Orientational phase transitions in liquid crystals. Critical dynamics

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We investigate the singularities of the dynamics of liquid crystals near orientational phase transitions. These are second-order phase transitions and can be conveniently used to demonstrate a general scheme developed by us for the description of critical dynamics. This scheme is based on nonlinear dynamic equations used to define an effective action with which to calculate macroscopic fluctuation effects by perturbation theory. The unrenormalized correlators are determined by the linearized dynamic equations, and the interaction vertices by nonlinear terms. Essentially, the proposed scheme is a procedure for excluding weakly-fluctuating variables from the effective action, so that the action is obtained for the order parameter. In the cases considered, this action describes purely relaxational dynamics and is renormalizable. We obtain the dispersion laws for all the natural modes near orientational phase transitions in smectics and nematics, and calculate their renormalization connected with fluctuations of the order parameter. This renormalization is determined by explicit expressions that contain one universal function having appropriate scaling properties. Damping of sound turns out to be the most sensitive to the fluctuations.

1. INTRODUCTION

An appreciable number of phases of varying symmetry are regarded as being in a liquid-crystal state. With respect to their properties, all these phases occupy an intermediate position between a liquid and a crystal. In addition, the liquid-crystal state is realized in a temperature interval intermediate between a liquid and a crystal, and liquid-crystal phases are therefore frequently called mesophases. Information on the main properties of liquid crystals can be found in de Gennes's classical monograph.[1] Liquid-crystal phases have been classified by symmetry in a survey by one of us (E. K.).[2]

It must be emphasized that matter in the liquid-crystal state exhibits a very extensive polymorphism. As the temperature varies it undergoes, as a rule, a number of phase transitions in an interval of a few tens of degrees. By using mixtures of different substances it is possible to make the phase diagram of the system even more detailed. All this makes it quite urgent to investigate effects connected with phase transitions in liquid crystals.

It can even be stated that without such an investigation none of the physical processes in liquid crystals can be understood. The point is that, in view of the relatively narrow region of its existence, matter in a liquid-crystal state is always close to some phase-transition point. Moreover, in the liquid-crystal state all transitions that are observed in practice are either second-order or weak first-order transitions. Allowance for critical phenomena is therefore obligatory for the description of the vicinities of these transitions.

The theoretical studies of phase transitions in liquid crystals have dealt so far almost exclusively with static properties. The singularities of many phase transitions in liquid crystals notwithstanding, the static properties of these transitions can by and large be described by the standard theory of phase transitions.[3,4] Much more diversified than the static critical phenomena are the dynamic ones, and their description is therefore more complicated.

A few words concerning the experimental situation. Detailed data are available by now on the behavior of ultrasound in various liquid-crystal phases.[5] One can deduce from these results the critical dependences of the elastic moduli and of the viscosity coefficients in various phase transitions. These results pertain to both the hydrodynamic and the critical regions. It is thus possible to present, on the basis of experiment, a certain picture of the critical dynamic behavior of liquid crystals.

The situation is much worse with the theoretical understanding of critical dynamic phenomena. There are practically no studies of this topic, owing both to the complexity of the dynamic phenomena in liquid crystals and to the unsatisfactory state of the theory of dynamic critical phenomena in general. We hope to fill this gap to some degree in the present paper.

Our starting point was a theoretical investigation of the singularities of the smectic *A*–smectic *C* phase transition, which is of second order. We investigated static critical phenomena[6] as well as the critical dynamics.[7] A very close examination has shown, however, that the theoretical scheme developed by us in the investigation of the smectic *A*–smectic *C* transition lends itself to a wide generalization and can be used to investigate practically all phase-transition types that occur in liquid crystals.

Moreover, the basic idea of the scheme in question, effective disregard of weakly fluctuating variables, can be used to construct a consistent general theory of critical dynamic phenomena. A logical consequence of such a construction would be a classification, as yet nonexistent, of the critical-dynamics types by universality classes, as is done for static critical phenomena.

We shall consider the following phase transitions: nematic–biaxial nematic, smectic *A*–smectic *C*, and smectic *A*–

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hexatic smectic B. These transitions are joined into a natural group which we call the group of orientational phase transition. The name stems from the fact that rotational symmetry is spontaneously broken in all these transitions.

The actual question is that of violation of the invariance of a system to rotation about the infinite-order axis possessed by the symmetry groups of an ordinary uniaxial nematic or smectic A. These axes run along the director in a nematic and along the normal to the smectic layers in smectic-A. Spontaneous violation causes the infinite-order axis to be replaced by a finite-order axis. It is convenient to designate the resultant states as $N_2,...,S_1,S_2,...$, where N and S denote respectively a nematic and a smectic, while the subscript denotes the order of the axis with respect to which the corresponding structure is invariant (respectively, the axis along the director in the N phases and along the normal to the layers in the S phases). The designations of initial phases, i.e., of the uniaxial nematic and smectic A, will be the traditional N and S_A.

In this notation, N_2 stands for a biaxial nematic, B–S_6 for a hexatic smectic, and S_1 for a smectic S_C in which the director is inclined to the normal to the layer. We shall use the latter designation along with the traditional S_C, i.e., $S_1 = S_C$.

It is also possible that some of the phases called smectic C may turn out to be S_2 phases, i.e., have a twofold axis in the direction normal to the layer. As a rule, the S_C phase constitutes a system of elongated molecules making an angle with the normal to the smectic layers. The S_2 phases can be visualized as a system of triaxial molecules whose principal axes are perpendicular to the smectic layers, but whose second axes are predominantly directed in the plane of the smectic layer. In optics both phases (S_1 and S_2) are biaxial and it is difficult to separate them experimentally.

Thus, the above transitions observed in liquid crystals are designated in our notation by N–N_2, S_A–S_6, S_A–S_1 (S_C), or S_A–S_2. The other types of phase transitions, N–N_n and S_A–S_2, have not yet been observed but they are not forbidden by symmetry and will hopefully be observed in experiment sooner or later. We shall consider all N–N_n, S_A–S_n transitions (both real and hypothetical) from a common viewpoint. This is justified, on the one hand, because all are of the same type from the theoretical standpoint, and on the other because the known orientational transitions have similar observable characteristics. We shall not discuss the N–N_1 transition, since it should be accompanied in a liquid crystal by a spontaneous dipole moment. The N–N_1 transition should therefore be considered separately.

All irreducible representations of the group of rotations around a preferred axis are known to be two-dimensional. The phase transitions N–N_n and S–S_n are therefore characterized by two-component order parameters Ψ. The order parameter can always be chosen to be complex, so that only the phase of Ψ and not its modulus is changed by rotation around the axis. The change of the phase Ψ by rotation through an angle φ should be equal to $n\varphi$. The integer n determines the rotation-group representation generated by Ψ. The number n is easily seen to coincide with the order of the symmetry axis of the low-temperature phase, in which the $\langle\Psi\rangle$ condensate differs from zero.

The free energy should be invariant under the group of rotations around a given axis. Therefore (disregarding weakly fluctuating variables) the expansion of the free energy in Ψ contains only terms even in Ψ, which are powers of the modulus of Ψ (since the phase of Ψ changes in the rotations). One should therefore expect the orientational transitions N–N_n and S_A–S_n to be of second order, in agreement with experiment.

The organization of this paper is the following. Section 2 describes the formal thermodynamics of systems near a second-order phase-transition point. The order parameter must then be included among the thermodynamic variables. We formulate the thermodynamic relations and investigate the character of the expansion of the energy in the order parameter.

Section 3 is devoted to a derivation of the nonlinear dynamic equations for the investigated nematic and smectic phases. Derivation of dynamic equations with allowance for the order parameter calls for a separate treatment. These equations must be used in investigations of the vicinity of the phase-transition point.

In Sec. 4 we consider the structure of the static correlators of the order parameter. We present results that are valid both in the mean-field theory and in the fluctuation region.

In Sec. 5 we consider the contributions of the order-parameter fluctuations to the dynamic characteristics of the system. For fully developed fluctuations these contributions agree with the dynamic-similarity hypothesis.

In Sec. 6 is analyzed the influence of order-parameter fluctuations on the spectrum of the natural modes of the system. Particularly strongly influenced are the acoustic-mode dispersion laws.

In the Conclusion we summarize the results and indicate directions for future research.

2. THERMODYNAMICS OF LIQUID CRYSTALS

Thermodynamic variables

We shall examine a liquid crystal from a macroscopic standpoint. This means that we are interested in scales and time intervals that are large compared with the molecular ones. In other words, the characteristic frequencies ω and the wave vector $\mathbf{q}$ must satisfy the inequalities

$$q \ll \Lambda, \quad \omega \ll \Omega.$$

The limiting wave vector Λ is determined by the molecular dimensions. It can be estimated to be 10^8 cm^{-1} for most liquid crystals. The limiting frequency can be estimated at $\Omega \sim c\Lambda \sim 10^{13}$ s^{-1}, where c is the speed of sound, of the order of 10^5 cm/s in all liquid crystals. The small parameter q/Λ is named hereafter hydrodynamic.

A few words concerning the thermodynamic variables that describe the macroscopic state of the systems. These variables are by definition slowly relaxing parameters (compared with the time Ω^{-1}), and include, in particular, the densities of the conserved quantities (energy, momentum, mass).

Another part of the slowly relaxing quantities is connected with spontaneous symmetry breaking. If this symmetry is continuous, its breaking makes the state of the system continuously degenerate and describable by a continuous degeneracy parameter. Of course, the uniform spatial distribution of this parameter does not relax, but in the inhomogeneous case the degeneracy parameter relaxes slowly to the extent that q/Λ is small.

The degeneracy parameter in a smectic is the displacement u of the smectic layers, which becomes a thermodynamic variable as a result of the spontaneous breaking of the translational symmetry. In a nematic, the degeneracy parameter connected with the spontaneous breaking of the rotational symmetry is the director $\mathbf{n}$. An angle φ must be added to these variables in the case of the S_A–S_n transitions. The variable is the degeneracy parameter connected with symmetry breaking with respect to rotation around a preferred axis, and has the meaning of the phase of the order parameter.

In the vicinity of a second-order phase transition it is necessary to include among the thermodynamic variables the order parameter Ψ, whose relaxation slows down near the phase-transition point. As already mentioned in the Introduction, a two-component order parameter corresponds to the orientational phase transitions we are considering. We shall dwell below in some detail on the structure of the order parameters for the N–N_n and S_A–S_n transitions.

It is convenient to set different regimes produced in the vicinity of a second-order phase-transition point in correspondence with regions on the T–q diagram (T is the temperature and q is the wave vector that defines the characteristic scale). These regions are shown in Fig. 1, where T_c is the transition temperature. Region 1 corresponds to the symmetric (high-temperature) phase. Region 2 is the critical one, where the relaxation rate of the order-parameter Ψ is comparable with the relaxation rates of the other thermodynamic variables. Region 3 corresponds to the asymmetric (low-temperature) phase, i.e., the phase with spontaneously broken symmetry.

In this last phase only a fraction of the degrees of freedom connected with the order parameter relaxes at a rate comparable with that of the other thermodynamic variables. The remaining degrees of freedom relax much more rapidly. The slowly relaxing degrees of freedom of the order parameter are none other than the degeneracy parameter discussed above. With regards to the transitions N–N_n and S_A–S_n considered by us it can be stated that the modulus of the order parameter "freezes" on going from region 2 to region 3, whereas its phase φ remains a "soft" variable.

Structure of the order parameters

The order parameters for the transitions N–N_n and S_A–S_n correspond, as already mentioned, to representations of the rotation group around a preferred axis and each has as a result two components. The situation is complicated by the fact that the direction of this preferred axis (which is determined by the director $\mathbf{n}$ in the nematic and by the by the normal $\mathbf{l}$ to the layers in the smectic) varies in space. It is therefore impossible in general to introduce the phase of the order parameter. One can only determine its variation (more below). The phase of the order parameter is well defined only for homogeneous $\mathbf{l}$ and $\mathbf{n}$. It is therefore necessary to determine correctly the order parameters for these transitions.

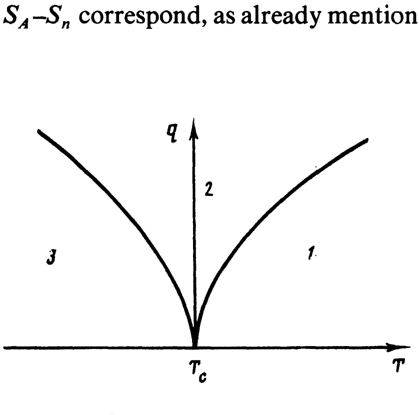

FIG. 1. Various regions on the T—q diagram. T_c—critical temperature. 1) High-temperature region, 2) critical region, 3) high-temperature region.

In the general case of inhomogeneous $\mathbf{l}$ and $\mathbf{n}$ the order parameters Ψ for these phase transitions are nth-rank tensors $\Psi_{ik...}$ satisfying the following conditions:

1) symmetry with respect to any pair of indices;

2) irreducibility, i.e., vanishing of the convolution with respect to any pair of indices;

3) orthogonality, i.e., $n_i\Psi_{i...k}=0$ for a nematic and $l_i\Psi_{i...k}=0$ for a smectic.

It is easy to verify that the number of independent components of the tensor $\Psi_{i...k}$ satisfying the above conditions is indeed equal to two.

Let us clarify the meaning of these tensor order parameters for smectic A–smectic C (S_A–S_1) and uniaxial nematic–biaxial nematic (N–N_2) phase transitions.

The order parameter for the S_A–S_1 transition is a vector defined as[6]

$$\boldsymbol{\Psi}=[\mathbf{n}\mathbf{l}]. \tag{2.1}$$

This vector is, as it should be, perpendicular to the normal to the smectic layers, and has two independent components. In the A phase the director $\mathbf{n}$ is collinear with $\mathbf{l}$, so that $\boldsymbol{\Psi}$ is zero. In the C phase the director $\mathbf{n}$ is inclined to $\mathbf{l}$, making $\boldsymbol{\Psi}$ different from zero. Therefore $\boldsymbol{\Psi}$ satisfies all the requirements imposed on the order parameter for the S_A–S_1 transition.

The order parameter for the N–N_2 transition is, in accord with the foregoing, the symmetric irreducible tensor Ψ_{ik}. It must be interpreted as the "biaxial part" of the nematic order parameter Q_{ik} represented in the form

$$Q_{ik}=Q_0(n_in_k-{}^1/_3\delta_{ik})+\Psi_{ik}. \tag{2.2}$$

Symmetry and irreducibility of Ψ_{ik} are ensured by the corresponding properties of Q_{ik}, while the condition $n_i\Psi_{ik}=0$ makes the partition (2.2) single-valued. In a uniaxial phase $\Psi_{ik}=0$, i.e., Ψ_{ik} also satisfies in this case all the requirements for the order parameter.

The order parameter of the smectic A–hexatic smectic B (S_A–S_6) transition is a sixth-rank tensor that is symmetric, irreducible, and orthogonal to $\mathbf{l}$.

A few words concerning the modulus and phase of the order parameter. Introduction of the phase $|\Psi|$ entails no difficulty: the square of this modulus is equal to the sum of the squares of the components of the corresponding tensor. The phase of the order parameter can in the general case not be introduced, and only the phase variation $\delta\varphi$ can be defined. In other words, the order-parameter phase is a nonholonomic variable.

By our definition, $\delta\varphi$ is such that when the changes of the modulus and of phase are respectively $\delta|\Psi|$ and $\delta\varphi$ the change of the order parameter (2.1) is

$$\delta\Psi_i=-\frac{1}{2}\delta\varphi\varepsilon_{ikn}l_k\Psi_n+\frac{\delta|\Psi|}{|\Psi|}\Psi_i, \tag{2.3}$$

where ε_{ikn} as an antisymmetric tensor. If the order parameter is a tensor of rank n, its variation with φ is a sum over all the indices of terms similar to the first term in the right-hand side of (2.3). For a nematic it is then necessary to replace the normal **l** in the definition introduced above by the director **n**. Thus, for example, for the order parameter corresponding to the N–N_2 transition we have

$$\delta\Psi_{ik}=-\frac{1}{2}\delta\varphi(\varepsilon_{imn}n_n\Psi_{nk}+\varepsilon_{kmn}n_m\Psi_{in})+\frac{\delta|\Psi|}{|\Psi|}\Psi_{ik}. \tag{2.4}$$

Nonholonomy of the angle φ raises no problems if a uniform spatial distribution can be assumed for the director **n** in the nematic or for the normal **l** in the smectic. This is precisely the situation with which we shall deal hereafter. We can then specify locally not only the variation $\delta\varphi$ but also the phase φ itself. In this case the order parameter is taken to be the two-component quantity

$$\Psi=(|\Psi|\cos 2\varphi,\ |\Psi|\sin 2\varphi). \tag{2.5}$$

Thermodynamic potential

The thermodynamic properties of the system are described by the thermodynamic potentials. We shall find it convenient to define as the thermodynamic potential the combination

$$\mathscr{H}=\int d^3r(E-\mu_T\rho-T_TS). \tag{2.6}$$

Here E is the energy density, ρ is the mass density, S is the entropy density, and μ_T and T_T are respectively the chemical potential and the temperature of the thermostat. We designate hereafter by $\mathscr{H}$ the Hamiltonian of the system (the meaning of this designation will be made clear in the derivation of the dynamic equations).

The energy density E is represented by the sum

$$E=j^2/2\rho+\varepsilon, \tag{2.7}$$

of the kinetic and internal energies. We designate by j the momentum density

$$\mathbf{j}=\rho\mathbf{v},$$

where **v** is the velocity. The internal energy ε depends on ρ and S. In a nematic ε is also a function of the director **n** and of its gradient, while in a smectic it is a function of the derivatives of the displacements u of the smectic layers. For low-symmetry phases it is necessary to add to these variables the phase φ of the order parameter. More accurately speaking, ε depends on the gradients of the degeneracy parameter φ. In the fluctuation region (region 2 of Fig. 1) account must be taken of both the phase and the modulus of the order parameter.

A nonuniform spatial distribution of the director in a nematic adds to the system energy a positive contribution called the Frank energy. The corresponding energy density can be expressed in the form[1]

$$E_F={}^1/{}_2K_1(\nabla\mathbf{n})^2+{}^1/{}_2K_2(\mathbf{n}[\nabla\mathbf{n}])^2+{}^1/{}_2K_3((\mathbf{n}\nabla)\mathbf{n})^2. \tag{2.8}$$

The coefficients K_1, K_2, and K_3 in this expression are called the Frank moduli.

In the low-temperature phases N_n and S_n we can introduce in similar fashion the energy due to inhomogeneity of the order parameter. The energy density takes the form

$$E_{or}={}^1/{}_2\alpha_\parallel(\nabla_\parallel\varphi)^2+{}^1/{}_2\alpha_\perp(\nabla_\perp\varphi)^2. \tag{2.9}$$

For a nematic we have here

$$\nabla_\parallel=n_i\nabla_i,$$
$$(\nabla_\perp\varphi)^2=(\delta_{ik}-n_in_k)\nabla_i\varphi\nabla_k\varphi.$$

For a smectic the director **n** in these expressions should be replaced by the normal **l**. The orientational energy has a somewhat more complicated form for the phase $S_1=S_c$, in which case the energy is characterized by three independent moduli.

We assume hereafter that in equilibrium the director **n** of a nematic or the normal **l** of a smectic are homogeneous in space and are directed along the z axis. The vector and tensor components along the axes x and y will be labeled by Greek subscripts. Note that that these are the only nonzero tensor order-parameter components if **n** or **l** is uniformly distributed in the tensor parameters introduced above.

It is convenient to describe the deformation of smectic layers by their displacements u along the z axis. The nonuniform deformation of these layers is the source of elastic energy whose density is given by[1,8]

$$E_s={}^1/{}_2B(\nabla_zu)^2+{}^1/{}_2K(\nabla^2u)^2. \tag{2.10}$$

Here B is the bulk modulus of the smectic layers, and the modulus K specifies the flexure energy. The modulus K is close in magnitude to the Frank moduli in nematics. The second term in the right-hand side of (2.10) contains higher powers of the spatial derivatives than the first term, and the hydrodynamic parameter in it is therefore smaller. We shall therefore as a rule neglect the term with modulus K. This term has to be introduced in the elastic energy (2.10) because there is no layer shear modulus in a smectic.

Expansion of energy near a phase transition point

The theoretical investigation of the properties of a phase transition is based on the well known Landau expansion of the energy in terms of the order parameter Ψ. Since the phase φ of the order parameter is changed by rotation in the orientational phase transitions considered by us, the expansion in question contains only terms even in the order parameter. The transitions N–N_n and S_A–S_n can therefore be expected to be of second order.

The first terms of the expansion of the energy density in terms of Ψ are of the form

$$E_\Psi={}^1/{}_2A\Psi^2+{}^1/{}_4U'\Psi^4. \tag{2.11}$$

The quantity A in (2.11) vanishes at the phase-transition point, so that near the temperature of this transition we have

$$A\propto T-T_c. \tag{2.12}$$

The factor U' preceding Ψ^4 in (2.11) has no critical behavior and can be regarded as constant near the phase transition.

The expansion (2.11) is valid if the order parameter Ψ is small. A typical value of Ψ in the mean-field theory is estimated to be $\Psi\approx(A/U')^{1/2}$. This value is indeed small because A is small in the vicinity of the phase-transition point. Allowance for the fluctuations of Ψ does not alter the situation qualitatively. Thus, in an investigation of a phase transition we can confine ourselves to the expansion (2.11) and discard higher powers of Ψ.

Beside the expansion terms in (2.11), allowance must be made in an investigation of a phase transition for the gradient contribution:

$$E_{grad}={}^1/_2L_\parallel(\nabla_z\Psi)^2+{}^1/_2L_\perp(\nabla_\alpha\Psi)^2. \tag{2.13}$$

Here $L_\parallel$ and $L_\perp$ are the elastic moduli. In (2.13), just as in (2.9), we have neglected the inhomogeneity of the director $\mathbf{n}$ or of the normal $\mathbf{l}$. The order parameter can accordingly be chosen in the form (2.5). The gradient term in the smectic S_1 (S_c) has a somewhat more elaborate form.

Note that the terms beyond (2.13) in the expansion in terms of the gradients of Ψ [e.g., the term proportional to $(\nabla^2\Psi^2)$] are smaller by the hydrodynamic parameter than those retained in (2.13). Since the coefficient A is small, it is expedient to retain the gradient term (2.13) itself alongside the first term of (2.11).

It will be convenient below to reckon the thermodynamic variables from their values at the critical point. We thus introduce the variables

$$\varphi_\rho=\rho-\rho_c,\quad \varphi_\sigma=\sigma-\sigma_c. \tag{2.14}$$

Here $\sigma=S/\rho$ is the specific entropy. It is analogously convenient to introduce in place of the displacement u of the smectic layers the variable

$$\varphi_u=-\nabla_z u, \tag{2.15}$$

representing the relative change (with temperature) of the distance between layers.

We shall designate the aggregate of variables (φ_ρ, φ_σ) for the nematic and (φ_ρ, φ_σ, φ_u) for the smectic by the symbol φ_a. The φ_a vanish at the phase transition point, but in its vicinity they are small parameters in terms of which physical quantities can be expanded.

Let us examine the principal terms of the expansion of $\mathcal{H}$ in terms of φ_a. The first term of this expansion is zero because of the equilibrium conditions. The quadratic term, however, can be written in the form

$$\mathcal{H}_{el}=\int E_{el}\,d^3r,$$

where the energy density is given by

$$E_{el}={}^1/_2\beta_{ab}\varphi_a\varphi_b. \tag{2.16}$$

Summation over the dummy indices a and b is implied throughout. By analogy with standard elaasticity theory, we can call (2.16) the elastic energy and the β_{ab} matrix the bare matrix of the elastic moduli. The β_{ab} coefficients have no substantial critical behavior and can be regarded as constants in the vicinity of a transition point.

For a nematic the components of the matrix β take the form

$$\beta_{\rho\rho}=\frac{1}{\rho}\left(\frac{\partial P}{\partial\rho}\right)_\sigma,\quad \beta_{\sigma\rho}=\beta_{\rho\sigma}=\frac{1}{\rho}\left(\frac{\partial P}{\partial\sigma}\right)_\rho,$$
$$\beta_{\sigma\sigma}=\rho\left(\frac{\partial T}{\partial\sigma}\right)_\rho. \tag{2.17}$$

Here P is the pressure and T is the (local) temperature. For a smectic it is necessary to consider in addition to (2.17) also the components

$$\beta_{uu}=B,\quad \beta_{u\rho}=\beta_{\rho u}=\frac{\gamma_\rho B}{\rho},\quad \beta_{u\sigma}=\beta_{\sigma u}=\frac{\gamma_\sigma B}{\rho}. \tag{2.18}$$

The modulus of B was introduced in (2.10), while γ_σ and γ_ρ are constants on the order of unity, and are given in terms of the derivatives of the distance l between the smectic layers by

$$\gamma_\rho=-\left(\frac{\partial\ln l}{\partial\ln\rho}\right)_\sigma,\quad \gamma_\sigma=-\left(\frac{\partial\ln l}{\partial\ln\sigma}\right)_\rho.$$

In the leading approximation, the coefficient A in expansion (2.11) is a linear combination of the values of φ:

$$A=\Xi_a\varphi_a. \tag{2.19}$$

Here Ξ_a are certain constants. As expected, expression (2.19) vanishes at the phase-transition point (when $\varphi_a=0$). The first terms of (2.11) take thus the form

$$E_{int}={}^1/_2\Xi_a\varphi_a\Psi^2. \tag{2.20}$$

This expression has the meaning of the energy of the interaction between the order parameters and other thermodynamic degrees of freedom.

3. DYNAMIC EQUATIONS

Poisson-brackets method

The nonlinear hydrodynamic equations for a classical fluid are well known. It is not simple to generalize these equations to the case of a liquid crystal with symmetry lower than a liquid. We must, in addition, include in the system of dynamic equations a nonlinear equation for the order parameter Ψ. We devote therefore a special section to the derivation of the dynamic equations.

It is simplest to obtain the nondissipative terms of these equations by using the method of Poisson brackets. A systematic exposition of this method can be found in a review by Dzyaloshinskiĭ and Volovik[9] and a monograph by Kats and Lebedev,[8] which deal mainly with liquid crystals. We explain here briefly the main ideas of this method.

In the Poisson-bracket method the nondissipative dynamic equations for the variables take the form

$$\frac{\partial\varphi_a}{\partial t}=\{\mathcal{H},\varphi_a\}. \tag{3.1}$$

Here $\mathcal{H}$ is the Hamiltonian of the system and the braces are the Poisson brackets. The quantities φ_a are in our case the thermodynamic variables of the system, and we use the Hamiltonian (2.6).

Note that the quantity $\mathcal{H}$ defined by (2.6) is not the total energy of the system. The difference, however, reduces to terms proportional to the system mass and entropy. Since these are conserved quantities (recall that we are dealing with a nondissipative regime in which the entropy is conserved), this difference does not affect the equations of motion. The advantage of using this definition of $\mathcal{H}$ will be made clear when fluctuation effects are considered.

A Poisson bracket can be defined for any pair of variables, and the bracket $\{\varphi_a,\varphi_b\}$ should be antisymmetric under permutation of the variables. In terms of $\{\varphi_a,\varphi_b\}$ the bracket in (3.1) takes the form

$$\{\mathscr{H}, \varphi_a(\mathbf{r})\} = \int d^3r_1 \frac{\delta\mathscr{H}}{\delta\varphi_b(\mathbf{r}_1)} \{\varphi_b(\mathbf{r}_1), \varphi_a(\mathbf{r})\}. \tag{3.2}$$

Summation over the dummy index b is implied. Using (3.2) it is easy to verify that antisymmetry of the bracket $\{\varphi_a,\varphi_b\}$ is ensured by the energy conservation law.

Consider a system of Poisson brackets for the hydrodynamic variables of a classical liquid. We choose these variables to be the momentum density j and the mass density ρ, as well as the specific entropy $\sigma = S/\rho$. The expressions for the nonzero brackets are

$$\begin{gathered} \{j_i(\mathbf{r}_1), j_k(\mathbf{r}_2)\} = j_k(\mathbf{r}_1)\nabla_i\delta(\mathbf{r}) + \nabla_k\delta(\mathbf{r})j_i(\mathbf{r}_1), \\ \{j_i(\mathbf{r}_1), \rho(\mathbf{r}_2)\} = \rho(\mathbf{r}_1)\nabla_i\delta(\mathbf{r}), \\ \{j_i(\mathbf{r}_1), \sigma(\mathbf{r}_2)\} = -\nabla_i\sigma\delta(\mathbf{r}). \end{gathered} \tag{3.3}$$

Here $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$.

If we choose for the Hamiltonian $\mathscr{H}$ Eq. (2.6) with the energy density E of a classical liquid, we obtain using (3.2) and (3.3) the well-known nondissipative equations of an ideal isotropic liquid. Expressions (3.3) are universal and are valid for arbitrary systems, including liquid crystals.

The nondissipative dynamic equations must be invariant under time reversal. Equations (3.1) meet this condition if the expression $\{\varphi_a(\mathbf{r}_1),\varphi_b(\mathbf{r}_2)\}$ for the bracket and the product $\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)$ respond differently to time reversal: one quantity reverses sign, and the other does not. This condition should be met by an expression for any Poisson bracket and is satisfied, of course, also by (3.3).

All the foregoing means that for these liquid-crystal systems only brackets of the form $\{j_i(\mathbf{r}_1),\varphi_a(\mathbf{r}_2)\}$ differ from zero in leading order. The point is that when time is reversed the only one of our thermodynamic variables, the momentum density, reverses sign. For the remaining variables, the expression for the bracket $\{\varphi_a,\varphi_b\}$ should therefore contain (as a result of Galilean invariance) a velocity gradient. Such terms can be neglected in the long-wave limit.

In the general case, the expression for the bracket $\{j_i(\mathbf{r}_1),\varphi_a(\mathbf{r}_2)\}$ takes the form

$$\{j_i(\mathbf{r}_1), \varphi_a(\mathbf{r}_2)\} = -\nabla_i\varphi_a\delta(\mathbf{r}) + \nabla_k\delta(\mathbf{r}) f_{a,ik}(\mathbf{r}_2). \tag{3.4}$$

Recall that $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$. The explicit form of the function $f_{a,ik}$ for the momentum density, and also for the variables φ_ρ and φ_σ introduced by us, follows from (3.3). The explicit form of $f_{u,ik}$ for our variable φ_u follows from the expression[8]

$$\{j_i(\mathbf{r}_1), u(\mathbf{r}_2)\} = -\nabla_i(u-z)\delta(\mathbf{r}). \tag{3.5}$$

We have thus for the variables introduced above

$$f_{\rho,ik} = \rho\delta_{ik}, \quad f_{\sigma,ik} = 0, \quad f_{u,zz} = 1 + \varphi_u, \quad f_{u,\alpha z} - \nabla_\alpha u. \tag{3.6}$$

The remaining components of $f_{u,ik}$ are equal to zero.

An expression for the order-parameter modulus is

$$\{j_i(\mathbf{r}_1), |\Psi|(\mathbf{r}_2)\} = -\nabla_i|\Psi|\delta(\mathbf{r}). \tag{3.7}$$

As for the nonholonomic phase φ of the order parameter, the form of the Poisson bracket $\{j,\varphi\}$ follows from the need to ensure conservation of the angular momentum:[10]

$$\{j_i(\mathbf{r}_1), \varphi(\mathbf{r}_2)\} = -\nabla_i\varphi\delta(\mathbf{r}) - \varepsilon_{ikn}\nabla_k\delta(\mathbf{r}) l_n(\mathbf{r}_2). \tag{3.8}$$

This expression pertains to smectics. For nematics the normal $\mathbf{l}$ to the layers must be replaced by the director $\mathbf{n}$. The expression for the bracket $\{\mathbf{j},\Psi\}$ is now derived on the basis of relations of the form (2.3) and (2.4). Expressions (3.7) and (3.8) are valid for N–N_n and S_A–S_n transitions at $n > 2$. The singularities of the Poisson bracket $\{\mathbf{j},\Psi\}$ for transitions with $n = 1$ and 2 are discussed at the end of the present section.

General dynamic equations

In the preceding section we have cited all the relations needed to construct the reactive (nondissipative) part of the dynamic equations. The nondissipative equations for the thermodynamic variables take the form (3.1). In the nondissipative terms it is necessary to add to the right-hand sides of the dynamic equations the kinetic (dissipative) terms. This is done in the usual manner using a dissipative function.[11]

Using the general form (3.4) of the Poisson bracket and taking into account the dissipation described by the rate coefficients, we can express the dynamic equation for all the thermodynamic variables φ_a (with exception of the momentum density $\mathbf{j}$) in the form

$$\frac{\partial\varphi_a}{\partial t} = -\mathbf{v}\nabla\varphi_a - \nabla_k v_i f_{a,ik} - \Gamma_{ab}\frac{\delta\mathscr{H}}{\delta\varphi}. \tag{3.9}$$

Here $\mathbf{v}$ is the mean mass velocity and Γ_{ab} is the differential operator determined by the set of rate coefficients. By virtue of the Onsager symmetry, the operator Γ_{ab} should be self-adjoint. Furthermore, this operator must have positive-definite eigenvalues to ensure positive entropy production.

The equation for the momentum density requires special consideration. The nondissipative term of this equation, constructed as prescribed by (3.1), reduces to the divergence of the reactive stress tensor. The explicit expression for this stress tensor, with allowance for (3.4), is

$$T_{ik} = -E\delta_{ik} + \frac{\partial E}{\partial\nabla_k\varphi_a}\nabla_i\varphi_a + \frac{\delta\mathscr{H}}{\delta\varphi_a} f_{a,ik}. \tag{3.10}$$

Here E is the energy density, and repeated indices imply summation over all the thermodynamic variables of the system, including the momentum density $\mathbf{j}$ and (in the critical region) the order parameter Ψ.

Taking also into account in the equation for $\mathbf{j}$ the viscosity-induced dissipation, we ultimately obtain

$$\frac{\partial j_i}{\partial t} = -\nabla_k T_{ik} - \nabla_k(\eta_{iknm}\nabla_n v_m). \tag{3.11}$$

Here η_{iknm} is the viscosity tensor. In view of angular-momentum conservation, this tensor is symmetric in both the first and the second pair of indices, and as a result of the Onsager symmetry it is symmetric under permutation of a pair of indices. The number of independent components of the viscosity tensor is quite large in an anisotropic sustem such as a liquid crystal. In uniaxial phases, such as N and S_A, η_{iknm} has five independent components.[1,8] In the biaxial phases N_n and S_n with $n \leqslant 4$ the number of independent components η_{iknm} increases to 13. Near the N–N_n, S_A–S_n transition point, however, the deviation of the viscosity tensor from uniaxial is small when T is close to T_c.

We present the hydrodynamic equations in explicit form. The simplest is the equation for the mass density

$$\frac{\partial\rho}{\partial t} = \nabla\mathbf{j}, \tag{3.12}$$

in which there is no dissipative term because of the Galilean invariance.

As a result of (3.3), Eq. (3.9) for the specific entropy takes the rather simple form

$$\frac{\partial\sigma}{\partial t}=-\mathbf{v}\nabla\sigma+\frac{1}{\rho}\nabla_i\left(\frac{\varkappa_{ik}}{T}\nabla_k T\right). \qquad (3.13)$$

Here $\varkappa_{ik}$ is the heat-conduction tensor. In the N and S_A uniaxial phases this tensor has two independent components, while in the N_n, S_n, $n\leqslant 2$ non-uniaxial phases the number of independent components $\varkappa_{ik}$ becomes larger. Near the phase-transition points, however, the deviation of the tensor $\varkappa_{ik}$ from uniaxial can be neglected. Generally speaking, the right-hand side of (3.13) should contain also a term proportional to the dissipative function and describing the entropy growth. This term, however, is of next-higher order in the hydrodynamic parameter, and we leave it out for simplicity.

We present now an equation for the director $\mathbf{n}$ in a nematic. The actual form of this equation is set by the angular-momentum conservation law.[8] It is convenient to use Eq. (3.9) for $\mathbf{n}$:

$$\frac{\partial n_m}{\partial t}=-(\mathbf{v}\nabla)n_m-\nabla_k v_i f_{m,ik}-\gamma_1^{-1}\frac{\partial\mathscr{H}}{\partial n_m}. \qquad (3.14)$$

Here

$$f_{m,ik}={}^1/_2(\delta_{km}n_i-\delta_{im}n_k)-\lambda(n_i\delta_{km}{}^\perp+n_k\delta_{im}{}^\perp),$$
$$\frac{\delta\mathscr{H}}{\delta n_m}=\delta_{mk}{}^\perp\left(\frac{\partial E}{\partial n_k}-\nabla\frac{\partial E}{\partial\nabla n_k}\right), \qquad (3.15)$$

where

$$\delta_{ik}{}^\perp=\delta_{ik}-n_in_k.$$

The quantity λ in (3.15) is a nondimensional reactive parameter of order unity, while γ_1 is known as the torsional viscosity coefficient.

The equation for φ_u in smectics is best found by differentiating the equation for the displacement vector $\mathbf{u}$. The nondissipative term in this equation can be found following the prescription (3.1) and using the bracket (3.5). By adding a kinetic term to this equation, we get

$$\frac{\partial u}{\partial t}=v_z-\mathbf{v}\nabla u-\xi_1\frac{\delta\mathscr{H}}{\delta u}. \qquad (3.16)$$

Here

$$\frac{\delta\mathscr{H}}{\delta u}=-\nabla\frac{\partial E}{\partial\nabla u}+\nabla_i\nabla_k\frac{\partial E}{\partial\nabla_i\nabla_k u}.$$

The kinetic coefficient $\xi_1>0$ is called the percolation coefficient, because the last term in (3.16) determines the difference between the displacement velocity of the smectic layer from the mean mass velocity, i.e., the "percolation" of the liquid crystal through the system of smectic layers. Generally speaking, the right-hand side of (3.16) contains one more thermomechanical dissipation cross-term that also describes percolation. This calls for introducing one more percolation coefficient.[8] To avoid complexity and bearing in mind that thermomechanical percolation changes nothing in our analysis, we have left out this term from (3.16).

In the low-temperature N_n and S_n phases, the independent soft variable is the angle φ (the phase of the order parameter). For $n>2$ the nondissipative part of the equation for φ can be obtained from (3.1) with the aid of (3.8). Adding the dissipative contribution to this equation, we obtain

$$\frac{\partial\varphi}{\partial t}=-(\mathbf{v}\nabla)\varphi-\nabla_k v_i n_j e_{jki}-\gamma^{-1}\frac{\delta\mathscr{H}}{\delta\varphi}. \qquad (3.17)$$

For smectics, the director $\mathbf{n}$ in (3.17) must be replaced by the normal $\mathbf{l}$. The singularities of the dynamic equation for φ in the phases S_n and N_n with $n=1$ and 2 will be considered below. The kinetic coefficient γ in (3.17) has the dimension of viscosity and can be called orientational viscosity.

Let us consider, finally, the order-parameter equation needed to investigate the critical dynamics. In accordance with (3.9), this equation has the form

$$\frac{\partial\Psi}{\partial t}=-(\mathbf{v}\nabla)\Psi-\nabla_k v_i f_{\Psi,ik}-\Gamma\frac{\delta\mathscr{H}}{\delta\Psi}. \qquad (3.18)$$

Here Γ is a rate coefficient with dimension of the inverse of viscosity. The expression for $f_{\Psi,ik}$ in (3.18) is determined by (3.7) and (3.8):

$$f_{\Psi,ik}=-e_{ikn}l_n\frac{\partial\Psi}{\partial\varphi}. \qquad (3.19)$$

For a nematic, $\mathbf{l}$ must be replaced here by $\mathbf{n}$. This expression is valid for S_A–S_n, and N–N_n transitions with $n>2$. The singularities of the $f_{\Psi,ik}$ structure for transitions with $n=1$ or 2 will be discussed at the end of this section.

Principal dynamic nonlinearities

The order parameter Ψ is small near the phase-transition point. In addition, φ_ρ, φ_σ, and φ_u are small parameters since they vanish at the transition point and are consequently small in its vicinity. In investigations of the critical dynamics, the general nonlinear equations formulated in the preceding section must be expanded in terms of these variables, with the principal terms of the expansion retained. The terms linear in φ_ρ, φ_σ, and φ_u should be retained together with those quadratic in Ψ.

The variation of the unit vector of the normal to the smectic layers is approximately

$$l_\alpha\approx-\nabla_\alpha u.$$

Recall that Greek subscripts label components along the x and y axes. In view of the last relation, $\mathbf{l}$ deviates little from equilibrium so that it can be assumed in practically all the equations that $\mathbf{l}$ is a unit vector along the z axis. For a phase transition in a nematic, the director $\mathbf{n}$ can in most equations also be assumed equal to its equilibrium value—a unit vector along the z axis. Some singularities are exhibited only by the transition N–N_2, which will be considered below.

We derive first an equation for the order parameter (3.18). Since we assume the vectors $\mathbf{n}$ and $\mathbf{l}$ to be uniform in space, we can introduce not only the variation $\delta\varphi$ of the phase of the order parameter Ψ, but also the phase φ itself. We assume the order parameter here to be the two-component quantity (2.5).

The transport (convective) term in (3.18)—the first term in the right-hand side—can be omitted as small relative to the hydrodynamic parameter. For the same reason we can omit the second term in (3.18) for the transitions N–N_n and S_A–S_n at $n>2$, for in this case $f_\Psi\propto|\Psi|$. We arrive thus at the following relaxation equation:

$$\frac{\partial\Psi}{\partial t}=-\Gamma(A\Psi+U'\Psi\Psi^2-L_\parallel\nabla_z^2\Psi-L_\perp\nabla_\alpha^2\Psi). \quad (3.20)$$

We have used here expressions (2.11) and (2.13) for the principal terms of the expansion of the energy density in terms of the order parameter.

Equation (3.20) is not a closed equation for the order parameter Ψ. The point is that the constant A in (3.20) depends, in accordance with (2.19), on the variables φ_ρ, φ_σ, and φ_u. Equation (3.20) must therefore be supplemented by the equation for these variables, which are defined by (3.10), (3.13), and (3.16)

These equations, with the principal nonlinearities retained, are

$$\frac{\partial\varphi_\rho}{\partial t}=-\rho\nabla\mathbf{v}, \quad (3.21a)$$

$$\frac{\partial\varphi_\sigma}{\partial t}=-\frac{1}{\rho^2T}(\varkappa_\parallel\nabla_z^2+\varkappa_\perp\nabla_\alpha^2)\left(\beta_{\sigma b}\varphi_b+\frac{1}{2}\Xi_\sigma\Psi^2\right), \quad (3.21b)$$

$$\frac{\partial\varphi_u}{\partial t}=-\nabla_zv_z+\xi_1\left(\beta_{ua}\varphi_a+\frac{1}{2}\Xi_u\Psi^2\right). \quad (3.22)$$

The last equation, with the subscripts a and b in (3.21) and (3.22) assuming the values ρ, σ, and u, should be used for the smectic phase. For the nematic phase, a and b assume the values ρ and σ. We have introduced in (3.21) the longitudinal and transverse components of the heat-conduction tensor. The matrix β_{ab} is defined by Eqs. (2.16), (2.17) and (2.18), and the coefficients Ξ_a by Eqs. (2.19) and (2.20).

Finally, we shall need Eq. (3.11) for the momentum density. Using the explicit expressions (3.6), we obtain for the reactive part of the stress tensor (3.10), in first-order approximation, the expression

$$T_{ik}\approx f_{a,ik}(\beta_{ab}\varphi_b+{}^1/{}_2\Xi_a\Psi^2). \quad (3.23)$$

Only the components $f_{\rho,ik}$ and $f_{u,ik}$ differ from zero, and it follows from (3.6) that their values, in the first-order approximation, are

$$f_{\rho,ik}=\rho\delta_{ik}, \quad f_{u,ik}=l_il_k. \quad (3.24)$$

For the nematic phase there are no terms in T_{ik} connected with elasticity of the smectic layers. They are replaced in the right-hand side of (3.23) by a term generated by the Frank energy (2.8) and by the function (3.15). An explicit expression for this term can be found in Katz and Lebedev's monograph[8] and will not be given here. We mention only that it is of next higher order in the hydrodynamic parameter, that in the first-order approximation the term connected with the Frank energy is simply added to (3.23), and that no cross terms are produced.

Dynamical behavior of the transitions S_A–$S_C(S_1)$, S_A–S_2, and N–N_2

A feature of these transitions is the low symmetry of the corresponding order parameter. It is a vector for the S_A–S_1 (S_C) transition and a second-rank tensor for the transitions N–N_2 and S_A–S_2 (see the discussion in Sec. 2). The low symmetry of Ψ for the S_A–S_C (S_1) transition manifests itself even in static effects. In the dynamics all the above transitions for which the distinguishing feature is the form of Eq. (3.18) for the order parameter are pronounced.

The point is that the quantity $f_{\Psi,ik}$ in (3.18) does not reduce to (3.19) for these transitions. This difference is very significant, since the quantity (3.19) is linear in the order parameter and is therefore small near a transition point. At the same time, the value of $f_{\Psi,ik}$ for the S_A–S_C (S_1), S_A–S_2, and N–N_2 transitions is not small near the transition point, and therefore plays a substantial role in the dynamics of Ψ. Let us present explicit expressions for those contributions to $f_{\Psi,ik}$ which remain finite at the phase-transition point.

The order parameter for the S_A–S_c phase transition is the vector Ψ_m. Expression (3.4) and Eq. (3.10) contain the quantity $f_{m,ik}$, the nonvanishing contribution to which is equal to

$$f_{m,ik}=\lambda_1l_j(\varepsilon_{jim}l_k+\varepsilon_{jkm}l_i). \quad (3.25)$$

This tensor is orthogonal to l_m and is symmetric in the indices i and k. The former property is due to the condition $l_i\Psi_i=0$, and the second ensures symmetry of the corresponding contribution to the stress tensor (3.11). Equation (3.25) contains a reactive parameter λ_1 analogous to the parameter λ in (3.15).

The order parameter for the phase transitions S_A–S_2 and N–N_2 is the second-rank tensor Ψ_{mn}. Equations (3.4) and (3.18) contain the quantity $f_{mn,ik}$, the nonvanishing contribution to which is

$$f_{mn,ik}=\lambda_2(\delta_{in}{}^\perp\delta_{mk}{}^\perp+\delta_{im}{}^\perp\delta_{km}{}^\perp-\delta_{ik}{}^\perp\delta_{mn}{}^\perp). \quad (3.26)$$

Here $\delta_{ik}^\perp=\delta_{ik}-l_il_k$ for a smectic and $\delta_{ik}^\perp=\delta_{ik}-n_in_k$ for a nematic. The tensor (3.26) is symmetric in the indices m and n, its trace over these indices is zero, and $\mathbf{l}$ or $\mathbf{n}$ is orthogonal in the same indices to (3.26). These properties reflect the structure of the tensor Ψ_{mn}. In addition, (3.26) is symmetric in the indices i and k, thereby ensuring the symmetry of the stress tensor. The reactive parameter λ_2 in (3.26) is analogous to the parameters λ and λ_1 introduced above.

4. STATIC FLUCTUATIONS

Effective Hamiltonian

We are interested in effects due to fluctuations of macroscopic (thermodynamic) quantities. To this end we must know the distribution function of these fluctuations. In the static case the distribution function is defined, apart from a normalization factor, as[12]

$$\exp(-\mathscr{H}/T_T). \quad (4.1)$$

Recall that the Hamiltonian $\mathscr{H}$ in (4.1) was defined in (2.6), and T_T is the temperature of the thermostat.

The Hamiltonian $\mathscr{H}$ is a functional of the complete set of the thermodynamic variables φ_a of the system. Since we are interested in effects due to fluctuations of the order parameter Ψ, this parameter must be included among the thermodynamic variables. The distribution function (4.1) makes it possible to calculate the correlation functions of φ_a and Ψ. These functions are represented in the form of the following path integral:

$$\langle\varphi_a\varphi_b\ldots\rangle=Z_0^{-1}\int D\varphi\, D\Psi\exp\left(-\frac{\mathscr{H}}{T_T}\right)\varphi_a\varphi_b\ldots, \quad (4.2)$$

where Z_0 is a normalization factor:

$$Z_0=\int D\varphi\, D\Psi \exp\left(-\frac{\mathscr{H}}{T_T}\right). \tag{4.3}$$

In the study of the correlation functions of the order parameter Ψ it is convenient to disregard from the outset the fluctuations of the remaining thermodynamic quantities φ_a, by introducing an effective Hamiltonian $\mathscr{H}^{\text{eff}}(\Psi)$ defined by

$$\exp\left(-\frac{\mathscr{H}^{\text{eff}}}{T_T}\right)=\int D\varphi \exp\left(-\frac{\mathscr{H}}{T_T}\right). \tag{4.4}$$

As a result of (4.2) the order-parameter correlation functions are expressed in terms of $\mathscr{H}^{\text{eff}}$ as follows:

$$\langle\Psi(\mathbf{r}_1)\Psi(\mathbf{r}_2)\rangle=Z_0^{-1}\int D\Psi \exp\left(-\frac{\mathscr{H}^{\text{eff}}}{T_T}\right)\Psi(\mathbf{r}_1)\Psi(\mathbf{r}_2), \tag{4.5}$$

containing only order-parameter fluctuations.

In the vicinity of the phase transition we are considering, the order parameter is a strongly fluctuating quantity. Strictly speaking, this statement does not hold for smectics. The point is that an important role is played in a smectic by long-wave fluctuations of the variable φ_u (displacements of the smectic layers).[13,14] However, all the contributions made to the observable quantities by order-parameter fluctuations develop in the critical region (region 2 in Fig. 1) where Ψ is indeed the only strongly fluctuating quantity. We are therefore not interested here in effects connected with the fluctuations of φ_u.

The weakness of the fluctuations of the remaining thermodynamic variables φ_a make it possible, when fluctuation effects are considered, to retain in the expansion of the Hamiltonian $\mathscr{H}$ only the terms quadratic and linear in φ_a. This means that the integrals over φ_a in (4.2) and (4.4) are Gaussian and can be evaluated explicitly. The kinetic energy generates a contribution in the Hamiltonian which is quadratic in the density of the momentum $\mathbf{j}$. For a nematic, similarly, the Frank energy (2.8) generates a contribution quadratic in the variation $\delta\mathbf{n}$ of the director. The integrations over these variables are therefore directly separable.

Matters are somewhat more complicated with the variables $\varphi_\rho=\rho-\rho_c$, $\varphi_\sigma=\sigma-\sigma_c$ and (for a smectic) $\varphi_u=-\nabla_z u$. The point is that in the expansion of the Hamiltonian $\mathscr{H}$ account must be taken of the terms linear in these variable. They are due, first, to the interaction energy (2.20), and second to the presence of the last two terms in the Hamiltonian (2.6). The linear contributions to $\mathscr{H}$ from these terms are equal to zero at the critical point, where the mean values of φ_σ, φ_ρ, and φ_u vanish [see (2.14), (2.15)].

These terms linear in φ_σ, φ_ρ, and φ_u can be eliminated from $\mathscr{H}$ by changing to new variables φ'_σ, φ'_ρ, and φ'_u, using the definition

$$\varphi_a=\varphi_a'+\beta_{ab}^{-1}\left((T_T-T_c)\frac{\partial P}{\partial\varphi_b}+(\mu_T-\mu_c)\frac{\partial S}{\partial\varphi_b}-\frac{1}{2}\Xi_b\Psi^2\right). \tag{4.6}$$

Here β_{ab}^{-1} is the inverse of the matrix β introduced by (2.15). The expansion of the Hamiltonian $\mathscr{H}$ in terms of φ'_a now contains only the quadratic term

$$\mathscr{H}_{el}=\frac{1}{2}\int d^3r\, \beta_{ab}\varphi_a'\varphi_b'. \tag{4.7}$$

The integration over φ'_a is therefore also separable.

Integration over the weakly fluctuating variables in (4.4) thus reduces to the fact that to obtain $\mathscr{H}^{\text{eff}}$ from $\mathscr{H}$ we must substitute in $\mathscr{H}$ the conditions $\mathbf{j}=0$ and $\varphi'_a=0$ (and also $\mathbf{n}=\text{const}$ for a nematic). Note that these equations are none other than the condition that the system be in local equilibrium with respect to the parameters $\mathbf{j}$, φ'_a, and $\mathbf{n}$. This aforementioned substitution leads to

$$\mathscr{H}^{\text{eff}}=\int d^3r\left(\frac{1}{2}A_0\Psi^2+\frac{1}{4}U\Psi^4+E_{\text{grad}}\right). \tag{4.8}$$

Here E_{grad} is defined by (2.13), and

$$U=U'-{}^1/_2\Xi_a\beta_{ab}^{-1}\Xi_b, \tag{4.9}$$

$$A_0=\Xi_a\{\beta_{a\sigma}^{-1}(T_T-T_c+(\mu_T-\mu_c)\sigma_c)+\beta_{a\rho}^{-1}\rho_c(\mu_T-\mu_c)\}. \tag{4.10}$$

Expression (4.9) means that interaction between weakly fluctuating degrees of freedom and the order parameter leads to a redefinition of the coefficient of Ψ^4 in the expansion of the energy. The coefficient A_0 in (4.8) is (as it should be) proportional to the deviations of the system temperature and chemical potential (or pressure) from the critical values.

Static correlation functions

We have concluded as a result of the analysis in Sec. 3 that the structure of the order-parameter correlation functions is set by the effective Hamiltonian (4.8). This Hamiltonian is the standard equation for the Ψ^4 model with a two-component order parameter. A model of this kind was actively investigated in the theory of second-order phase transitions in connection with the scaling problem. Note that these phase transitions considered belong to the same universality class as the transition of ^{4}He to the superfluid state.

In contrast to the standard models, the gradient energy (2.13) is anisotropic. This anisotropy, however, is immaterial to the analysis, since it can be eliminated by a simple redefinition of the scale along the z axis. The situation is somewhat more complicated for the S_A–S_C transition. The gradient energy does not reduce in this case to (2.13). We shall discuss this situation at the end of this section.

The principal structural properties of the order-parameter correlators in Ψ^4 models are well known. Their main distinguishing feature is scaling, i.e., a power-law dependence of the correlation functions on the coordinates and on the critical parameters. A survey of the properties of the correlation functions in the Ψ^4 model can be found in Refs. 3 and 4. We present here without derivation some results of the theory.

A distinction must be made between two regimes—mean-field and fluctuation. In the mean-field regime the order-parameter fluctuations are weak, but in the fluctuation regime they are strong and determine the main features of the correlation functions. The limits of the fluctuation region are determined by the inequality

$$|A_0|+Lq^2<\frac{T^2U^2}{L^3}. \tag{4.11}$$

The parameters here are those of the effective Hamiltonian (4.8), while $\mathbf{q}$ is the characteristic wave vector. The fluctuation region is thus located near the origin in Fig. 1.

The mean value is $\langle\Psi\rangle=0$, but above the phase-transition point (for $A_0 < 0$), it becomes nonzero. We shall assume that the phase of this mean value is zero, i.e., in accordance with (2.5) we have $\langle \Psi_1 \rangle \neq 0$, and $\langle \Psi_2 \rangle = 0$. In the mean-field theory

$$\langle \Psi \rangle^2 = A_0/U. \tag{4.12}$$

In the fluctuation region

$$\langle \Psi \rangle \propto |A_0|^\beta, \tag{4.13}$$

where β is the critical exponent of the order parameter (we shall introduce below many additional critical exponents). The proportionality coefficient in (4.13) is determined by "matching" (4.12) and (4.13), in accordance with (4.11), at $|A_0| \approx T^2U^2/L^3$.

Consider the structure of an irreducible paired correlation function

$$D(\mathbf{r}) = \langle\!\langle \Psi(\mathbf{r})\Psi(0) \rangle\!\rangle = \langle \Psi(\mathbf{r})\Psi(0) \rangle - \langle \Psi \rangle^2. \tag{4.14}$$

It is easy to find an explicit expression for this correlation function when the mean-field theory is valid. It suffices to retain in the Hamiltonian (2.6) the term quadratic in the fluctuations of Ψ, so that the integration in (4.5) becomes Gaussian and can be carried out explicitly. It is convenient to write the result for the Fourier component [denoted $D(\mathbf{q})$] of the function (4.14):

$$D(\mathbf{q}) = T_T(A_0 + L_\parallel q_z^2 + L_\perp q_\alpha^2)^{-1}, \quad A_0 > 0, \tag{4.15}$$

$$D_{11}(\mathbf{q}) = T_T(2|A_0| + L_\parallel q_z^2 + L_\perp q_\alpha^2)^{-1}, \quad A_0 < 0, \tag{4.16a}$$

$$D_{22}(\mathbf{q}) = T_T(L_\parallel q_z^2 + L_\perp q_\alpha^2)^{-1}, \quad A_0 < 0. \tag{4.16b}$$

Recall that for $A_0 < 0$ the mean value $\langle \Psi_1 \rangle$ is assumed to differ from zero while $\langle \Psi_2 \rangle = 0$.

The paired correlation functions (4.14) can be represented in the fluctuation region (4.11) in the form

$$D(\mathbf{r}) = r_c^{-(1+\eta)} d(r/r_c). \tag{4.17}$$

Here r_c is the correlation radius,

$$r_c \propto |A_0|^{-\nu}. \tag{4.18}$$

Note that expressions (4.15) and (4.16) agree formally with (4.17) if one puts

$$r_c = |L/A_0|^{1/2}. \tag{4.19}$$

The proportionality coefficient in (4.18) can be obtained by joining (4.18) and (4.19) at the value $A_0 \approx T^2U^2/L^3$ defined by (4.11).

The asymptotic forms of the Fourier component of the correlation function (4.14) in the fluctuation region have the form:

$$\begin{aligned} &D(\mathbf{q}) \propto |A_0|^{-\gamma}, \quad qr_c \ll 1, \\ &D(\mathbf{q}) \propto q^{-(2+\eta)}, \quad qr_c \gg 1. \end{aligned} \tag{4.20a}$$

The long-wave asymptotic form is valid here for $A_0 < 0$ for the D_{11} component, while the D_{22} component has another asymptotic form:

$$D_{22}(\mathbf{q}) \propto r_c^{-\eta} q^{-2}, \quad qr_c \ll 1. \tag{4.20b}$$

This asymptotic form [just like expression (4.16) for D_{22}] reflects the presence, in the low-temperature phase, of a soft degree of freedom connected with the phase φ of the order parameter Ψ.

Consider now the correlation function

$$F(\mathbf{r}) = \frac{1}{4T_T} \langle\!\langle \Psi^2(\mathbf{r})\Psi^2(0) \rangle\!\rangle. \tag{4.21}$$

It is convenient to formulate the properties of this correlation function for the Fourier component $F(\mathbf{r})$, which we denote by $F(\mathbf{q})$. In the mean-field theory there exists at $A_0 < 0$ the following long-wave contribution to F:

$$F(\mathbf{q}) = 1/2U, \quad q \ll (|A_0|/L)^{1/2}, \tag{4.22}$$

and for $A_0 > 0$ we can neglect $F(\mathbf{q})$ compared with (4.22). In the functional region (4.11) the correlation function F has a structure similar to (4.17):

$$F(\mathbf{q}) = r_c^{\alpha/\nu} f(qr_c). \tag{4.23}$$

The asymptotic forms of F are

$$\begin{aligned} &F(\mathbf{q}) \propto |A_0|^{-\alpha}, \quad qr_c \ll 1, \\ &F(\mathbf{q}) \propto q^{-\alpha/\nu}, \quad qr_c \gg 1. \end{aligned} \tag{4.24}$$

We have introduced in the above relations many critical exponents, designated by the standard symbols β, η, ν, α. The scaling relations described by these exponents are formally valid in the mean-field theory if one puts

$$\beta = 1/2, \quad \eta = 0, \quad \nu = 1/2, \quad \gamma = 1, \quad \alpha = 0.$$

In the fluctuation region (4.11), the introduced exponents are related as follows:

$$\nu = \frac{2-\alpha}{d}, \quad \gamma = (2-\eta)\nu, \quad \beta = 1 - \frac{\alpha+\gamma}{2}, \tag{4.25}$$

where $d = 3$ is the dimensionality of the space. Numerical simulation and experiment show that in the Ψ^4 model with a two-component order parameter the exponents α and η are close to zero, while the remaining ones, in accordance with the relations above, have the values

$$\nu \approx 2/3, \quad \gamma \approx 4/3, \quad \beta \approx 1/3. \tag{4.26}$$

Note that these exponents differ from the mean-field ones, even though it was assumed in their derivation that $\alpha = \eta = 0$, just as in the mean-field theory.

Finally we consider the behavior of the moduli $\alpha_{\parallel,\perp}$ introduced by Eq. (2.9). Comparing expression (2.13) for the gradient energy with (2.9), with account taken of (2.3) and (2.4), we arrive in the mean-field theory at

$$\alpha_{\parallel,\perp} = 4L_{\parallel,\perp} \langle \Psi \rangle^2 \sim L|A_0|/U. \tag{4.27}$$

In the fluctuation region we have

$$\alpha_{\parallel,\perp} \propto |A_0|^\nu. \tag{4.28}$$

Correlation functions of weakly fluctuating quantities

Consider now the contributions made to the correlation functions φ_a of weakly fluctuating quantities by the order-parameter fluctuations. We can use for this purpose the relation (4.6). Averaging (4.6) and recognizing that $\langle \varphi'_a \rangle = 0$, we get

FIG. 2. Diagram representation of paired correlation function of weakly fluctuating quantities.

$$\langle\varphi_a\rangle=\beta_{ab}^{-1}\left[(T_T-T_c)\frac{\partial P}{\partial\varphi_b}+(\mu_T-\mu_c)\frac{\partial S}{\partial\varphi_b}-\frac{1}{2}\Xi_b\langle\Psi^2\rangle\right]. \tag{4.29}$$

The first two terms in the right-hand side of (4.29) are regular, while the last one is connected with the order parameter and thus determines the singular critical behavior of $\langle\varphi_a\rangle$.

We can also use (4.6) to calculate the irreducible paired correlation function of weakly fluctuating quantities. It must be borne in mind here that the pair correlation function of the quantities φ'_a is calculated from Eqs. (4.2) and (4.7). As a result we get

$$D_{ab}(\mathbf{r})=\langle\langle\varphi_a(\mathbf{r})\varphi_b(0)\rangle\rangle=T_T\beta_{ab}^{-1}\delta(\mathbf{r})+T_T\beta_{ac}^{-1}\Xi_c\Xi_d\beta_{ab}^{-1}F(\mathbf{r}). \tag{4.30}$$

Here $\langle\langle\varphi_a\varphi_b\rangle\rangle=\langle\varphi_a\varphi_b\rangle-\langle\varphi_a\rangle\langle\varphi_b\rangle$, $\mathbf{r}=\mathbf{r}_1-\mathbf{r}_2$, while F is determined by (4.21). We point out that in diagram language (4.30) means that the correlation function $\langle\langle\varphi_a\varphi_b\rangle\rangle$ is represented by the sum of the two diagrams shown in Fig. 2. The line in this figure denotes the unrenormalized correlation function, i.e., the first term in the right-hand side of (4.30), the points stand for Ξ_a, and the hatched block denotes the correlation function (4.21).

This diagram representation calls for some clarification, since the second diagram of Fig. 2 has the form of the first term of a self-energy series, and the question of summing this entire series is raised. An example of the next diagram of this series is shown in Fig. 3. However, the diagrams having the structure shown in Fig. 3 have already been taken into account in the second diagram of Fig. 2. The point is that the intermediate middle line in Fig. 3 is none other than the contribution to the quaternary vertex of the self-action Ψ, connected with the interaction with weakly fluctuating quantities. A contribution of this kind was already taken into account in the redefinition $U'\to U$ specified by Eq. (4.9).

We discuss now the behavior of the correlation functions of the weakly fluctuating quantities φ_ρ, φ_σ, φ_u near a phase-transition point. The mean values of these quantities are determined by (4.29). In the mean-field theory we have $\langle\Psi^2\rangle\propto|A_0|$, i.e., the quantities $\langle\varphi_a\rangle$ as functions of T_T-T_c or $\mu_T-\mu_c$ exhibit kinks at the transition point. The mean values $\langle\varphi_a\rangle$ in the fluctuation region (4.11) have a more complicated singular behavior, determined by

$$\langle\varphi_a\rangle\propto|A_0|^{1-\alpha}. \tag{4.31}$$

Note that this singular contribution to $\langle\varphi_a\rangle$ takes place both below the transition (for $A_0<0$) and above it (for $A_0>0$), and only the proportionality coefficients of $|A_0|^{1-\alpha}$ are different.

FIG. 3. Diagram representation of one of the contributions already taken into account on the diagram of Fig. 2.

The contribution of the Ψ fluctuations to the irreducible paired correlation function of the weakly fluctuating variables is determined by Eq. (4.30). Let us examine the Fourier transform of (4.30), which we designate by $D_{ab}(\mathbf{q})$, and which is expressed in terms of the function F whose behavior was discussed above. The explicit expression is

$$D_{ab}(\mathbf{q})=T_T[\beta_{ab}^{-1}+\beta_{ac}^{-1}\Xi_c\beta_{bd}\Xi_dF(\mathbf{q})]. \tag{4.32}$$

We rewrite this expression in the form $T_T\tilde\beta_{ab}^{-1}$, where

$$\tilde\beta_{ab}(\mathbf{q})=\beta_{ab}-\frac{\Xi_a\Xi_bF(\mathbf{q})}{1+\Xi_a\Xi_bF(\mathbf{q})}. \tag{4.33a}$$

The quantity $\tilde\beta$ can be called the matrix of the renormalized elastic moduli.

Let us dwell in greater detail on the properties of the correlation functions $D_{ab}(\mathbf{q}=0)$ which determine system properties such as heat capacity or compressibility. Thus, for example,

$$D_{\rho\rho}(\mathbf{q}=0)=T\rho\left(\frac{\partial\rho}{\partial P}\right)_T,\qquad D_{\sigma\sigma}(\mathbf{q}=0)=\frac{T}{\rho}\left(\frac{\partial\sigma}{\partial T}\right)_P. \tag{4.33b}$$

In the mean-field theory, $F(\mathbf{q}=0)$ has a discontinuity given by (4.22). A corresponding discontinuity appears in $D_{ab}(\mathbf{q}=0)$, i.e., the heat capacity and the compressibility, as well as the elastic moduli (4.33a). This mean-field contribution is illustrated by the diagram shown in Fig. 4 (the dash-dot line corresponds to $\langle\Psi\rangle$).

The behavior of $F(\mathbf{q}=0)$ in the fluctuation region is determined by Eq. (4.24), and $F(\mathbf{q}=0)$ diverges for $a>0$ near the phase-transition point. Accordingly, the fluctuation contributions to the heat capacity and the compressibility, given by the second terms in the right-hand side of (4.32), diverge with an exponent α. Note that in this case the renormalized elastic moduli (4.33a) remain finite at the transition point.

Singularities of the S–$S_c(S_1)$ and N–N_2 transitions

The S_A–S_1 phase transition is characterized by the vector order parameter (2.1), while the order parameters for the S_A–S_n and N–N_n phase transitions with $n>1$ are tensors of rank n, and this causes the singularities of the transition in question.

The gradient energy for the phase transition S_A–$S_C(S_1)$ is somewhat more complicated in form than for the other orientational phase transitions. We write for the density of this energy, assuming the vector $\mathbf{l}$ of the normal to be uniform,

$$E_{\text{grad}}={}^1/_2L_1(\varepsilon_{\alpha\beta}\nabla_\alpha\Psi_\beta)^2+{}^1/_2L_2(\nabla_\alpha\Psi_\alpha)^2+{}^1/_2L_3(\nabla_z\Psi_\alpha)^2. \tag{4.34}$$

Recall that the z axis is directed along $\mathbf{l}$, the indices α and β

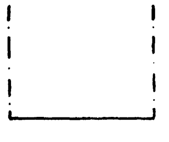

FIG. 4. Diagram representation of mean-field contribution to the correlation function.

assume all the values x and y, while $\varepsilon_{\alpha\beta}$ is an antisymmetric tensor: $\varepsilon_{xy} = -\varepsilon_{yx} = 1$. Expression (4.34) can be obtained from the Frank energy (2.8) by substituting in (2.8) the director $\mathbf{n}$ expressed in terms of Ψ in accordance with (2.1). It is therefore logical to refer to $L_{1,2,3}$ as Frank constants. They are of the same order of magnitude as $K_{1,2,3}$ in nematics.

In contrast to (2.13), which is valid for the S_A–S_n and N–N_n transitions with $n > 1$, the order-parameter exponents are linked with the gradient exponents. This linkage is described by the second term in the right-hand side of (4.34). This is also the reason why (4.34) contains three moduli L as against the two in (2.13). One more consequence of this linkage is that the form of the orientational energy in the S_C phase is more complicated than in (2.9):

$$E_{or}={}^1/_2[\alpha_1(\delta_{ik}-l_il_k)+(\alpha_2-\alpha_3)n_{1i}n_{1k}+\alpha_3l_il_k]\nabla_i\varphi\nabla_k\varphi. \quad (4.35)$$

Here $n_{1i} = \Psi_i/|\Psi|$ and the angle φ is introduced in accordance with (2.3).

We examine now the singularities of the critical behavior of the system in an S_A–S_C transition. In the mean-field theory there are no qualitative differences from the other S_A–S_n transitions. The only difference is that, in accordance with (4.34), the components of the correlation function $\langle\Psi_\alpha\Psi_\beta\rangle$ longitudinal and transverse to the wave vector are determined by different moduli L, viz., L_1 and L_3 for the transverse component and L_2 and L_3 for the longitudinal one.

Certain properties of the S_A–S_C transition are manifested in the fluctuation region (4.11), owing to the smallness of the exponent η introduced above. In view of this smallness, the corrections to the gradient energy (4.32) can be neglected if the inequality

$$\ln\left(\frac{1}{qr_{fl}}+\frac{r_c}{r_{fl}}\right)<\frac{1}{\eta} \quad (4.36)$$

holds. Here $\mathbf{q}$ is the characteristic wave vector, r_c is the critical radius, and in accordance with (4.11) $r_{fl} \sim L^2/UT$ determines that value of the critical radius for which fluctuation effects connected with Ψ self-action start to become substantial.

Satisfaction of conditions (4.11) and (4.36) brings about scaling described by the exponents introduced above. In view of the small corrections to the gradient energy in this region, we can assume $\eta = 0$ in it. Among the remaining exponents β, γ, ν, and α only one is independent in accordance with (4.25). In the region (4.36) all these exponents are functions of the ratio L_1/L_2, i.e., they are not universal. An estimate in the framework of the renormalization-group method[6] shows that these exponents do not differ very strongly from those given in (4.26).

Universal critical behavior sets in when the inequality opposite to (4.36) is satisfied. The singularities are then specified by the standard exponents for a two-component order parameter (i.e., the situation considered in the preceding subsections takes place). However since the exponent η is small the universal-behavior region defined by the inequality opposite to (4.36) is located in an exceedingly narrow vicinity of the phase transition and can hardly be attained in experiment.

Singularities similar to those of the phase transition S_A–$S_C(S_1)$ are connected with the transition N–N_2. The low symmetry of the order parameter Ψ_{mn} for this transition leads to the presence in the expansion of the energy of the next gradient term

$$(\mathbf{n}\nabla)n_k\nabla_n\Psi_{kn}.$$

After eliminating the weakly fluctuating director $\mathbf{n}$ we return to the effective energy (4.8). Now, however, the constants L in the effective energy become complicated functions of the wave-vector direction. This circumstance leads to no qualitative differences from other phase transitions in the mean-field theory. In the fluctuation region (4.11) (intermediate-scaling region) the critical exponents β, γ, ν, α are complicated functions of the unrenormalized elastic moduli K and L. Finally, in the universal-behavior region the transition N–N_2 reduces to the standard Ψ^4 model.

Note that the S_A–S_2 phase transition does not have the singularities of the N–N_2 transition. The point is that the displacement u of the smectic layer is a much more "rigid" variable than the director $\mathbf{n}$, so that no new contributions to the gradient energy of the order parameter are produced when u is eliminated.

5. DYNAMIC FLUCTUATIONS

Diagram technique

The first to develop a diagram technique for the calculation of long-wave fluctuation effects was Wyld.[15] This technique was later[16] generalized to include a large class of systems. A generating functional describing the dynamic fluctuational effects for an arbitrary hydrodynamic system was derived in Ref. 17. A consistent exposition of the derivation of a dynamic generating functional can be found in Ref. 8. We present here for reference only a number of relations needed for our exposition.

The dynamic diagram technique is generated by the effective action

$$I=\int dt\,d^3r\left\{p_a\left(\frac{\partial\varphi_a}{\partial t}+\{\varphi_a,\mathscr{H}\}+\Gamma_{ab}\frac{\delta\mathscr{H}}{\delta\varphi_b}+iTp_a\Gamma_{ab}p_b\right)\right\}. \quad (5.1)$$

Here φ_a is the set of hydrodynamic variables and p_a is the set of auxiliary fields. Recall that summation over dummy indices is implied. The first three terms in the right-hand side of (5.1) are directly generated by the dynamic equation for φ_a, the second term specifies the reactive term in the equation, Γ_{ab} is the kinetic operator defined by the set of kinetic coefficients, and $\delta\mathscr{H}/\delta\varphi_b$ is the variational derivative of the Hamiltonian (2.6). The actual structure of the bracket $\{\varphi,\mathscr{H}\}$ can be found from Eq. (3.9) which is valid for all the variables considered here. The form of the last term in (5.1) is determined by the fluctuation-dissipation theorem.

We introduce the following pair correlation functions

$$D_{ab}(t,\mathbf{r})=\langle\varphi_a(t,\mathbf{r})\varphi_b(0,0)\rangle,\quad G_{ab}(t,\mathbf{r})=\langle\varphi_a(t,\mathbf{r})p_b(0,0)\rangle. \quad (5.2)$$

These correlation functions are expressed in terms of the effective action by functional integration. Thus, for example,

$$G_{ab}(t,\mathbf{r})=\int D\varphi\,Dp\,\exp(iI)\varphi_a(t,\mathbf{r})p_b(0,0). \quad (5.3)$$

The integration here is over all the functions $\varphi_a(t,\mathbf{r})$ and

$p_b(t, \mathbf{r})$. Note that in this technique the correlation function $\langle p_a p_b \rangle$ vanishes identically.

The function D_{ab} is simply a pair correlation function of thermodynamic quantities. The correlation function G_{ab}, on the other hand, is the generalized susceptibility of the system and determines the response of the mean values $\langle \varphi_a \rangle$ to the addition of an external "force" δF_a to the equation for φ_a. It follows hence that the Fourier component $G_{ab}(\omega, \mathbf{q})$ is analytic in the frequency in the upper half-plane, while the singularities of G_{ab} in the lower half plane determine the spectrum of the eigenmodes of the system. The correlation functions D_{ab} and G_{ab} are related by the fluctuation–dissipation theorem. The functions G_{ab} are therefore fully indicative of the dynamic properties of the system.

The definition (5.3) of the correlator in terms of the effective action permits the standard[18] formulation of the diagram technique in which the dynamic correlation function can be represented by a perturbation-theory series. This series contains the paired correlation functions (5.2) whose unrenormalized values are determined by linearized dynamic equations, while the unrenormalized vertices in this series are determined by the nonlinear terms in the dynamic equations.

Effective action

The thermodynamic parameters used in an investigation of the vicinity of a second-order phase transition must include the order parameter Ψ. Just as in statics, to investigate the dynamic correlation functions of the order parameter it is convenient to introduce an effective action I_{eff} that depends only on the order parameter Ψ and on the corresponding auxiliary field p_Ψ. This action is introduced by analogy with (4.4):

$$\exp(iI_{eff}) = \int D\varphi\, Dp \exp(iI). \qquad (5.4)$$

The integration here is over all the φ_a and p_a variables except Ψ and p_Ψ. The paired correlation function $\langle \Psi\Psi \rangle$ now takes the form

$$D(t, \mathbf{r}) = \langle \Psi(t, \mathbf{r}) \Psi(0, 0) \rangle$$
$$= \int D\Psi Dp_\Psi \exp(iI_{eff}) \Psi(t, \mathbf{r}) \Psi(0, 0). \qquad (5.5)$$

Just as in statics, the integration in (5.4) can be carried out explicitly. To this end it must be recognized that the quantities φ_a and p_a in (5.4) fluctuate weakly. This means that it suffices to retain in the action I the terms linear and quadratic in φ_a and p_a, so that the integration in (5.4) becomes Gaussian. We shall retain also in I the terms principal with respect to Ψ. This means in fact that the action must be constructed, in accordance with the definition (5.1), using analytic equations obtained by expansion in terms of φ_a and Ψ and presented in Sec. 3. Just as in statics, it is convenient to transform from the variables φ_a to the variables φ'_a in accordance with the definition (4.6).

It should be mentioned here that the long-wave displacement fluctuations of the smectic-layers u lead in the long-wave limit to corrections proportional to ω^{-1} in the viscosity coefficients.[19,20] These corrections, however, accumulate outside the critical region, where the order parameter is indeed the only strongly fluctuating variable. Primary account must therefore be taken of the critical effects considered in the present paper, in whose calculations the u fluctuations can be neglected and replaced by the long-wave u fluctuations whose contributions were calculated in Refs. 19 and 20.

It must now be recognized that in the critical region (region 2 of Fig. 1) the order parameter is the "softest" variable. The terms with $\partial\varphi_a/\partial t$ of the action I can can therefore be omitted in the investigation of the critical mode. The so-transformed action I breaks up then into a sum of parts with the pairs p_a, φ'_b and p_Ψ, Ψ as the variables. The first part vanishes when the integral (5.4) is taken, and the second yields I_{eff} in the form

$$I_{eff} = \int dt\, d^3r \left(\Gamma^{-1} p \frac{\partial \Psi}{\partial t} + p \frac{\delta \mathscr{H}_{eff}}{\delta \Psi} + i\Gamma^{-1} T_T p_\Psi^2 \right). \qquad (5.6)$$

We have introduced here in place of p_Ψ the variable $p = \Gamma p_\Psi$, with the effective Hamiltonian $\mathscr{H}_{\text{eff}}$ defined by Eq. (4.8).

Note that the effective action (5.6) is determined here in accordance with the general expression (5.1) with the aid of the equation

$$\partial\Psi/\partial t = -\Gamma \delta \mathscr{H}_{eff}/\delta\Psi. \qquad (5.7)$$

In other words, after eliminating the weakly fluctuating variables we are left here with purely dissipative dynamics of the order parameter.

Equation (5.7), of course, can be derived from (3.19) with allowance for the softness of the order-parameter dynamics. This softness means that the dynamics of the order parameter can be investigated with the terms containing $\partial/\partial t$ in the equations for φ_ρ, φ_σ, and φ_u. In other words, the equations for these quantities will reduce to the conditions that the right-hand sides of (3.21) and (3.22) and the divergence (3.23) of the stress tensor be zero. These equations have a simple physical meaning, being the conditions for local equilibrium of the system with respect to ρ, σ, and u:

$$P = \text{const}, \quad T = \text{const}, \quad \delta\mathscr{H}/\delta u = \text{const}.$$

Using these conditions to express φ_ρ, φ_σ, and φ_u and substituting the result in (3.20) we arrive at (5.7).

By analogy with (5.2) we introduce the correlation function

$$G(t, \mathbf{r}) = \langle \Psi(t, \mathbf{r}) p(0, 0) \rangle. \qquad (5.8)$$

In accordance with the foregoing, the singularities, with respect to the frequency ω, of the Fourier representations G of this correlator determine the dispersion law of the critical mode. As a result of the fluctuation–dissipation theorem, the correlation functions (5.8) and (5.5) are interrelated. The structure of the action (5.6) leads to the following relation between the Fourier components G and D:

$$D(\omega) = -\frac{T_T}{\omega} [G(\omega) - G(-\omega)]. \qquad (5.9)$$

This relation has the same form as the standard connection between the susceptibility (whose role is assumed here by G) and the paired correlation function D in the classical limit.[12]

We introduce now the correlation function

$$F(t, \mathbf{r}) = {}^1/_2 \langle \Psi^2(t, \mathbf{r}) \Psi(0, 0) p(0, 0) \rangle. \qquad (5.10)$$

It is connected, in view of the fluctuation-dissipation theorem, with the correlation function $\langle\Psi^2\Psi^2\rangle$. It is convenient to write this connection, which is similar to (5.9), for Fourier components with respect to time:

$$\langle\Psi^2\Psi^2\rangle_\omega=\frac{4iT_T}{\omega}[F(\omega)-F(-\omega)]. \qquad (5.11)$$

Integrating this relation over the frequency ω and recognizing that the function F is analytic in ω in the upper half plane, we get

$$\frac{1}{4T_T}\int\frac{d\omega}{2\pi}\langle\Psi^2\Psi^2\rangle_\omega=F(\omega)\,|_{\omega=0}. \qquad (5.12)$$

The left-hand side here is none other than the equal-time correlation function (4.21) introduced in the preceding section. This justifies the use of the same symbol F for both.

The effective action (5.6) allows us to write a perturbation-theory series for the correlation functions introduced above. The terms of this series contain the unrenormalized values of the correlators and the quaternary interaction vertex U—the same quantity (4.9) as in the static case. Therefore the diagram structures will be the same as in statics, but the diagrams will now contain two types of pair correlation functions, (5.5) and (5.8).

Dynamic correlation functions

We investigate now the structure of the correlation functions (5.5), (5.8), and (5.10), which contain the primary information on the order-parameter dynamics. The unrenormalized values of these correlations can be found by limiting the effective action I_{eff} in integrations of the form (5.5) to terms quadratic in p and in $\Psi-\langle\Psi\rangle$. As a result, this integral becomes Gaussian and can be calculated in general form. Thus, for example, for the correlation function (5.8) we obtain in the Fourier representation

$$G(\omega,\mathbf{q})=[\Gamma^{-1}\omega+i(A_0+L_\parallel q_z^2+L_\perp q_\alpha^2)]^{-1},\quad A_0>0, \qquad (5.13)$$

$$G_{11}=-[\Gamma^{-1}\omega+i(2|A_0|+L_\parallel q_z^2+L_\perp q_\alpha^2)]^{-1},\quad A_0<0, \qquad (5.14a)$$

$$G_{22}=-[\Gamma^{-1}\omega+i(L_\parallel q_z^2+L_\perp q_\alpha^2)]^{-1},\quad A_0<0. \qquad (5.14b)$$

The explicit form of the correlation function (5.5) can now be found by using (5.9).

Expressions (5.13) and (5.14) correspond to the static expressions (4.15) and (4.16) and are valid, just as the latter are, in the mean-field picture. In the fluctuation region (4.11) the unrenormalized values (5.13) and (5.14) require large corrections due to the fluctuations of Ψ. Let us discuss the structure of the correlation functions in this region.

The relaxational dynamics described by Eq. (5.7) is in accord with the dynamic-scaling hypothesis.[21] According to this hypothesis, the dynamic correlation functions in the fluctuation region are functions of the time (or of the frequency ω) with power-law asymptotic limits. The order parameter Ψ has here only one characteristic relaxation time, with the following dependence on the proximity to the transition point:

$$\tau\propto r_c^z. \qquad (5.15)$$

Here z is a new critical exponent, called dynamic.

In accordance with the dynamic scaling hypothesis, the structure of the correlation function (5.5) in the fluctuation region is given by

$$D(t,\mathbf{r})=r_c^{1-\eta}d(t/\tau,\mathbf{r}/\mathbf{r}_c). \qquad (5.16a)$$

Expression (5.16a) is a generalization of (4.17). Similarly, the expression (4.23) for the Fourier component of the correlation function is now

$$F(\omega,\mathbf{q})=r_c^{\alpha/\nu}f(\omega\tau,qr_c). \qquad (5.16b)$$

Expression (5.16a) coincides with (4.17) at $t=0$, while (5.16b) coincides with (4.23) at $\omega=0$.

It follows from (5.13) and (5.14) that the scaling relations cited above are formally valid also in the region where the mean-field theory is valid, if we put

$$\tau=(A_0\Gamma)^{-1}. \qquad (5.17)$$

It can thus be stated that in this region the critical exponent z is equal to 2. Expressions (5.13) and (5.14) should join (5.16a) at the boundary (4.11) of the fluctuation region. This enables us to estimate the proportionality coefficient in (5.15). We should have $\tau\sim L^3/\Gamma T^2U^2$ for $r_c\sim L^2/UT$.

We emphasize that the frequency ω plays exactly the same role as the wave vector $\mathbf{q}$ or the proximity to the transition point, viz., a high frequency suppresses the fluctuation effects. The limiting frequency can be estimated as ΓA_0, where A_0 lies on the boundary (4.11) of the fluctuation region. We thus arrive at the inequality

$$\omega\ll\Gamma T^2U^2/L^3, \qquad (5.18)$$

which, along with (4.11), characterizes the fluctuation region.

We present now the asymptotes of the Fourier component of the correlation function (5.16) for $qr_c\ll1$:

$$\begin{aligned}&D(\omega,\mathbf{q})\propto|A_0|^{-\gamma-\nu z},\quad \omega\tau\ll1,\\&D(\omega,\mathbf{q})\propto\omega^{(\eta-2-z)/z},\quad \omega\tau\gg1.\end{aligned} \qquad (5.19a)$$

The high-frequency asymptotic form of the correlation function (5.16b) for $qr_c\ll1$ is

$$F(\omega,\mathbf{q})\propto\omega^{-\alpha/z},\quad \omega\tau\gg1. \qquad (5.19b)$$

We emphasize that whereas the high-frequency asymptotic form (5.19a) is formally valid also in the mean-field theory, the asymptote (5.19b) is valid only in the fluctuation region, i.e., when the condition (5.18) is met.

The dynamic exponent z can be approximately calculated in the framework of the ε expansion in $4D$ space. The corresponding formalism was developed in detail for the static case.[3] The ε expansion procedure is applicable in critical dynamics to our problem because the effective action (5.6) is renormalizable in $4D$ space. The exponent z was calculated in Ref. 21 in a two-loop approximation for the relaxational dynamics of the order parameter in the Ψ^4 model. The result of this calculation is

$$z=2+\left(6\ln\frac{4}{3}-1\right)\frac{N+2}{2(N+8)^2}\varepsilon^2. \qquad (5.20)$$

Here N is the number of the order-parameter components, equal to two for orientational phase transitions. Expression (5.20) indicates that in a real system the dynamic critical exponent should be close to its unrenormalized value 2.

Fluctuation contribution to the susceptibility

We consider here the fluctuation contributions, induced by the order parameter, to the dynamic correlation functions G_{ab} introduced in (5.2) and having the meaning of generalized susceptibilities of the system. It follows from the above equations that the degrees of freedom interacting most strongly with the order parameter Ψ are those connected with φ_ρ, φ_σ, φ_u. We shall therefore be interested in correlation functions G_{ab} with $a = \rho, \sigma, u$. It is the structure of these correlation functions which most strongly exhibits effects connected with order-parameter fluctuations.

These variables are contained in the stress tensor (3.23). We shall therefore be interested in the contribution made to the effective action (5.1) by Eq. (3.11) for the momentum density. We write down this contribution, using the explicit expression (3.23) for the stress tensor. As a result we obtain

$$I_{mom}=\int dt\,d^3r\left[p_i\frac{\partial j_i}{\partial t}+\nabla_i p_k f_{a,ik}\left(\beta_{ab}\varphi_b+\frac{1}{2}\Xi_a\Psi^2\right)\right.$$
$$\left.+\nabla_i p_k \eta_{iknm}\nabla_m(v_n+iTp_n)\right]. \qquad (5.21)$$

We have introduced here an auxiliary variable p_i conjugate to j_i. The nonzero components in (5.21) are f_ρ and f_u given explicitly in (3.24), and the meaning of the coefficients β_{ab} is made clear by (2.16), (2.17), and (2.18).

The action (5.21) contains, in addition to the variables of interest to us, the momentum density j_i. The variables φ_ρ and φ_σ can be connected with $\mathbf{j}$ by Eqs. (3.21) and (3.22). For our accuracy requirements, they can be rewritten in the form

$$\frac{\partial\varphi_a}{\partial t}=-\frac{1}{\rho}f_{a,ik}\nabla_i j_k. \qquad (5.22)$$

The notation here is the same as in (3.9), and terms nonlinear in the weakly fluctuating quantities, as well as the term describing percolation, have been omitted. The point is that percolation-related effects are as a rule small in liquid crystals compared with viscosity effects.

We consider now the contribution made to the effective action (5.1) by Eq. (3.13) for the specific entropy. Introducing the auxiliary variable p_σ conjugate to σ, we can express this contribution, in our approximation, in the form

$$I_\sigma=\int dt\,d^3r\,p_\sigma\left[\frac{\partial\varphi_\sigma}{\partial t}-\frac{1}{\rho^2T}(\varkappa_\parallel\nabla_z^2+\varkappa_\perp\nabla_\alpha^2)\right.$$
$$\left.\times\left(\beta_{\sigma b}\varphi_b+\frac{1}{2}\Xi_\sigma\Psi^2\right)\right]. \qquad (5.23)$$

We have used here the explicit form of Eq. (3.21) for φ_σ.

Beside the terms already given, we shall need in the effective action (5.1) one more term that describes the interaction of φ_ρ, φ_σ, and φ_u with the critical degrees of freedom. Recalling relation (2.19), we obtain the explicit expression

$$I_{int}=\int dt\,d^3r\,\Xi_a\varphi_a p_\Psi\Psi. \qquad (5.24)$$

Here p_Ψ is the auxiliary variable conjugate to the order parameter Ψ and contained in (5.6).

We are interested in the structure of the correlation functions

$$\langle\varphi_a p_i\rangle,\quad \langle\varphi_a p_\sigma\rangle, \qquad (5.25)$$

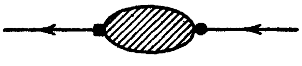

FIG. 5. First contribution to the G-function for weakly fluctuating quantities.

where $a = \rho, \sigma, u$. The unrenormalized values of these correlation functions are determined by the quadratic parts of the contributions (5.21) and (5.23) to the effective action, with allowance for Eqs. (5.22). The fluctuation corrections to these unrenormalized values are due to the terms of the interactions of the variables φ_a, p_a with Ψ, p in (5.25). The principal terms of such an interaction are those proportional to Ψ^2 in the contributions (5.21) and (5.23) to the effective action and the term (5.24). We emphasize that, just as in the static case, these principal interaction terms are cubic.

We shall calculate the fluctuation corrections to the correlation functions (5.25) in the form of a perturbation series in the interaction. The first term of this series is shown in Fig. 5. The solid line in this diagram denotes the unrenormalized values of the correlation functions (5.25), with the arrow directed from p_a to φ_a, the circle denotes Ξ_a, the square denotes vertices generated by the interaction terms in (5.21) and (5.23), and the shaded block denotes the correlation function (5.10). We shall use the same notation below.

The contribution to the correlation functions (5.25), which is shown in Fig. 5, becomes large near poles of unrenormalized functions. We are interested, however, in just this vicinity. Its investigation calls for summation of the higher-order contributions to (5.25). All the significant contributions are determined by the perturbation-theory series terms that account for the self-energy blocks. An example is the diagram in Fig. 6. However, the contribution to (5.25) corresponding to this diagram is already partly taken into account in the term defined by the diagram of Fig. 5.

The point is that the intermediate line in Fig. 6 is connected with the contribution made to the $U' \to U$ renormalization by the quaternary vertex of the self-action of the order parameter (4.9). Recall that it is in fact the vertex U which is contained in the effective action (5.6) that effects the averaging in (5.10). It can be tracked that this contribution to U arises when the Fourier components of the unrenormalized values of the correlation functions (5.25) on the intermediate line are replaced by their values at $\omega = 0$. This situation is perfectly analogous to the static case analyzed in Sec. 4.

This double allowance for the diagrams must be eliminated. Its result in statics was that it sufficed to retain only one diagram of the type shown in Fig. 5. The situation in dynamics is more complicated, since the correlation functions on the diagram depend on the frequency, and a contribution to the $U' \to U$ renormalization corresponds to substitution of the values $\omega = 0$ on the intermediate lines. In the calculation of the correlation functions (5.25) it is therefore necessary to sum the infinite series of diagrams shown in Fig. 7. The intermediate lines should represent the differences between the values of the correlation functions (5.25) at a real fre-

FIG. 6. Example of higher-order contribution to the G-function for weakly fluctuating quantities.

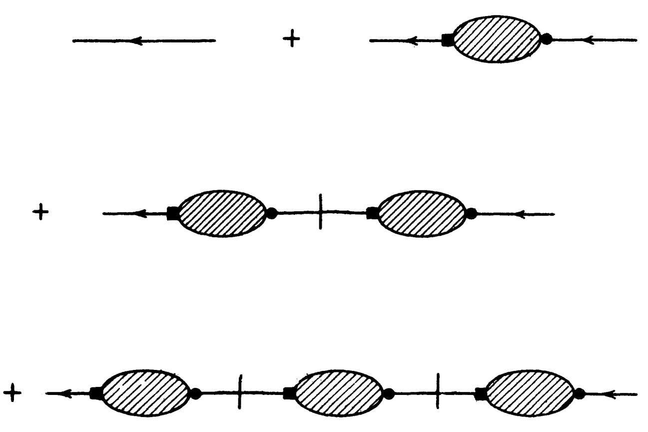

FIG. 7. Diagram series for G-function of weakly fluctuating quantities. The crossed lines represent the difference between the unrenormalized G function and its value at zero frequency ω.

quency ω and $\omega = 0$.[7] This difference is marked in Fig. 7 by a crossed line.

The sum of Fig. 7 reduces to a geometric progression and can be calculated explicitly. A straightforward, albeit somewhat cumbersome, calculation shows that when the fluctuations are taken into account the expressions for the correlation functions (5.25) (in the Fourier representation) differ from the unrenormalized values only by the substitution $\beta_{ab} \to \tilde{\beta}_{ab}(\omega, \mathbf{q})$. It is natural to call $\tilde{\beta}_{ab}$ a matrix of renormalized elastic moduli, the expression for which is[22]

$$\tilde{\beta}_{ab}(\omega, \mathbf{q}) = \beta_{ab} - \frac{\Xi_a \Xi_b F(\omega, \mathbf{q})}{1 + \Xi_a \Xi_d \beta_{ad}^{-1} F(\omega, \mathbf{q})} \cdot \tag{5.26}$$

The matrix (5.26) has the same structure as the static matrix (4.33) and coincides with it at $\omega = 0$.

We emphasize that expression (5.26) describes the correlators (5.25) in the presence of both small and large corrections to the unrenormalized value. This expression agrees with the ideas of Fixman,[23] who proposed to describe long-wave dynamics by replacing the static compressibility and the heat capacity by complex dynamic quantities that depend on the frequency ω. Specific expressions for the correlators (5.26) will be analyzed in the next section.

6. CRITICAL BEHAVIOR OF THE SYSTEM SPECTRUM

Critical mode

We consider first the mode describing the order-parameter relaxation. The dispersion law of this mode is determined by the singularities of the correlation function $G(\omega, \mathbf{q})$ introduced by (5.8).

In fact, assume that we have added to the Hamiltonian (2.6) the term

$$-\int d^3r\, h\Psi.$$

Here h has the meaning of a field thermodynamically conjugate to Ψ. A corresponding term appears in the action (5.1), and hence in the effective action (5.6). Using next the representation (5.3), it is easily shown that application of a small external field $\delta h(t, \mathbf{r})$ changes the mean value of $\Psi(t, \mathbf{r})$ by an amount

$$\delta\langle\Psi(\omega, \mathbf{q})\rangle = -iG(\omega, \mathbf{q})\delta h(\omega, \mathbf{q}). \tag{6.1}$$

Relation (6.1) pertains to Fourier components. It follows from it that the dispersion law of a critical mode is defined as

$$\det G^{-1}(\omega, \mathbf{q}) = 0. \tag{6.2}$$

We know the explicit expressions (5.13) and (5.14) for $G(\omega, \mathbf{q})$ in the region where the mean-field theory is applicable. Using them we can write down directly the critical-mode dispersion laws, which take the form

$$\omega = -i\Gamma(A_0 + L_\parallel q_z^2 + L_\perp q_\alpha^2),\ A_0 > 0, \tag{6.3}$$

$$\omega_1 = -i\Gamma(2|A_0| + L_\parallel q_z^2 + L_\perp q_\alpha^2),\quad A_0 < 0, \tag{6.4a}$$

$$\omega_2 = -i\Gamma(L_\parallel q_z^2 + L_\perp q_\alpha^2),\quad A_0 < 0. \tag{6.4b}$$

The onset of a zero-gap mode of frequency ω_2 at $A_0 < 0$ is due to the appearance of the Goldstone degree of freedom which we have specified above with the aid of the order-parameter phase φ.

The unrenormalized dispersion laws (6.3) and (6.4) are subject in the fluctuation region (4.11) to large corrections. To establish the critical-mode dispersion law in this region we must use the data given in Sec. 5 on the structure of the correlation function G and based on dynamic-scaling relations. As a result, we obtain for the high-frequency asymptotic behavior

$$\omega \propto iq^z,\quad \omega\tau \gg 1, \tag{6.5}$$

where τ is the characteristic time introduced in the preceding section. To find the proportionality coefficient in (6.5), this dispersion law must be matched to (6.3) and (6.4) at the value $q \sim TU/L^3$ at which the fluctuation regime begins according to (4.11).

We consider now the long-wave case corresponding to $qr_c \ll 1$. For $A_0 > 0$ both branches of the critical mode describe relaxation of the order parameter, with a relaxation time of order τ. For $A_0 < 0$ the same pertains to the mode describing the relaxation of the magnitude of the order parameter. The rate of relaxation of the phase φ of the order parameter depends on the wave vector $\mathbf{q}$, and the damping rate of this mode can be estimated as follows:

$$i\omega \sim \tau^{-1}(qr_c)^2,\quad qr_c \ll 1. \tag{6.6}$$

On the other hand, the dynamics of φ in the low-symmetry phase is described by Eq. (3.17). When orientational dynamics is investigated, one can omit from this equation the terms containing the mean-mass velocity. Linearizing the remaining term, we obtain, taking (2.9) into account, the following dispersion law:

$$\omega = -i\gamma^{-1}(\alpha_\parallel q_z^2 + \alpha_\perp q_\alpha^2). \tag{6.7}$$

Comparing (6.7) with the second dispersion law in (6.4) we obtain, with allowance for (4.27),

$$\gamma = 4\langle\Psi\rangle^2/\Gamma \propto |A_0|. \tag{6.8}$$

This expression is valid in the mean-field theory. In the fluctuation region we should compare (6.7) with the dispersion law (6.6). Taking the proportionality law (4.28) into account, we get

$$\gamma \propto |A_0|^{(3-z)\nu}. \tag{6.9}$$

Relations (6.8) and (6.9) solve the problem of the critical behavior of the "orientational" viscosity coefficient γ.

Acoustic modes

Acoustic modes are connected with density oscillations of the momentum **j**, so that the properties of these modes are specified by the correlation function

$$G_{ik}(t,\ \mathbf{r})=\langle j_i(t,\ \mathbf{r})p_k(0,\ 0)\rangle. \tag{6.10}$$

Here p_k is an auxiliary variable serving as the conjugate to j_k in the action (5.1).

It is expedient to discuss in greater detail the physical meaning of the correlation function (6.10). Assume that an external force density F_i has been added to the right-hand side of Eq. (3.12) for the momentum density. In this case the system acquires, by way of response, a mean value $\langle j_i \rangle$. Adding the corresponding term to the effective action (5.1) and using the representation (5.3), it is easy to show that the relation

$$\langle j_i(\omega,\ \mathbf{q})\rangle=iG_{ik}(\omega,\ \mathbf{q})F_k(\omega,\ \mathbf{q}), \tag{6.11}$$

holds for small F_i and is valid for the Fourier components. The correlation function G_{ik} thus determines the susceptibility of the system in respect to an external force.

This statement means, in particular, that the dispersion equation for the system modes connected with **j** is

$$\det G_{ik}{}^{-1}(\omega,\ \mathbf{q})=0. \tag{6.12}$$

Here the superscript -1 denotes the inverse of the matrix G_{ik}. Equation (6.12) holds for acoustic modes as well as for viscous modes describing relaxation of velocity components not connected with sound.

The unrenormalized value of the correlator (6.10) is determined by the quadratic part of the effective action (5.12). Since the acoustic modes are more rigid than the thermodiffusion mode, in acoustic investigations we can assume that the adiabaticity condition $\varphi_\sigma = \text{const}$ is satisfied. With this taken into account, the quadratic part of the action (5.12) is expressed after substitution of (5.22) only in terms of p_i and j_i. The resultant expression can be used to calculate G_{ik} directly in accordance with (5.3).

Performing the transformations described above, we obtain an explicit equation for the matrix of the reciprocal of the Fourier component G_{jk}:

$$G_{ik}^{-1}=\omega\delta_{ik}+\frac{1}{\rho\omega}f_{a,in}f_{b,km}q_mq_n\tilde{\beta}_{ab}(\omega,\mathbf{q})-\frac{1}{\rho}\eta_{iknm}q_mq_n. \tag{6.13}$$

Here $f_{a,ik}$ is determined by Eq. (3.24). In accord with the analysis of Sec. 5, we have replaced the unrenormalized matrix $\tilde{\beta}$ of the elastic moduli in the derivation by the renormalized matrix given by (5.26). The result is an expression for the correlation function G_{ik} with account taken of the main contributions due to the order-parameter fluctuations.

Expression (6.13) makes possible a complete analysis of the critical behavior of the acoustic-mode dispersion relations defined by Eq. (6.12). This expression, moreover, in accord with (6.11) specifies the critical behavior of the system susceptibility with respect to external forces. We shall present below results of an analysis based on (6.13) and pertaining to various frequency and value ranges of the critical parameter A_0.

We note first of all that, owing to the linear dispersion law, the acoustic oscillations are "stiffer" than the critical mode in the critical region. This means that at $\omega = cq$ the dynamic correlation functions depend more strongly on the frequency than on the wave vector **q**. The latter pertains, in particular, to the Fourier component of the correlation function (5.10), since it determines in accordance with (5.26) the renormalized values of the elastic moduli $\tilde{\beta}_{ab}$. In other words, we can neglect the dependence of $\tilde{\beta}_{ab}$ on **q** in the analysis of the acoustic modes, i.e., substitute the value $\tilde{\beta}_{ab}(\omega,\ \mathbf{q}=0)$ in (6.13).

Let us first examine the low-frequency limit $\omega\tau \ll 1$, where τ is the characteristic order-parameter relaxation time introduced in the preceding section. In this case to first approximation we can use $\tilde{\beta}_{ab}(0,\ 0)$, in (6.13) i.e., the static renormalized elastic moduli.

The dispersion equation in (6.12) (with viscosity neglected) determines in this case the sound-wave velocities $c = \omega/q$, which are expressed, as they should, in terms of the renormalized adiabatic moduli $\tilde{\beta}_{ab}$.

Only one acoustic mode is present in a nematic. Its velocity is isotropic and is given according to (6.12) by

$$c^2=\rho\tilde{\beta}_{\rho\rho}=\left(\frac{\partial P}{\partial\rho}\right)_\sigma, \tag{6.14}$$

where p is the pressure, i.e., we arrive at the standard expression for the speed of sound in terms of the compressibility (an expression valid, in particular, for an ordinary liquid). The second equality in (6.14) was discussed for the case of unrenormalized quantities at the end of Sec. 2, and is valid also for renormalized quantities. The same holds also for the relation $\tilde{\beta}_{uu} = B$ which will be used below.

A smectic permits, besides ordinary sound (whose velocity we designate by c_1), propagation of what is called second sound connected with the compression of the smectic layers. The propagation velocity c_2 of this sound is strongly anisotropic. We present expressions for the velocities c_1 and c_2, assuming that $c_2 \ll c_1$:

$$\begin{aligned}c_2{}^2&=\frac{1}{\rho}\tilde{\beta}_{uu}\frac{q_z{}^2q_\alpha{}^2}{q^4}=\frac{B}{\rho}\frac{q_z{}^2q_\alpha{}^2}{q^4},\\ c_1{}^2&=\rho\tilde{\beta}_{\rho\rho}-2\tilde{\beta}_{\rho u}\frac{q_z{}^2}{q^2}+\tilde{\beta}_{uu}\frac{1}{\rho}\frac{q_z{}^4}{q^4}.\end{aligned} \tag{6.15}$$

Here B is the compression modulus of the smectic layers, the subscripts z and α label respectively the components of the wave vector **q** along the normal to the smectic layers (along the z axis) and in the plane of the layers. The propagation velocity of first sound produced in a smectic by oscillations of the mass density ρ is determined for $c_2 \ll c_1$ in first order by the same equation (6.14) as for a nematic.

The critical behavior of the propagation velocities of the acoustic waves is determined by Eqs. (6.14) and (6.15) with allowance for the critical behavior discussed in Sec. 4. In the mean-field theory the velocities c, c_1, and c_2 are discontinuous at the phase-transition point. In the fluctuation region (4.11), the velocities have the rather complicated critical behavior defined by (4.33b) (one must put $\mathbf{q} = 0$ in the calculation of c_1 and c_2). We note only that, with allowance for fluctuation effects, c_1 and c_2 remain finite, according to (4.33b), at the phase-transition point.

We examine now, in the low frequency region, the first corrections to the dynamic correlation functions in terms of the parameter $\omega\tau$. For small $\omega\tau$ the Fourier component of the correlation function (5.10) can be written as

$$F(\omega, \mathbf{q}) = F_0 + iF_1\omega\tau. \tag{6.16}$$

Here $F_0 = F(0,0)$ and its critical behavior was discussed in Sec. 4; F_1 has the same critical behavior as F_0. Expanding expression (5.26) for the renormalized dynamic moduli in terms of the second small parameter of (6.16), we get

$$\tilde{\beta}_{ab}(\omega, 0) - \tilde{\beta}_{ab}(0, 0) = \frac{-iF_1\Xi_a\Xi_b\omega\tau}{(1+\Xi_c\beta_{cd}{}^{-1}\Xi_d F_0)^2}. \tag{6.17}$$

Comparison of this expression with (6.13) leads to the conclusion that the presence of the contribution (6.17) in the dynamic moduli denotes renormalization of the viscosity tensor. Denoting this renormalized tensor by $\tilde{\eta}$, we obtain from (6.13) and (6.17)

$$\tilde{\eta}_{iklm} = \eta_{iklm} + \frac{F_1\Xi_a\Xi_b\tau(f_{a,ik}f_{b,lm} + f_{a,im}f_{b,kl})}{2(1+\Xi_c\beta_{cd}{}^{-1}\Xi_d F_0)^2}. \tag{6.18}$$

This equation means that the viscosity coefficients have much more singular critical velocities than the sound velocities. Note that the explicit expressions (3.23) for $f_{a,ik}$ show that only the so called bulk viscosity coefficients contain large fluctuation corrections. It is precisely these coefficients which enter in the dispersion laws of the acoustic modes and are the cause of their damping:

$$\operatorname{Im}\omega \sim -\tilde{\eta}q^2/\rho. \tag{6.19}$$

In the mean-field theory, the quantity F_1 in (6.18), unlike F_0, has no discontinuity and is small compared with the F_0 discontinuity given by (4.22). Calculation of the first nonvanishing fluctuating contribution to F_1 shows that $F_1 \ll F_0$ holds in the region where the mean-field theory is applicable. In this region the fluctuation contributions to the bulk-viscosity coefficients are thus given, according to (5.15) and (6.18), by

$$\tilde{\eta}_{1,4,5} - \eta_{1,4,5} \propto |A_0|^{-3/2}. \tag{6.20}$$

The critical behavior of the viscosity coefficients in the fluctuation region (4.11) is given in accordance with (6.18) by Eqs. (4.18), (4.24), and (5.15), which lead to the proportionality

$$\tilde{\eta} - \eta \propto |A_0|^{-z\nu\pm\alpha}. \tag{6.21}$$

The choice of the plus or minus sign in the exponent of (6.21) depends on whether the combination $\Xi_c\beta_{cd}^{-1}\Xi_d F_0$ is large or small compared with unity.

We consider now the high-frequency case $\omega\tau \gg 1$. The high-frequency asymptotic form of the function $F(\omega, \mathbf{q} = 0)$ in the fluctuation region is determined by (5.19b). In the region where the mean-field theory is valid, the first nonvanishing fluctuation correction to $F(\omega, \mathbf{q} = 0)$ is proportional to $\omega^{-1/2}$. In both cases, the function F has real and imaginary parts of equal order. We can therefore analyze on the basis of (5.26) and (6.13) the sound-wave dispersion laws (6.12) in the low-frequency region. Various situations are possible, depending on the sizes of the fluctuation corrections to the unrenormalized values of β_{ab}.

If the corrections to β_{ab} are small, the sound waves propagate with high-frequency velocities that differ from the low-frequency ones. The presence of a fluctuation term gives rise to corrections, proportional to $F(\omega, \mathbf{q} = 0)$, to both the real and imaginary parts of the dispersion law $\omega(\mathbf{q})$. If the corrections to β_{ab} are appreciable, the sound wave propagate at the low-frequency (renormalized) velocities (6.14) and (6.15). The dispersion law $\omega = cq$ is subject in this region to corrections $\propto F^{-1}$ (to both the real and imaginary parts of the dispersion law).

In addition to the above corrections, it is necessary to take into account in the high-frequency region the sound damping $\sim \eta q^2/\rho$ due to the viscosity terms in (6.13). We emphasize that this damping is due to the unrenormalized viscosity coefficient and consequently has no critical behavior.

A preliminary report of the foregoing results was published earlier.[22]

Singularities of the critical dynamics of the transitions S_A–$S_C(S_1)$, S_A–S_2, and N–N_2

These singularities are due to the low symmetry of the order parameters corresponding to these phase transitions. The order parameter for the transition S_A–$S_C(S_1)$ is a vector, while for the transitions S–S_2 and N–N_2 it is a second-rank tensor specified in real space.

The singularities of the transitions S_A–S_C and N–N_2 come into play even in statics, making the critical exponents nonuniversal in a wide intermediate region defined by (4.11) and (4.36). Qualitatively, however, they do not alter the qualitative picture of the transition. More significant in these transitions are the dynamic singularities connected with the presence in $f_{\Psi,ik}$ of the contributions (3.25) and (3.26) which vanish near the transition point. These contributions enter both in Eq. (3.18) for the order parameter and in expression (3.10) for the stress tensor. Since the $f_{\Psi,ik}$ remain finite at the transition point, the terms containing them cannot be neglected (as was done above) in the analysis of critical dynamics.

Cross terms thus appear in the equations for the velocity and the order parameter. Since the critical mode is soft, these cross terms play no significant role in the formation of the dispersion laws of the acoustic or velocity-relaxation modes. The presence of these cross terms, however, strongly influences the form of the dynamic equation for the order parameter.

Cross terms other than the above appear also in the equations for $\mathbf{v}$ and the director $\mathbf{n}$, which are of dissipative origin.

After eliminating the weakly fluctuating variables, which include the velocity relaxation component and/or the director, Eq. (5.7) for Ψ is replaced by

$$\frac{\partial\Psi}{\partial t} = -\Gamma^{eff}\frac{\delta\mathcal{H}^{eff}}{\delta\Psi}. \tag{6.22}$$

Here Γ^{eff} is a matrix of the order-parameter components and has a complicated angular dependence on the wave-vector direction. We have approximately

$$\Gamma^{eff} - \Gamma \sim \eta^{-1},\ \gamma_1{}^{-1}, \tag{6.23}$$

where Γ is the kinetic coefficient in Eq. (3.9) for the order parameter, η is determined by the viscosity coefficients that specify the relaxation rate of the transverse velocity component, and γ_1 is the torsional-viscosity coefficient introduced in (3.14). Recall that these viscosity components have no critical behavior.

The correlation-function dynamic-singularity components connected with the unusual angular dependence and with the matrix structure of Γ^{eff} are "extinguished" in the fluctuation region. This extinction, however, is slow when $z-2$ is small (z is the dynamic critical exponent). Therefore, in particular, the kinetic coefficient γ indicative of the phase relaxation of the order parameter φ in the low-temperature phase, has a nontrivial angular dependence. This dependence vanishes only very close to the transition point.

We have discussed how the director mode and of the relaxation mode connected with the shear component of the velocity affect the behavior of the critical mode in the vicinity of the transitions S_A–$S_C(S_1)$, S_A–S_2, and N–N_2. In turn, the connection of the order parameter with the director and with the shear component of the velocity modifies the spectra of the latter. Each dispersion law contains a correction of the form

$$iLq^2/\eta. \tag{6.24}$$

Here L and η stand for a complicated combination of elastic moduli and viscosity coefficients. This correction changes the spectrum of the director mode somewhat, but can be neglected in spectrum of the relaxation modes.

We note finally that in the scaling region, where the critical mode is greatly softened, the correction (6.24) vanishes from the spectra of the nonrenormalized diffusion modes. This region, however, can hardly be reached in experiment.

7. CONCLUSION

We have investigated theoretically the critical dynamics of a number of phase transitions that occur in both the nematic and smectic phases of liquid crystals. All these phase transitions, in which the rotational symmetry is spontaneously broken, are described by a two-component order parameter that is purely relaxational for the transitions in question. It is therefore natural to gather all these transitions, which we shall call orientational, into a special group and treat them within the framework of a single formalism. This has been done in the present paper.

The acoustic modes, or more accurately their damping, turn out to be most sensitive to critical fluctuations. Theory makes it possible to determine the critical contribution to the dispersion laws of the acoustic modes that contain one universal function F of $\omega\tau$, where τ is the characteristic damping time of the critical mode and depends likewise universally on the proximity to the transition point. The function $F(\omega\tau)$ cannot be obtained in explicit form, but our expression for the critical contribution makes it possible to relate the frequency dependences of the sound-wave dispersion law at various temperatures, and also for various substances and different orientational phase transitions.

Detailed experimental data are available at present for the first- and second-sound dispersion laws near the smectic-A–smectic-C phase transition.[5] The entire aggregate of these data agrees splendidly with the results of the proposed theory. A discussion of the results of the theory for the A–C transition can be found in our earlier paper.[24] Comparison of the theory with experiment[5] yields for $F(\omega\tau)$ an explicit expression that could be used in the future to compare the theory with experimental data, and for other orientational phase transitions.

In the investigation of orientational phase transitions we have used a method of effectively excluding, from the action in dynamic fluctuations, weakly fluctuating degrees of freedom whose dynamic correlation functions can be explicitly expressed in terms of correlation functions for the order parameter. This method is universal and can be used to investigate the dynamics of any system with well developed low-frequency fluctuations. Thus, for example, it was used to investigate anomalous sound damping in smectics[20] or near a weak-crystallization phase transition.[25]

This method can also be used to study theoretically the dynamic singularities of substances near a number of phase transitions outside the scope of our analysis. These include second-order crystallization transitions such as the nematic–smectic transition, as well as the critical point on the smecitic A_1–smectic A_d diagram. Their treatment, however is outside the scope of the present paper and can be the subject of a special investigation.

[1] P. G. De Gennes, *Physics of Liquid Crystals*, Pergamon, Oxford, 1974.

[2] E. I. Kats, Usp. Fiz. Nauk **142**, 99 (1984) [Sov. Phys. Uspekhi **27**, 42 (1984)].

[3] K. C. Wilson and J. Kogut, Phys. Rep. C **12**, 76 (1974).

[4] A. Z. Patashinskii and V. L. Pokrovskii, *Fluctuation Theory of Phase Transitions*, Pergamon, Oxford, 1974.

[5] V. A. Balandin, E. V. Gurovich, and A. S. Kashitsyn, Zh. Eksp. Teor. Fiz. **98**, 485 (1990) [Sov. Phys. JETP **71**, 270 (1990)].

[6] E. I. Kats and V. V. Lebedev, *ibid.* **90**, 111 (1986) [**63**, 63 (1986)].

[7] E. V. Gurovich, E. I. Kats, and V. V. Lebedev, *ibid.* **94**, No. 4, 167 (1988) [**67**, 741 (1988)].

[8] E. I. Kats and V. V. Lebedev, *Dynamics of Liquid Crystals* [in Russian], Nauka (1988).

[9] I. E. Dzyaloshinskii and G. E. Volovik, Ann. Phys. (NY) **88**, 823 (1980).

[10] E. I. Kats and V. V. Lebedev, Zh. Eksp. Teor. Fiz. **88**, 823 (1985) [Sov. Phys. JETP **61**, 484 (1985)].

[11] L. D. Landau and E. M. Lifshitz, *Hydrodynamics*, Pergamon, Oxford, 1988.

[12] L. D. Landau and E. M. Lifshitz, *Statistical Physics*, Part 1, Pergamon, Oxford, 1980.

[13] G. Grinstein and R. A. Pelcovits, Phys. Rev. Lett. **47**, 856 (1981). Phys. Rev. A **26**, 915 (1982).

[14] E. I. Kats, Zh. Eksp. Teor. Fiz. **83**, 1376 (1982) [Sov. Phys. JETP **56**, 791 (1982)].

[15] H. W. Wyld, Ann. Phys. (N.Y.) **14**, 143 (1961).

[16] P. C. Martin, E. D. Siggia, and H. A. Rose, Phys. Rev. A **8**, 423 (1973). C. de Dominicis, J. de Phys. Colloque, No. 1, 247 (1976). H. K. Janssen, Z. Phys. B **23**, 377 (1976).

[17] V. V. Lebedev, A. I. Sukhorukov, and I. M. Khalatnikov, Zh. Eksp. Teor. Fiz. **90**, 1249 (1981) [Sov. Phys. JETP **63**, 728 (1981)].

[18] V. N. Popov, *Functional Integrals in Quantum Field Theory and Statistical Physics* Reidel, Amsterdam, 1983.

[19] G. F. Mazenko, S. Ramaswamy, and J. Toner, Phys. Rev. Lett. **49**, 51 (1982). Phys. Rev. A **28**, 1618 (1983).

[20] E. I. Kats and V. V. Lebedev, Pis'ma Zh. Eksp. Teor. Fiz. **37**, 594 (1983) [JETP Lett. **37**, 709 (1983)]. Zh. Eksp. Teor. Fiz. **85**, 2019 (1983) [Sov. Phys. JETP **58**, 1172 (1985)].

[21] D. Halperin and P. I. Hohenberg, Rev. Mod. Phys. **49**, 435 (1977).

[22] E. V. Gurovich, E. I. Kats, and V. V. Lebedev, Pis'ma Zh. Eksp. Teor. Fiz. **52**, 1196 (1990) [JETP Lett. **52**, 610 (1990).

[23] M. Fixman, J. Chem. Phys. **36**, 1961 (1962).

[24] E. V. Gurovich, E. I. Kats, and V. V. Lebedev, J. Phys. Condens. Matter **2**, 9155 (1990).

[25] E. I. Kats, V. V. Lebedev, and A. R. Muratov, Physica (Utrecht) A **160**, 98 (1989).

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