fourier spatial component. We have retained in this expression the dependence on the frequency ω, since apart from the zero term, we will also need the first term of the expansion of $F(\omega)$ in the frequency

$$F(\omega) \simeq F_0 + \mathrm{i}\gamma\omega\,. \tag{2.181}$$

These two terms of the expansion produce effects, different by their physical meaning, i.e., renormalization of the real part of the spectrum of the modes and their damping.

Firstly consider the term F_0 in the r.h.s. of eq. (2.181). A relation of the type (2.161) makes it possible to express this term via the integral of the one-time correlation function

$$F_0 = \frac{1}{2T}\int \mathrm{d}\boldsymbol{r}\, \langle\varphi^2(0,\boldsymbol{r})\varphi^2(0,0)\rangle\,. \tag{2.182}$$

Equation (2.182), with the irrelevant factor omitted, coincides with the quantity (2.126), determining the fluctuation contribution to the heat capacity, compressibility, etc. The method of calculating this one-time correlation function has been discussed in subsection 2.3. Inserting eq. (2.128) into eq. (2.182), we find

$$F_0 = TZq_0^2/4\pi\alpha^{1/2}\Delta^{3/2}\,, \tag{2.183}$$

where we employ the quantity, introduced in eq. (2.119),

$$Z = (1 + \lambda T q_0^2/8\pi\alpha^{1/2}\Delta^{3/2})^{-1}\,. \tag{2.184}$$

Prior to the analysis of the second term in (2.181), let us clarify the structure of the diagram determining the correlation function (2.179). Like in the static case, in the main approximation the dynamic correlation function (2.179) is determined by the sum of the ladder diagrams depicted in fig. 10. Remember that the dashed line stands for the correlation function (2.157), the solid line for the correlation function (2.158) and the black dot labels the vertex λ.

To obtain the first term of the expansion of the correlation function (2.179) in ω, it is necessary to expand the expression determined by one of the loops of the ladder diagram in ω, in the other loops we can put $\omega = 0$. This operation is depicted in fig. 11, where the loop in which the expansion

Fig. 10. "Ladder" diagrams determing relevant corrections to the dynamic correlation function $\langle\varphi^2 p\varphi\rangle$.

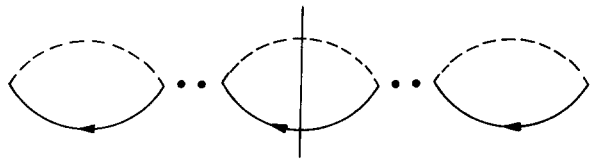

Fig. 11. A "ladder" contribution to $\langle\varphi^2 p\varphi\rangle$ expanding in ω (the crossed loop designates the term linear in ω.

in ω is performed, is crossed out. The sum of blocks to the left of the crossed loop gives the factor (2.184). The same factor is given also by the sum of blocks to the right of the crossed loop.

Transforming the first term of the expansion of the loop in ω by means of the relation (2.162), we get the representation

$$\gamma = \frac{Z^2}{16T\pi^3}\int d\omega\, d\boldsymbol{q}\, D^2(\omega, \boldsymbol{q})\,. \tag{2.185}$$

The integral in (2.185) after the insertion of (2.166) and (2.162) is calculated explicitly, which yields

$$\gamma = T\Gamma Z^2/32\pi\alpha^{1/2}\Delta^{5/2}. \tag{2.186}$$

Now we can insert (2.186) into (2.177), obtaining from (2.176) an expression for the function G_{ik}. Having in mind the inequalities (2.180), in $\tilde{\beta}$ one should retain only the zero and first terms of the expansion in ω, defined by (2.181). Comparing the derived expression for G_{ik}^{-1} with the bare value (2.170), we arrive at the following conclusions.

Fluctuations of φ bring about a renormalization of the velocity of sound $c_0 \to c$, where the velocity of sound c is defined by

$$c^2 = c_0^2 - \rho^{-1}\tau_\rho^2 F_0/(1 + F_0 Y)\,. \tag{2.187}$$

Here all the coefficients, except F_0, behave regularly near the transition point. Therefore the singular behaviour of the velocity c near the transition point and its jump in this point are determined by the function F_0, expressed via the gap Δ by means of eqs. (2.183) and (2.184).

Besides, fluctuations of φ contribute to the viscosity coefficients. In our approximation there is only a contribution to the second viscosity coefficient η_2, having singular behaviour,

$$\eta_2 = \eta_{20} + \rho^{-1}\tau_\rho^2\gamma(1 + F_0 Y)^{-2}, \tag{2.188}$$

where γ is defined by eq. (2.186).

The analysis, analogous to the one performed in subsection 2.3, reveals that the constant $Z \sim 1$ and under the natural assumption that $F_0 Y \sim 1$ will be $c \sim c_0$. Thus, the singular part of the second viscosity is

$$\eta_2 - \eta_{20} \sim 10^{-2} T\Gamma\tau_\rho^2/\rho\alpha^{1/2}\Delta^{5/2}.$$

It is difficult to say something definite about the value of this contribution, since it depends on the value of the kinetic coefficient Γ, determining the dynamics of the field φ. Yet, the singular part of η_2 has a larger power of Δ in the denominator than the singular part of c^2 in eq. (2.187).

Therefore one can expect that near the weak crystallization phase transition, the singular part of η_2 will exceed the regular part.

The second viscosity coefficient η_2 has the strongest singularity over Δ among all quantities studied by us. In the approximation we are using, the first viscosity coefficient η_1 does not possess any singular behaviour. To investigate the singular behaviour of η_1 one should go beyond the scope of this approximation. As a result, we conclude that under the natural assumptions the singular part of η_1 has a value of the order of magnitude of the regular part of η_1.

2.4.7. Conclusion

Let us now formulate the main results obtained in this subsection. Fluctuations of the soft field φ induce abnormal contributions to the dynamic characteristics of the system which, as a consequence shows singular behaviour near the transition point. The contributions are of the same order both in the high-temperature liquid phase and in the low-temperature ordered phases.

All the contributions may be expressed through the fundamental quantity, characterizing fluctuations of the soft field the gap Δ. The dynamics of the soft field is purely relaxational. The relaxation time is inversely proportional to the gap Δ.

The temperature dependence of the sound velocities is related to the temperature dependence of the appropriate elasticity modules. The second viscosity coefficient has the most singular dependence on the temperature, this coefficient being proportional to $\Delta^{-5/2}$. The appropriate viscosity coefficient in the ordered phase has the same dependence on Δ. In other words, in the vicinity of the phase transition the attenuation of (longitudinal) sound will noticeably increase.

3. Strongly anisotropic nematics and smectics-A

3.1. Introduction

As has been mentioned, known isotropic liquids are crystallized by strong first-order phase transitions. That is why the theory, developed in section 2 is not straightforwardly applicable to these liquids. At the same time, in the liquid-crystalline state one can observe diverse phase transitions which are accompanied by partial or complete crystallization and in fact are weak first-order transitions. To describe these phase transitions it is necessary to generalize the developed weak crystallization theory to the case of an anisotropic system, which is a liquid crystal. Having this in mind we will briefly describe the structure of known types of liquid crystals, which combine properties of a crystal and of a liquid.

3.1.1. Types of liquid crystals

The liquid crystalline phases (mesophases) are observed in substances, consisting of molecules of a rod-like or of a disc-like shape. The anisotropy of molecules on the macroscopic level leads to the appearance between the solid and the liquid states of mesophases possessing a strong anisotropy revealing itself in the anisotropy of different tensor characteristics such as polarizability. A review of the properties of liquid crystals may be found in the monographs by de Gennes [1974], Stephen and Straley [1974], Chandrasekhar [1977] and Pikin [1981].

The liquid crystalline phases most close to liquids are called nematics. One can imagine a nematic as a system of molecules whose mass centers are positioned chaotically in space, but whose main axes have a preferred direction. Molecules then can slip freely with respect to one another and

rotate around their long axes. The unit vector $\boldsymbol{n}$ characterising this preferred direction is called director.

In substances, consisting of rod-like molecules, between the nematic and solid phases there usually exists a smectic phase, where in comparison with the nematic phase, a violation occurs of the translational symmetry along one of the directions. In other words smectic can be represented as an ordered system of liquid (or liquid-crystalline) layers. Then the mass centers of molecules are arranged regularly in the direction of the normal to the layers but chaotically in the plane of the layer. Smectic layers can slip freely with respect to one another in a liquid-like manner.

In the simplest case the smectic layers are isotropic, which corresponds to the so-called A-phase. Smectic-A can be represented as a system of liquid layers of molecules whose main axes are perpendicular to smectic layers. The layers of so-called smectics-C possess a lower rotational symmetry. This is a consequence of the fact that the main axes of molecules in smectics-C are tilted by a certain angle to the normal of the layer. In other words, in smectics-A the director is perpendicular to layers and in smectics-C it is not.

In hexatic smectics-B (or hexatics) the main axes of the molecules are perpendicular to the layer (like in smectics-A), but in contrast to smectics-A molecules cannot freely rotate around their main axes with respect to one another. Usually, in this case the layer has a sixth-order axis, which explain the notation of these smectics. We will denote smectics-A as SA, smectics-C as SC and hexatic smectics-B as SB.

Experimentally it is difficult to distinguish the latter smectics from layered hexagonal crystals which are also often called smectics-B, or more accurately, crystalline smectics-B. There also exists a number of layered crystalline phases of different symmetry, which are labelled as smectics-E, F, G, H, I. Note that the designation smectics-D is attributed to complex cubic crystalline structures possessing weak density modulation. Besides these phases, also phases are observed which can be considered as smectics with one-dimensional density modulation in a layer [Sigaud et al. 1981, Hardouin et al. 1982]. These phases are usually called modified smectics (smectics-A_m, smectics-C_m etc.) and are distinguished by layer structures and by tilting of the director. The main experimental data concerning smectic phases may be found in the works [Hardouin et al. 1983, de Jeu 1992].

Violation of the translational symmetry of the nematic phase, consisting of disc-like molecules, occurs fairly specifically. The prolate shape of molecules brings about the fact that the translational symmetry is violated in the plane of the preferred orientation of molecules. Thus there appears a columnar liquid-crystalline phase, which can be represented as a system of columns or threads, forming a regular two-dimensional lattice in the plane orthogonal to the threads. The mass centers of molecules in each thread are positioned chaotically, therefore the threads can slip with respect to one another in a liquid-like manner.

Let us stress that because of intensive thermal motion of molecules in liquid crystals the pictures of molecule arrangement in these phases have little to do with the experimental situation. These pictures can be used for illustration only. Therefore we will pay attention to the structure of the density modulation which is a directly observable quantity. These structures are characterized by their symmetry. Here we present a short symmetry classification of liquid-crystalline phases.

The symmetry of any phase set by the spatial group $S = G \wedge T$, which is a semi-direct product of the translation group T and of the rotation group G, rendering the structure invariant. For instance, for an isotropic liquid $G = O(3)$ or $G = O_h(3)$, i.e., three-dimensional group of rotations, and $T = R^3$, i.e., a group of three-dimensional translations. All possible types of liquid crystals are classified according to subgroups of this semi-direct product $O(3) \wedge R^3$.

The mesophases with the symmetry group $G \wedge R^3$, where G is a subgroup of the total group of rotations, should naturally be called nematics. Among this class there are classical uniaxial nematics

with $G = D_{\infty h}$, orthorhombic biaxial nematics with $G = D_{2h}$ and other orientationally ordered phases whose existence has not yet been reliably confirmed: icosahedral, hexatic and tetragonal nematics. Any other subgroups of O(3) or any other types of nematics are not in principle prohibited. We will denote them as follows: conventional uniaxial nematics as N, as it is usually done in the literature on liquid crystals, and the others in accordance with the largest order of the symmetry axis of the subgroup G, i.e., orthorhombic biaxial nematics as N_2, hexatic as N_6, etc.

Similarly, all mesophases, where $T = R^2 \otimes Z^1$ (where $\otimes$ denotes the direct product of the two-dimensional group of continuous translations R^2 and of the one-dimensional group of discrete translations Z^1) can naturally be termed smectics, whereas all mesophases, where $T = R^1 \otimes Z^2$ are termed columnar phases. Smectic-A, for instance, is characterized by the symmetry group $D_{\infty h} \wedge R^2 \otimes Z^1$, smectic-C by the group $C_{2h} \wedge R^2 \otimes Z^1$, hexatic smectic-B by the group $D_{6h} \wedge R^2 \otimes Z^1$, hexagonal columnar phases by the group $D_{6h} \wedge R^1 \otimes Z^2$ and tetragonal columnar phases by the group $D_{4h} \wedge R^1 \otimes Z^2$. Note that the modified smectic phases mentioned above have the symmetry $G \wedge R^1 \otimes Z^2$ (where G is a discrete rotation group) coinciding with the symmetry of rhombic or monoclinic columnar phases.

3.1.2. Peculiarities of weak crystallization of liquid crystals

Recall that the main peculiarities of the weak crystallization of liquids are accounted for by the fact that the crystalline order parameter softens in the vicinity of a sphere in the reciprocal space. In this section we will dwell upon the case when the order parameter softens in the vicinity of a circle (or a couple of circles) in the reciprocal space. This can occur in systems possessing the symmetry axis C_∞. We speak about the weak crystallization of uniaxial nematics and smectics-A.

To avoid confusion, note that nematics and smectics-A can get crystallized by different mechanisms. So, in the result of the phase transition they can transform into molecular crystals (not possessing a pronounced layered structure). If such a transition is weak crystallization, it occurs at a sufficiently weak anisotropy of the system. This case is studied in section 4.

On the other hand, one can also observe the nematic–smectic-A transition at which the crystalline order parameter softens in the vicinity of two isolated points in the reciprocal space. This transition can be described in the framework of the conventional phase transition theory. In terms of the mean field theory this transition is a second-order transition. However, in this transition an important role is played by fluctuations of the director [Halperin, Lubensky and Ma 1974, Wiegmann and Filev 1975], which apparently result in the transformation of this transition into a first-order transition [Anisimov et al. 1987, 1990]. We will not discuss in detail the nematic–smectic-A or the analogous smectic-C–smectic-$\tilde{C}$ transitions in our review.

In this section we consider two possibilities of crystallization of smectics-A and nematics dictated by their symmetry. The first possibility is associated with the softening of the order parameter in the vicinity of a circle in the reciprocal space. This possibility will be called simple crystallization, it is usually realized in smectics-A. The nematic–columnar phase transition is analogous to the simple crystallization of smectics-A and is described by the same model. The second possibility is associated with the softening of the order parameter in the vicinity of two circles in the reciprocal space. The nematic–smectic-C transition gives such a example. In smectics a realization of the second possibility is accompanied by such effects as doubling of the interlayer period or even formation of an incommensurate structure.

To study the crystallization of a smectic-A or a nematic we will make use of the weak crystallization theory of an isotropic liquid, described in section 2. However it is in need ofsome modification

because of anisotropy of a smectic-A or a nematic phase. Our approach will be grounded on the works [Kats, Lebedev and Muratov 1988, 1989; Lebedev and Muratov 1991].

3.2. Simple crystallization. Mean field theory

As we have already mentioned, weak crystallization is associated with the softening of the short-wave density modulation. In the case of the liquid possessing full rotational invariance the softening occurs near a sphere in the reciprocal space. In the case of a smectic-A or a nematic possesing uniaxial symmetry the softening occurs near the circle (or circles) in the reciprocal space. In this and in the next subsections we will consider the case of softening near one circle which we will call simple crystallization.

As previously, we will start from the Landau functional set by eqs. (2.10), (2.17) and (2.18). But the character of the dependence of the coefficients in these expressions on wave vectors will be different. Particularly, we should to add to eq. (2.16) an anisotropic term of the form

$$F'^{(2)} = \frac{\alpha_{\|}}{2} \int \mathrm{d}\boldsymbol{r}\, (\boldsymbol{l}\nabla\varphi)^2 . \tag{3.1}$$

Here the unit vector $\boldsymbol{l}$ determines the direction of the normal to a smectic layer (for the nematic it should be replaced by the director $\boldsymbol{n}$), $\alpha_{\|}$ is the expansion coefficient. We suppose that $\alpha_{\|} > 0$. In the opposite case $\alpha_{\|} < 0$, the softening of the order parameter will take place near two circles in the reciprocal space. We will consider this case in the next subsection.

It will be our assumption that at equilibrium the layers are orthogonal to the Z-axis. Then $(\boldsymbol{l}\nabla) = \nabla_z$. In the case of a strong anisotropy, typical of smectics and nematics, the coefficient $\alpha_{\|}$ must be of the order of the coefficient α, figuring in eqs. (2.12) and (2.16). It means that for the characteristic values of τ at which the transition takes place, the inequality

$$|\tau| \ll \alpha_{\|} q_0^2 \tag{3.2}$$

is fulfilled. The case of weak anisotropy, when the inequality (3.2) is not fulfilled, will be discussed in section 4.

3.2.1. Interaction term

The short-wavelength field $\varphi(\boldsymbol{r})$, describing the density distribution, can be written as a Fourier expansion,

$$\varphi(\boldsymbol{r}) = \sum_{\boldsymbol{q}} \varphi(\boldsymbol{q}) \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}), \tag{3.3}$$

where now the components of $\varphi(\boldsymbol{q})$ with the wave vectors, lying in the vicinity of a circle in the reciprocal space $q_z = 0, |\boldsymbol{q}| = q_0$ are relevant. Thus, at the crystallization of smectics-A there is a loss of translational invariance in the smectic layer plane.

Now consider the fourth-order term in the Landau expansion (2.18),

$$F^{(4)} = \frac{V}{24} \sum_{\boldsymbol{q}} \lambda(\boldsymbol{q}_1, \boldsymbol{q}_2, \boldsymbol{q}_3, \boldsymbol{q}_4) \varphi(\boldsymbol{q}_1)\varphi(\boldsymbol{q}_2)\varphi(\boldsymbol{q}_3)\varphi(\boldsymbol{q}_4) . \tag{3.4}$$

The summation in (3.4) is performed over a set of vectors, obeying the condition $\boldsymbol{q}_1 + \boldsymbol{q}_2 + \boldsymbol{q}_3 + \boldsymbol{q}_4 = 0$. Since all vectors $\boldsymbol{q}_i$ are lying in the same plane and are identical over the absolute value, they

can be arranged as a rhombus. The quantity λ which can be treated as the scattering vertex, is a function of the value of angle θ of the rhombus, obeying the self-evident relations

$$\lambda(\theta) = \lambda(-\theta) = \lambda(\pi - \theta) = \lambda(2\pi + \theta). \tag{3.5}$$

This function can be written as a Fourier expansion,

$$\lambda(\theta) = \lambda_0\left(1 + \sum_k \lambda_k \cos(2k\theta)\right). \tag{3.6}$$

Henceforth, as a rule, we will consider some particular cases of the dependence $\lambda(\theta)$, when in the series (3.6) only one term with $k = 1, 2, 3$ is non-zero, and describe the phase diagrams thus obtained.

Naturally, the theory we are employing, is applicable only if $\lambda(\theta) > 0$. In the opposite case $\lambda(\theta) < 0$ the functional F is not positively defined and as a result the usual first-order phase transition with the condensation of the field φ in the region corresponding to the negative $\lambda(\theta)$ will take place. In this case it is necessary to take into account higher-order terms of the expansion of F in the field φ. We will not consider this case. For the dependence $\lambda(\theta)$ of the form

$$\lambda(\theta) = \lambda_0(1 + \lambda_k \cos(2k\theta)),$$

the condition $\lambda(\theta) > 0$ implies that the condition $|\lambda_k| < 1$ must be fulfilled.

With fluctuations of the field φ neglected, the problem of crystallization of smectics-A is virtually a problem of a conventional two-dimensional crystallization. Then all the arguments given in subsection 2.2 hold. The simple crystallization of smectics-A or nematics in the mean-field approximation is described analogously to the weak crystallization of an isotropic liquid. Particularly the sequence of smectic phases appearing at the increasing of temperature may be deduced by renaming of the sequence of phases found for the crystallization of the liquid (certainly without phases with three-dimensional ordering).

3.2.2. The case $\lambda = const.$

Firstly, consider the case when in the series (3.6) all coefficients λ_k are zero, i.e., the quartic scattering vertex does not depend on the angle between the wave vectors. In this case in the phase diagram there emerge phases with the same condensates as the averages, found in subsection 2.2 for a three-dimensional system, with the exception of the condensate, describing the BCC_1 phase. It means that at increasing τ there occurs the sequence of phases

$$SA_m\text{–}SB\text{–}SA.$$

Here SA is the original smectic-A phase, SB is a hexagonal layered crystal, which it is more natural to call a crystalline smectic-B, SA_m is the so-called modified smectic-A, i.e., a smectic phase where the density in a smectic layer is modulated in one direction. The symmetry of the SA_m phase is the same as the symmetry of columnar phases since it is characterized by the two-dimensional translational order.

The difference between the energy of the crystalline smectic-B phase and the energy of the original smectic-A is defined by eq. (2.59), and the difference between the energy of the modified smectic-A_m and the latter energy by eq. (2.50). The amplitudes of the arising density waves in SB

and SA_m are also defined by eqs. (2.59) and (2.49), respectively. The phase transitions take place at the following values of the parameter τ:

$$\tau(SA_m\text{–}SB) = -\tfrac{1}{5}(7 + 3\sqrt{6})\mu^2/\lambda_0), \quad \tau(SB\text{–}SA) = -\tfrac{4}{45}\mu^2/\lambda_0. \tag{3.7}$$

Recall that the simple crystallization of a nematic is described by the same model as the simple crystallization of a smectic-A. It means for example that the sequence of phases for the simple crystallisation of nematic may be deduced from the one for smectic by denomination of the phases. The SA phase corresponds to the nematic phase, the SB phase to the columnar one and the modified smectic-A could correspond to the smectic-C phase with the tilt angle $\pi/2$. Unfortunately we do not know experiments in which such C phases were observed.

3.2.3. Anisotropic λ

Let us assume now that the vertex λ depends on the angles between the wave vectors and analyse consequences of this dependence. It is convenient, like it has been done in subection 2.2. (see eqs. (2.69)), to represent the energy of the inhomogeneous phase as

$$\Omega/V = A\tau + \tfrac{1}{4}\lambda(\theta = 0)A^2 + f', \tag{3.8}$$

where A is the sum (2.42) and the function f' is defined by

$$f' = \sum_{n>m}[\lambda(\theta_n - \theta_m) - \tfrac{1}{2}\lambda(\theta = 0)]a_n^2 a_m^2 - \tfrac{1}{6}\mu\sum_{nml} a_n a_m a_l. \tag{3.9}$$

With this definition the function f' is zero for the modified smectic-A_m.

Let only one term with $k = 1$ in the series of eq. (3.6) be non-zero. It is clear that in this case the tetragonal phase Te with the condensate

$$\langle\varphi(\boldsymbol{r})\rangle = 2[a_1\cos(q_0 x) + a_2\cos(q_0 y)]$$

can become absolutely stable. The function f' for this phase equals

$$f' = \lambda_0(1 - 3\lambda_1)a_1^2 a_2^2/2. \tag{3.10}$$

The total energy of the tetragonal phase and the amplitude of the density

$$\Omega_{Te}/V = -\tau^2/2\lambda_0(1 - \lambda_1), \quad a_1 = a_2 = \sqrt{A/2}. \tag{3.11}$$

For $\lambda_1 > 1/3$ the value of Ω for the tetragonal phase becomes lower then for the modified smectic-A (because for SA_m $f' = 0$ and for Te it follows from eq. (3.10) that $f' < 0$ at $\lambda_1 > 1/3$). So, for $\lambda_1 > 1/3$, the sequence of transitions at increasing temperature is

Te–SB–SA.

Let us now describe the phase diagrams, occurring at the crystallization of smectics-A for the case, when in the series (3.6) the terms with $k = 2, 3$ are non-zero. Skipping simple calculations, we present only results. For $k = 2$ at $\lambda_2 > 3$ the modified smectic-A is replaced by a rhombic phase R with the condensate

$$\langle\varphi(\boldsymbol{r})\rangle = 2a[\cos(q_0 x) + \cos(q_0(x + y)/\sqrt{2}))].$$

For $k = 3$ there are two transitions. Firstly, at $\lambda_3 > 1/3$ the modified smectic-A is replaced by a tetragonal phase. Note that in this case in our approximation there is a degeneration: the energies of the tetragonal and rhombic phase R′ with the condensate

$$\langle\varphi(\boldsymbol{r})\rangle = 2a[\cos(q_0 x) + \cos(q_0(x + \sqrt{3}y)/2)]$$

identically coincide. Secondly, at $\lambda_3 > 0.224$ on the phase diagram between the regions of stability SA_m and SB there emerges a quasicrystal with the condensate

$$\langle\varphi(\boldsymbol{r})\rangle = 2a\sum_{n=1}^{6}\cos(\boldsymbol{q}_n\cdot\boldsymbol{r}),$$

where the six vectors $\boldsymbol{q}_n$ are equal in absolute value and have the angles $\pi/6$ between each other.

Thus, the cascades of transitions

$$SA_m\text{–}Q_6\text{–}SB\text{–}SA, \quad Te\text{–}Q_6\text{–}SB\text{–}SA$$

become possible. All phase transitions in these sequences are first-order phase transitions.

As is seen from the above analysis, new phases emerge only for positive values of the parameter λ_k. At negative values of λ_k the phase diagram does not qualitatively change in comparison with the the diagram at $\lambda = \text{const}$. This is accounted for by the fact that for $\lambda_k < 0$ the modified smectic-A always has a smaller energy than the tetragonal or rhombic phase.

3.2.4. Quasicrystals

We now study the problem under what conditions the emergence of absolutely stable quasicrystalline phases is possible. We will confine ourselves to the case when the triple vertex μ in the Landau expansion is small and can be neglected. Following the work [Malomed, Nepomnyashiy and Tribelsky 1989] where the authors studied the problem of structures appearing at convective instabilities, it is easy to get a necessary but not sufficient condition for absolute stability of quasicrystalline phases. As an illustration of this statement let us consider, as competing structures, the structures with the condensate

$$\langle\varphi(\boldsymbol{r})\rangle = 2a\sum_{i=1}^{n}\cos(q_0\boldsymbol{e}_i\cdot\boldsymbol{r}), \tag{3.12}$$

Here $\boldsymbol{e}_i$ are unit vectors, having angles π/n with each other. The phase with $n = 1$ is the modified smectic-A. The phase with $n = 2$ and $\boldsymbol{e}_1 \perp \boldsymbol{e}_2$ is the tetragonal phase Te and under the condition $(\boldsymbol{e}_1\boldsymbol{e}_2) = 1/2$ is the rhombic phase R. Finally, the structure with $n = 4$, where the angles between vectors $\boldsymbol{q}$ are $\pi/4$, is the quasicrystal Q_4.

Let a certain dependence of the vertex λ on the angle θ between the wave vectors be set. To investigate the problem of stability of the mentioned phases in the framework of the mean field theory, suffice it to know the two values

$$\lambda(3\pi/4)/\lambda(0) = \lambda(\pi/4)/\lambda(0) = \gamma_1, \quad \lambda(\pi/2)/\lambda(0) = \gamma_2. \tag{3.13}$$

Note that from the condition $\lambda(\theta) > 0$ it ensues that both $\gamma_1 > 0$ and $\gamma_2 > 0$.

Next, calculate the functions f' for the four phases under consideration in conformity with the definition (3.9),

$$f'(A_m) = 0, \quad f'(R) = \lambda(0)(2\gamma_1 - 1)A^2/8,$$

$$f'(Te) = \lambda(0)(2\gamma_2 - 1)A^2/8, \quad f'(Q_4) = \lambda(0)(2\gamma_1 + \gamma_2 - 3/2)A^2/8. \tag{3.14}$$

Comparing eqs. (3.14) with each other, we see that the most energetically favourable out of the four phases are

(a) $\gamma_1 > 1/2$, $\gamma_2 > 1/2$, SA_m,
(b) $\gamma_1 < 1/2$, $\gamma_2 < 1/2$, R,
(c) $\gamma_1 > (2\gamma_2 + 1)/4$, $\gamma_2 < 1/2$, Te,
(d) $\gamma_1 < (2\gamma_2 + 1)/4$, $\gamma_2 < 1/2$, Q_4.

The two latter inequalities restrict the region of the parameters where the absolutely stable phase is a quasicrystal Q_4.

Note that above when we have used the parametrisation $\lambda(\theta) = \lambda_0[1 + \lambda_k \cos(2k\theta)]$, the stability region of a quasicrystal Q_4 was unatainable, since the inequalities (d) could not be simultaneously satisfied. At the same time if the two non-zero harmonics in the series (3.6) are taken into account it is possible to attain the stability region of a quasicrystal. The quasicrystal Q_6 proves to be absolutely stable for $k = 3$, due to the cubic term of the Landau expansion, which for other considered phases was identically equal to zero. The described simple analysis can easily be carried out for other cases, e.g., for pentagonal quasicrystals.

Let us recall that all above described results can be applyed to a simple crystallization of strongly anisotropic nematics (with the evident redesignations of phases). At the crysallization of a nematic of considering type a two-dimensional density modulation appear corresponding to different columnar phases, observing usually in the discotic liquid crystals. It is interesting to note that the sequence D_t–D_h–N (where D_t is the tetragonal columnar phase and D_h is the hexagonal columnar phase) corresponding to the above formulated sequence Te–SB–SA for smectics, is actually observed in discotics [Levelut 1979, 1983].

3.3. Simple crystallization. The role of fluctuations

In this subsection we will go on with the analysis of the crystallization of smectics-A and nematics in the framework of the developed model. Remember that all conclusions of this analysis are applicable to the nematic–columnar phase transition. In contrast to subsection 3.2, where the analysis has been carried out in the framework of the mean field theory, now we will take into consideration fluctuations of the order parameter φ, which play an important role in the weak crystallization theory. The diagram technique, necessary for this purpose, has been developed in subsection 2.3. This diagram technique involves vertices μ and λ as well as the pair correlation function $\langle\varphi\varphi\rangle$. The analysis of the role of fluctuations in the anisotropic case largely repeats the analysis, performed in section 2 for an isotropic system, therefore our consideration here will be more brief and schematic.

Note that with fluctuations taken into account, the weak crystallization of films will not be analogous to the weak crystallization of the systems under study since the strength of fluctuations in a two-dimensional system is larger. In this sense a two-dimensional system resembles rather an isotropic liquid. Certain peculiarities of the weak crystallization of films were investigated in the work [Lebedev and Muratov 1990].

3.3.1. Equation for the gap

The analysis of corrections to the correlation function $\langle\varphi\varphi\rangle$ enables one to come to the conclusion that at the softening of φ in the vicinity of a circle in the reciprocal space, in the main approximation, like in the isotropic case, it suffices to confine oneself to the self-energy contribution represented by

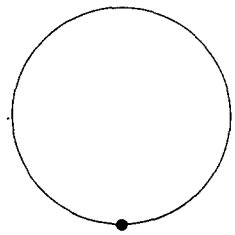

Fig. 12. Main self-energy correction to the correlation function $\langle\langle\varphi\varphi\rangle\rangle$.

the diagram given in fig. 12. The account of this diagram leads to the expression for the correlation function

$$\langle\langle\varphi(\boldsymbol{q})\varphi(-\boldsymbol{q})\rangle\rangle = T/[\Delta + \alpha_{\parallel}q_z^2 + \alpha(q - q_0)^2]. \tag{3.15}$$

The bare value of Δ is equal to τ, the account of the diagram in fig. 12 reduces to the renormalization of the gap in eq. (3.15).

Henceforth, we will assume that the conditions

$$\Delta \ll \alpha_{\parallel}q_0^2, \quad \Delta \ll \alpha q_0^2 \tag{3.16}$$

are fulfilled. These conditions generalize eqs. (3.2) to the case under discussion. These inequalities are necessary to make the weak crystallization theory applicable. They also will enable us to perform analytical calculations to the end. Besides, if the first condition in (3.16) is fulfilled, it is possible to confine ourselves only to the one anisotropic term (3.15) in the Landau functional, since higher-order terms of the expansion in $(\boldsymbol{l}\cdot\nabla)$ bring about the effects, small in the parameter $\Delta/\alpha_{\parallel}q_0^2$.

First consider the case λ = const. Calculating the self-energy contribution, depicted in fig. 12, we arrive at the equation for the gap Δ in the smectic-A phase

$$\Delta_{\mathrm{A}} = \tau + \tilde{\beta}\ln(4\alpha_{\parallel}q_0^2/\Delta_{\mathrm{A}}), \quad \tilde{\beta} = \lambda q_0 T/8\pi\sqrt{\alpha\alpha_{\parallel}}. \tag{3.17}$$

Note that instead of the power of Δ, figuring in the equation for the isotropic system, here there arises a logarithm, which is a consequence of the structure of the correlation function (3.15). As for the weak crystallization of isotropic liquids, this equation has a solution for the gap at any value of τ. It means that the SA phase is always at least metastable. This fact allows us to use the energy of the SA phase as the reference point for the energy of different phases.

In low-symmetry phases the condensate $\langle\varphi(\boldsymbol{r})\rangle$ is non-zero,

$$\langle\varphi(\boldsymbol{r})\rangle = \sum_m 2a_m\cos(q_0\boldsymbol{e}_m\cdot\boldsymbol{r}), \tag{3.18}$$

where $\boldsymbol{e}_m$ are the unit vectors determining the type of lattice and lying in the XY-plane, and a_m are the amplitudes of density waves. Explicitly, the equation for the gap in the low-symmetry phases reads

$$\Delta = \tau + \lambda A + \tilde{\beta}\ln(4\alpha_{\parallel}q_0^2/\Delta). \tag{3.19}$$

The relation between the parameter A, introduced in (2.42), and the value of the gap Δ for modified smectics-A and crystalline smectics-B may be found from the equation $\mathrm{d}\Omega'/\mathrm{d}A = 0$. Using this

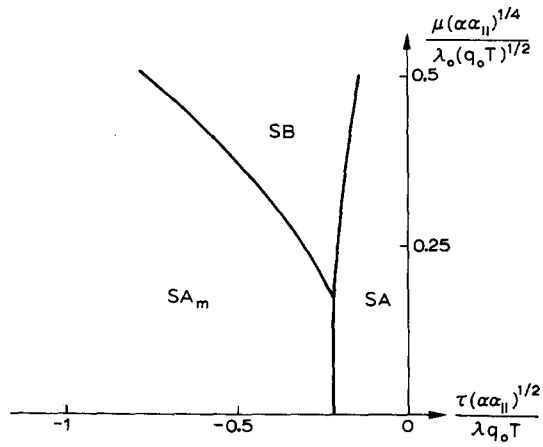

Fig. 13. Phase diagram of weak crystallization of smectics-A in the case λ = const.

relation, it is easy to get from (3.19) a closed equation for the gap. For example for the modified smectic-A it is

$$\tilde{\beta}\ln(4\alpha_\parallel q^2/\Delta_{A_m}) + \tau + \Delta_{A_m} = 0. \tag{3.20}$$

The calculation of the energy of the phases is analogous to that presented in section 2. As a result we find

$$(\Omega_{A_m} - \Omega_{SA})/V = -(\Delta_A^2 + \Delta_{A_m}^2)/2\lambda + \tilde{\beta}(\Delta_A - \Delta_{A_m})/\lambda,$$

$$(\Omega_B - \Omega_{SA})/V = (\Delta_B^2 - \Delta_A^2)/2\lambda + (\tilde{\beta}/\lambda)(\Delta_B - \Delta_A) - 2|\mu|(\Delta_B/3)^{3/2} - \lambda\Delta_B^2/12. \tag{3.21}$$

Employing eqs. (3.21), it is not difficult to determine the diagram of states, emerging at the crystallization of smectics-A. It is given in fig. 13. For the case under discussion the characteristic value of the parameter μ is the ordinate of the triple point in the phase diagram,

$$\mu_0 \cong 0.17(\lambda^2 q_0 T)^{1/2}/(\alpha\alpha_\parallel)^{1/4}.$$

Note that the difference of μ_0 from zero is purely a fluctuation effect; in mean field theory $\mu_0 = 0$. The general features of the influence of fluctuations on the weak crystallization phase transition are the same as in the isotropic system. We see that fluctuations do not create new stable (or metastable) phases. All phases in the phase diagram have corresponding three-dimensional analogues. The most important qualitative fluctuation effect is the presence of a direct first-order SA_m–SA transition in the region of strong fluctuations $\mu < \mu_0$.

The value of the gap Δ can be computed numerically using presented equations. Figure 14 gives the dependence of the gap Δ on the parameter τ for two values of the triple vertex $\mu = 0$ and $\mu = 2.65\mu_0$. Besides a continuous behaviour of the gap we see jumps: the value of the gap Δ increases at a transition to a low-temperature phase.

3.3.2. Account of anisotropy

Next, we generalize the above described results to the case when the quartic vertex λ depends on the angle between the wave vectors. Take the dependence $\lambda(\theta)$ to be of the form of (3.6), where

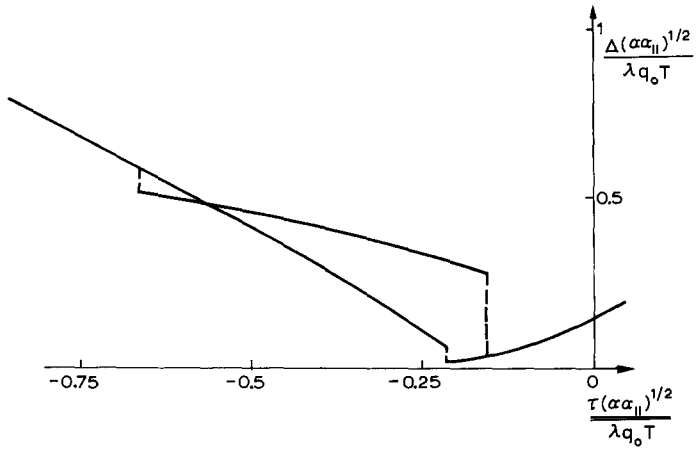

Fig. 14. Dependence of the gap Δ in the correlation function $\langle\langle\varphi\varphi\rangle\rangle$ on the value of the parameter τ at the weak crystallization of smectics-A for the values $\mu = 0$ and $\mu = 0.45\lambda\sqrt{q_0 T}(\alpha\alpha_\parallel)^{-1/4}$.

in the Fourier series only one term is non-zero. From the calculation performed in the mean field theory we know structures which then can be absolutely stable. Let first $k = 1$. Apart from the phases, stable at $\lambda = \text{const.}$, for $\lambda_1 > 1/3$ in the phase diagram there emerges a region of stability of a tetragonal crystal. Derive the equations for the gap Δ and find energy values for all the four phases: SA, SA_m, SB, Te.

The correlation function $\langle\langle\varphi\varphi\rangle\rangle$ has, as usual, the form (3.15). The equation for the gap in the smectic-A phase is derived analogously to (3.17),

$$\Delta_A = \tau + \beta_0 \ln(4\alpha_\parallel q_0^2/\Delta_A), \tag{3.22}$$

where $\beta_0 = \lambda_0 q_0 T/8\pi\sqrt{\alpha\alpha_\parallel}$, and λ_0 is the zero Fourier harmonics of the vertex $\lambda(\theta)$.

In the low-symmetry phase the gap Δ becomes anisotropic. Its dependence on the angle θ, referred to from one of the directions of crystallization $\boldsymbol{e}_1$, is governed by the equation

$$\Delta(\theta) = \tau + \sum_m \lambda(\theta - \theta_m) a_m^2 + \frac{\beta_0}{2\pi\lambda_0}\int_0^{2\pi} d\theta'\, \lambda(\theta - \theta') \ln[4\alpha_\parallel q_0^2/\Delta(\theta')]. \tag{3.23}$$

For the tetragonal and hexagonal phases eq. (3.23) reads

$$\Delta(\theta) = \tau + \lambda_0 A + \frac{\beta_0}{2\pi}\int_0^{2\pi} d\theta'\, [1 + \lambda_1 \cos(2(\theta - \theta'))] \ln[4\alpha_\parallel q_0^2/\Delta(\theta')], \tag{3.24}$$

where $A_{Te} = 2a^2, A_{SB} = 3a^2$. It has the trivial solution $\Delta(\theta) = \Delta$, where the value of Δ satisfies

$$\Delta = \tau + \lambda_0 A + \beta_0 \ln(4\alpha_\parallel q_0^2/\Delta). \tag{3.25}$$

The relation between A and Δ is

$$A_{Te} = 4\Delta_{Te}/\lambda_0(1 + \lambda_1),$$

$$A_B = 3\{[\mu^2 + 2\lambda_0(1 + \lambda_1)\Delta_B]^{1/2} - |\mu|\}/\lambda_0(1 + \lambda_1).$$

Hence, to define the value of the gap, we get the system of equations

$$\beta_0 \ln(4\alpha_\parallel q_0^2/\Delta_{\mathrm{Te}}) + (3-\lambda_1)\Delta_{\mathrm{Te}}/(1+\lambda_1) + \tau = 0,$$

$$\beta_0 \ln(4\alpha_\parallel q_0^2/\Delta_{\mathrm{B}}) + \lambda_0 A_{\mathrm{B}} - \Delta_{\mathrm{B}} + \tau = 0. \tag{3.26}$$

Out of the two solutions of the system of equations (3.26) one should choose the largest by absolute value. It is clear from these equations that solutions for the tetragonal phase and crystalline smectic-B exist at any λ and μ, although these phases can be metastable.

Recall that the difference between the energies of low-symmetry phases and the energy of the high-energy phase (namely smectic-A) can be computed the most easily. For the tetragonal and hexagonal structures, they, respectively, equal

$$\frac{\Omega_{\mathrm{Te}} - \Omega_{\mathrm{SA}}}{V} = -\frac{[(3-\lambda_1)/(1+\lambda_1)]\Delta_{\mathrm{Te}}^2 + \Delta_{\mathrm{A}}^2}{2\lambda_0} + \frac{\beta_0}{\lambda_0}(\Delta_{\mathrm{Te}} - \Delta_{\mathrm{A}}),$$

$$\frac{\Omega_{\mathrm{B}} - \Omega_{\mathrm{SA}}}{V} = \frac{\Delta_{\mathrm{B}}^2 - \Delta_{\mathrm{A}}^2}{2\lambda_0} + \frac{\beta_0}{\lambda_0}(\Delta_{\mathrm{B}} - \Delta_{\mathrm{A}}) - 2|\mu|(\tfrac{1}{3}A_{\mathrm{B}})^{3/2} - \tfrac{1}{12}\lambda_0(1+\lambda_1)A_{\mathrm{B}}^2. \tag{3.27}$$

These expressions will be used later.

3.3.3. Modified smectic phase

Now let us consider a one-dimensional structure, i.e., smectic-A_m. In this case the gap will not be isotropic. Therefore we should use eq. (3.23) for an anisotropic gap. For the phase considered it is

$$\tilde{\Delta}_{\mathrm{A_m}}(\theta) = \tilde{\tau} + \frac{1}{16\pi^2}\int_0^{2\pi} \mathrm{d}\theta' \,[1 + \lambda_1 \cos(2(\theta - \theta'))] \ln[4/\tilde{\Delta}_{\mathrm{A_m}}(\theta')]. \tag{3.28}$$

In the following, for convenience, we will use the dimensionless variables $\tilde{\Delta}, \tilde{\tau}, \tilde{\mu}$, defined by

$$\tau = \tilde{\tau}\frac{\lambda_0 q_0 T}{\sqrt{\alpha\alpha_\parallel}}, \quad \Delta = \tilde{\Delta}\frac{\lambda_0 q_0 T}{\sqrt{\alpha\alpha_\parallel}}, \quad \mu = \tilde{\mu}\frac{\lambda_0\sqrt{q_0 T}}{(\alpha\alpha_\parallel)^{1/4}}. \tag{3.29}$$

Equation (3.28) has the solution $\tilde{\Delta} = x + y\cos(2\theta)$, where the quantities x and y obey the system of equations

$$x = \tilde{\tau} + \tilde{A}_{\mathrm{A_m}} + (1/8\pi)\ln[8/(x + (x^2 - y^2)^{1/2})],$$

$$y = \tilde{A}_{\mathrm{A_m}} - y/8\pi[x + (x^2 - y^2)^{1/2}]. \tag{3.30}$$

The relation between the parameter $\tilde{A}_{\mathrm{A_m}}$ and the value of the gap is determined by

$$\tilde{A}_{\mathrm{A_m}} = 2\frac{\tilde{\Delta}_{\mathrm{A_m}}(\theta = 0)}{1+\lambda_1} = 2\frac{x+y}{1+\lambda_1}.$$

Thus, we get a system for defining both harmonics x and y of the gap of the modified smectic-A_m,

$$x(1-\lambda_1) + 2y = -(1+\lambda_1)\{\tilde{\tau} + (1/8\pi)\ln[8/(x + (x^2 - y^2)^{1/2})]\},$$

$$2\lambda_1 x - y(1-\lambda_1) = \lambda_1\frac{1+\lambda_1}{8\pi}\frac{y}{x + \sqrt{x^2 - y^2}},$$

which after the replacement $y = x \sin\alpha$ results in

$$\ln\left(\left|\frac{64\pi[2\lambda_1 - (1-\lambda_1)\sin\alpha]}{\lambda_1(1+\lambda_1)\sin\alpha}\right|\right) + 8\pi\tilde{\tau} + \lambda_1\tan(\alpha/2)\frac{1-\lambda_1+2\sin\alpha}{2\lambda_1-(1-\lambda_1)\sin\alpha} = 0. \tag{3.31}$$

The quantity x is related to the root of this equation as

$$x = \frac{1+\lambda_1}{8\pi}\frac{\lambda_1\tan(\alpha/2)}{2\lambda_1-(1-\lambda_1)\sin\alpha}.$$

An analysis of eq. (3.31) shows that in the case $\lambda_1 < 1/3$ at a sufficiently low temperature there are two solutions for α from which the largest in absolute value corresponds to the energy minimum. If $\lambda_1 > 1/3$, the solution that is interesting for us vanishes at decreasing temperature. The disappearance of the solution is connected with the fact that $\Delta(\theta)$ becomes zero in the direction orthogonal to the direction of crystallization, i.e., with the loss of stability of the smectic-A_m.

Now we have to calculate the energy of the modified smectic-A. The difference between this energy and the energy of the smectic-A phase is determined by

$$\frac{\tilde{\Omega}_{A_m} - \tilde{\Omega}_A}{V} = \int_0^A \frac{d\tilde{\Omega}}{dA'}\,dA' = \int_0^{\tilde{A}} (x+y)\,d\tilde{A}' - \frac{(x+y)^2}{1+\lambda_1},$$

where the relation between x, y and A' is set by eq. (3.30). The integral is calculated analytically, and we finally obtain

$$\frac{\tilde{\Omega}_{A_m} - \tilde{\Omega}_A}{V} = \frac{x^2 - \tilde{A}_A^2}{2} + \frac{\overline{x-\tilde{A}_A}}{8\pi} + \frac{y^2}{2\lambda_1} - \frac{(x+y)^2}{1+\lambda_1}. \tag{3.32}$$

The dimensional value of Ω is equal to $(\lambda_0 q_0^2 T^2/\alpha\alpha_\parallel)\tilde{\Omega}$.

3.3.4. Phase diagram

Now it is possible to obtain the total phase diagram for the case under study. fig. 15a shows the phase diagram of the system for $\lambda_1 = 0.34$. It is clear that fluctuations modify the mean field behaviour in the region of small μ. If in the mean field theory at increasing λ_1 at $\lambda_1 = 1/3$ there occurs a continuous transition and the modified smectic is replaced by a tetragonal phase. With fluctuations taken into account, the modified smectic-A remains absolutely stable in a certain region of parameters also for $\lambda_1 > 1/3$. The temperature of the SA_m–Te transition becomes dependent on λ_1 and tends to $-\infty$ at $\lambda_1 \to 1/3 + 0$. The modified smectic looses its stability at τ_{in} somewhat smaller than the value of τ at the transition, namely

$$\tau_{in} = -\left[\ln\left(\left|\frac{64\pi q_0\sqrt{\alpha\alpha_\parallel}(3\lambda_1-1)}{T\lambda_0\lambda_1(1+\lambda_1)}\right|\right) + \lambda_1\frac{3-\lambda_1}{3\lambda_1-1}\right]\beta_0. \tag{3.33}$$

Thus, fluctuations render the SA_m–Te transition a first-order transition. At a further increase of λ_1 the modified smectic vanishes and, for instance, for $\lambda_1 = 0.6$ the diagram acquires the form, plotted in fig. 15b.

Similarly, one can consider the cases $k = 2, 3$. We will not give all formulas but give the results only for a few values of the parameter λ_k, and discuss the form of the obtained diagrams.

Above all, the value of the gap in the tetragonal phase depends on the angle θ only at $k = 2$, and in the smectic-B only at $k = 3$. In the modified smectic-A the gap is always anisotropic, however,

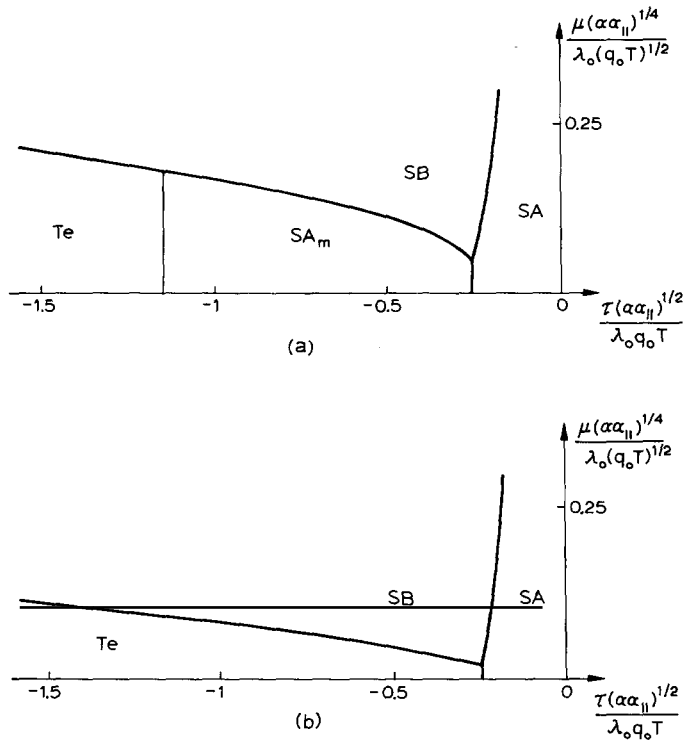

Fig. 15. Phase diagram of weak crystallization of smectics-A for the case (a) $\lambda_1 = 0.34$; (b) $\lambda_1 = 0.6$.

the final formulas for this phase do not at all depend on the number of the harmonics k to be taken into account with the accuracy up to the replacement $\lambda_1 \to \lambda_k$. In all other cases the gap in the correlation function $\langle\varphi\varphi\rangle$ remains isotropic and the calculation only slightly differs from the one for the case $\lambda = \text{const}$.

The structure of the phase diagram for $k = 2$, i.e., for $\lambda(\theta) = \lambda_0(1 + \lambda_2\cos(4\theta))$, identically coincides with the diagram for $k = 1$, if $\lambda_1 = \lambda_2$. The only distinction is that in the latter case instead of the tetragonal phase in the diagram there is a rhombic phase R, described in subsection 3.2.

The phase diagrams for $k = 3$, $\lambda_3 = 0.34$, 0.4, 0.6 are given in figs. 16a–16c. As has been explained in subsection 3.2, in the given case there arise two new structures. As for an absolutely stable tetragonal phase, it emerges similarly to what has been described above for $k = 1$. Note only that in the approximation we have employed for $k = 3$ the energies of the tetragonal phase and rhombic crystal R′ coincide both in the mean field theory and with fluctuations taken into account. Apart from the tetragonal phase at $\lambda_3 > 0.22$ in the phase diagram there emerges a quasicrystalline phase Q_6, described in subsection 3.2.

Above we have constructed phase diagrams only for the simplest dependences $\lambda(\theta)$. As has been explained in subsection 3.2, for more sophisticated dependences in the phase diagrams there may appear phases, missing in figs. 15 and 16. So, for instance, instead of rhombic phases at large negative τ quasicrystalline phases can be absolutely stable. Unfortunately, more general cases of the dependence $\lambda(\theta)$ require more numerically bulky calculations. Therefore we will confine ourselves

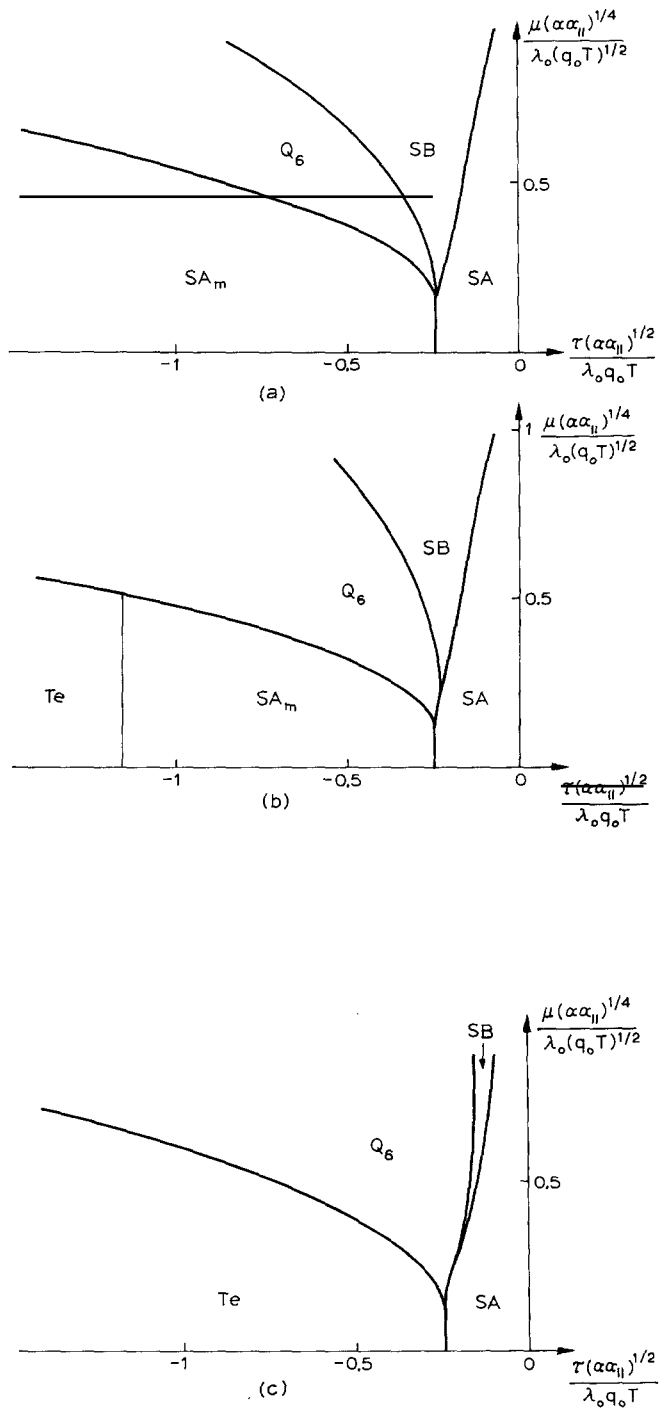

Fig. 16. Phase diagram of weak crystallization of smectics-A for the case (a) $\lambda_3 = 0.3$; (b) $\lambda_3 = 0.34$; (c) $\lambda_3 = 0.6$.

to a qualitative discussion of the structure of the phase diagram.

In the mean field theory all lines of phase equilibria on the plane τ, μ are parabolas $\tau \sim \mu^2$. Taking into account fluctuations leads to the fact that in the region of strong fluctuations (at small μ) all intermediate phases vanish and a direct first-order transition from the smectic-A phase into a phase, stable at large negative τ, takes place.

For the case of an isotropic vertex (i.e., at λ = const.) the phase diagram is given in fig. 13. The presence of anisotropy in the function $\lambda(\theta)$ essentially alters the phase diagram. It is, as usual, composed of three sectors, yet now the rhombic (tetragonal) or quasicrystalline phase can serve as the low-temperature phase. Besides, between this phase and the smectic-B phase there may be a quasicrystal. In the mean field theory transitions of this kind occur irrespective of τ and μ upon a variation of the parameters describing the anisotropy of the function $\lambda(\theta)$. The dependence of this transition point on τ, μ arises if fluctuations are taken into account. The said-above also concerns the dependence $\lambda(\theta)$, having deep minima at some non-zero angles. If these minima are absent, the phases remain qualitatively the same as in the theory with λ = const., although the transition lines, naturally, become shifted. Remind that all said above is valid also for the simple crystallization of a nematic.

3.4. Nematic–smectic-C transition

The nematic–smectic-C phase transition often takes place in a sequence of polymorphic transformations in liquid crystals. This is a case of one-dimensional crystallization. We have already considered the alternative scenario of crystallization of a nematic in the previous subsections. The difference is that in the examined case the fluctuations of the order parameter were "softened" near the one circle in the reciprocal space but near the nematic–smectic-C transition the fluctuations soften near two circles symmetric with respect to the plane perpendicular to the director.

It is clear that it is impossible to construct a closed triangle from wave vectors lying near the circles. Hence the term of the third order (and all odd terms) will be absent in the expansion of the free energy in the order parameter. Therefore the phase transition has to be a second-order phase transition in the framework of mean field theory. But fluctuations of the order parameter make the transition a first order one. The important role of fluctuations of the field φ at this transition was noticed by Swift [1976]. In this subsection we will largely follow his work.

3.4.1. Main equations

As has already been noted, at the nematic–smectic-C transition the order parameter φ softens in the vicinity of two circles in the reciprocal space. The second order term in the Landau functional, describing this softening, can be written as

$$F_{\mathrm{L}}^{(2)} = \frac{1}{8}\int \mathrm{d}\boldsymbol{r}\left(4\tau\varphi^2 + \alpha_{\parallel}\frac{[((\boldsymbol{n}\nabla)^2 + q_1^2)\varphi]^2}{q_1^2} + \alpha_{\perp}\frac{[(\nabla_{\perp}^2 + q_0^2)\varphi]^2}{q_0^2}\right). \tag{3.34}$$

Here $\boldsymbol{n}$ is the director, $\nabla_{\perp}^2 = \nabla^2 - (\boldsymbol{n}\nabla)^2$. In considering the phase transition, the gradient term (3.34) should be analysed alongside with the terms (2.16)–(2.18) of the Landau expansion.

We may neglect fluctuations of the director $\boldsymbol{n}$ at the nematic–smectic-C transition and therefore assume that $\boldsymbol{n}$ = const. Below we will assume that the Z-axis is directed along the director.

The gradient energy (3.34) has a minimum for fluctuations with the wave vectors

$$q_z = \pm q_1\,, \quad q_{\perp} = \sqrt{q_x^2 + q_y^2} = q_0\,. \tag{3.35}$$

These conditions define two circles in the reciprocal space. At the condensation of the field φ, i.e., at the phase transition under study, there emerges a harmonics of φ with a wave vector, obeying the conditions (3.35). Thus, this wave vector proves to be tilted to the Z-axis. This condensate corresponds to the smectic-C phase, where the director $\boldsymbol{n}$ is tilted to the normal $\boldsymbol{l}$ to the smectic layers.

Using the quadratic part of the Landau functional (3.34), it is easy to find the bare expression for the pair correlation function of the field φ (2.84), which in the Fourier representation reads

$$D(\boldsymbol{q}) = T/[\Delta + \alpha_\perp(|\boldsymbol{q}_\perp| - q_0)^2 + \alpha_\parallel(|q_z| - q_1)^2]. \tag{3.36}$$

Here, as previously, the bare value of the gap $\Delta = \tau$. In the derivation of eq. (3.36) we have assumed that the conditions

$$\Delta \ll \alpha_\parallel q_1^2, \quad \Delta \ll \alpha_\perp q_0^2 \tag{3.37}$$

are fulfilled. This makes it possible to confine oneself to the consideration of a narrow vicinity of the circles (3.35) in the reciprocal space. In essence, the inequalities (3.37) are the applicability conditions for the weak crystallization theory for the given case.

Note that in the vicinity of the triple point "nematic–smectic-A–smectic-C" the inequality holds

$$\alpha_\perp q_0^2 \ll \alpha_\parallel q_1^2.$$

The Landau functional for this case was formulated in the work [Chen and Lubensky 1976]. There it was demonstrated that this functional has a low critical dimensionality, equal to three. The consequences of this fact were studied in the work [Gorodetsky and Podnek 1989]. In our opinion, however, this question requires some additional investigation. In particular, the role of fluctuations of the director, neglected by the authors of the above mentioned work, is quite obscure.

The inequalities (3.37) permit to confine oneself in the analysis of the phase transition to Fourier components of the field φ with the wave vectors near the circles (3.35) in the reciprocal space. These wave vectors cannot form a closed triangle. Hence it follows that at this phase transition the cubic term (2.17) in the Landau expansion is irrelevant, since it vanishes in the integration over the volume. The same assertion holds also for other terms, odd in the field φ.

The said-above means that in the mean field theory the transitions we are studying are second-order phase transitions. This assertion is valid both for the crystallization of nematics into smectics-C and for the transitions into phases of more complex symmetries (see below). Yet, due to fluctuations of the field φ, this phase transition becomes a first-order transition.

To analyse the role of fluctuations of the field φ, it is necessary to employ the diagram technique, developed in subsection 2.3. The inequalities (3.37) permit to confine oneself to the one-loop approximation for the effective field h and the self-energy function Σ. In the case under study the problem is simplified due to the absence of the terms, cubic in the field φ, therefore in the diagram equations, plotted in figs. 2 and 3 one can omit the terms with the triple vertex μ.

As previously, alterations in the structure of the pair correlation function $\langle\langle\varphi\varphi\rangle\rangle$ due to fluctuations reduce to the replacement of the bare value of the gap $\Delta = \tau$ in eq. (3.36) with its renormalized value. The equations for the gap Δ can be easily written out analytically in the case, when the quartic vertex $\lambda = \text{const}$. This equation reads

$$\Delta = \tau + \lambda A + \beta' \ln(4\alpha_\perp q_0^2/\Delta), \tag{3.38}$$

where $\beta' = \lambda q_0 T/4\pi\sqrt{\alpha_\perp \alpha_\parallel}$. The quantity A here is defined by eq. (2.42). Recall that the first term in the r.h.s. of eq. (3.38) is a bare contribution, the second a mean field contribution and the last one is a fluctuation contribution.

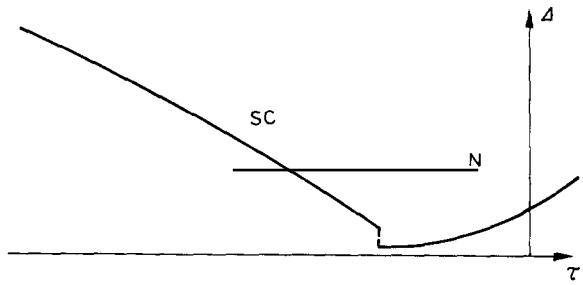

Fig. 17. Dependence of the gap Δ in the correlation function $\langle\langle\varphi\varphi\rangle\rangle$ on the value of the parameter τ at the nematic–smectic-C phase transition.

Like in subsection 3.3, the fluctuation contribution to the gap is defined by the integral, logarithmically diverging in the upper limit. The final results are not sensitive to the method of cutting off this integral. We have performed this cutting by analogy with subsection 3.3. The resulting equation (3.38) for the gap Δ is analogous to eqs. (3.17) and (3.20). Therefore the analysis relevant to the nematic–smectic-C transition largely repeats the one covered in subsection 3.3. We will give here only the main results in brief.

3.4.2. Results

If the vertex λ = const., the Landau expansion (2.16), (2.18), (3.34) gives rise a phase transition at the variation of the parameter τ, associated with the formation of the condensate of the field φ of the form

$$\langle\varphi(\boldsymbol{r})\rangle = \sqrt{A}\cos(q_0 x + q_1 z + \Phi), \tag{3.39}$$

where Φ is an arbitrary phase. The density modulation (3.39) corresponds to the smectic-C phase. Let us discuss the main features of this transition.

The dependence of the gap Δ_N on τ in the nematic phase is determined by eq. (3.38) where one should put $A = 0$. As in previous cases, there exists a solution of the equation for all values of τ. Therefore the energy of the nematic phase may serve as a reference point at computing of the energies of low-symmetry phases.

The dependence of the gap Δ_{SC} on τ in the smectic-C phase is determined by eq. (3.38), where the relation between the amplitude A and the gap Δ_{SC} is determined by the condition $h = 0$. The field h, conjugated to φ, is defined as in subsection 2.3. At the transition point, the gap Δ experiences a jump of the order

$$\Delta \sim \beta'. \tag{3.40}$$

The gap in the nematic and smectic phases has the same order near the transition point. For the theory to be correct, the quantity β' must satisfy the inequalities (3.37). The qualitative form of the dependence of the gap on the temperatures in depicted in fig. 17.

At the nematic–smectic-C phase transition point the thermodynamic potentials Ω of the both phases must be equal to each other. The difference of the potentials of the smectic and nematic phases is given by

$$(\Omega_{SC} - \Omega_N)/V = -(\Delta_{SC}^2 + \Delta_N^2)/2\lambda + \beta'(\Delta_{SC} - \Delta_N)/\lambda. \tag{3.41}$$

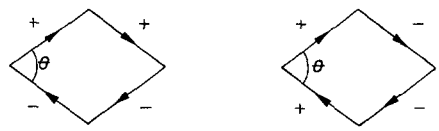

Fig. 18. Configurations of wave vectors entering in the equation for the gap.

The equation $\Omega_{SC} = \Omega_N$ can be solved only numerically. The fluctuation contribution into Ω gives rise to the fact that the transition under study is a first-order phase transition with the latent heat of the transition of the order Δ^2/λ, where Δ is estimated from (3.40).

The conclusion from the theory that the nematic–smectic-C transition is a first-order phase transition tallies with the experimental situation. The latent heat of this phase transition was measured in the works of several authors (see the monograph by Anisimov [1992] and the literature referred to therein). Note that the experimentally found value of the latent heat of this transition proves to be rather small, which justifies the applicability of the weak crystallization theory to this transition.

We now discuss the influence of the angular dependence of the quartic vertex λ on the phase transition. This dependence for the case we are studying will be somewhat more complicated than in subsections 3.2 and 3.3. The component q_z of the wave vector of the field φ is non-zero, it is close either to $+q_1$ or $-q_1$. Although the dependence of λ on absolute values of the Z-components of the wave vectors can, as previously, be omitted, the dependence of λ on their signs must be retained. Therefore λ can be treated as a function of the transversal components of the wave vectors (lying in the smectic layer plane) and the signs of $\boldsymbol{q}$ (labelled by the subscripts + and −).

The gap Δ now becomes a function of the wave vectors, one of which has the subscript + and the other has the subscript −. It is clear that the equation for the gap involves a sum of the values of the vertex λ for the configurations of the wave vectors, depicted in fig. 18. This sum is a function of the angle θ of the rhombus and possesses all symmetry properties (3.5). Thus, with the angular dependence of λ taken into account, the problem reduces to the one analysed in subsections 3.2 and 3.3. That is why one can reformulate the results of these subsections, bearing in mind that the components of the emerging condensate have the wave vectors with $q_z \neq 0$ and regarding the triple vertex $\mu = 0$. Recall that although the analysis of subsections 3.2 and 3.3 is based on a concrete form of the angular dependence of the vertex $\lambda(\theta)$, the conclusions of this analysis are more or less general.

Repeating the considerations of subsection 3.3, we conclude that at the crystallization of nematics a monoclinic (M) or quasicrystalline (Q) phases can arise. The monoclinic phase is a genuine crystalline phase with the C_2 axis along the director. The quasicrystalline phase possesses a crystalline order along the director and a quasicrystalline order in the orthogonal plane. The following sequences of phase transitions are possible:

M–N, Q–N, M–SC–N, Q–SC–N.

All these phase transitions are first-order transitions with the characteristic latent heats of the order of Δ^2/λ, where the gap Δ is estimated from eq. (3.40).

The possibility of transitions, where the symmetry $z \to -z$ is broken is not excluded. This possibility is in need of a special analysis and will not be discussed here.

The performed analysis of the crystallization of nematics is also applicable to the crystallization of smectics-A for the case when the softening of the field φ occurs near the two circles in the reciprocal

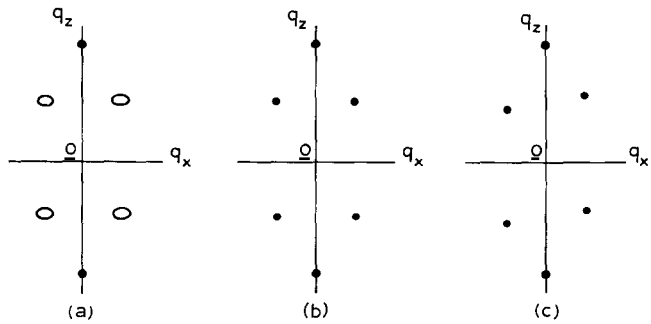

Fig. 19. Diffraction patterns for the three smectic phases: (a) smectic A_1 phase with the quasi-Bragg peak at $\boldsymbol{q} = k\boldsymbol{e}_z$ and two diffusion spots at $|\boldsymbol{q}_\perp| = q_0$, $|q_z| = q_1$, (b) smectic-$\tilde{A}$ phase with quasi-Bragg peaks at $k\boldsymbol{e}_z$ and $\boldsymbol{k}_1, \boldsymbol{k}_2, k_{1z} = k_{2z}$, (c) smectic-$\tilde{C}$ phase with quasi-Bragg peaks at $k\boldsymbol{e}_z, \boldsymbol{k}_1, \boldsymbol{k}_2, k_{1z} \neq k_{2z}$; the sum $\boldsymbol{k}_1 + \boldsymbol{k}_2 = 0$.

space. All above formulated conclusions hold also for the crystallization of smectics-A, if then there occurs a period along the Z-axis, incommensurate with the initial density modulation period in smectics-A. This weak crystallization model is qualitatively consistent with the experimental data [Ema et al. 1989b]. If at the transition the period increases twice (three or four times) as much, this strongly complicates the theoretical investigation. We will not consider this situation here.

3.5. *Smectic-A–smectic-$\tilde{A}$, smectic-A–smectic-$\tilde{C}$ phase transitions*

Here we will study the weak crystallization of smectics-A for the case when the order parameter φ softens in the vicinity of two circles in the reciprocal space whose centres are lying roughly in the middle between the origin and the boundaries of the Brillouin zone. In this case effects of commensurability become important, inducing the appearance of such unusual phases as smectics-$\tilde{A}$, smectics-$\tilde{C}$.

These phases emerge in the phase diagram of substances consisting of polar molecules. Such phase diagram, as a rule, gives a few different smectic-A phases. Following the conventional notation, we will call the smectic-A phase which at the crystallization generates the $\tilde{A}$ and $\tilde{C}$ phases, smectic-A_1. The X-ray patterns for the smectic-A_1, -$\tilde{A}$, -$\tilde{C}$ phases are given in fig. 19. In the smectic-A_1 phase there is one quasi-Bragg peak with the wave vector $\boldsymbol{q} = \boldsymbol{k} = k\boldsymbol{e}_z$. This peak corresponds to the original density modulation with the period, close to the length of the molecule. Near the phase transitions, investigated here, apart from this peak, there also emerge diffusion spots near the circles $|\boldsymbol{q}_\perp| = q_0$, $|q_z| = q_1$, where $\boldsymbol{q}_\perp$, q_z are components of the wave vector $\boldsymbol{q}$, orthogonal and parallel to $\boldsymbol{e}_z$ (q_0, q_1 are positive constants).

The appearance of these spots shows that in the vicinity of the phase transition density fluctuations with the wave vectors near the spots "soften down". At decreasing temperature the intensity of fluctuations increases and in the phase transition point in the "soft" regions there emerge two new quasi-Bragg peaks with the wave vectors $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$. If $|\boldsymbol{k}_1| = |\boldsymbol{k}_2|$, the new phase is smectic-$\tilde{A}$, if $|\boldsymbol{k}_1| \neq |\boldsymbol{k}_2|$, this is smectic-$\tilde{C}$.

In the mean field theory the A_1–$\tilde{A}$, A_1–$\tilde{C}$, $\tilde{A}$–$\tilde{C}$ transitions are second-order phase transitions [Prost 1984]. However due to fluctuation effects, the A_1–$\tilde{A}$, A_1–$\tilde{C}$ transitions become first-order phase transitions, as was noted in the work [Wang and Lubensky 1984]. The description of these phase transitions is very close to that of the nematic– mectic-C transition, studied in subsection 3.4. Yet, the presence of the original density modulation in smectics-A_1 brings about a number of

peculiarities, distinguishing the A_1–$\tilde{A}$, A_1–$\tilde{C}$ transitions from the nematic–smectic-C transition.

A few words about the experimental situation. Safinya et al. [1986] noticed that the structure factor of the A_1 phase near the A_1–$\tilde{A}$ transition exhibits a sophisticated behaviour. The measurements of the heat capacity show that the $A_1 - \tilde{A}$ transition is a weak first-order transition [see Ema et al. 1989a]. This result is confirmed also by the recent X-ray studies on 7CBAAB [Ostrovsky and Said-Achmetov 1990].

In this subsection we will construct the weak crystallization theory for the A_1–$\tilde{A}$, A_1–$\tilde{C}$ transitions, incorporating the influence of fluctuations. We will find the phase diagram and analyse the behaviour of the physical quantities near these phase transitions. Our analysis will follow the work by Lebedev and Muratov [1991].

3.5.1. Landau expansion

As previously, we will describe the density modulation, emerging at the A_1–$\tilde{A}$, A_1–$\tilde{C}$ transitions, by means of the order parameter $\varphi(\boldsymbol{r})$, characterizing the value of the density modulation with the wave vectors in the "soft" regions. The mean value of the field φ is zero in the high-temperature phase, i.e., in smectics-A_1, and is non-zero in the low-temperature phase, i.e., in smectics-$\tilde{A}$ or smectics-$\tilde{C}$. We will consider only components of the field φ with the wave vectors close to the mentioned two circles in the reciprocal space. In this case, as for the nematic–smectic-C phase transition, all odd terms of the Landau expansion of the free energy of the system in the order parameter $\varphi(\boldsymbol{r})$ are zero. That is why the A_1–$\tilde{A}$, A_1–$\tilde{C}$ phase transitions in the mean field theory are second-order phase transitions.

We stress that the thus defined order parameter describes the so-called bilayer density modulation. Alongside with it, in the phases we are studying, there is also a monolayer density modulation which is assumed to be rather insensitive to the emergence of the bilayer density modulation. Peculiarities of these transitions are accounted for by the interaction of these two types of modulation.

In this situation the leading terms of the expansion of the free energy F in the order parameter can be represented as

$$F = F_{\varphi} + F_{1-2}. \tag{3.42}$$

Here the first term is defined by eqs. (2.18) and (3.34), and the second term describes the interaction of the density modulation, emerging at the phase transition, with the original monolayer density modulation in smectics-A_1. In conformity with the experimental situation we believe that $|\boldsymbol{k}|$ is close to $2q_1$. Then in the Landau expansion one should take into account a cross term of the form

$$F_{1-2} = -\zeta_0 \int \mathrm{d}\boldsymbol{r}\, \cos(kz + \Phi_0)\, \varphi^2(\boldsymbol{r}). \tag{3.43}$$

Here ζ_0 is the coefficient, proportional to the density modulation amplitude in the smectic-A_1 and Φ_0 is an arbitrary phase. This phase can be made zero by an appropriate choice of the origin of the reference system, this choice will be assumed henceforth.

Let us discuss the applicability regions of our model. We are interested in the narrow vicinity of the A_1–$\tilde{A}$, A_1–$\tilde{C}$ phase transitions where fluctuations are important. Thus, we study only a small part of the phase diagram, which was analysed in the mean field approximation in the works [Prost 1979, Barois, Coulon and Prost 1981, Wang and Lubensky 1984]. We will assume also that the fluctuation region we are analysing is far from other phase transition lines, in particular, from the nematic–smectic-A_1 phase transition line. In this case one can treat all parameters appearing

in the Landau expansion as temperature-independent. In particular, we will regard the quantities, determining the position of the "soft" regions in the reciprocal space as constant.

3.5.2. Main relations

The A_1–$\tilde{A}$, A_1–$\tilde{C}$ phase transitions occur upon a variation of the parameters τ and ζ_0, entering the Landau expansion. Consequently, we must study the phase diagram of the system on the plane (τ, ζ_0). At $\zeta_0 = 0$ we come back to the situation discussed by Swift [1976], devoted to the nematic–smectic-C transition (see the previous subsection).

In the original smectic-A_1 phase the mean value of the bilayer order parameter φ is zero. At decreasing parameter τ there arises a non-zero condensate of the field φ. In smectics-$\tilde{C}$ it reads

$$\langle \varphi(\boldsymbol{r}) \rangle = 2a_1 \cos(\boldsymbol{k}_1 \cdot \boldsymbol{r}) + 2a_2 \cos(\boldsymbol{k}_2 \cdot \boldsymbol{r}) . \tag{3.44}$$

In eq. (3.44) a_1 and a_2 are density modulation amplitudes. The wave vectors $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ obey the relation

$$\boldsymbol{k}_1 + \boldsymbol{k}_2 = k\boldsymbol{e}_z .$$

This condition ensures the presence of a non-zero contribution to the interaction energy (3.43) of the field φ with the monolayer density modulation. For the smectic-$\tilde{A}$ phase the condensate of the field φ also has the form of (3.44), where now

$$a_1 = a_2 , \quad k_{1z} = k_{2z} = k/2 . \tag{3.45}$$

From these conditions, the smectic-$\tilde{A}$ phase has the second-order symmetry axis, which makes it macroscopically distinct from the smectic-$\tilde{C}$ phase.

Consider the structure of the pair correlation function $\langle\langle \varphi\varphi \rangle\rangle$. Above we have taken into account only the average $\langle\langle \varphi(\boldsymbol{q})\varphi(-\boldsymbol{q}) \rangle\rangle$. Yet, in the situation we are investigating now, due to the presence of the monolayer density modulation, the average of the form $\langle\langle \varphi(\boldsymbol{q})\varphi(-\boldsymbol{q} \pm \boldsymbol{k}) \rangle\rangle$ should be taken into account. Since we have assumed that $2q_1 \simeq k$, i.e., that the diffusion spots in the smectic-A phase are almost in the middle between $\boldsymbol{q} = 0$ and the peak of the monolayer modulation, then both the vectors $\boldsymbol{q}$ and $-\boldsymbol{q} \pm \boldsymbol{k}$ may lie in the vicinity of the circles $|\boldsymbol{q}_\perp| = q_0, |q_z| = q_1$. We will take into account the average $\langle\langle \varphi(\boldsymbol{q})\varphi(-\boldsymbol{q} \pm \boldsymbol{k}) \rangle\rangle$ only under this condition.

Let the vector $\boldsymbol{q}$ lie in the vicinity of a circle with $q_z = q_1$. Then we must consider the correlation functions

$$D_{++}(\boldsymbol{q}) = \langle\langle \varphi(\boldsymbol{q})\varphi(-\boldsymbol{q}) \rangle\rangle , \quad D_{--}(\boldsymbol{q}) = \langle\langle \varphi(\boldsymbol{q}-\boldsymbol{k})\varphi(\boldsymbol{k}-\boldsymbol{q}) \rangle\rangle ,$$

$$D_{+-}(\boldsymbol{q}) = \langle\langle \varphi(\boldsymbol{q})\varphi(\boldsymbol{k}-\boldsymbol{q}) \rangle\rangle , \quad D_{-+}(\boldsymbol{q}) = \langle\langle \varphi(\boldsymbol{q})\varphi(\boldsymbol{q}-\boldsymbol{k}) . \tag{3.46}$$

Naturally, the function D_{--} can be obtained from D_{++} by means of complex conjugation, the same is valid for the pair D_{-+}, D_{+-}. The technique, exploiting correlation functions of the type of (3.46), is close to the technique, proposed by Nambu [1960] in the superconductivity theory [see also Wang and Lubensky 1984].

The final expressions for the correlation functions (3.46) can be written as

$$\begin{pmatrix} D_{++}(\boldsymbol{q}) & D_{+-}(\boldsymbol{q}) \\ D_{-+}(\boldsymbol{q}) & D_{--}(\boldsymbol{q}) \end{pmatrix} = \begin{pmatrix} \Delta + b(\boldsymbol{q}) & -\zeta \\ -\zeta^* & \Delta + b(\boldsymbol{k}-\boldsymbol{q}) \end{pmatrix}^{-1} . \tag{3.47}$$

Fig. 20. (a) Main mean field correction to the gap Δ in the correlation function $\langle\langle\varphi\varphi\rangle\rangle$. (b) Main fluctuation correction to the gap Δ.

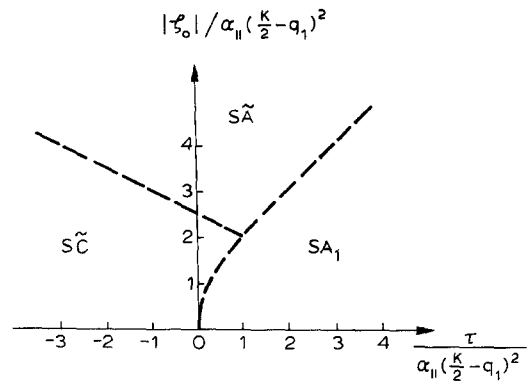

Fig. 21. Phase diagram for the SA$_1$–SÃ–SC̃ transitions, obtained in the Landau approximation. All transitions are second-order transitions.

Here the function $b(\boldsymbol{q})$ equals

$$b(\boldsymbol{q}) = \alpha_\perp(|\boldsymbol{q}_\perp| - q_0)^2 + \alpha_\parallel(|q_z| - q_1)^2, \tag{3.48}$$

and Δ and ζ are new parameters. The bare values of these quantities are, respectively, equal to τ and ζ_0. Note that in the dependence on the values of the parameters in the r.h.s. of eq. (3.48), the determinant of the matrix in the r.h.s. can have minima either on two or on four circles in the reciprocal space. It means that the maxima of the pair correlation function can be achieved either on two or four circles in the q-space.

The parameters Δ and ζ in the smectic-A_1 phase are distinct from their bare values due to fluctuation effects. In ordered phases there emerge additional terms, associated with the presence of the condensate (3.44). The main contribution of this type is given by the diagram in fig. 20a. The main fluctuation contribution to Δ and ζ is represented in fig. 20b, where the solid line stands for the correlation function (3.47).

The weak crystallization theory is applicable for the case under study if the conditions

$$\Delta, \zeta \ll \alpha_\perp q_0^2, \alpha_\parallel q_1^2 \tag{3.49}$$

are fulfilled. In this case fluctuations of the field φ are concentrated in a narrow vicinity of the circles $|\boldsymbol{q}_\perp| = q_0$, $|q_z| = q_1$. Recall that for the mean value of the order parameter the estimate $\langle\varphi\rangle \sim \sqrt{\Delta/\lambda}$ holds. The fulfillment of the conditions (3.49) thus ensures the small value of the density modulation arising at the phase transition and validates our approach.

3.5.3. Phase diagram

First consider the phase transition in the mean field approximation. Inserting the condensate (3.44) into the Landau functional (3.42), we get the expression for the potential Ω

$$\Omega/V = A\tau + \zeta_0 A x + \alpha_\parallel(k/2 - q_1)^2 A x^2 + \lambda A^2(1 + x^2/2)/4. \tag{3.50}$$

Here $A = a_1^2 + a_2^2, x = 2a_1a_2/A$. The parameter A varies from zero up to $+\infty$, and the parameter x from -1 up to 1. In deriving eq. (3.50) we have made use of the expressions for the wave vectors of the condensate $\boldsymbol{k}_1$, $\boldsymbol{k}_2$

$$k_{1z} = q_1 + (k - 2q_1)a_2^2/A, \quad k_{2z} = q_1 + (k - 2q_1)a_1^2/A. \tag{3.51}$$

These expressions can be derived as the result of the procedure of energy minimization over all independent parameters. From eq. (3.51) it follows that in the smectic-$\tilde{C}$ phase, where $k_{1z} \neq k_{2z}$, also $a_1 \neq a_2$.

To find the values of A and x, it is necessary to minimize the expression for the potential Ω, defined in eq. (3.50). The value $A = 0$ corresponds to the smectic-A_1 phase, the values $A \neq 0$, $x = 1$ to the $\tilde{A}$ phase and the values $A \neq 0$, $x < 1$ to the $\tilde{C}$ phase. The finally obtained phase diagram is depicted in fig. 21. The boundaries between the phases are determined by

$$\tau(A_1\text{–}\tilde{A}) = |\zeta_0| - \alpha_{\|}(k/2 - q_1)^2, \quad \tau(A_1\text{–}\tilde{C}) = \zeta_0^2/\alpha_{\|}(k - 2q_1)^2,$$

$$\tau(\tilde{A}\text{–}\tilde{C}) = -2|\zeta_0| + 5\alpha_{\|}(k/2 - q_1)^2. \tag{3.52}$$

The triple point has the coordinates

$$|\zeta_0| = 2\alpha_{\|}(k/2 - q_1)^2, \quad \tau = \alpha_{\|}(k/2 - q_1)^2. \tag{3.53}$$

In the mean field theory all A_1–$\tilde{A}$, A_1–$\tilde{C}$, $\tilde{A}$–$\tilde{C}$ transitions are second-order phase transitions.

Now consider the role of fluctuations near the phase transitions. Assume that the influence of fluctuations is much stronger that the influence of commensurability, i.e., that the condition

$$\beta' \gg \alpha_{\|}(k/2 - q_1)^2 \tag{3.54}$$

is fulfilled. Here the parameter β' is defined by eq. (3.38). In this case one can put $k = 2q_1$.

The equations for the parameters Λ and ζ are derived as it has been described above. They read

$$\Lambda = \tau + \lambda a_1^2 + \lambda a_2^2 + \tfrac{1}{2}\beta' \ln[\Lambda^2/(\Lambda^2 - \zeta^2)],$$

$$\zeta = \zeta_0 + \lambda a_1 a_2 + \tfrac{1}{4}\beta' \ln[(\Lambda - \zeta)/(\Lambda + \zeta)]. \tag{3.55}$$

Here Λ is the upper cutoff, determined by the limits of applicability of eq. (3.48). The variation of Λ is equivalent to a redefinition of the parameter $\tau \to \tau +$ const. Therefore we may put $\lambda = \beta'$, which is a convenient choice.

The thermodynamic potential Ω is now a function of the parameters Λ, ζ, a_1, a_2. The relation between a_1, a_2 and Λ, ζ is found from the conditions $h_1 = 0$, $h_2 = 0$ where

$$h_1 = \partial\Omega/\partial a_1, \quad h_2 = \partial\Omega/\partial a_2. \tag{3.56}$$

Using eqs. (3.55) one can write the expressions for the fields as

$$h_1 = a_1(\Lambda - \lambda a_1^2/2 - \lambda a_2^2) + \zeta_0 a_2,$$

$$h_2 = a_2(\Lambda - \lambda a_2^2/2 - \lambda a_1^2) + \zeta_0 a_1. \tag{3.57}$$

From eqs. (3.55) and from the conditions $h_1 = 0$, $h_2 = 0$ by means of numerical calculations one can find the dependence of the quantities Λ, ζ, a_1, a_2 on τ and ζ_0.

To construct the phase diagram we need to calculate thermodynamic potentials for different phases. The difference of the thermodynamic potentials Ω for two given phases is the integral

$$V \int (h_1 \, \mathrm{d}a_1 + h_2 \, \mathrm{d}a_2). \tag{3.58}$$

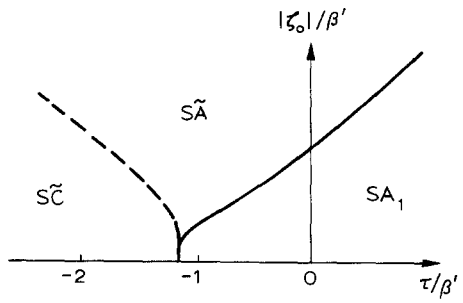

Fig. 22. Phase diagram for the SA$_1$–SÃ–SC̃ transitions, obtained with fluctuations taken into account. The SA$_1$–SÃ, SA$_1$–SC̃ transitions are first-order transitions, the SÃ–SC̃ transition is a second-order transition.

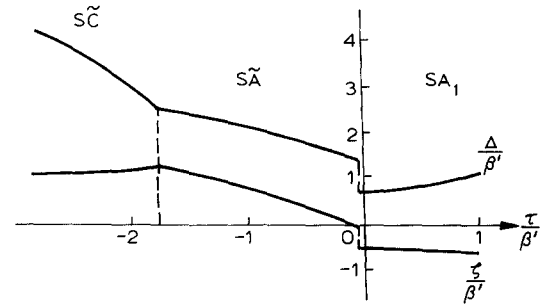

Fig. 23. Dependence of the parameters Δ, ζ on τ.

The limits in this integral are determined by the values of the parameters a_1, a_2 in these phases. The fields h_1, h_2 are related to the parameters a_1 and a_2 via (3.57).

The integral in (3.58) can be calculated analytically. As a result, the difference of free energies of a low-temperature phase and the smectic-A$_1$ phase can be represented in the form

$$(\Omega - \Omega_{A_1})/V = \lambda^{-1}[(\Delta^2 - \Delta_1^2)/2 + \zeta^2 - \zeta_1^2 + \beta'(\Delta - \Delta_1) - \lambda^2 A^2(2 + x^2)/8]. \tag{3.59}$$

The quantities A and x have been defined above (see (3.50)). The phase transition lines are determined by the conditions

$$\Omega_{\tilde{A}} - \Omega_{A_1} = 0, \quad \Omega_{\tilde{C}} - \Omega_{A_1} = 0, \quad (\Omega_{\tilde{A}} - \Omega_{A_1}) - (\Omega_{\tilde{C}} - \Omega_{A_1}) = 0. \tag{3.60}$$

It is easy to derive the equation for the phase transition line between the Ã and C̃ phases,

$$\tau = -2|\zeta_0|\beta' \ln[\beta'/(\tfrac{1}{4}\beta' \ln 3 + |\zeta_0|)]. \tag{3.61}$$

The position of other transition lines can be found only numerically. The numerically calculated phase diagram is depicted in fig. 22. It involves the three phases A$_1$, Ã and C̃. Note that the A$_1$–Ã, A$_1$–C̃ transitions, with fluctuations taken into account, become first-order phase transitions whereas the Ã–C̃ transition remains continuous like in the mean field theory. At the Ã–C̃ transition the second-order symmetry axis is broken. Such type of symmetry breaking leads to the second-order phase transition. A similar situation takes place at the smectic-A–smectic-C transition.

The renormalized quantities Δ and ζ are nontrivial functions of the variables τ and ζ_0. The typical form of the dependence of Δ and ζ on τ at a fixed ζ_0 is given in fig. 23. In the A$_1$–Ã, A$_1$–C̃ phase transition points the quantities Δ and ζ experience jumps of the order β'. In the Ã–C̃ phase transition point the quantities Δ, ζ, a_1, a_2 vary continuously. At $\zeta \to 0$ we have $a_2 \to 0$ and, consequently, we come back to the situation described by Swift [1976].

In the smectic-C̃ phase, the value of the wave vector of the condensate k_{1z}, as follows from the relation (3.51), depends on τ. It varies from $k/2$ on the smectic-Ã–smectic-C̃ phase transition line up to q_1 at $\zeta_0 = 0$.

3.5.4. Discussion

We now analyse the dependence of the heat capacity on the temperature in the vicinity of the phase transitions we are studying. Since the parameter τ is proportional to $T - T^*$, the singular part

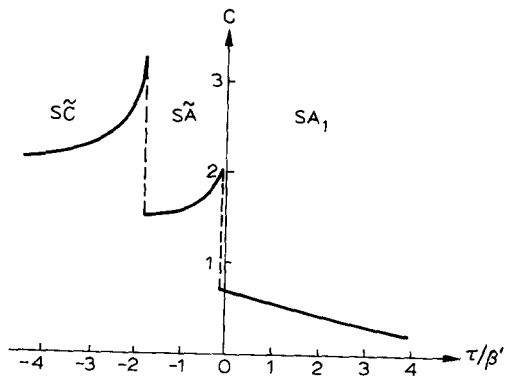

Fig. 24. Dependence of the heat capacity on τ in the vicinity of the SA_1–SÃ–SC̃ phase transitions.

of the heat capacity is proportional to $\partial^2\Omega/\partial\tau^2$, where Ω is the singular part of the thermodynamic potential Ω. Calculating this derivative and using the expressions for the derivatives of the quantities Δ and ζ over τ, ensuing from eqs. (3.55), we get

$$C_{\text{sing}}(A_1) \propto T\beta'(2\Delta + \beta')/\lambda[(2\Delta + \beta')(\Delta + \beta') - 2\zeta^2],$$

$$C_{\text{sing}}(\tilde{A}) \propto T\frac{8(\Delta^2 - \zeta^2) + 8\beta'\zeta + 2\beta'\Delta - 3\beta'^2}{\lambda[6(\Delta^2 - \zeta^2) + 8\beta'\zeta - \beta'\Delta - 3\beta'^2]},$$

$$C_{\text{sing}}(\tilde{C}) \propto T\frac{4(\Delta^2 - \zeta^2) - 4\beta'\Delta + \beta'^2}{\lambda[2(\Delta^2 - \zeta^2 - 3\beta'\Delta + \beta'^2]}. \tag{3.62}$$

An example of the dependence of the heat capacity on τ at a fixed ζ_0 is depicted in fig. 24, where the heat capacity is measured in arbitrary units. The singular part of the heat capacity in the low-symmetry Ã and C̃ phases is larger than in the smectic-A_1 phase due to the contribution of the condensate.

Let us to mention that in the general case we have to take into acount the role of two factors – fluctuations and effects of an incommensurability. If the incommensurability effects are small we may neglect them. In the opposite limit we may neglect fluctuations of the order parameter. The simultaneous consideration of both effects can be done only numerically. However using the explicit expressions for these two limit cases, one can consider the general case as a certain interpolation.

Thus, the use of the weak crystallization theory for the analysis of phase transitions between the smectic-A_1, Ã and C̃ phases permits to obtain the phase diagram, to determine the order of the transitions and to investigate the temperature dependence of the structural factor and heat capacity. The then obtained results are in qualitative agreement with the experimental data. A quantitative comparison with experiment, apparently, requires a certain generalization of the model.

In our phase diagram there are only three smectic-A_1, Ã and C̃ phases. To include into the weak crystallization scheme other smectic phases, also present, for instance, in the global phase diagram [see Prost 1984], we have to give up some inequalities, formulated above. The phase diagram will also be modified if the dependence of the vertex λ on the wave vectors is taken into account.

3.6. Macroscopic effects

At the end of this section we will discuss macroscopic and, in particular, dynamic manifestations of the studied types of weak crystallization of nematics and smectics-A. Actually this study is a repetition of the analysis, performed in subsection 2.4 for the isotropic liquid, therefore here we will cover only the results.

Like in subsection 2.4, in studying the macroscopic effects, associated with the field φ, in the expansion of the free energy, one should incorporate the terms, describing the interaction of the field φ with the long-wavelength degrees of freedom. In smectics-A these degrees of freedom are described by the mass density ρ, specific entropy σ, velocity v and the smectic layer displacement u along the Z-axis. In the weak crystallization transition point the mass density, specific entropy as well as $\nabla_z u$, i.e., interlayer spacing, experience a jump. This jump is small in virtue of the fact that this first-order phase transition is close to a second-order transition.

Apart from this trivial effect, the interaction of φ with the long-wavelength degrees of freedom induces a fluctuational softening of the system. So, fluctuations of the field φ bring about the decrease of the smectic layer compressibility modulus B and of the quantity $c^2 \equiv (\partial P/\partial \rho)_\sigma$ (P is the pressure), which is inversely proportional to the compressibility. This means that fluctuation contributions to the quantities B^{-1}, c^{-2} arise. These contributions are of the order

$$q_0^2 T/4\pi \Delta \alpha . \tag{3.63}$$

A similar contribution emerges also into the quantity C_P^{-1}, where C_P is the specific heat at constant pressure.

Let us give some relations, valid for the simple crystallization of smectics-A. The energy (3.1) explicitly depends on the vector of the normal to the layers, which for smectics coincides with the director $\boldsymbol{n}$. Expanding (3.1) in deviations of $\boldsymbol{n}$ from the equilibrium value and taking into account that $n_\alpha = -\nabla_\alpha u$ (where $\alpha = x, y$), we get

$$F_{\text{int}} = -\alpha_\parallel \nabla_z \varphi \nabla_\alpha \varphi \nabla_\alpha u + \alpha_\parallel \nabla_\alpha u \nabla_\beta u \nabla_\alpha \varphi \nabla_\beta \varphi / 2 . \tag{3.64}$$

This energy describes the interaction of the field φ with the smectic layer displacement u. At the condensation of the field φ due to the second term of (3.64), in the energy there emerges a contribution, associated with the shear elasticity. In the smectic-B phase this contribution implies the presence of the shear modulus,

$$C_{44} = \alpha_\parallel q_0^2 A . \tag{3.65}$$

The presence of the interaction energy (3.64) gives rise to various fluctuation effects, in particular, induces the emergence of the following fluctuation contribution to the energy density,

$$K_{\text{fl}} (\nabla_\alpha^2 u)^2 / 2 . \tag{3.66}$$

The fluctuation contribution appearing in eq. (3.66), to the Frank constants equals

$$K_{\text{fl}} = (3/32\pi) \sqrt{\alpha \alpha_\parallel}\, q_0^3 T/\Delta . \tag{3.67}$$

Thus, fluctuations of φ generate an anomalous contribution to the only smectic Frank constant K.

To investigate how fluctuations of φ influence the long-wavelength dynamics of the system, we must take into account the interaction with all long-wavelength degrees of freedom. This procedure

is described in subsection 2.4. It is not difficult to make sure that all static effects, associated with the field φ, are also reproduced in dynamic equations. In particular, it implies the appearance of anomalous contributions, defined in eq. (3.63), to c_1^{-2} and c_2^{-2}, where c_1 and c_2 are velocities of the first and second sound in the smectic phase or velocities of the respective acoustic modes in the crystalline phase. Thus, these modes soften near the transition point.

Besides, fluctuations of the field φ induce a purely dynamical effect, i.e., increase of the viscosity coefficients of the system near the transition point. In subsection 2.4, it has been shown that at the weak crystallization of isotropic liquids in the main approximation there is only a contribution to the coefficient of the so-called second viscosity. This contribution in the vicinity of the transition behaves as $\Delta^{-5/2}$. At the weak crystallization of smectics, the situation is somewhat more complex. The dissipative stress tensor in smectics is characterized by five viscosity coefficients and fluctuations corrections arise to all the five coefficients. Omitting fairly cumbersome calculations [see Kats, Lebedev and Muratov 1989], we will give only the results.

It proves that the bulk viscosity coefficients, determining the sound absorption, η_1, η_4, η_5 (we are employing the notation of Martin et al. [1972]) grow most of all. The fluctuation contributions to these coefficients are proportional to

$$q_0 T/\Gamma \Delta^2 \sqrt{\alpha \alpha_\parallel}. \tag{3.68}$$

Here Γ is the kinetic coefficient, describing the relaxation of φ. Fluctuation corrections to the shear viscosity coefficients η_2, η_3 have a less pronounced singular character, by the order of magnitude they are equal to

$$q_0^3 T \sqrt{\alpha}/\Gamma \Delta \sqrt{\alpha_\parallel}. \tag{3.69}$$

The existent experimental data do not permit to carry out a quantitative comparison with our results. Nevertheless there is, no doubt, qualitative agreement. For instance, in the works [Calder et al. 1980, Oswald 1986] a considerable growth of the sound absorption was observed at the smectic-A–crystalline smectic-B transition, whereas the anomalies in the velocity of sound and the shear viscosity coefficients are less marked. This fact agrees with our results, since the softening of the velocity of sound and the increase of the shear viscosity coefficients are determined by a weaker dependence on the small parameter of the theory Δ than the main contribution to the bulk viscosity coefficients, proportional to Δ^{-2}, determining the sound absorption.

All predictions concerning macroscopic manifestations of fluctuations of the order parameter φ at the simple weak crystallization of smectics-A are qualitatively valid for all other weak crystallization transitions, discussed in this section, in particular, for the nematic–columnar phase and nematic–smectic-C, as well as smectic-A_1–smectic-$\tilde{A}$, smectic-A_1–smectic-$\tilde{C}$ transitions.

4. Weakly anisotropic nematics and smectics-C

Here we will construct the crystallization theory of weakly anisotropic systems. By "weakly anisotropic systems" we will denote substances which possess a high-temperature phase with weakly broken rotational or uniaxial symmetry. The softening of the order parameter in the weakly anisotropic systems also occurs in the vicinity of a sphere or of a circle (or circles) in the reciprocal space but the angular distribution of fluctuations will not be isotropic even in the high-temperature phase. Nevertheless the phase volume of fluctuations in weakly anisotropic systems

will, as previously, be large and the scenario of a weak crystallization transition in such substances will be similar to the one considered in the previous two sections.

It is useful to compare weakly anisotropic systems with systems with a strong anisotropy where the softening of the order parameter takes place in the vicinity of isolated points in the reciprocal space. The crystallization of such a system is as usual a continuous transition and may be considered in the framework of the conventional theory of second-order phase transitions.

We consider the following examples of weakly anisotropic systems. The crystallization of weakly anisotropic nematics is analysed in subsections 4.1 and 4.2 and in subsection 4.3 the crystallization of smectics-C is studied. Whereas weakly anisotropic nematics are largely model systems, the smectics-C in reality possess weakly anisotropic layers.

The first attempt to investigate theoretically the crystallization of nematics was made by Gorodetsky and Podnek [1985]. They made use of the mean field theory. However, as it has been proved in sections 2 and 3, fluctuations of the order parameter play an essential role in the weak crystallization theory. Fluctuation effects for the crystallization of nematics and smectics-C were studied in the works [Kats and Muratov 1988, Kats, Lebedev and Muratov 1989] which we will stick to in what follows.

4.1. Nematics. The mean field theory

In this and following subsections we will consider the case of weakly anisotropic nematics. The weak crystallization of such a system is close to the case of isotropic liquids, but its consideration reveals some peculiarities due to the presence of anisotropy.

For weakly anisotropic nematics the Landau functional, describing both the orientational and crystallization transitions, can be written as the sum

$$F = F_\varphi + F_N + F_{int}. \tag{4.1}$$

Here F_φ is the isotropic crystallization energy, associated with the short-wavelength field φ, F_N is the orientational energy, associated with the nematic order parameter, F_{int} is the interaction energy, containing the cross terms in both order parameters. The energy F_φ is defined by eq. (2.10).

4.1.1. Character of anisotropy

As it is well known, a nematic is a phase with spontaneously broken rotational symmetry. In the simplest case of uniaxial nematics the anisotropy of the system is described by director $\boldsymbol{n}$, which is a unit vector oriented along the preferred direction. All physical characteristics of the nematic are invariant with respect to the transformation $\boldsymbol{n} \to -\boldsymbol{n}$. In the general case the nematic order parameter is a symmetric traceless 2-rank tensor Q_{ik}. It can be represented as

$$Q_{ik} = Q_0\{(n_i n_k - \delta_{ik}/3) - Y(m_i m_k - [\boldsymbol{n} \times \boldsymbol{m}]_i [\boldsymbol{n} \times \boldsymbol{m}]_k)/2\}. \tag{4.2}$$

Here Q_0, Y are scalar parameters, $\boldsymbol{n}$, $\boldsymbol{m}$, $[\boldsymbol{n} \times \boldsymbol{m}]$ is a triad of unit mutually orthogonal vectors, the unit vector $\boldsymbol{n}$ is the director.

The parameter Q_0 in eq. (4.2) characterizes the degree of ordering of the long axes of the molecules. At $Y = 0$, eq. (4.2) describes the conventional uniaxial nematic order, the parameter Y characterizes the biaxiality of the system. To avoid confusion, let us mention that the value of $Y = \pm\sqrt{3}Q_0$ also corresponds to uniaxial phases but with the director, coinciding with $\boldsymbol{m}$ or $[\boldsymbol{n} \times \boldsymbol{m}]$. Henceforth we will take only a uniaxial phase with $Y = 0$. The nematic part of the

Landau functional F_N contains only even powers of the expansion in Y. This is a consequence of the invariance of the order parameter (4.2) with respect to the transformation

$$Y \to -Y, \quad \boldsymbol{m} \to [\boldsymbol{n} \times \boldsymbol{m}]. \tag{4.3}$$

Due to this, the function F_N is invariant with respect to the transformation $Y \to -Y$, i.e., this function must be even with respect to Y.

Henceforth we will assume that the original nematic phase is uniaxial, i.e., in this phase $Y = 0$. The quantity Y may become non-zero under crystallization, that is, the low-temperature phases may be biaxial. We will also assume the nematic phase to be weakly anisotropic, i.e., the parameter Q_0 to be small. Therefore the problem we are studying has a model character, nevertheless it has an undoubted methodical significance. Besides, most results, obtained for weakly anisotropic nematics, can be generalized to the case of a weak anisotropy of smectics-C (see subsection 4.3), whose smectic layers are always weakly anisotropic.

In the main approximation in the small parameter Q_{ik} the interaction term F_{int} can be written out as

$$F_{int} = \frac{1}{2} \int d\boldsymbol{r}\, g_0 Q_{ik} \nabla_i \varphi \nabla_k \varphi . \tag{4.4}$$

Equation (4.4) is the first non-vanishing term of the expansion of F_φ in Q_{ik}. Since the field Q_{ik} in eq. (4.4) is a long-wavelength field, F_{int} reduces to the sum of the products of the Fourier components of the field φ with the opposite wave vectors. In this situation the dependence of g_0 on the direction of this wave vector is absent and the coefficient g_0 in (4.4) can be regarded as constant.

Here our analysis is carried on in the framework of the mean field theory. In this case the effects, associated with fluctuations of the order parameters φ, Q_{ik} are neglected. The mean value of the nematic order parameter Q_{ik}, in contrast to φ, is homogeneous. Therefore, henceforth all parameters, entering in (4.4) will be treated as constants, independent of the radius vector.

Rewrite the interaction term (4.4), using the representation (2.19) for the condensate φ and eq. (4.2) for Q_{ik},

$$F_{int} = \tfrac{3}{2} g \sum_i [(\boldsymbol{n}\boldsymbol{e}_i)^2 - 1/3 + Y((([\boldsymbol{n} \times \boldsymbol{m}]\boldsymbol{e}_i)^2 - (\boldsymbol{m}\boldsymbol{e}_i)^2)]|a_i|^2 . \tag{4.5}$$

The summation here is performed over the components of the expansion of the condensate of the field φ, $e_i = q_i/|\boldsymbol{q}|$ is a unit vector in the direction of the respective wave vector and the quantity

$$g = -g_0 q_0^2 Q_0/3 \tag{4.6}$$

has the meaning of the interaction constant. In the derivation of eq. (4.5), we have taken advantage of the fact that due to the weak anisotropy of the system the absolute values of the wave vectors $\boldsymbol{q}_n$ are close to q_0.

Now we can formulate the criterion for the weak anisotropy of the system. The criterion is that for the interaction constant g, defined above, there is the estimate

$$|g| \leq \tau_{char} . \tag{4.7}$$

Here τ_{char} is the characteristic value of the parameter τ, determining the crystallization transition points. Recalling that the inequality (2.99) is the condition of applicability for the weak crystallization theory, we conclude that

$$|g|/\alpha q_0^2 \ll 1 . \tag{4.8}$$

This inequality, in particular, ensures that the absolute value of $\boldsymbol{q}_n$ is close to q_0.

Note that the inequality, opposite to (4.7), corresponds to the case of a strongly anisotropic nematic, described in section 3.

4.1.2. Influence of anisotropy

At crystallization transitions under the condition (4.7) the interaction term (4.5) induces the mutual orientation of the nematic and crystalline order parameters. Besides, this term changes the value of the energy of the respective phases in comparison with the isotropic case. Let us analyse these effects, having in mind that the result depends on the sign of g in eq. (4.5).

Take a smectic phase whose condensate has the form of (2.48). If $g < 0$, the density modulation wave vector will be oriented along the director $\boldsymbol{n}$, which corresponds to the smectic-A phase. In this case the interaction energy (4.5) equals $2gA$, where the value of the parameter A is defined by eq. (2.42). In other words, the distinction from the isotropic case reduces to the replacement $\tau \to \tau + 2g$ in the expression for the energy of the smectic-A phase, derived for the isotropic system.

If $g > 0$, the wave vector of the one-dimensional density modulation proves to be oriented orthogonally to the director. It is natural to call this structure the smectic-C phase. In this case the interaction energy (4.5) has the value $-gA$, which leads to the replacement $\tau \to \tau - g$ in the expression for the energy of the smectic-A phase, derived for the isotropic case. Besides, for $g > 0$, the nematic order parameter becomes biaxial with $Y \sim gA$. We may neglect the corresponding contribution to the energy of the smectic-C phase since it is proportional to the squared small interaction constant g.

Now consider the hexagonal columnar phase D_h, whose condensate is determined by the three wave vectors, forming a perfect triangle (see subsection 2.2). At $g > 0$, the wave vectors of the condensate φ are orthogonal to the director $\boldsymbol{n}$. Then the amplitudes of density waves remain equal to each other, and the interaction energy $F_{\text{int}} = -gA$. Thus, to take into account the interaction energy F_{int} one should replace $\tau \to \tau - g$ in the expression for the energy of the D_h phase for the isotropic case. Note that in this case the orientational order parameter does not become biaxial.

The case $g < 0$ is more intricate. Then the director proves to be orthogonal to columns, i.e., it is lying in the same plane as the wave vectors of the density modulation. There are two options; either the director $\boldsymbol{n}$ is parallel to one of the crystallization directions $\boldsymbol{q}_1$, or is orthogonal to it. The first phase with $\boldsymbol{n} \parallel \boldsymbol{q}_1$ will be denoted by D_1, the second phase with $\boldsymbol{n} \perp \boldsymbol{q}_1$ by D_2. In these phases the density wave amplitudes are not identical by value, that is why the columnar phases will have the rhombic symmetry.

We now calculate the energies of these phases under the condition $\lambda = \text{const}$. Designate $a_2 = a_3 = a$, then $A = 2a^2 + a_1^2$. Like in section 2, it is convenient to represent the energy of the phase in the form of (2.41). Then we will include the contribution, associated with F_{int} to the function f. For the rhombic phases we get

$$f_{D_1} = -\lambda((A - a_1^2)^2 + 2a_1^4)/8 - |\mu|a_1(A - a_1^2) + g(9a_1^2 - A)/4,$$

$$f_{D_2} = -\lambda((A - a_1^2)^2 + 2a_1^4)/8 - |\mu|a_1(A - a_1^2) + g(5A - 9a_1^2)/4. \tag{4.9}$$

The energy of the D_1, D_2 phases can be obtained by the minimization of eqs. (4.9) over a_1, and then by the minimization of the sum $F + f$ over A. A numerical analysis reveals that the energy of the D_1 phase is lower than that of the D_2 phase. Therefore at $\lambda = \text{const}$. the D_1 phase may arise in the phase diagram of the system.

Now we analyse how the anisotropy affects the cubic BCC phase. In virtue of the high symmetry of this phase, the interaction of the crystalline and nematic order parameters is very weak (see

below) therefore the presence of Q_{ik} does not practically affect the structure of the condensate φ. This phase apparently corresponds to the crystalline smectic-D phase, and we will denote it as SD.

The insertion into eq. (4.5) of the condensate φ, corresponding to the cubic BCC_1 phase, yields a zero value for F_{int}. It means that both the orientation of the nematic order parameter Q_{ik} with respect to the crystal axes and the variation of the energy of this phase as compared to the isotropic case are determined by quadratic effects, which are small in the parameter (4.8). Note that these effects cannot be correctly analysed in the framework of our approach, since the term of the expansion of the crystalline energy, quadratic in Q_{ik}, omitted by us in eq. (4.4), brings about effects of the same order.

4.1.3. Phase diagram

Here we describe the phase diagram of the system. At very small g the nematic and crystalline order parameters behave independently. Therefore we may construct the sequence of phases basing on previous results. At $\lambda = \text{const.}$ and $g > 0$ we have the cascade of transitions

$$SC\text{–}D_h\text{–}SD\text{–}N. \tag{4.10}$$

At $\lambda = \text{const.}$ and $g < 0$ this sequence is

$$SA\text{–}D_1\text{–}SD\text{–}N. \tag{4.11}$$

At the increase of the interaction constant g the smectic-D phase disappears from the cascade (4.10). At negative g with increasing absolute value of g the smectic-D phase in (4.11) is replaced by the smectic-A and then the D_1 phase vanishes in such a way that there is only one direct second order transition SA–N. All other phase transitions are weak first-order transitions, except for the SA–D_1 transition, which in a certain range of values of g can be continuous. The phase diagram, constructed in the framework of the mean field approximation, is depicted in fig. 25.

The analysis of the phase diagram given above concerns the case $\lambda = \text{const.}$ If the quartic vertex λ sufficiently strongly depends on the angles between the wave vectors $\boldsymbol{q}$, then in the sequence of phases (4.10), (4.11) only the phase, stable at large negative values of τ, may change. Instead of the smectic-C and -A phases with the one-dimensional density modulation, columnar rhombic phases or quasicrystals can be stable. For $g > 0$ in the main approximation the latter phases are not tilted since the symmetry of the lattice is high enough for the interaction energy (4.4) to become zero. The value of the constant g then does not affect the sequence of transitions with the exception of the disappearance of the smectic-D phase. At large negative values of g the smectic-A becomes stable instead of columnar rhombic and quasicrystalline phases.

4.2. Nematics. Fluctuation effects

Here we will analyse the role of fluctuations of the order parameter φ at the crystallization of weakly anisotropic nematics. A simple analysis reveals that fluctuations of the nematic order parameter Q_{ik} can be neglected in considering weak crystallization transitions. This means that Q_{ik} can be treated, as previously, as a homogeneous quantity.

Thus, when one includes the nematic order parameter into the theory, the anisotropic term (4.5), quadratic in φ, emerges in the Landau expansion. Recall that it is our assumption that the original nematic phase is uniaxial. As has been shown in subsection 4.1, the crystallization makes the emergence of biaxiality possible. The mechanism of the emergence of biaxiality is not affected by fluctuations of φ, that is why the conclusions of subsection 4.1 hold also if fluctuations are

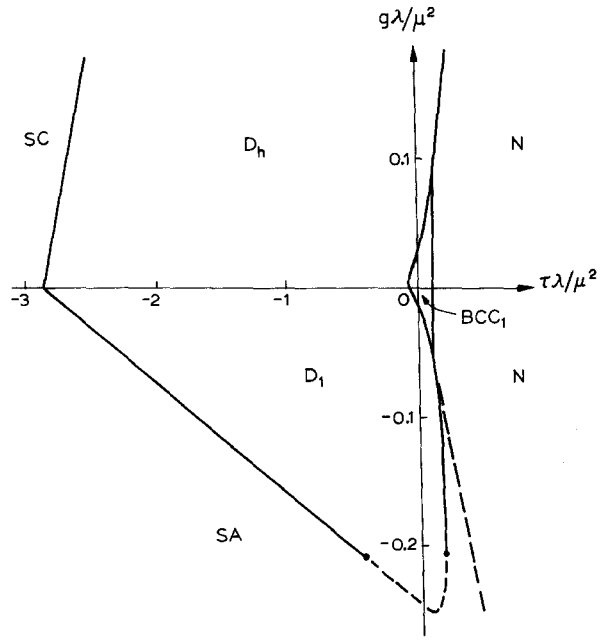

Fig. 25. Phase digram of crystallization of nematics, obtained in the Landau approximation.

taken into account. The influence of the biaxial contribution into Q_{ik} on the form of the Landau expansion in φ manifests itself only in the second order in the interaction constant and it can be discarded when fluctuations of φ are studied. Therefore in this section we will assume $Y = 0$.

4.2.1. Equation for the gap

As has been explained above, the only modification of the theory, in comparison with the isotropic case, is the replacement

$$\tau \to \tau + g(3\cos^2\theta - 1).$$

Here θ is the angle between the director $\boldsymbol{n}$ and the wave vector of the field φ. In other words, the parameter τ in eq. (2.12) becomes anisotropic. Yet, from the relations (4.7) and (4.8), the softening of the components of the field φ, as usual, occurs in the vicinity of the sphere $|\boldsymbol{q}| = q_0$ in the reciprocal space. Therefore the procedure, developed in subsection 2.1 to investigate the role of fluctuations of φ can almost without any changes be generalized to the case of crystallization of weakly anisotropic nematics. Therefore we will in brief give the main elements of this procedure, dwelling in detail only on the distinctive features of the crystallization of nematics.

The calculation of the bare pair correlation function (2.89) of the field φ in this case is completely analogous to that of the isotropic case. In the Fourier representation for this correlation function we have an expression, similar to (2.89)

$$D(\boldsymbol{q}) = T/[\Delta + \alpha(q - q_0)^2 + 3gt^2]. \tag{4.12}$$

Here we have introduced the notation $t = \cos\theta$, where θ is the angle between the director $\boldsymbol{n}$ and the wave vector $\boldsymbol{q}$. In the nematic phase the bare value of the gap equals $\Delta = \tau - g$, in phases

with the broken translational symmetry in Δ there appears an additional term, associated with the condensate of the field φ.

If fluctuations are taken into account, in the main approximation the irreducible correlation function $\langle\langle\varphi\varphi\rangle\rangle$ has the same structure as (4.12), only the gap Δ proves to be renormalized. Corrections to Δ are determined by the diagrams, given in fig. 3. Like in the isotropic case, it is possible to confine oneself to these diagrams if $\Delta \ll \alpha q_0^2$. This inequality is equivalent to the applicability condition (4.8) of the weak crystallization theory since with (4.7) taken into account, in the vicinity of the transition point $\Delta \sim \tau_{\text{char}}$.

Let us explicitly write out the equation for the gap Δ, defined by these diagrams, assuming $\lambda = \text{const}$. In this case the quantity Δ remains isotropic, however, the correlation function (4.12) is anisotropic, which leads to a modification of eq. (2.102),

$$\Delta = \tau - g + \lambda A + \beta \int_0^1 \mathrm{d}t\, (\Delta + 3gt^2)^{-1/2}$$

$$= \begin{cases} \tau - g + \lambda A + \beta(3|g|)^{-1/2} \arcsin(\sqrt{3|g|/\Delta}), & g < 0, \\ \tau - g + \lambda A + \beta(3|g|)^{-1/2} \ln[(\sqrt{\Delta + 3g} + \sqrt{3g})/\sqrt{\Delta}], & g > 0. \end{cases} \tag{4.13}$$

The quantity A, figuring in eq. (4.13), is introduced by eq. (2.42), and the parameter β equals $\beta = \lambda T q_0^2/4\pi\sqrt{\alpha}$.

To get a closed system, one should add to eq. (4.12) another equation, relating A and Δ. This equation ensues from the condition $h = 0$, where h is the field, conjugated to φ. In our approximation the field φ is determined by the diagrams, plotted in fig. 2. Equating it to zero, one can derive the relations

$$\Delta_S + 3g\Theta(-g) = \lambda A_S/2, \quad \Delta_D = \lambda A_D/6 + |\mu|(A_D/3)^{1/2}. \tag{4.14}$$

Here $\Theta(x)$ is a step function, the subscript S implies that the respective expression concerns the smectic phase, and the subscript D the hexagonal columnar phase. The second equation in (4.14) is valid only at $g > 0$.

Inserting eqs. (4.14) into (4.13), we get closed equations for the gap Δ. For the original nematic phase they result from eqs. (4.13) at the replacement $A = 0$. We will also give the explicit form of these equations for the gap for the smectic phases:

$$\Delta_S + \tau + 5g + \beta(3|g|)^{-1/2} \arcsin(\sqrt{3|g|/\Delta_S}) = 0, \quad g < 0, \tag{4.15}$$

$$\Delta_S + \tau - g + \beta(3g)^{-1/2} \ln[(\sqrt{\Delta_S + 3g} + \sqrt{3g})/\sqrt{\Delta_S}] = 0, \quad g > 0. \tag{4.16}$$

For $g > 0$, the described procedure can be easily generalized to the case of the hexagonal columnar phase. At $g < 0$, when the appearing columnar phase possesses the rhombic symmetry, the situation becomes more complicated (see below).

4.2.2. Phase diagram

The calculation of the energies of inhomogeneous phases is performed similarly to the one performed in section 2. It is convenient to write the thermodynamic potential of the system in the form of a sum of two terms

$$\Omega/V = F + f. \tag{4.17}$$

The second term in eq. (4.17) depends on the structure of the emerging phase and is defined by eq. (2.43). For the smectic and columnar phases the function f is equal to

$$f_S = -\lambda A_S^2/4, \quad f_D = -\lambda A_D^2/12 - 2|\mu|(A_D/3)^{3/2}. \tag{4.18}$$

To calculate the first term in eq. (4.17), employ the relation

$$dF/dA = \Delta + 3g\Theta(-g), \tag{4.19}$$

which is obtained in the same way as in section 2. Integrating eq. (4.19) over the parameter A from zero up to the equilibrium value in the inhomogeneous phase, found from eqs. (4.14). In integrating let us make use of the relation (4.13). As a result, we get

$$F - F_N = \frac{\Delta^2 - \Delta_N^2}{2\lambda} + \frac{\beta}{\lambda}(\sqrt{\Delta + 3g} - \sqrt{\Delta_N + 3g}), \quad \text{for } g > 0,$$

$$F - F_N = \frac{\Delta^2 - \Delta_N^2}{2\lambda} + \beta(\sqrt{\Delta + 3g} - \sqrt{\Delta_N + 3g}) + 3g(\Delta - \Delta_N)$$

$$-\beta\sqrt{3|g|}\left[\arctan\left(\frac{\Delta + 3g}{\sqrt{3|g|}}\right) - \arctan\left(\frac{\Delta_N + 3g}{\sqrt{3|g|}}\right)\right] \quad \text{for } g < 0. \tag{4.20}$$

Using eqs. (4.17), (4.18), (4.20), (4.14) and the analogous formulas for the smectic-D phase, identically coinciding with the ones derived in section 2, for the BCC_1 phase one can calculate the phase diagram of the system. Figure 26 gives the phase diagram of the system for the value $g = \mu^2/2\lambda$. This figure illustrates the fact that the increase of fluctuations makes the intermediate columnar phase disappear and diminishes the phase transition temperature. The smectic-D phase, having the cubic symmetry, at this value of g is metastable.

For $g < 0$, we have to take into consideration the rhombic columnar phases D_1 and D_2 discussed in the previous subsection. For these phases the relation between A and Δ following from $h = 0$ becomes complicated in comparison with (4.14) since the field h depends not only on A but also on a_1 (the amplitude of the preferred harmonics). The energy of the rhombic columnar phases D_1 and D_2 can be found only numerically. Comparing the energies of different phases we can find a phase diagram of the system. All phase transitions between the phases are weak first-order transitions. The phase diagram for the value $g = -\mu^2/2\lambda$ is given in fig. 27. Note that with decreasing parameter τ after the D_1 phase again there arises a smectic-A phase in the diagram.

As previously fluctuations stabilize a high-symmetry phase (nematic in our case) but not at arbitrary values of parameters g, τ. It may be checked that for $g < 0$ at decreasing τ eq. (4.15) loses its solution at a certain value of τ which means that the nematic phase becomes absolutely unstable. This instability reveals itself at the value $\tau = \tau_c$,

$$\tau_c = -2g - \pi\beta(12|g|)^{-1/2}. \tag{4.21}$$

It is clear from this formula that only at $g \to 0$ the value $\tau_c \to -\infty$. The line of the nematic phase stability loss is pictured by the dashed line in fig. 27. Let us stress that the crystallization which is the transition from the nematic into SA or D_1 phase occurs before the nematic loses its stability what justifies our consideration of these transitions. The investigation of the phase diagram in the region where the nematic phase is absolutely unstable is based upon the relation (4.20) where instead of the nematic gap Δ_N the smectic gap Δ_S should be used.

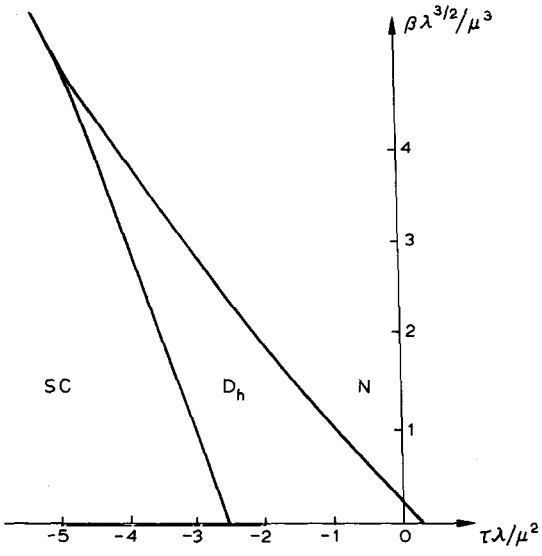

Fig. 26. Phase diagram of crystallization of nematics, obtained with fluctuations taken into account for $g = 0.165\mu^2/\lambda$.

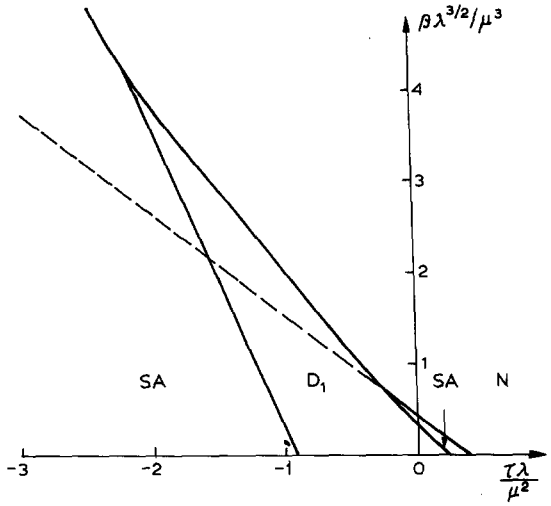

Fig. 27. Phase diagram of crystallization of nematics, obtained with fluctuations taken into account for $g = -0.165\mu^2/\lambda$.

The effects, induced by the dependence of the vertex λ on the angles between wave vectors, have been qualitatively discussed in subsection 4.1 in the framework of the mean field theory. The incorporation of fluctuations in this case may lead to the fact that at increasing anisotropy of λ the smectic phase will not be simply replaced by a rhombic columnar or quasicrystalline structure, but will be ousted from the phase diagram gradually, starting from large negative τ (cf. the results of section 3).

So, at increasing fluctuations the sequences of phases get simplified since the smectic and columnar phases disappear.

4.3. Weak crystallization theory of smectics-C

In section 3 of this survey the weak crystallization of smectics-A has been elucidated. Here we will discuss peculiarities of the weak crystallization of smectics-C. Smectics-C are characterized by the fact that the molecules, packed into smectic layers, are arranged not along the normal to the layers, like in smectics-A, but at a certain angle to the normal. This generates anisotropy in a smectic layer. Since the tilt angle, as a rule, is small, the anisotropy is also small. That is why we are studying the crystallization theory of smectics-C in this section.

To describe the anisotropy of a smectic layer in smectics-C, it is convenient to use the order parameter $\boldsymbol{s}$, defined by the relation

$$\boldsymbol{s} = [\boldsymbol{l} \times \boldsymbol{n}], \tag{4.22}$$

where $\boldsymbol{l}$ is the normal to smectic layers, and $\boldsymbol{n}$ is the director. The vector $\boldsymbol{s}$ lies in the smectic layer plane. In smectics-A there is $\langle \boldsymbol{s} \rangle = 0$, in smectics-C $\langle \boldsymbol{s} \rangle$ is non zero. In all known smectics-C

$|\langle s \rangle| \ll 1$, which means that the value of the tilt angle between the molecules and the normal to the smectic layers is small. In other words, real smectics-C are close to the smectic-A phase. Henceforth we will bear this case in mind.

To describe the crystallization of smectics-C, introduce also, like it has been done in section 3, a short-wavelength field φ, characterizing the density modulation in a smectic layer. In smectics $\langle \varphi \rangle = 0$, in crystals $\langle \varphi \rangle$ is non zero. This average has harmonics with wave vectors lying in the smectic layer plane and having a value of the order of the mutual molecular distance.

4.3.1. Free energy

It is convenient to represent the energy of smectics-C, like for weakly anisotropic nematics, as the sum

$$F = F_\varphi + F_s + F_{int}. \tag{4.23}$$

In eq. (4.23) F_φ is defined by the Landau expansion (2.16)–(2.18) and (3.1). The second term F_s is the energy, associated with the tilt of the molecules to the smectic layer. Having in mind that the value of s is small, it is sufficient to confine oneself in this energy to the first nonvanishing terms of the expansion in s. In virtue of the invariance of the energy with respect to the replacement $s \to -s$, in F_s there are only terms, even in s

$$F_s = \tau_s s^2/2 + \lambda_s s^4/24. \tag{4.24}$$

In eq. (4.24) λ_s is the quartic vertex of the self-interaction of the field s. At a variation of the parameter τ_s there occurs a transition from the A to the C phase: at positive τ_s the average $\langle s \rangle = 0$, which corresponds to smectics-A, and at negative τ_s, $\langle s \rangle \neq 0$, which corresponds to smectics-C.

The third term in eq. (4.24) is the energy of interaction of the fields φ and s. In the main approximation over s, it is described by the expression

$$F_{int} = \gamma_0 s^2 \varphi^2/24 + \gamma_1 (s \nabla \varphi)^2/24 q_0^2. \tag{4.25}$$

Here γ_0 and γ_1 are the interaction constants, q_0 is the absolute value of the wave vector, figuring in F_φ. Note that the second term in (4.25) is anisotropic in the smectic layer plane. We will be interested in sufficiently small values of the constants τ, τ_s. The applicability condition for the weak crystallization theory is (3.2). For the value of the tilt angle of the director to the normal to the smectic layers to be small in smectics-C, it is necessary that the condition $|\tau_s| \ll \lambda_s$ be fulfilled. Besides, on the constants γ_0 and γ_1 one must impose the following constraint:

$$\gamma \equiv \gamma_0 + \gamma_1 \Theta(-\gamma_1) > -\sqrt{6\lambda\lambda_s}, \tag{4.26}$$

where $\Theta(x)$ is the step function. If (4.26) is violated, the form, quadratic in s^2 and φ^2, introduced in eq. (4.25), will not be positively defined.

4.3.2. Phase diagram

We will analyse the structure of the phase diagram in the coordinates τ and τ_s at different values of γ_0 and γ_1. Let us focus ourselves on the case $\lambda = \text{const}$. It is easy to construct the phase diagram, obtained in the mean field theory for small γ_0 and γ_1. In the result the sequence of phases SA_m–SB–SA, obtained in section 3 for the crystallization of smectics-A, at $\tau_s < 0$ transforms into the sequence of tilted phases SC_m–SB_c–SC. Smectics-C_m differ from the above described smectics-C by the presence of the one-dimensional density modulation in the smectic layer. The smectic-B_c

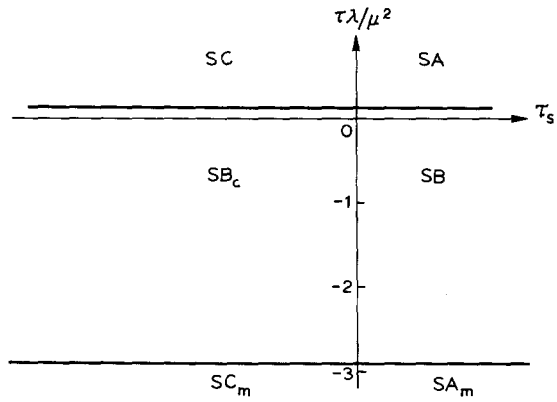

Fig. 28. Mean field phase diagram of crystallization of smectics-A and -C for small values of the parameters γ_0 and γ_1.

phase is a hexagonal layered crystal, where the molecules are tilted to the smectic layer plane. Recall also that smectics-B are hexagonal layered crystals, where the molecules are orthogonal to the layer, and SA_m differs from smectics-A by the presence of the one-dimensional density modulation in the layer. Note that from the symmetry viewpoint the A_m and C_m phases are equivalent, and from the viewpoint of the dimensionality of their lattice, belong to columnar phases but not to smectics.

The interaction term (4.25) for small values of γ_0 and γ_1 leads to the mutual orientation of the vector $\boldsymbol{s}$ and crystallization directions. For $\gamma_1 < 0$. the density modulation in the smectic-C phase is oriented along the vector $\boldsymbol{s}$, and for $\gamma_1 > 0$ in the direction orthogonal to $\boldsymbol{s}$. Likewise, in the tilted smectic-B_c phase for $\gamma_1 < 0$ one of the vectors $\boldsymbol{q}$ is parallel to $\boldsymbol{s}$, and for $\gamma_1 > 0$ orthogonal to it. The phase diagram for the case when the interaction (4.25) is small, is given in fig. 28. Recall that in obtaining this diagram we have assumed that the vertex λ is constant and fluctuations are neglected.

Now consider the question how the phase diagram is modified for the case when the interaction term (4.25) is not small. To illustrate this case, first analyse the phase diagram in the range of values of the parameters τ and τ_s, defined by the inequality

$$|\tau| \gg \mu^2/\lambda, \quad |\tau_s| \gg \mu^2\lambda_s/\gamma\lambda.$$

In this region one can ignore the contribution of the term $\mu\varphi^3$ into the energy F_φ. Then it is sufficient to study the competition of the four phases: SA, SC, SA_m, SC_m. For $\tau_s > 0$ we come back to the problem of the crystallization of smectics-A, discussed in section 3. The sequence of phases at increasing τ has the form: SA_m–SB–SA.

At $\tau_s > 0$, in the region under study there are three phases: SC, SA_m, SC_m. The boundaries of the stability regions of these phases are given by the relations

$$\tau(SC\text{–}SC_m) = \gamma\tau_s/2\lambda_s, \quad \tau(SA_m\text{–}SC_m) = 3\tau_s\lambda/\gamma. \tag{4.27}$$

With increasing parameter γ, defined by eq. (4.26), the stability region of SC_m diminishes, and at $\gamma > (6\lambda\lambda_s)^{1/2}$ this phase vanishes from the phase diagram. As a result, the latter acquires the form depicted in fig. 29.

The complete calculation of the phase diagram with the cubic term in F_φ can be performed only numerically. Figure 30 gives the diagrams of states, obtained for the values of the parameters

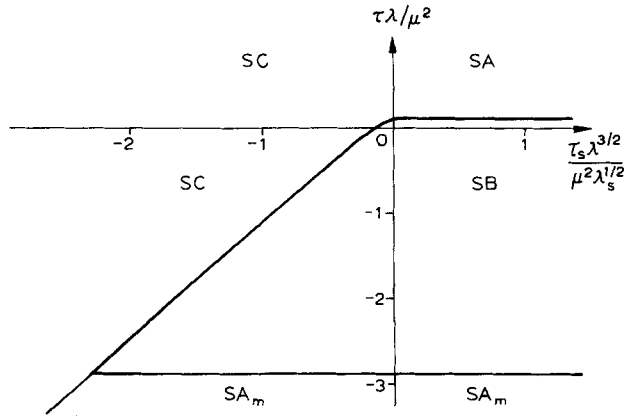

Fig. 29. Mean field phase diagram of crystallization of smectics-A and -C for the value of the parameter $\gamma > \sqrt{6\lambda\lambda_s}$.

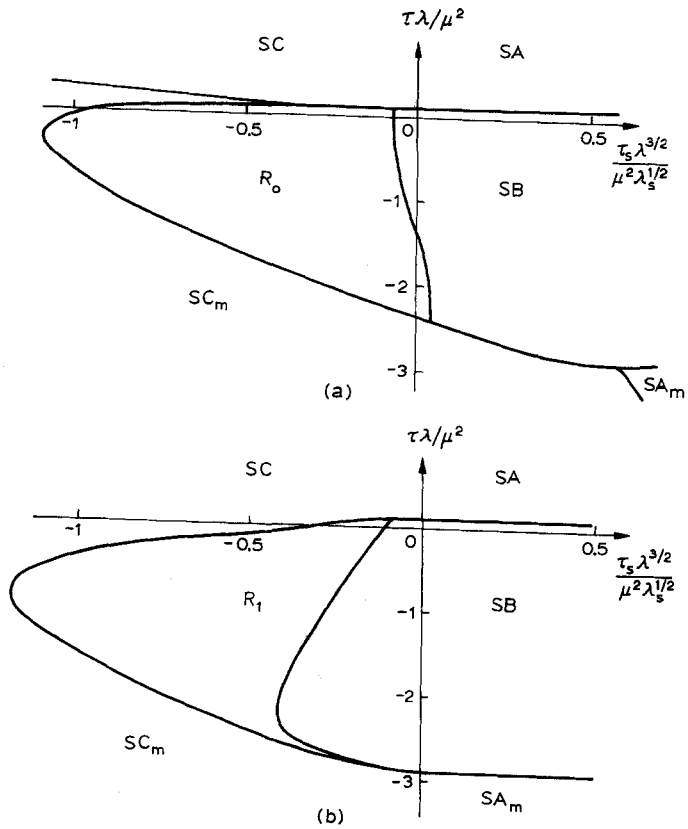

Fig. 30. Mean field phase diagrams of crystallization of smectics-A and -C for the following values of the parameters γ: (a) $\gamma_0 = 0$, $\gamma_1 = -\sqrt{6\lambda\lambda_s}/4$, (b) $\gamma_0 = 0$, $\gamma_1 = \sqrt{6\lambda\lambda_s}/4$.

$\gamma_0 = 0$, $\gamma_1 = -\sqrt{6\lambda\lambda_s}/4$ (fig. 30a), and $\gamma_0 = 0$, $\gamma_1 = \sqrt{6\lambda\lambda_s}/4$ (fig. 30b). In these diagrams there are crystalline rhombic phases R_0 and R_1, characterized by the condensate of the field φ, having in the main approximation the form

$$\langle\varphi\rangle = 2[a_1\cos(\boldsymbol{q}_1\boldsymbol{r}) + a_2\cos(\boldsymbol{q}_2\boldsymbol{r}) + a_2\cos(\boldsymbol{q}_3\boldsymbol{r})] \tag{4.28}$$

Here the vectors $\boldsymbol{q}_1$, $\boldsymbol{q}_2$, $\boldsymbol{q}_3$, lie in the smectic layer plane and form a equilateral triangle with the side q_0. In the R_0 phase the vector $\boldsymbol{s}$ is parallel to $\boldsymbol{q}_1$, then $a_1 < a_2$, in the R_1 phase the vector $\boldsymbol{s}$ is orthogonal to $\boldsymbol{q}_1$, then $a_1 > a_2$. Since the values of a_1 and a_2 are different, the R_0 and R_1 phases are rhombic but not hexagonal.

The phase diagrams, given in fig. 30, reflect a number of common features, inherent in weakly anisotropic systems. The tilted smectic-C_m phase exhibits a re-entrant behaviour. In the interval between the stability regions of this phase there emerge tilted rhombic structures: R_0 at $\gamma_1 < 0$ and R_1 at $\gamma_1 > 0$. Note that an analogous behaviour is observed at the crystallization of nematics. This analogy, however, is existent only for $\gamma_1 < 0$ and, correspondingly, for $g < 0$.

At small values of the parameter γ_1, the amplitudes a_1 and a_2 in eq. (4.28) are only slightly different, therefore in X-ray difraction patterns the phases R_0 and R_1 can hardly be distinguished from hexagonal. At the same time in these phases the director $\boldsymbol{n}$ is tilted to the normal $\boldsymbol{l}$ to the smectic layers. Such phases are traditionally termed as tilted smectics-B (SB_c), as we actually did in considering small values of γ. In the framework of the mean field theory the SA–SC, SA_m–SC_m, SC–SC_m phase transitions are continuous. All the other transitions at $\mu \neq 0$ are first-order transitions.

4.3.3. Influence of fluctuations and anisotropy of λ

We now discuss the influence of fluctuations of the field φ_0 These fluctuations are concentrated near the circle $|\boldsymbol{q}| = q_0$, $\boldsymbol{l}\cdot\boldsymbol{q} = 0$ in the reciprocal space. The theory, incorporating these fluctuations, can also be constructed, as it has been done in subsection 4.2 for nematic liquid crystals.

A slight distinction is in the form of gradient terms in the energy expansion. If the applicability conditions (3.2) for the weak crystallization theory are fulfilled, in calculating corrections to the correlation function $\langle\langle\varphi\varphi\rangle\rangle$, suffice it to confine oneself to the self-energy corrections of the form, given in subsection 2.4. The correlation function $\langle\langle\varphi\varphi\rangle\rangle$ then reads

$$\langle\langle\varphi\varphi\rangle\rangle = T/[\Delta + \alpha_\parallel(\boldsymbol{l}\boldsymbol{q})^2 + \alpha(q - q_0)^2 + \tfrac{1}{12}\gamma_1(\boldsymbol{q}\langle\boldsymbol{s}\rangle)^2]\,. \tag{4.29}$$

Here Δ is the gap in the fluctuation spectrum. In the mean field theory the gap is determined by the sum $\tau + \gamma_0\langle\boldsymbol{s}\rangle^2/12$, in the crystalline phases one should add another term, associated with the condensate of the field $\langle\varphi\rangle$, into this expression. The fluctuations of φ generate a contribution to Δ, pictured in the diagram of fig. 20b.

Quantitatively the relative strength of fluctuations is characterized by the dimensionless parameter

$$P_f = \lambda q_0 T/10\Delta\sqrt{\alpha\alpha_\parallel}\,. \tag{4.30}$$

The fluctuations should be taken into account at $P_f \sim 1$. The account of fluctuations leads to a number of qualitative effects as compared with the mean field approximation. The influence of fluctuations at the crystallization of smectics-A, i.e., at $\tau_s > 0$, has been elucidated in section 3. At negative τ_s fluctuations may transform the continuous (in the mean field approximation) SC–SC_m transition into a first-order transition at sufficiently small $|\tau_s|$. Thus, on the equilibrium SC–SC_m line there appears a tricritical point whose coordinate τ_s is estimated as

$$\tau_s \sim \lambda\lambda_s T/10|\gamma|\sqrt{\alpha\alpha_\parallel}\,. \tag{4.31}$$

As long as the parameter P_f is growing, the intermediate SB and SB_c (R_0 and R_1) phases tend to vanish from the phase diagram. In the long run at a sufficient intensity of fluctuations in the phase diagram there are only four phases left, namely: SA, SC, SA_m, SC_m. The SA–SA_m, SC–SC_m transitions then become weak first-order transitions.

So far we have treated the interaction vertex λ in F_φ as constant. As soon as the dependence of the vertex on the angle between the wave vectors appears, new phases may also emerge in the phase diagram. At a sufficiently strong anisotropy instead of smectic phases rhombic or quasicrystalline phases can become stable. The absolute stability of these phases will now depend not only on the form of the dependence $\lambda(\theta)$ but also on the value of the parameter γ_1. The influence of fluctuations on the phase diagram in the case when the vertex λ is angle-dependent, as in the case $\lambda = \text{const.}$, reduces to the fact that as long as P_f is growing, the intermediate rhombic phases vanish, and the value of the parameter τ at which the transitions take place, diminishes.

The above given analysis has been qualitative. The described phenomenological theory involves many unknown parameters, which makes it possible to describe a large number of phase diagrams but makes it hard to formulate the conclusions quantitatively. Nevertheless, this analysis permits to make the following conclusion about the structure of the phase diagram of the crystallization of smectics-C. We will confine ourselves to the case $\tau_s < 0$, since at $\tau_s > 0$ we come back to the situation, discussed in section 3.

The sequence of phases, observed at decreasing τ, consists, as a rule, of three phases. The first one is the original smectic-C. At decreasing τ a transition into the phase with a rhombic crystalline structure in the smectic layer plane may occur. This phase can in experiment be identified as the tilted smectic-B_c. The latter, low-temperature phase is smectic-C_m. For a certain anisotropy of λ it may be replaced by a rhombic or quasicrystalline phase. The increase of the smectic layer anisotropy, i.e., the decrease of τ_s, gives rise to the fact that the latter phase arises between the smectic-C and tilted smectic-B_c. At a sufficiently strong anisotropy the tilted smectic-B_c (i.e., R_0 or R_1) vanishes, and there is only one direct SC_m–SC transition left. In the mean field theory this transition is continuous. With fluctuations taken into account, this transition becomes a weak first-order transition.

Now a few words about fluctuations of the long-wavelength field s. They are, in principle, relevant in the whole region under study since we have assumed the condition $|\tau_s| \ll \lambda_s$ to be fulfilled, i.e., in essence we assumed that the system is close to the line of the continuous SA–SC transition. At the same time the fluctuations of s inducing the renormalization of the parameters of the theory do not qualitatively affect the structure of the phase diagram. For this reason we will not examine the role of the fluctuations of s all the more because it is a bulky procedure.

4.4. Macroscopic consequences

In fact, all what has been said in sections 2 and 3 about the influence of the order parameter fluctuations on macroscopic properties of the system, also holds for the case of weakly anisotropic systems, investigated in this section. The main characteristic, describing fluctuations of the field φ, is the gap Δ, which is small in the vicinity of the transition point as long as the transition is a weak first-order transition.

For the case of weakly anisotropic nematics we have studied, the field φ softens on the sphere in the reciprocal space. The distinction from the isotropic case is the fact that the "depth" of this softening is different in different points of the sphere. However the gap Δ, figuring in the correlation function, remains isotropic in the main approximation, therefore all the physical conclusions of section 2 concerning the influence of the order parameter fluctuations on macroscopic properties,

are also valid for the crystallization of weakly anisotropic nematics. It is natural that all formulas of section 2 must be modified in terms of the symmetry of structures resulting from the crystallization. As has been shown in subsection 4.1, the modification reduces to the redefinition, e.g., $\tau \to \tau + 2g$ for the transition into the smectic-A phase, and to some analogous redefinitions for other types of low-symmetry phases.

Therefore, for the weak crystallization of slightly anisotropic nematics, as well as for all other systems studied in our review, via the gap Δ we express the contributions, associated with the order parameter fluctuations, into the physical characteristics of the system. These contributions behave anomalously near the transition points. The contribution to such characteristics as the density or entropy proves to be $\Delta^{-1/2}$. The contribution to the heat capacity or compressibility is $\Delta^{-3/2}$. The coefficients of the bulk viscosity, associated with the sound absorption, exhibit the most pronounced singular behaviour near the phase transition. The anomalous contribution into these coefficients is $\Delta^{-5/2}$.

A similar behaviour is observed at the crystallization of weakly anisotropic smectics-C. The interaction of the order parameter fluctuations with the long-wavelength degrees of freedom brings about the softening of the system near the phase transition. This softening is, for instance, characterized by the contributions, proportional to Δ^{-1}, to c_1^{-2} and c_2^{-2}, where c_1 and c_2 are the velocities of the first and second sound in the smectic-C phase. Thus, these modes soften down near the phase transition point, i.e., the respective velocities or elasticity modules decrease. Fluctuations also lead to the growth of the bulk viscosity coefficients as Δ^{-2} and shear viscosity coefficients as Δ^{-1}.

A detailed comparison of the theoretical results, derived in this section, with the experimental data is hard at present. Firstly, our scheme involves a large number of unknown parameters. Secondly, the experimental studies of the vicinity of the crystallization transitions in liquid crystals are not numerous and scattered. Nevertheless, within the framework of our approach it is easy to qualitatively describe all observed sequences of phase transitions in liquid crystals. It is also easy to verify on the qualitative level all our predictions of the fluctuation softening near the crystallization phase transition points and of the increase of the viscosity coefficients. Note also that there are grounds to believe (see the concluding part of the work [Brazovsky, Dzyaloshinsky and Muratov 1987]) that the general conclusions of the model concerning the influence of fluctuations do not depend on its simplifying assumptions.

5. Conclusion

We have come to the end of our survey of the weak crystallization theory. Let us summarize: Weak crystallization is associated with a softening of the order parameter φ, describing the short-wavelength density modulation. This softening can occur in the vicinity of certain points or of certain lines or surfaces in the reciprocal space. The first case can be described in the framework of the conventional phase transition theory and is beyond the scope of our research. The softening of φ in the vicinity of a line or a surface in the reciprocal space induces a number of characteristic peculiarities of the transition the study of which is actually the subject of the weak crystallization theory.

The main characteristic of the system in the vicinity of such a transition is the value of the gap Δ, figuring in the expression for the pair correlation function $\langle\langle\varphi\varphi\rangle\rangle$. In the weak crystallization theory it is assumed that the value of Δ near the phase transition is small, i.e., much smaller than the characteristic values of Δ far from the phase transition. This small value actually expresses the "softening" of the field φ near the transition point.

In the weak crystallization theory the Landau expansion of the energy of the system in φ has, as a rule, a cubic term. It means that the phase transition over φ is a first-order phase transition. The value of this cubic term in the weak crystallization theory is assumed to be small enough, or else near the phase transition the softening of φ is not observed. There are also cases when the cubic term in the Landau expansion is equal to zero. In both cases the weak crystallization transition appears to be a first-order phase transition, close to a continuous one. This situation is realized in most crystallization phase transitions in liquid crystals.

Although the description of weak crystallization phase transitions is similar to that of conventional second-order phase transitions there is a rather important distinction. At conventional phase transitions (e.g., in magnets) the order parameter is a macroscopic long-wavelength variable (e.g., magnetization). At weak crystallization phase transitions the order parameter is a short-wavelength variable, which even in the mean field approximation determines a whole series of specific properties of these transitions, in particular, diversity of phase diagrams with various ordered phases.

A peculiarity of the weak crystallization theory is the important role of fluctuations of φ, accounted for by the large phase volume of fluctuations occurring in the vicinity of the mentioned line or surface in the reciprocal space. Fluctuation effects are strong due to the small value of Δ and generate a number of qualitative effects. For instance, fluctuations make the crystallization phase transition a first-order transition even in the absence in the Landau expansion of the term cubic in φ. Fluctuations also give rise to a fairly nontrivial behaviour of the gap Δ in the vicinity of the phase transition.

The phase diagram of the system in the weak crystallization theory is rather versatile. In this diagram there arise both crystalline phases of different symmetry as well as smectic, columnar and even quasicrystalline phases. At decreasing temperature there may occur a cascade of phase transitions. Typical sequences of transitions for the crystallization of various high-temperature phases are given in the text of the survey. Note only that the low-temperature phase of this cascade, as a rule, is a low-symmetry phase (e.g., for the crystallization of a liquid this is the smectic-A).

At decreasing temperature the behaviour of the gap Δ is quite universal. The gap Δ diminishes in the high-temperature phase, achieving its minimum in the point of transition into a consecutive phase. In this point Δ experiences a jump and at a further decrease of the temperature, grows experiencing positive jumps in all the points of consecutive first-order phase transitions.

The dynamics of the parameter φ is purely relaxational. The respective kinetic coefficient proves to be insensitive to the phase transition, therefore the relaxation time of φ is proportional to Δ^{-1} and achieves its maximum near the phase transition from the disordered phase. All physical characteristics of the system in some degree depend on how close it is to the crystallization phase transition. The contributions, associated with the parameter φ, to physical characteristics of the system, which exhibit an anomalous behaviour in the vicinity of the crystallization transition, are expressed via the gap Δ. The most marked singular behaviour near the phase transition is inherent in the viscosity coefficients, associated with the attenuation of acoustic modes.

In the weak crystallization theory it is possible to explain the amazing diversity of liquid-crystalline phases, emerging in a relatively narrow temperature range in real substances. Apart from this, a consequence of the theory is the anomalous behaviour of various physical characteristics, and, in the first place, the large values of the viscosity coefficients, which are one of the principal experimental characteristics of liquid crystals. Unfortunately, a straightforward comparison of theory and experiment is not easy.

Firstly, concrete peculiarities of phase transitions in the framework of the weak crystallization theory depend on a number of parameters. Among them one should mention parameters, characterizing the intensity of fluctuations of φ and the angular dependence of the quartic interaction

constant λ. Most of the results, cited in this survey, are obtained for the case λ = const.; some particular cases of the angular dependence of λ are also analyzed. A still larger number of parameters arise in the theory when one considers phase transitions, associated, for instance, with variation of the smectic density modulation period. A quantitative comparison of the theory with experiment requires a detailed knowledge of all these parameters.

Secondly, the phase transition picture in real liquid crystals is more complicated than the one given here. Alongside with crystallization transitions, there occur also orientational phase transitions in them (e.g., smectic-A–smectic-C or smectic-A–hexatic). At decreasing temperature different types of crystallization transitions may compete. Since the liquid-crystalline state is realized in a relatively narrow temperature range, all these phase transitions influence each other. An attempt to study the mutual influence of the orientational and crystallization phase transitions has been made in subsection 4.3. Besides, the sequences of phases, given in the main text of this survey can be violated due to the transition of a liquid crystal into a solid molecular crystal, which, as a rule, is a strong first-order transition.

Despite the difficulties of comparing theory with experiment, a number of concrete predictions of the theory (e.g., concerning the behaviour of the elasticity coefficients or viscosity) can be directly compared with experimental data. Besides, the theory makes it possible to connect the results of various (calorimetric, dynamic and X-ray) experiments. Near the weak crystallization point all quantities, measured in these experiments are expressed via the fundamental characteristics of the transition, i.e., the value of the gap Δ in the fluctuation spectrum.

Ultimately, we would like to stress that the presented theory reveals a number of universal peculiarities determining the qualitative picture of the weak crystallization.

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