Heterophase states in physical systems

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The main experimental data on the observation of heterophase states in physical systems are reviewed. Phenomenological theories and approaches to the study of the dynamics of heterophase nucleation centers are described. The essence of Bogolyubov's concept of quasiaverages is investigated, and principles of a microscopic equilibrium theory of heterophase states are formulated on its basis. The thermodynamic behavior of heterophase systems is illustrated by model problems in the theory of magnetism, superconductivity, and relativistic nuclear physics.

INTRODUCTION

In recent years, much attention has been paid to the investigation of phase transitions and the critical phenomena associated with them. The main reasons for this are the following circumstances. First, the study of phase transitions in condensed media has a strong influence on the development of modern technology. Second, the very concept of a phase transition and the methods of its theory have penetrated and, in recent years, have become firmly established in the most varied fields in physics—in quantum field theory, elementary-particle physics, nuclear physics, etc. Particularly important is the fact that phase transitions and critical phenomena that occur in systems having different physical natures possess common features and can be described in the framework of a unified approach. This circumstance makes it possible to treat the theory of phase transitions as an independent discipline.

The traditional approach is associated with the study of phase transitions between pure (homogeneous in the sense of the phase composition) states and critical phenomena due to homogeneous fluctuations, i.e., collective excitations in a pure phase. Such critical phenomena can be described by means of the Fisher-Widom-Kadanoff-Wilson approach,[1,2] which is intimately related to the Bogolyubov-Shirkov renormalization-group method.[3,4]

But in numerous cases it is possible to observe experimentally the phenomenon of interpenetration and equilibrium coexistence of different phases. For example, as water approaches the boiling point, macroscopic vapor bubbles can be observed in it. Above 0 °C, water is an equilibrium mixture of water and ice present in macroscopic amounts but unobservable by ordinary methods because of the rapid fluctuations in the volume of the system. It is the presence of the ice, in which the molecules do not have the same packing as water, that makes it possible to explain the well-known anomaly of the water density in the temperature range from 0 to 4 °C.

Such phase mixing—heterophase states—are observed in the most varied systems: in superconductors, magnets, ferroelectrics, crystals, liquids, etc. The fluctuations of the water density above 0 °C have a direct analogy with Blokhintsev's fluctons in nuclei.[5] Heterophase ideas have also found an application in traditional nuclear theory in connection with the problem of intermediate values of the angular momenta of heavy nuclei.[6] Finally, the existence of multiquark objects in nuclei, predicted by Baldin[7] and confirmed experimentally, can be interpreted as a manifestation of a heterophase state of quark matter.[8]

The experimental and theoretical study of heterophase states has been carried out already for more than one decade. The first phenomenological theories of states that are an equilibrium mixture of phases were proposed in the thirties.[9] The concept of heterophase fluctuations was introduced at the end of the thirties by Frenkel, whose studies laid the foundation of the investigation into the kinetics of the nucleation centers of competing phases. An interesting and important approach, taking into account scaling ideas, was developed in the middle of the sixties by Fisher[10,11] ("drop model"). The investigation of the kinetics of heterophase systems using computer simulation[12,13] has been widely used in recent years.

However, it is only comparatively recently that a microscopic theory of the heterophase state has been successfully developed.[14–22] The basis of this theory is Bogolyubov's concept of quasiaverages,[23,24] which plays a fundamental role in the theory of phase transitions. This concept makes it possible to resolve constructively the problem of the nonuniqueness in the choice of the state space of a macroscopic system[25] and to treat a phase transition as a spontaneous breaking of symmetry.

The method of microscopic description of heterophase states developed on the basis of the concept of quasiaverages makes it possible to treat from a unified point of view systems that are completely different in their physical natures. In essence, the method is a general approach to the construction of microscopic models of heterophase states in physical systems and makes it possible to understand how they arise. An important circumstance here is the fact that any of the known methods of statistical mechanics can be used to calculate particular characteristics of a heterophase system.

The present paper attempts a systematic exposition of the present status of the physics of heterophase systems, including experimental results, phenomenology, dynamical approaches (including computer simulation), Bogolyubov's concept of quasiaverages for global and local symmetry breakings, the principles of the microscopic theory of heterophase states, and examples of its application for different physical objects.

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1. OBSERVATION OF HETEROPHASE STATES

We have already said that heterophase states—equilibrium mixtures of phases—are observed in the most varied physical systems. We here consider a number of examples that support this assertion.

Superconductors

It is well known that the superconducting state is characterized by the presence of a condensate state of an "electron fluid" that extends to the complete volume of the system.[26,27] The condensate is formed by Cooper pairs, but down to very low temperatures the "normal fluid"—a macroscopic fraction of electrons not in the condensate—persists in the system. The properties of such electrons in no way differ from their properties in the normal state. The normal fluid is also extended to the complete volume of the system (in superconductors of the first kind). In other words, in a superconductor the phase components are mixed. Thus, superconductivity is a remarkable example of a heterophase state.

Such a two-fluid picture is the basis of the phenomenological theories of Gorter and Casimir,[9] the Londons,[28] the nonlocal generalization of the London theory by Pippard,[29] and the Ginzburg-Landau theory.[30] This picture of superconductors is well confirmed experimentally.

In the first place, we must mention the observations of the rather appreciable low-temperature thermal conductivity, which cannot always be explained by just one background contribution (Ref. 31).[1)] To a large degree, this thermal conductivity is due to the normal electrons. This is illustrated particularly clearly by investigations of the dependence of the thermal conductivity on the concentration of impurities in superconductors. It is found that an increase in the amount of impurities in tin single crystals below 3.72 °K leads to an increase in the thermal conductivity as a result of the scattering of the normal electrons by the impurities.[32]

In the supercooled normal state (in an external magnetic field) in tin and aluminum, nucleation centers of the superconducting phase can be observed.[33]

In the interval between the upper and lower critical fields, superconductors of the second kind constitute a thermodynamically equilibrium state in which the electron components (superconducting and normal) are spatially localized.[34] This phenomenon can be observed by various methods, the simplest of which employs the Faraday effect in glass containing a paramagnetic admixture of ceric nitrate and placed on a smooth surface of the superconductor.[35] Application of a magnetic field leads to a rotation of the plane of polarization of plane-polarized light incident on the glass in regions in which magnetic flux penetrates into the sample (superconducting regions). The normal regions then appear dark.

Of great interest was Staudenmann's experiment[36] to study the distribution of the density of valence electrons at different temperatures in V_3Si crystals by the x-ray diffraction method. This showed that quite different pictures of the electron bonds in the crystal correspond to the different phases. Thus, the bond between the Si atoms and the V–V chain which exists at room temperature is absent at 13.5 °K, i.e., in the superconducting phase (which arises below the transition point 16.85 °K). Unfortunately, the experiments were made only for two temperatures (13.5 and 300 °K). We emphasize that study of the distribution of the electron density in its dependence on the temperature in a wide range, including the transition point, would make it possible to obtain detailed information about the mechanism of phase generation and the phase transition. This method, making it possible to "see" the interactions in the crystal from within, so to speak, is very promising for the investigation of phase transitions not only in superconductors but also, for example, in vanadium compounds, which undergo a metal-insulator transition, and magnets based on *3d* elements. Particularly convenient is the combination of the methods of x-ray diffraction and neutron scattering, since the use of the latter makes it possible to fix precisely the position of the nuclei, this being necessary for the correct analysis of x-ray data.[2)]

Before we turn to the discussion of other objects, we note that what we have said above entails the existence of heterophase states in superconductors in transitions of both the first and the second kind. We emphasize this particularly, since traditionally heterophase phenomena are associated only with transitions of the first kind, an association by no means always in agreement with the experimental data.

Magnets

An equilibrium mixture of different phases is also observed in magnets. We mention, for example, the spin-echo experiments in the method of nuclear magnetic resonance for the cobalt compounds $CoTi_{1-x}Al_x$ and $CoTi_{1-y}Ga_y$,[37–39] in which it was shown that below the Curie point, at definite x and y, there is coexistence of "magnetic" and "nonmagnetic" cobalt[39] (in these compounds, the magnetic moments are localized at the Co sites, as is confirmed by neutron diffraction experiments[40]). Measurements of the magnetization show that at $x \sim 0.57$–0.6 and $y \sim 0.6$–0.7 and temperature 4.2 °K the spontaneous magnetization is always far from saturation, although the corresponding Curie points exceed 100 °K. This also indicates a partial disordering, i.e., the presence of paramagnetic regions (of nonmagnetic Co).[39]

In a Au_4Mn crystal, it is possible, by annealing from an initial state with temperature 753 °K, to prepare a ferromagnetic state diluted by regions of antiferromagnetic ordering or, possibly, paramagnetic regions.[41] In such a ferromagnet, the Curie point is of order 120 °K, approximately half of that for ordinary samples. The magnetization near the ground state in this case is also half of that for ordinary samples at the same temperature. There is a similar effect for Cu_3Mn.[42]

In the ferro- and antiferromagnetic crystals DyH_2 and EuB_6 there is also a partial disordering below the Curie point, this being manifested in anomalous behavior of the magnetization, which has a maximum below the transition point, and the specific heat[43–45] (see also Ref. 46).

We emphasize that in magnets too the heterophase states are not associated with transitions of the first kind.

Ferroelectrics

By nuclear quadrupole resonance in HCl crystals and mixed HCl–DCl crystals it is possible not only to detect heterophase fluctuations but also to determine the temperature dependence of the mean concentration of ferroelectric clusters near the transition.[47,48] Such clusters arise in these compounds at about 0.5 °K above the transition point, i.e., in the paraelectric phase.[48]

It was also recently shown that heterophase states play an important part in the repolarization of ferroelectrics.[49]

Crystals

A crystal is a periodically ordered state of a system of particles with a well-defined symmetry, such symmetry being absent in the liquid phase. Therefore, particles displaced from one site to another in the crystal lattice by self-diffusion must be regarded as part of the liquid phase. To a greater or lesser degree, actually existing crystals possess the features of solid (localized) and liquid (nonlocalized) substances. The delocalization of particles associated with their hopping from site to site is particularly pronounced in quantum crystals.[50] Something similar must also be observed in crystallized neutron stars.[51]

However, elements of localization (of the crystal state) are also observed in the liquid phase.[52] For example, investigation of the propagation of hypersound in supercooled water (bidistillate) at the temperature − 27 °C makes it possible to identify a heterophase state—a mixture of water and ice[53] revealed by anomalous behavior of the specific heat, thermal conductivity, and isothermal compressibility (see also Refs. 54 and 55).

Heterophase states can also occur when there are structure transitions (a change in the ordering in a crystal). For example, the behavior of the central phonon peak for $SrTiO_3$ can be explained by the presence of heterophase fluctuations (nucleation centers of the competing phase) in a fairly wide temperature range near the point of the structure transition.[56]

Nuclear systems

An infinitesimally small change in the rotation frequency can be accompanied by the observation of a qualitative change in the behavior of the angular momentum of a nucleus. For example, at a rotation frequency approximately equal to 0.28 MeV there is a jump in the angular momentum of the ^{152}Dy nucleus, which can be interpreted as a phase transition.[57] This interpretation is justified, since the states of the ^{152}Dy nucleus above and below this point differ qualitatively—at low frequencies, the nucleus is spherical, whereas when the transition point is reached deformation occurs and the nucleus becomes elliptic. This phenomenon is explained by the mechanism of nucleon pairing, which was first proposed by Bogolyubov[58] (see also Ref. 59). Below the phase-transition frequency Ω_0, the nucleus is in the state of a Bose condensate by virtue of nucleon pairing, whereas above Ω_0 the rotation destroys the pairing, and this leads to a jump in the angular momentum.[57]

However, at low rotation frequencies the angular momentum of the nuclei is not always zero.[6] Such behavior indicates the presence of not only the condensate state but also a certain fraction of unpaired nucleons, i.e., the presence of a certain amount of the phase formed at high values of the rotation frequency. It is such nucleons that create the nonzero value of the angular momentum.[6]

As another example of heterophase states in nuclear systems, we can mention the clusters that arise in nucleon matter when the density is raised[60]; evidence for these is provided by experiments on the interaction of heavy ions with energies around 2 GeV.[61]

Deconfinement and multiquark states

Study of the problem of deconfinement in quantum chromodynamics suggests that multiquark states may arise when the temperature and density of a hadronic system are raised.[62,63] A system of nucleons may go over to a six-quark state, nine-quark state, etc., this even going so far as to deconfinement. The different states in this sequence can be interpreted as phase states of quark matter.

The cumulative effect, predicted by Baldin[64] and discovered experimentally,[65] was the first sign of the existence in nuclei (nucleon systems) of multiquark states, i.e., different coexisting phases. The presence in nuclei of the six-quark and, possibly, the nine-quark state was subsequently confirmed by various experiments,[66–69] the most convincing of which are the studies on deep inelastic scattering of leptons by nuclei[66,68,69] (see also Ref. 70).

Thus, these examples show that heterophase states are indeed realized in different physical systems and are not associated with any particular type of phase transition, for example, one of the first kind.

2. EQUILIBRIUM PHENOMENOLOGICAL THEORIES

As already mentioned in the Introduction, the first phenomenological model of a heterophase state was proposed in 1934 by Gorter and Casimir[9] in connection with the development of the thermodynamics of the superconducting phase transition. The ideas of Gorter and Casimir's two-fluid model are simple and transparent and can be applied to the phenomenological description of heterophase states in arbitrary systems. We briefly explain the basic principles of this approach.

We consider a system in which one of n phase states (pure phases) can be realized under certain conditions. We denote by $G_i(\Theta, x)$ the free energy per unit volume (or the Gibbs potential) of phase $i (i = 1,...,n)$. Here, Θ is the temperature, having the dimensions of energy ($\Theta = k_B T$), and x are external parameters of the system, for example, fields acting on it. Suppose that in the system a heterophase state is realized in the form of an equilibrium mixture of n phases. By w_i we denote the relative fraction of the particles in phase i,

$$w_i = N_i/N, \tag{1}$$

where $N = \Sigma_i N_i$ is the total number of particles in the system.

It is clear that

$$\sum_i w_i = 1 \tag{2}$$

The basic assumption of the Gorter-Casimir theory[9] (see also Refs. 27 and 31) is that there exist functions $\varphi_i(w_i)$ such that the free energy per unit volume of the heterophase state is

$$G(\{w_i\};\ \Theta,\ x) = \sum_i \varphi_i(w_i)\, G_i(\Theta,\ x). \tag{3}$$

The parameters w_i are found self-consistently as functions of Θ and x from the condition of minimality of $G(\{w_i\}; \Theta, x)$ corresponding to the assumption of equilibrium of the heterophase state. It is clear that the minimization problem must be solved subject to the condition (2), and solutions of the type $w_j \equiv 1$, $w_{i\neq j} \equiv 0$ must be compared with other (nontrivial) solutions. In all cases, the stable state will be the one (pure or mixed) whose free energy has the smallest of the possible values for the given Θ and x.

In the case of a superconductor, $n = 2$ (there exist only two phases—the superconducting phase $i = 1$ and the normal phase $i = 2$). The Gibbs potential of the superconducting electrons is taken to be equal to[9,27,31]

$$G_1(\Theta) = -g = \text{const.}$$

For the normal electron component, the Gibbs potential has the same form as for ordinary electrons in a normal metal,

$$G_2(\Theta) = -\frac{1}{2}\gamma\Theta^2,$$

where γ is Sommerfeld's constant.

We write $w_1 \equiv w$; then, by virtue of (2), $w_2 \equiv 1 - w$. We make a remark concerning the choice of the functions $\varphi_i(w_i)$. It is clear that the only way of determining the form of the functions $\varphi_i(w_i)$ involves fitting to experimental data. This method of choice leaves a certain arbitrariness in the determination of the heterophase free energy (3). The simplest choice of these functions in the case of a superconductor is[9]

$$\varphi_1(w) = w; \quad \varphi_2(1-w) = (1-w)^\alpha,$$

where the parameter α is usually taken to be $\frac{1}{2}$ in order to ensure reasonable agreement with the experimental data.

Substituting these relations in the expression for the total free energy (3) and minimizing with respect to w, we find

$$w = 1 - \gamma^2\Theta^4/16g^2.$$

If we now assume that above Θ_c the pure normal phase is realized,[9,27,31] i.e., that $w \to 0$ as $\Theta \to \Theta_c$, then

$$g = \gamma\Theta_c^2/4.$$

Further, we assume that $w \to 1$ as $\Theta \to 0$ and use the thermodynamic relation obtained from the Meissner effect,[31]

$$G_2(\Theta) - G_1(\Theta) = H_c^2/8\pi,$$

where $H_c = H_c(\Theta)$ is the critical magnetic field. From this we have

$$w = 1 - (\Theta/\Theta_c)^4$$

and

$$H_c(\Theta) = H_0[1-(\Theta_0/\Theta_c)^2]; \quad H_0 = \sqrt{g/8\pi} = \Theta_c\sqrt{\gamma/32\pi}.$$

The last relation agrees fairly well with experiment.[27,31] From these relations it is possible to determine other thermodynamic characteristics of the state. For example, for the specific heat

$$C = -\Theta\frac{\partial^2 G}{\partial\Theta^2} = 3\gamma\Theta_c(\Theta/\Theta_c)^3.$$

Such a cubic dependence of the specific heat agrees only roughly with the experimental results,[31] indicating the presence of an exponential dependence.

Subsequently, attempts were made to improve the results for superconductors obtained in the framework of the Gorter-Casimir model.[71] The two-fluid model was also used in the theory of superconductors of the second kind in connection with the problem of the motion of vortex filaments.[72,73]

It is obvious that the Gorter-Casimir theory can be improved by calculating the free energies of the phase components on the basis of microscopic models. We mention in this connection the model proposed by Mikhaĭlov *et al.*[6] to explain the intermediate values of the angular momentum of heavy nuclei. They assumed that such a nucleus contains both a condensate (superfluid) and a normal component, the total Hamiltonian being chosen in the matrix form

$$H = \begin{pmatrix} H_1 & \Delta \\ \Delta & H_2 \end{pmatrix}, \tag{4}$$

where H_i are the Hamiltonians of the corresponding components, and Δ is a phenomenological term describing the interaction between the components. The form of this term and the concentrations of the components were determined here too by fitting, so that the model of Ref. 6 can be regarded as a semiphenomenological form of the Gorter-Casimir theory.

The weakest point in the Gorter-Casimir theory is the assumption that the dependence on the parameters w_i occurs in the expression (3) for the total free energy in the form of certain factors. But in no way does it follow that the dependence is so trivial. Strictly speaking, it would be more consistent to determine the total free energy by the relation

$$G(\{w_i\};\ \Theta,\ x) = \sum_i G_i(w_i;\ \Theta,\ x), \tag{5}$$

and seek the functions $G_i(w_i; \Theta, x)$ on the basis of microscopic considerations. We shall return to the discussion of this question below when considering the microscopic theory of heterophase states.

An undoubted achievement of the Gorter-Casimir theory is that it correctly reflects the qualitative picture of the heterophase state at the thermodynamic level. Particularly fruitful is the idea of introducing an additional parameter w, determined self-consistently, from the equilibrium condition. In the modern theory of phase transitions, each phase is associated with an order parameter— in a superconductor, a gap ($\Delta = 0$ in the normal phase and $\Delta \neq 0$ in the superconducting phase); in a ferromagnet, the magnetization ($M = 0$ in the paramagnetic phase and $M \neq 0$ in the ferromagnetic phase), etc. However, in a heterophase state, an equilibrium mixture of phases, ordinary order parameters are clearly inadequate. One also needs some additional parameter to indicate what fraction of the particles of the system is in a given phase. Just such a specific heterophase parameter is w.

We give one further example of the application of the Gorter-Casimir theory—the reaction by which three-quark bags (baryons) fuse into six-quark bags: $3q + 3q \leftrightarrow 6q$. Such a process is to be expected in nuclear matter when its density is raised or its temperature is increased.[8] If matter is regarded as a quark-gluon system, the formation of bound states (nucleons, quark sextets, etc.) can be interpreted as the condensation of quarks, like the condensation of liquid drops from a gas. Therefore, nucleons and six-quark states can be regarded as different phases of quark matter.[8]

Let the number of three- and six-quark bags be N_{3q} and N_{6q}, respectively. The total number of quarks in the system is

$$N = 3N_{3q} + 6N_{6q}.$$

Then the concentration of the baryon phase, determined in accordance with (1), is

$$w = 3N_{3q}/N.$$

The Gibbs potential of the heterophase baryon–six-quark mixture has a form that agrees with (5):

$$G = \mu_{3q}N_{3q} + \mu_{6q}N_{6q}.$$

Here, μ_i are the chemical potentials of the components. From the condition of equilibrium of the heterophase system

$$(\delta G)_{\Theta,\,p} = 0$$

we have

$$\mu_{3q}\delta N_{3q} + \mu_{6q}\delta N_{6q} = 0.$$

Taking into account the conservation of the total number N of the quarks, we then obtain

$$2\mu_{3q}(\Theta, p, w) = \mu_{6q}(\Theta, p, w), \tag{6}$$

which can be used as an equation to determine $w = w(\Theta, p)$. For this, it is necessary to have explicit expressions for μ_i, which can be obtained either phenomenologically on the basis of experimental data or by means of a microscopic model. We shall discuss the second approach below when considering the microscopic theory of heterophase states.

We consider one further form of phenomenological equilibrium theory of heterophase states—Fisher's so-called droplet approach.[10,11,74] The basic idea of this approach is that any configuration of particles in any state of some system can be formed by a collection of individual "droplets"—fairly large regions with a definite thermodynamic state. For example, in a ferromagnet, whose ground state corresponds to complete ordering of the magnetic moments, the droplets are regions of reverse magnetization whose existence at nonzero temperatures leads to a decrease in the mean magnetization.[74] In other words, the droplets can be regarded as the nucleation centers of a different state in the main phase.

The simplest form of the model is associated with the assumption that there is no interaction.[11] In this case, the equation of state of a system containing n droplets can be written in the form[11,74]

$$p/\Theta = V^{-1}\ln \Xi(z, \Theta) = \sum_{n=1}^{\infty} (q_n(\Theta)/V)\, z^n.$$

Here, p is the pressure, V is the volume, Ξ is the grand partition function of the system, $z = e^{\mu/\Theta}$ is the activity (μ is the chemical potential), and $q_n(\Theta)$ is the partition function of an n-particle droplet. Obviously,

$$F_n = -\Theta \ln [q_n(\Theta)/V],$$

where F_n is the free energy of the droplet. It is further assumed that F_n contains a volume contribution,

$$F_n^{(1)} = n(E_1 - S_1),$$

where E_1 is the binding energy of a particle in the droplet and S_1 is the corresponding entropy of the surface contribution,

$$F_n^{(2)} = S(n)(E_2 - S_2),$$

where $S(n)$ is the effective area of the droplet surface, chosen in the form

$$S(n) \approx an^{\sigma}, \quad a = \text{const}, \quad \sigma \in (0, 1)$$

[for a two-dimensional system $\sigma \approx \frac{1}{2}$, and for a three-dimensional system $\sigma \approx 2/3$ (Ref. 11)]; E_2 is the surface energy due to the decrease in the binding energy on the surface, and S_2 is the surface entropy[74]; there is also a "geometrical contribution"

$$F_3 = -\tau \ln n + \ln q_0,$$

whose introduction is due to the necessity of making a special choice of the surface.[11] Here, τ is a parameter whose value is assumed to be greater than 1,[11] and $q_0 = \text{const}$ is the amplitude factor in $q_n(\Theta)$.

The equation of state now takes the form

$$p/\Theta = q_0 \sum_{n=1}^{\infty} n^{-\tau} x^{n^{\sigma}} y^n, \tag{7}$$

$$x \equiv \exp\{-a(E_2 - S_2)/\Theta\}, \quad y \equiv z\exp\{(E_0 - S_0)/\Theta\}.$$

For the density $\rho = z(d/dz)(p/\Theta)$ we then obtain

$$\rho = q_0 \sum_{n=1}^{\infty} n^{1-\tau} x^{n^{\sigma}} y^n. \tag{8}$$

The main achievement of this model is that all the critical exponents can now be expressed on the basis of (7) and (8) in terms of the parameters σ and τ. Using the definition of the critical exponents (see, for example, Ref. 75)

$$\alpha = \lim_{\varepsilon\to 0}\frac{\ln C}{\ln(-\varepsilon)}, \quad \varepsilon \equiv \frac{\Theta - \Theta_c}{\Theta_c},$$

$$\beta = \lim_{\varepsilon\to 0}\frac{\ln \Delta\rho}{\ln(-\varepsilon)}, \quad \gamma = \lim_{\varepsilon\to 0}\frac{\ln K_0}{\ln(-\varepsilon)},$$

where C is the specific heat, $\Delta\rho$ is the change in the density, and K_0 is the isothermal compressibility $(K_0 \equiv \rho^{-1}(\partial\rho/\partial p)_{\Theta})$, we can obtain from (7) and (8) the relations[11]

$$\alpha = 2 - (\tau - 1)/\sigma, \quad \beta = (\tau - 2)/\sigma, \quad \gamma = (3 - \tau)/\sigma$$

Hence $\sigma = 1/(\beta + \gamma)$. The values of σ chosen above agree fairly well with the well-known results for the two-dimensional Ising model and with some experimental results for three-dimensional real gases.[74] However, there is still a certain arbitrariness in the choice of the parameter τ.

For the droplet model, one obtains the well-known relations for the critical exponents and, in addition, one can show that the equation of state that follows from (7) and (8) satisfies the homogeneity hypothesis.[74] The droplet approach has been used to study critical behavior in various systems.[74,76] We mention here the work of Wagner,[77] who used it to investigate the three-dimensional Ising model on a compressible lattice in the approximation linear in the displacement of the spins. Later, an attempt was made to improve the droplet approach by taking into account the interaction between the droplets.[78]

Fisher's approach is an attempt to treat critical fluctuations in a microscopic language, but it contains many phenomenological assumptions (the choice of the free energy of the droplet). In addition, the "droplet" is, as we have already said, a region of ordering with a direction different from that in the remaining volume of the system (region of reverse magnetization in a ferromagnet). On the other hand, if one of the phases is an ordered state, while the other is disordered, it is natural to speak of heterophase fluctuations as nucleation centers of disordering in an ordered phase (Fig. 1). It is such a picture that is considered in the Gorter-Casimir model, and it is such states that we consider below.

3. DYNAMICS OF HETEROPHASE STATES

The simplest forms of the dynamical theory of heterophase states are also associated with the phenomenological concept of a "droplet" of one phase in another. Thus, in the classical Becker-Dehring theory,[79] one considers a droplet consisting of a group of n particles that interact strongly with one another and weakly with the remaining system (analog of the Fisher droplet). The dynamics of such droplets satisfies the continuity equation

$$\frac{\partial \overline{w}_n(t)}{\partial t} + \frac{\partial J_n}{\partial n} = 0, \tag{9}$$

where $\overline{w}_n(t)$ is the concentration of the n-particle droplets and J_n is the flux of the droplets:

$$\left.\begin{aligned} J_n &= -R_n w_n \nabla(\overline{w}_n(t)/w_n); \\ w_n &= w_1 e^{-F_n/\Theta}. \end{aligned}\right\} \tag{10}$$

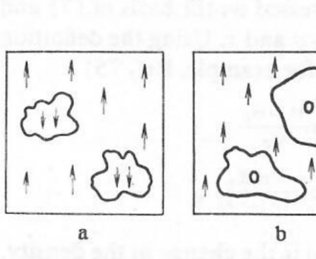

FIG. 1. Fisher droplets (a) and nucleation centers of the paramagnetic phase (b) in a ferromagnet.

Here, w_1 is the number density of individual particles ("monomers"), the parameter R_n is proportional to the droplet surface area, and F_n is the energy of the formation of an n-particle cluster. The parameters w_1, R_n, F_n are phenomenological. The main shortcoming of such an approach is the possibility of treating the dynamics of clusters of only one size, the droplets of other sizes being ignored.[80]

We note that relations of the type (9) and (10) can also be obtained in the framework of statistical mechanics from first principles.[81]

Other forms of dynamical theories involving the use of the continuity equation (9) and Fisher's approach were developed in Refs. 82 and 83 (see also the review of Ref. 84).

Also used is the approach based on a kinetic equation of master type[80]:

$$\frac{\partial P(x, t)}{\partial t} = -\int_0^t d\tau \sum_{x'} \{w_{t,\tau}(x \to x') P(x, \tau) - w_{t,\tau}(x' \to x) P(x', \tau)\}. \tag{11}$$

Here, $P(x,t)$ is the probability that at the time t the system is in the state x, and $w_{t,\tau}(x \to x')$ is the probability of transition from the state x to the state x', this probability usually being taken to be Markov[80]:

$$w_{t,\tau}(x \to x') = \delta(t - \tau)\, w(x \to x').$$

In the case of a dynamical heterophase system, each cluster (droplet) is described by a set of "cluster coordinates" $\{n, s, \{\alpha\}\}$, where n is the number of particles or the volume of the cluster, s are "fundamental" coordinates (area of the cluster surface, kinetic energy, etc.), and $\{\alpha\}$ is a set of certain "nonfundamental" coordinates. For the complete set of cluster coordinates, the variable x in (11) can be defined as[80]

$$x = (\{n_1, s_1, \{\alpha_1\}\}, \{n_2, s_2, \{\alpha_2\}\} \ldots). \tag{12}$$

We emphasize that the cluster concept as used here generally expresses the same idea as Fisher's droplet concept,[80] although the definition (12) leaves a certain arbitrariness.

Such an approach was used, in particular, to investigate relaxation phenomena in one-dimensional systems.[85,86]

Both approaches to the kinetics of heterophase systems involve a classical description. This is evidently justified for the majority of condensed media. An exception is the case of quantum crystals, in which a distinctive quantum diffusion occurs at low temperatures,[87,88] and possibly even superfluidity too.[87]

In order to make clearer the difference between homophase and heterophase states, we consider the classical kinetic equations for the nonequilibrium distribution functions. Suppose that a system consists of identical particles coupled by a two-body interaction $\Phi(|\mathbf{r} - \mathbf{r}'|)$. The equation for the single-particle distribution function $f_1(\mathbf{r}, \mathbf{p}, t)$ has the form[89]

$$\left(\frac{\partial}{\partial t} + \frac{\mathbf{p}}{m}\frac{\partial}{\partial \mathbf{r}}\right) f_1(\mathbf{r}, \mathbf{p}, t) - \frac{\partial}{\partial \mathbf{p}} I(\mathbf{r}, \mathbf{p}, t) = 0, \tag{13}$$

where $\mathbf{p}$ is the momentum,

$$I(\mathbf{r}, \mathbf{p}, t) \equiv \int f_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}', t) \frac{\partial}{\partial \mathbf{r}} \Phi(|\mathbf{r} - \mathbf{r}'|)\, d\mathbf{r}'\, d\mathbf{p}',$$

and $f_2(\cdot)$ is the two-particle distribution function, symmetric with respect to the variable interchange $(\mathbf{r}, \mathbf{p}) \leftrightarrow (\mathbf{r}', \mathbf{p}')$. In addition, normalization conditions must be satisfied:

$$\int f_1(\mathbf{r}, \mathbf{p}, t)\, d\mathbf{r}\, d\mathbf{p} = N,$$

$$\int f_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}', t)\, d\mathbf{r}\, d\mathbf{p}\, d\mathbf{r}'\, d\mathbf{p}' = N^2.$$

To close Eq. (13), we use the Tyablikov decoupling[90]:

$$f_2(\mathbf{r}, \mathbf{p}, \mathbf{r}', \mathbf{p}', t) \approx f_1(\mathbf{r}, \mathbf{p}, t)\, f_1(\mathbf{r}', \mathbf{p}', t)\, g(|\mathbf{r} - \mathbf{r}'|),$$

where $g(\cdot)$ is a smoothing function.

Further, we go over to an effective interaction potential (pseudopotential), determining it by the equation

$$\frac{\partial}{\partial r} \widetilde{\Phi}(r) = g(r) \frac{\partial}{\partial r} \Phi(r)$$

with the boundary conditions

$$\widetilde{\Phi}(r_0) = \Phi(r_0) = 0.$$

Hence

$$\widetilde{\Phi}(r) = \int_{r_0}^{r} g(r) \frac{\partial \Phi(r)}{\partial r}\, dr.$$

The smoothing function can, for example, be chosen in the form

$$g(r) = \exp\{-\Phi(r)/\gamma\}, \qquad \gamma > 0.$$

Frequently, however, one chooses, not the smoothing function, but the pseudopotential itself on the basis of phenomenological considerations, as, for example, in nuclear theory.[91]

The interaction integral in (13) now has the form

$$I(\mathbf{r}, \mathbf{p}, t)$$

$$= f_1(\mathbf{r}, \mathbf{p}, t) \quad \frac{\partial}{\partial \mathbf{r}} \int \widetilde{\Phi}(|\mathbf{r} - \mathbf{r}'|)\, f_1(\mathbf{r}', \mathbf{p}', t)\, d\mathbf{r}'\, d\mathbf{p}'. \tag{14}$$

The relations (13) and (14) determine a nonlinear integro-differential equation for the single-particle distribution function. As is well known, such an equation can have infinitely many different solutions. However, all its solutions can be divided into two classes, which are physically distinct. The solutions of the first class describe elementary excitations, i.e., they correspond to homophase fluctuations. The solutions of the second class are of soliton type and correspond to heterophase nucleation centers. There is here a direct analogy with the fact that in the theory of condensation of a complex field it is possible to obtain from the same equations both Goldstone excitations and vortex filaments like those in a superfluid Bose liquid.

The homophase solutions are sought as deviations from the equilibrium distribution with a function $f_0(\mathbf{r}, \mathbf{p})$ satisfying the stationary equation [Eq. (13) with $(\partial/\partial t) f_0(\mathbf{r}, \mathbf{p}) = 0$]

$$f(\mathbf{r}, \mathbf{p}, t) = f_0(\mathbf{r}, \mathbf{p}) + \varphi(\mathbf{r}, \mathbf{p}, t).$$

By means of (13) and (14), an equation for $\varphi(\cdot)$ can now be readily obtained.

In contrast to the homophase solutions, the heterophase (soliton) solutions describe, not elementary, but macroscopic excitations consisting of a large number of particles. Such objects can have very different natures and can be, for example, quantized vortices (including point vortices in ^{3}He)[92], domains or domain walls,[93] etc.

Equations (13) and (14) contain a class of solutions of soliton type that have the form of self-similar waves,

$$f_1(\mathbf{r}, \mathbf{p}, t) = f(\mathbf{r} - \mathbf{v}t, \mathbf{p}), \tag{15}$$

propagating in space with velocity $\mathbf{v}$. Indeed, making the substitution $\boldsymbol{\xi} = \mathbf{r} - \mathbf{v}t$, we can transform (14) to the form

$$I(\mathbf{r}, \mathbf{p}, t) = f(\boldsymbol{\xi}, \mathbf{p}) \frac{\partial}{\partial \boldsymbol{\xi}} U(\boldsymbol{\xi}) \equiv I(\boldsymbol{\xi}, \mathbf{p});$$

$$U(\boldsymbol{\xi}) \equiv \int \widetilde{\Phi}(|\boldsymbol{\xi} - \boldsymbol{\xi}'|)\, f(\boldsymbol{\xi}', \mathbf{p}')\, d\boldsymbol{\xi}'\, d\mathbf{p}'.$$

Instead of (13), we now have the equation

$$\left(\frac{\mathbf{p}}{m} - \mathbf{v}\right) \frac{\partial}{\partial \boldsymbol{\xi}} f(\boldsymbol{\xi}, \mathbf{p}) - \frac{\partial}{\partial \mathbf{p}} I(\boldsymbol{\xi}, \mathbf{p}) = 0,$$

for which the self-similar waves (15) are a solution. Such solutions correspond to stable solitons, i.e., solitary waves that do not change their shape as they move.

Generally speaking, real heterophase nucleating centers are not stable—they do not exist for ever and unchanged but can grow, change their shape, merge with other nucleating centers, decay, decrease, and disappear. Therefore, with such nucleating centers it is more natural to associate so-called quasisolitons (unstable solitons). We note that at the present time many nonlinear equations are known that have quasisoliton solutions, which possess a rich and extremely interesting dynamics.[94]

Another approach widely used recently is the computer simulation of the dynamics of heterophase states. The most transparent approach here is the method of molecular dynamics, in which the computer is used to integrate the Newtonian equations of motion for a large number of particles coupled by a two-body interaction and placed in a finite volume. The number of particles in the volume can indeed be large. It was in fact possible to obtain a result for 1372 particles in a cubic box, interacting through the Lennard-Jones potential.[84] By changing the size of the box for given parameters of the potential one can simulate a change in the density, i.e., consider different phases and a density transition of the liquid-gas type. Of course, in real liquids and gases the number of particles is much greater than 1372. Therefore, to improve the agreement with the real situation, a periodic continuation is usually made, this making it possible, in particular, to take into account the contribution of inhomogeneities with a size exceeding that of the cubic box.[84]

Such an approach makes it possible to simulate the generation of one phase in another (the nucleation phenomenon) and to determine the nucleation densities that are the boundaries of the region of phase coexistence (of the heterophase state).

In such computer experiments, one can change the number of particles, the size and geometry of the cavity, the interaction potential, and even the shape of the particles.[95]

A further method of computer simulation is associated with the use of the Monte Carlo method[13] on the basis of the algorithm of Metropolis.[96] In this approach, one specifies an initial state of a system of N particles in a certain volume V, for example, a three- or two-dimensional lattice that simulates a homogeneous crystal at a certain fixed temperature. If $U(\xi)$ is the potential energy of the system in the configuration $\xi = (\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$, then the probability density of such a configuration is

$$P(\xi) = e^{-U(\xi)/\Theta} \Big/ \int e^{-U(\xi)/\Theta}\, d\xi,$$

and the mean energy is determined by

$$\langle U \rangle = -\int U(\xi)\, P(\xi)\, d\xi. \qquad (16)$$

The initial state is perturbed by a random displacement Δ, and the potential energy δU of this perturbation is calculated. If $\delta U < 0$, then one chooses a new configuration for which a random displacement is again generated. Such a process simulates the evolution from an initial "nonequilibrium" configuration to the state of equilibrium. The displacement parameter Δ is chosen to optimize the convergence of the mean values (16) to the equilibrium mean value.

A similar approach is used in quantum field-theory problems on a lattice.[97]

Such an approach makes it possible to simulate fairly well, for example, the process of melting of a heated Lennard-Jones crystal[98] and to show that such a process is associated with the development of nucleation centers of the liquid phase.

We end by giving one other way of simulating a crystal—liquid phase transition—using a purely mechanical model. The system is a collection of "particles" (molecules) in a finite region on a plane. Each particle is an equilateral triangle made of a sufficiently tough material. The interaction between the particles is realized by their collisions. The motion of the particles is produced by random vibrations of the plane. For example, one could have a tissue spanned over a dynamic loudspeaker that generates random noise. A change in the number of triangles in a region of given size simulates a change in the density.

At the highest density, the particle configuration will correspond to close packing (Fig. 2a), which can be associated with the crystal phase. If the density is slightly reduced, we obtain a more realistic picture of a crystal—on the average, the triangles are ordered but execute certain fluctuations about the equilibrium positions, the lattice sites, which coincide with the centers of hexagons (Fig. 2b). A further decrease in the density has the consequence that, while the general ordered picture persists, individual triangles begin to jump from site to site, gradually migrating over the crystal (Fig. 2c). Averaging the motion of such migrating particles over a sufficiently long time interval, we obtain, as it were, the motion of the liquid component in the crystal. Finally, with a further decrease in the density the ordering disappears entirely and the purely liquid phase sets in (Fig. 2d).

Recorded on a movie film, such a process very clearly demonstrates the existence of the heterophase state—the liquid—crystal mixture—in a fairly wide range of densities.[3)]

4. BOGOLYUBOV'S CONCEPT OF QUASI AVERAGES

Before we formulate the principles of the equilibrium microscopic theory of heterophase states, let us consider Bo-

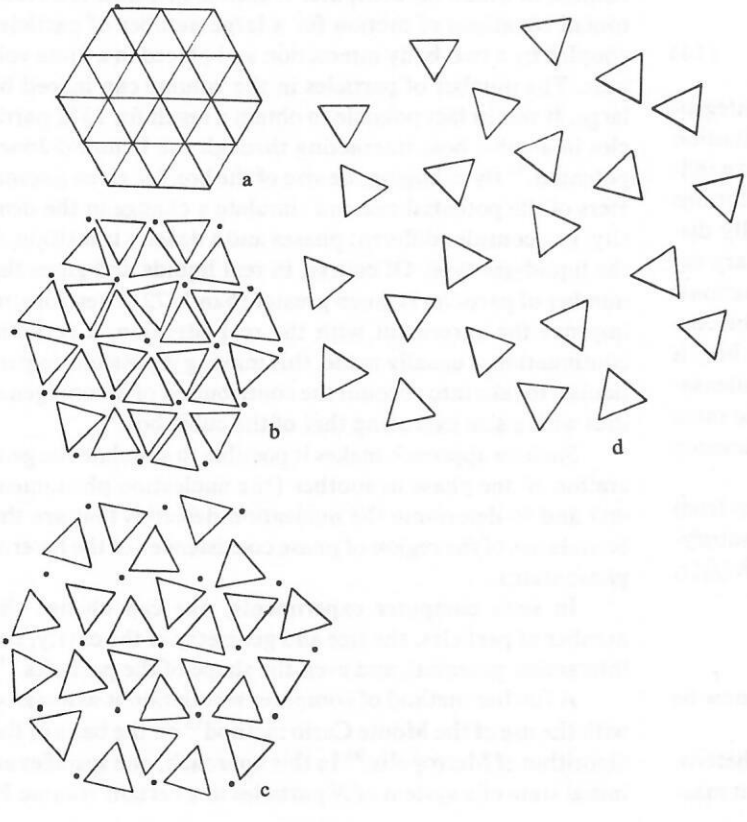

FIG. 2. Mechanical model of the melting of a crystal. The points represent lattice sites.

golyubov's concept of quasiaverages.[23,24] This concept, the basis of the theory of phase transitions, makes it possible to establish a connection between the thermodynamic concepts of phase, the conditions of stability of an equilibrium state, and a microscopic description based on a choice of the state space and concepts of operator algebras.

We analyze the concept by considering the simplest example of the Ising model,[25] which admits both a classical and a quantum treatment. The Hamiltonian of the model has the form

$$H_N = -\frac{1}{4}\sum_{ff'} J_{ff'}\,\sigma_f^z\sigma_{f'}^z, \tag{17}$$

where the indices f and f' denote the lattice sites, the total number of which is N; σ_f^z is the z component of the Pauli spin operator, and the exchange integral corresponds to the ferromagnetic case: $J_{ff'} = J_{f'f} \geqslant 0$, $J_{ff} = 0$.

For the concept of quasiaverages, it is immaterial how the summation is performed in (17) and what the dimension of the lattice is. The Hamiltonian (17) is invariant with respect to the group Z_2, which consists of the identity transformation $\sigma_f^z \to \sigma_f^z$ and the inversion $\sigma_f^z \to -\sigma_f^z$. We shall denote the spin functions describing the states with spin up and down at site f, respectively, by

$$\psi_{f+} = \begin{pmatrix}1\\0\end{pmatrix}_f = \underset{f}{\uparrow}, \quad \psi_{f-} = \begin{pmatrix}0\\1\end{pmatrix} = \overset{f}{\downarrow}.$$

These functions form a basis in the space $\mathscr{C}_f^2$. The total N-particle state space for the Hamiltonian (17) is

$$\mathscr{H} = \bigotimes_{f=1}^{N} \mathscr{C}_f^2 = (\mathscr{C}^2)^N. \tag{18}$$

In this space, it is possible to have states with spins oriented upward,

$$\psi_+^N = \bigotimes_{f=1}^{N} \psi_{f+} = \underset{1}{\uparrow}\underset{2}{\uparrow}\cdots\underset{N}{\uparrow}, \tag{19}$$

with spins oriented downward,

$$\psi_-^N = \bigotimes_{f=1}^{N} \psi_{f-} = \overset{1}{\downarrow}\overset{2}{\downarrow}\cdots\overset{N}{\downarrow}, \tag{20}$$

and with disoriented spins:

$$\psi_0^N = \underset{1}{\uparrow}\overset{2}{\downarrow}\underset{3}{\uparrow}\cdots\overset{N}{\downarrow}. \tag{21}$$

We emphasize that the successive arrangement of the spins in the symbolic form on the right-hand sides of Eqs. (19)–(21) corresponds to the manner chosen to label the sites in the lattice of arbitrary dimension, and a linear chain is by no means all we have in mind.

The functions (19)–(21) are eigenfunctions for the operator of the reduced spin

$$\sigma = N^{-1}\sum_{f=1}^{N}\sigma_f^z,$$

and

$$(\psi_\pm^N, \sigma\psi_\pm^N) = \pm 1, \quad (\psi_0^N, \sigma\psi_0^N) = 0.$$

For the Ising model, one can introduce the concept of an elementary excitation of the state ψ^N, defining it as the flipping of one spin with respect to ψ^N, i.e., it is a flippon.[25] The flippon excitation above the state ψ_+^N is described by the function

$$\psi_+^N(f) = \underset{1}{\uparrow}\cdots\underset{f-1}{\uparrow}\overset{f}{\downarrow}\underset{f+1}{\uparrow}\cdots\underset{N}{\uparrow}.$$

One can similarly define the function of a many-flippon excitation $\psi_+^N(f_1, f_2, \ldots, f_n)$. Obviously

$$\psi_+^N(12\ldots N) = \psi_-^N, \quad \psi_+^N(246\ldots) = \psi_0^N.$$

Proceeding in this manner, one can show that all the functions of the space (18) can be transformed into each other by means of a sequence of flippon states. Note that flippon excitations above the ordered states ψ_+^N and ψ_-^N correspond to the occurrence of disordered clusters and clusters of reversed spin (regions of "countermagnetization," i.e., Fisher droplets), while flippon excitations in the case of the disordered state ψ-$_0^N$ equivalent to the appearance of ordered clusters. The states ψ_+^N and ψ_-^N are vacuum states, since from them one can, by means of elementary excitations, construct the complete state space, and the energy of elementary excitations above them is non-negative. From the state ψ_0^N one can also construct the complete space (18), but it is only a pseudovacuum, since the energy of an elementary excitation above it is nonpositive. In the Ising model with finite N, any function in the space (18) can serve as a pseudovacuum.

The thermodynamic characteristics of the system with the Hamiltonian are determined by means of the operation

$$\mathrm{Sp}\ \ldots\ e^{-H_N/\Theta}, \tag{22}$$

where Sp is taken over an arbitrary basis of some space. For finite N, our system has a unique unitarily irreducible basis (i.e., a basis that cannot be reduced to another by a unitary transformation). Therefore, such a system has a unique free energy (for $\Theta > 0$)

$$F = -\Theta N^{-1}\ln \mathrm{Sp}\, e^{-H_N/\Theta}. \tag{23}$$

It is the uniqueness of the unitarily irreducible basis that explains the absence of a phase transition in the system with finite N.

It is a different matter in the thermodynamic limit, when $N \to \infty$. We denote the limits of the corresponding functions by

$$\psi_{\underset{0}{\pm}}(f_1\ldots f_n) = \lim_{N\to\infty}\psi_{\underset{0}{\pm}}^N(f_1\ldots f_n). \tag{24}$$

There are obviously infinitely many such states. Thus, proceeding from any of the three functions $\psi_{\underset{0}{\pm}} = \lim_{N\to\infty}\psi_{\underset{0}{\pm}}^N$, we can construct by flippon excitations three different countable bases $\{\psi_{\underset{0}{\pm}}(f_1 \ldots f_n)\}$, over which separable Hilbert spaces can be spanned. We choose here these three states, ψ_+, ψ_-, ψ_0, since only they possess the property of translational invariance inherent in the Hamiltonian (17).

Thus, in the thermodynamic limit we have instead of the unique space (18) three spaces, $\mathscr{H}_+, \mathscr{H}_-, \mathscr{H}_0$, with translationally invariant vacua (pseudovacua). We emphasize that these spaces are mutually orthogonal (the corresponding pseudovacua are unitarily irreducible).

The operation (22) can now be performed on the different spaces, and this leads to nonuniqueness of the free energy (23) and the other thermodynamic quantities.

We consider the symmetry properties of each of the spaces. For the state ψ_+, the Z_2 symmetry is broken. All flippon excitations above ψ_+ determine functions belonging to the same space $\mathscr{H}_+$. In accordance with the concept of quasiaverages, we shall assume that each thermodynamic phase has a definite symmetry, distinguishing it from the other phases. One can then say that the space $\mathscr{H}_+$ corresponds to the ordered phase with mean spin

$$\langle\sigma\rangle_+ = \lim_{N\to\infty}\left\{\underset{(+)}{\mathrm{Sp}}\,\sigma e^{-H_N/\Theta}\Big/\underset{(+)}{\mathrm{Sp}}\,e^{-H_N/\Theta}\right\}$$

(magnetization) directed upward. For $\Theta = 0$,

$$\langle\sigma\rangle_+\,|_{\Theta=0} \equiv \langle\psi_+,\ \sigma\psi_+\rangle = 1.$$

A nonvanishing temperature $\Theta > 0$ leads to the appearance of flippon excitations corresponding to states in the same space $\mathscr{H}_+$. Such excitations, described by the functions of one space with given symmetry, are homophase fluctuations in a homogeneous phase.

In the state ψ_-, the Z_2 symmetry is also broken. The space $\mathscr{H}_-$ corresponds to an ordered phase with mean spin directed downward:

$$\langle\sigma\rangle_-\,|_{\Theta=0} \equiv \langle\psi_-,\ \sigma\psi_-\rangle = -1.$$

These two states are usually said to be ferromagnetic. We emphasize that these states differ only by the direction of the magnetization, whereas the free energy (23) and the other thermodynamic variables have for them the same values (at a given temperature Θ). Such a picture corresponds to macroscopic degeneracy.

The pseudovacuum ψ_0 has the Z_2 symmetry, as a consequence of which

$$\langle\sigma\rangle_0\,|_{\Theta=0} = \langle\psi_0,\ \sigma\psi_0\rangle = 0.$$

Moreover, $\forall\Theta\langle\sigma\rangle_0 = 0$. Such behavior corresponds to the paramagnetic (disordered) phase.

It is clear that flippon excitations over ψ_+ and ψ_- can lead to partial disordering of the spins, but in the case of ψ_0 to partial ordering. However, one cannot say (as, unfortunately, is sometimes done) that the regions of the elementary excitations correspond to nucleation centers of one phase in the other. We have already made it clear that all the flippon excitations above a certain state belong to one state space and therefore correspond to only a single unique phase with a definite symmetry property. Such regions are homophase fluctuations. In addition, a phase is, by definition, always macroscopic, whereas the sizes of the flippon regions are microscopic.

Thus, the spaces $\mathscr{H}_+$, $\mathscr{H}_-$ and $\mathscr{H}_0$ describe pure phases.

We can now define three free energies (23) and, generally, three sets of thermodynamic variables corresponding to different phases. Which of them is to be given preference to the others? The answer to this question is also given by the concept of quasiaverages, in accordance with which it is necessary to choose the state that under the given conditions (definite temperature, etc.) is thermodynamically the most advantageous, i.e., has the smallest free energy.

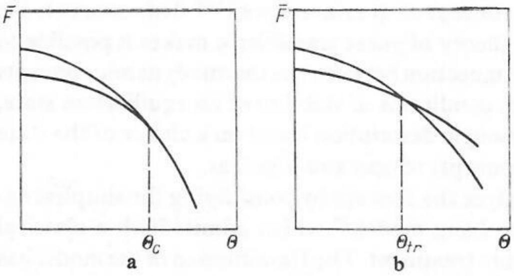

FIG. 3. Temperature dependence of the free energy in the case of transitions of the second (a) and first (b) kinds.

At low temperatures, it is well known that in the model (17) the ordered state is advantageous (and this is why the state ψ_0 is a pseudovacuum), whereas at high temperatures it is the disordered state (Fig. 3a). The situation shown in Fig. 3a corresponds to a phase transition of continuous type, in which the free energies of the ordered and disordered states are equal above the critical point. In transitions of the first kind, there is no such equality (Fig. 3b). This last circumstance emphasizes the importance of taking into account not only the vacua but also the pseudovacua corresponding to disordering.

Below the phase-transition point, the physical system described by the Ising model must be in one of two states: $\mathscr{H}_+$ or $\mathscr{H}_-$. But in which? These states are thermodynamically equivalent (have the same free energy). Physically, this degeneracy is lifted by external and internal factors. The external factors are associated with the presence of small external perturbations, for example, weak external fields.[24] The internal factors are associated with the circumstance that the equilibrium state is a mathematical idealization, the result of averaging over an infinite time interval.[99] A system observed during a finite time interval is, strictly speaking, not in equilibrium. In it, different states arise as fluctuations. Most of the time, the system will be in that state of the two $\mathscr{H}_+, \mathscr{H}_-$ that arises first, i.e., from the equilibrium point of view, it goes over spontaneously into one of the states with broken Z_2 symmetry.

The transition of a system with a Hamiltonian invariant with respect to a certain symmetry group to a state that is not invariant with respect to this group is usually called spontaneous symmetry breaking. In accordance with the concept of quasiaverages, which associates with a phase the symmetry properties of the state space of a macroscopic system, spontaneous symmetry breaking is a phase transition.

A mathematical device which makes it possible to lift the macroscopic degeneracy was developed by Bogolyubov[23,24] and reduces to an infinitesimal violation of the symmetry by the inclusion in the Hamiltonian of an additional term having the physical meaning of an external field or sources.[100] Subsequently, other methods of introducing quasiaverages were developed,[25,101] among which an important one is the method of N. N. Bogolyubov, Jr.[102] (see also Ref. 103), who introduced the procedure of quasiaveraging by means of asymptotic violation of the canonical commutation relations, i.e., by the introduction of unitarily inequivalent representations of the operators.

We consider other examples. In the Heisenberg model with the Hamiltonian

$$H = -\sum_{ff'} J_{ff'} \mathbf{S}_f \mathbf{S}_{f'}, \tag{25}$$

where S_f is a vector spin operator at site f, there is invariance with respect to the group SU(2).[104] Therefore, in the limit $N \to \infty$ we no longer have here two equivalent vacua ("up" and "down"), as in the Ising model (17), but a continuum of such vacua, each of them characterized by a unit vector **e** specifying a certain direction in the three-dimensional spin space.[19,20] The vector **e**, determined by two spherical angles, fixes the direction of the magnetization in the system. Since the values of the angles vary continuously on a certain set, there is a continuum of vacua $\psi_{\mathbf{e}}$. Over each vacuum one can construct a state space $\mathscr{H}_{\mathbf{e}}$ analogous to the spaces $\mathscr{H}_{\pm}$ in the Ising model. It is true that in this case, as is well known, the elementary excitations will no longer be flippons.[105] As in the case of the Ising model, for (25) one can also introduce the space $\mathscr{H}_0$ with disordered directions. In addition, one can construct spaces that do not have analogs in the Ising model, for example, spaces of the type $\mathscr{H}_{\mathbf{e}_1\mathbf{e}_2\ldots\mathbf{e}_n}$ $(n \geqslant 1)$, which are generated by pseudovacua which change their direction in different macroscopic sections of the system. If we introduce the variable φ, which belongs to the set

$$\varphi = \{\varphi_1 \varphi_2 \ldots \varphi_n \colon n \geqslant 1,\ \varphi_j = 0,\ \mathbf{e}_j\},$$

then the different admissible spaces can be denoted by $\mathscr{H}_\varphi$ (included here are spaces of the type $\mathscr{H}_{\mathbf{e}_1\mathbf{e}_2\ldots 0 \ldots \mathbf{e}_n}$ corresponding to all possible mixed states). The complete state space is constructed as the direct integral[19,20]

$$\mathscr{H} = \int^{\oplus} \mathscr{H}_\varphi \, d\varphi, \tag{26}$$

where

$$\int d\varphi = \sum_{n=1}^{\infty} \int d\varphi_1 \ldots d\varphi_n, \quad \int d\varphi_j = 1 + \int d\mathbf{e}_j.$$

Thus, there is here a continuum of ordered, thermodynamically equivalent states and a disordered (paramagnetic) state, i.e., there is the possibility of a phase transition, a spontaneous symmetry breaking at a certain temperature.

A further important example is the Bogolyubov-Bardeen-Cooper-Schrieffer (BBCS) model in the theory of superconductivity,

$$H = \sum_k \varepsilon_k a_k^+ a_k - \sum_{kk'} J_{kk'} a_k^+ a_{-k}^+ a_{-k'} a_{k'}, \tag{27}$$

where a_k^+ and a_{-k}^+ are the operators of creation of an electron with momentum **k** and spin up and down, respectively; only electrons with oppositely directed spins and momenta interact.[26] Similar models are also used in nuclear theory.[59] Such a model problem admits a quasispin formulation.[106,107] Indeed, we have the relations

$$\sigma_k^- = a_k^+ a_{-k}^+, \quad \sigma_k^+ = a_{-k} a_k, \quad \sigma_k^z = \hat{1} - 2\,(a_k^+ a_k + a_{-k}^+ a_{-k}),$$
$$\sigma^\pm \equiv (\sigma^x \pm i\sigma^y)/2,$$

where σ^α $(\alpha = x, y, z)$ are the Pauli operators and $\hat{1}$ is the identity operator.

It is readily seen that the Hamiltonian (27) is invariant with respect to the group $U(1)$; therefore, here, as in the Heisenberg model, there is a continuum of vacua characterized by a continuous parameter $\varphi \in [0, 2\pi]$, the polar angle in the xy plane of the space of the quasispins.

Let ψ be a vector in the space $\mathscr{C}^2$ and 1_φ be a unit vector of the three-dimensional space of the quasispins whose projection onto the xy plane has the direction φ. If $\psi_{\varphi k}$ is the single-particle vacuum in the φ direction, the equation

$$(\sigma_k \cdot 1_\varphi)\, \psi_{\varphi k} = \psi_{\varphi k}$$

determines $\psi_{\varphi k}$ up to the phase factor $e^{i\gamma}$.[108] The N-particle vacuum is

$$\psi_\varphi = \bigotimes_k \psi_{\varphi k}, \quad \psi_\varphi \in \mathscr{H} = \bigotimes_k \mathscr{C}_k^2 = (\mathscr{C}^2)^N.$$

For the scalar product in $\mathscr{H}$ we have[108,109]

$$(\psi_\varphi \psi_{\varphi'}) = \prod_k e^{i\gamma_k} \sqrt{\frac{1 + 1_\varphi \cdot 1_{\varphi'}}{2}} = e^{i\sum_k \gamma_k} \left(\cos\frac{\varphi - \varphi'}{2}\right)^N,$$

from which it follows that in the limit $N \to \infty$ the vacua with different values of φ and φ' are orthogonal. Therefore, on the spaces $\mathscr{H}_\varphi$ obtained from the vacua ψ_φ by means of elementary excitations, called bogolons,[110] unitarily inequivalent representations of the canonical commutation relations of the algebra of local observables are realized.[109]

As in the cases considered above, here too it is possible to introduce the space $\mathscr{H}_0$ of disordered states possessing $U(1)$ invariance that describes the normal phase. The simplest way of quasiaveraging for such a model is to linearize it, i.e., to introduce an approximating Hamiltonian that makes it possible to obtain an exact (as $N \to \infty$) solution.[101]

Thus, the concept of quasiaverages gives us a rigorous definition of a phase as a macroscopic state with a definite symmetry and makes it possible to resolve constructively the problem of the nonuniqueness in the choice of the state space in accordance with the requirement of its being thermodynamically advantageous.

The above treatment also makes it possible to formulate a necessary and sufficient condition for a phase transition. Such a condition consists of: 1) the presence in the system of macroscopic degeneracy; 2) spontaneous breaking of the symmetry being advantageous at certain values of the thermodynamic variables and disadvantageous for other values.

We note that the symmetry properties are not always so readily defined as in the examples considered above. In a number of cases, for example, for the liquid-vapor transition, it is necessary to introduce the concept of a hidden symmetry.[111]

5. LOCAL SYMMETRY BREAKINGS

In the previous section, we considered in detail the case of so-called global symmetry breaking, when the breaking occurs simultaneously in the complete volume of the system. In other words, the transition takes place between pure phase states. However, as the study of the experimental data made in Sec. 1 shows, such a situation is by no means always realized, and in a number of cases there is penetration of one phase into another, i.e., there is only local symmetry breaking. The idea of describing states with locally broken symmetry is due to Bogolyubov.[112]

We investigate such states for the examples considered in the previous section. For the Ising model (17), for example, proceeding from the state ψ_{+}^{N}, we can, by using flippon excitations, construct the state

$$\psi_{+0}^{NN_1} = \overset{\uparrow}{1}\,\overset{\uparrow}{2}\cdots\overset{\uparrow}{N_1}\downarrow\overset{\uparrow}{}\downarrow\overset{\uparrow}{}\cdots\overset{\uparrow}{N},$$

which is formed by N_1 sites with ordered spins and $N_2 = N - N_1$ with disordered spins. In such a state, the energy of the flippon depends on its localization; for a flippon that arises in a region of ordering has positive energy, but in a region of disorder has negative energy. The states $\psi_{-0}^{NN_1}$ can be constructed similarly. The thermodynamic limit for such functions can be defined in such a way that $N_1 \to \infty$ and $N \to \infty$ simultaneously. From the states

$$\psi_{+0} = \lim_{\substack{N_1\to\infty \\ N_2\to\infty}} \psi_{+0}^{NN_1},\ N_1 + N_2 = N, \quad N_1/N_2 \to \text{const}$$

formed in this manner one can, using flippon excitations, construct a countable basis $\{\psi_{+0}(f_1 \dots f_n)\}$ and over it span a separable space $\mathscr{H}_{+0}$. Varying the position of the ordered and disordered regions on the lattice and varying the values of N_1 and N_2 subject to the condition $N_1 + N_2 = N$, it is possible to obtain (as $N \to \infty$) a countable set of spaces of the type $\mathscr{H}_{+0}$, which we shall denote by $\{\mathscr{H}_{+0}\}$. One can construct similarly the set of spaces $\{\mathscr{H}_{-0}\}$. Note that the pseudovacua ψ_{+0} and ψ_{-0} are in this case no longer translationally invariant, since the heterophase states described by them are spatially inhomogeneous (in the phase sense). It is readily seen that spaces in the sets $\{\mathscr{H}_{+0}\}, \{\mathscr{H}_{-0}\}$ are orthogonal to the spaces $\mathscr{H}_{+}, \mathscr{H}_{-}, \mathscr{H}_{0}$ and to each other.

For the Ising model (17), heterophase states corresponding to a mixture of ferromagnetic and paramagnetic states are specified on the spaces $\mathscr{H}_{+0}, \mathscr{H}_{-0}$. In the case of the Heisenberg model (25), spaces of the type $\mathscr{H}_{e_1 \dots 0 \dots e_n}$ correspond to the heterophase states. Similar state spaces can also be constructed for the superconductor model (27).

How is the quasiaveraging procedure to be introduced for mixed states? We said above that the simplest method of global symmetry breaking is to include in the Hamiltonian an additional term of the type of an external field or sources.[23,24] In the case of the Ising model (17), for example, it is sufficient to go over to the Hamiltonian

$$H_N(B) = -\frac{1}{4}\sum_{ff'} J_{ff'}\sigma_f\sigma_{f'} - \sum_f B\sigma_f, \tag{28}$$

where B is an infinitesimally weak external magnetic field. The Ising Hamiltonian (28) is then no longer Z_2 invariant and describes only the ordered phase.

If the symmetry breaking is not global but local in nature, the corresponding field must also be local,

$$H_N(B) = -\frac{1}{4}\sum_{ff'} J_{ff'}\sigma_f\sigma_{f'} - \sum_f B_f\sigma_f, \tag{29}$$

where

$$B_f = \begin{cases} B, & f \in \tilde{V} \subset V, \\ 0, & f \in V \setminus \tilde{V}. \end{cases}$$

Here, V is the total volume of the system of spins (the set of lattice sites), and $\tilde{V}$ is a part of the volume, containing N_1 spins in the ordered state. Here, as usual,[23,24] it is assumed that $B \to 0$ after the limit $N \to \infty$.

Thus, the introduction of local fields (sources) is a simple, although not the only, way of realizing the procedure of quasiaveraging for mixed states of macroscopic systems.

To conclude this section, we note that the idea of local symmetry breaking is also used in quantum field theory.[113]

We now turn to the consideration of the principles of the equilibrium microscopic theory of heterophase states.

6. THE PRINCIPLE OF SPACE EXTENSION

We have seen that if we remain in the framework of the spaces that correspond to the pure phases, it is impossible to describe heterophase states. In general, study of the complete picture of phase transitions must include the possibility of forming both pure and mixed phase states. An adequate complete state space can be constructed as follows.

We again consider the Ising model (17). Suppose that the ferromagnetic state corresponds to ordering of the spins up (the vacuum ψ_{+}). Obviously, in the extended space

$$\mathscr{H} = \mathscr{H}_{+} \otimes \mathscr{H}_{0} \tag{30}$$

there exist states of not only pure ferromagnetic and paramagnetic phases but also a heterophase mixture described by the set $\{\mathscr{H}_{+0}\}$. For the description of the situation when there is a ferromagnetic phase, a ferromagnetic phase with macroscopic disordered states, and a paramagnetic phase such an extended space (30) is complete.

Since the factor spaces in (30) are orthogonal (see Sec. 4), there is realized on each of them a unitarily inequivalent representation of the operators σ, which can be constructed by means of the operation of orthogonal projection:

$$P_i\mathscr{H} = \mathscr{H}_i \quad (i = +,\ 0). \tag{31}$$

The representation of the operator σ_f on the ith factor space in (30) is

$$\sigma_{fi} = \sigma_f P_i. \tag{32}$$

Therefore, on each of the spaces it is possible to construct a representation of the Ising Hamiltonian (17):

$$H_i = H(\sigma_i),$$

by making the substitution $\sigma_f \to \sigma_{fi}$ in (17). For reasons of generality, we augment the operator H_i by a term containing a chemical potential:

$$H_i \to H_i(\mu) = H_i - N_i\mu_i \otimes \hat{1}_i,$$

where N_i is the number of particles in phase i, μ_i is the corresponding chemical potential, and $\hat{1}_i$ is the identity operator in the ith factor space in (30). The introduction of such a term makes it possible to take into account the possibility of transition of particles from one pure phase state to another.

On the space (30), the Hamiltonian can now be defined as follows:

$$H(\mu)=H_+\otimes\hat{1}_0+\hat{1}_+\otimes H_0\equiv H_+\oplus H_0. \tag{33}$$

It is clear that such a definition of the total Hamiltonian corresponds to the structure of the extended space (30).

For the Hamiltonian (33), we can in the standard manner define the thermodynamic potential

$$\Omega(\Theta,\ \mu)=-\Theta\ln\underset{(\mathscr{H})}{\mathrm{Sp}}\,\mathrm{e}^{-H(\mu)/\Theta}.$$

By virtue of the definitions (30) and (33), we then obtain

$$\left.\begin{aligned}\Omega(\Theta,\ \mu)&=\Omega_+(\Theta,\ \mu)+\Omega_0(\Theta,\ \mu);\\ \Omega_i&\equiv-\Theta\ln\underset{(\mathscr{H}_i)}{\mathrm{Sp}}\ \mathrm{e}^{-H_i(\mu)/\Theta}.\end{aligned}\right\} \tag{34}$$

Such phase additivity also holds for the other thermodynamic potentials (free energy, internal energy, etc.). We recall that the assumption of phase additivity of the thermodynamic potentials is included in phenomenological theories of heterophase states (see Sec. 2). In the microscopic theory, this additivity is a consequence of the extension of the state space.

In the general case, when there are n phases in the system, the extended space has the form

$$\mathscr{H}=\bigotimes_i^n\mathscr{H}_i,$$

and the corresponding Hamiltonian and thermodynamic potential are defined by analogy with (33) and (34) as

$$\left.\begin{aligned}H(\mu)&=\bigoplus_i^n H_i(\mu);\\ \Omega(\Theta,\ \mu)&=\sum_i^n\Omega_i(\Theta,\ \mu);\ \ \Omega_i=-\Theta\ln\underset{(H_i)}{\mathrm{Sp}}\,\mathrm{e}^{\frac{-H_i(\mu)}{\Theta}}.\end{aligned}\right\} \tag{35}$$

For an equilibrium mixture of the phases (heterophase state) the following equilibrium condition must also be satisfied:

$$\mu_i=\mu_j,\quad i\neq j\quad(i,\ j=1,\ \ldots,\ n) \tag{36}$$

(see Sec. 2).

We note that the idea of extending the state space in order to describe heterophase systems was proposed in Ref. 14. In this connection, we also mention Refs. 19, 20, 22, and 114–118.

7. PRINCIPLE OF PHASE MIXING

We now turn to the problem of constructing a representation of the Hamiltonian for a definite phase. To describe a mixture of the paramagnetic and ferromagnetic phases in the considered example of the Ising model, it is simplest to use the method of local quasiaveraging, introducing in accordance with (29) ordering of the spins in a certain volume $\tilde{V}$. But how is this volume $\tilde{V}$ to be chosen?

In our discussion of experiments in Sec. 1 we noted that each of the phase components is usually extended to the complete volume of the system. This means that the volume $\tilde{V}$ occupied by the ferromagnetic component may be situated in an arbitrary manner in the complete volume V of the system; for example, there may be formed one macroscopic region or several such regions separated by paramagnetic regions, although the mean value $\tilde{V}$ of the volume for given conditions must evidently be the same. Thus, in (29) we already have an infinite set of volumes $\{\tilde{V}_\alpha\}$ corresponding to the ordered phase component. One can say that the index α that characterizes the method of choosing $\tilde{V}_\alpha\subset V$ corresponds to the time, and the different configurations of the phase components in the complete volume of the system correspond to the dynamical picture of the heterophase fluctuations.

Since in the description of the phase transitions and states of the system we are in the first place interested in the equilibrium thermodynamic characteristics, we must obviously average over all possible configurations of the phase components in (29). This corresponds in essence to averaging over an infinitely long time of observation of the system.

Of course, for the Ising model this time has a nominal nature. In more realistic cases corresponding to the soliton dynamical picture of the heterophase fluctuations described in Sec. 3, it is possible, assuming that the time of measurement of some quantity (which may even be a local quantity) is much greater than the lifetime of the quasisolitons or that the system contains a large number of randomly distributed solitons, to ignore the details of their motion.[119] To this end, it is necessary to average over the solitons or quasisolitons. Naturally, each quasisoliton, interpreted as the nucleation center of a thermodynamic phase, must have a lifetime longer than the time of establishment of local equilibrium.

Let us consider how such averaging can be realized. Suppose that a system of N particles is described by the Hamiltonian H_N. Then the mean value of the operator $\mathcal{O}$ corresponding to an observable is, as is well known,

$$\langle\mathcal{O}\rangle_{N,\,t}=\mathrm{Sp}\,\rho_N(t)\,\mathcal{O},$$

where $\rho_N(t)$, the statistical operator, satisfies the Liouville equation

$$i\hbar\frac{\partial}{\partial t}\rho_N(t)=[H_N,\ \rho_N(t)].$$

If, as we have already said, the measurement lasts for a time Δt much greater than the lifetime of an individual nucleation center (quasisoliton), one can usefully consider the time average

$$(\mathcal{O})_{N,\,t}=\lim_{\Delta t\to\infty}\frac{1}{\Delta t}\int_t^{t+\Delta t}\langle\mathcal{O}\rangle_{N,\,\tau}\,d\tau. \tag{37}$$

Instead of the time averaging (37), one can go over in accordance with the ergodic hypothesis[99] to ensemble averaging. To do this, we recall that the Hamiltonian of the system, like the other operators of physical variables, is a functional of the field operators ψ:

$$H_N=H_N\{\psi\},\quad\mathcal{O}=\mathcal{O}\{\psi\}.$$

The ensemble average can now be defined as the functional integral[120]

$$[\mathcal{O}]_N=Z_N^{-1}\int\mathrm{e}^{-H_N\{\psi\}/\Theta}\mathcal{O}\{\psi\}\,D\{\psi\}, \tag{38}$$

with partition function

$$Z_N=\int\mathrm{e}^{-H_N\{\psi\}/\Theta}D\{\psi\}.$$

We write here $D\{\psi\}$, understanding that the integration must be performed over the field operators, both of creation and annihilation, independently, but with allowance for the commutation properties.

Unfortunately, the representation of the average in the form of the functional integral (38)—on which the statistical physics of solitons[121] is actually based—presupposes that the explicit form of the soliton solutions for physical fields is known. At the present time, it is known how to construct soliton statistics only for some classical one-dimensional systems. Moreover, the soliton ensemble is usually represented as an ideal gas. However, if the number of nucleation centers is large, their interaction cannot be ignored.

In a more realistic treatment, one should separate the soliton from the nonsoliton degrees of freedom, representing the set of all possible fields $\{\psi\}$ as the union of the soliton and nonsoliton subsets,

$$\{\psi\}=\{\psi_{\mathrm{sol}}\}\cup\{\widetilde{\psi}\},$$

so that at the same time

$$D\{\psi\}=D\{\psi_{\mathrm{sol}}\}\,D\{\widetilde{\psi}\},$$

and then integrate the partition function over the soliton degrees of freedom and determine the effective Hamiltonian $\widetilde{H}_N\{\widetilde{\psi}\}$ as a functional of the nonsoliton fields. After this, one could integrate over $\{\psi_{\mathrm{sol}}\}$ in (38) and determine the effective operator $\widetilde{\mathcal{O}}\{\widetilde{\psi}\}$.

It is evident that the implementation of such a program in a fairly general case is hardly possible. In terms of its complexity, this problem is comparable with the justification of statistical mechanics on the basis of Newton's equations.

Therefore, we make here the assumption of mixing,[14,115,118] according to which the effective system obtained after integration over the soliton degrees of freedom is a mixture of thermodynamic phases and is defined on an extended state space. The field operator of the mixed system is represented by the direct sum

$$\widetilde{\psi}=\bigoplus_i\widetilde{\psi}_i,$$

where ψ_i are the field operators of the pure phases. In a number of cases, in order to preserve the correct normalization of the operators, it is convenient to make a renormalization of the form[22,118]

$$\widetilde{\psi}_i\rightarrow\sqrt{w_i}\,\psi_i\ (w_i\equiv N_i/N), \tag{39}$$

so that

$$H_{N_i}\{\widetilde{\psi}_i\}\rightarrow H_N\{\psi_i\}.$$

Such a renormalization leads to the appearance in the Hamiltonian of the factors w_i, which have the meaning of phase probabilities or concentrations. These are essentially the same phase concentrations as arose in the Gorter-Casimir theory (see Sec. 2). The appearance of such factors in the Hamiltonian can be readily understood by again considering the Ising model (29). On the transition to the extended space and the representation of the corresponding phase, we have in the Hamiltonian an expression of the form

$$\sum_{1\leqslant f\leqslant N_i}\sigma_{fi},\quad\sum_{1\leqslant f,\,f'\leqslant N_i}\sigma_{fi}\sigma_{f'i}.$$

Averaging over all ways of choosing the set V_i, we replace the sums by the equivalent expressions[22]

$$w_i\sum_{1\leqslant f\leqslant N}\sigma_{fi},\quad w_i^2\sum_{1\leqslant f,\,f'\leqslant N}\sigma_{fi}\sigma_{f'i},$$

preserving the normalization of the Pauli operators σ_{fi} to unity. The concentration w_i need not be introduced explicitly into the Hamiltonian; one can instead work with operators having a nonstandard normalization. In such an approach, the w_i appear in the definition of the averages.[114]

Thus, the transition to the equilibrium description of the heterophase state on the extended space required the introduction of the following hypotheses:

the stationarity hypothesis

$$(\mathcal{O})_{Nt}=(\mathcal{O})_{Ns}$$

i.e., the result of an observation does not depend on the time at which it is commenced;

the ergodicity hypothesis

$$(\mathcal{O})_N=[\mathcal{O}]_N,$$

by virtue of which time averages can be replaced by ensemble averages;

and the mixing hypothesis

$$[\mathcal{O}]_N=\langle\widetilde{\mathcal{O}}\rangle_N,$$

which makes it possible to go over from studying the soliton dynamics to considering the heterophase averages of operators of the type (39).

8. PRINCIPLE OF COMPETITION OF INTERACTIONS

Before we turn to the consideration of specific examples, we attempt to answer this question: What physical reasons cause the appearance of heterophase states?

It is clear that the occurrence of such states cannot be due solely to a change in the temperature. First, as we have seen above, such changes generate only homophase fluctuations. Second, heterophase states are evidently not always observed in phase transitions.

It is here appropriate to recall that in the description of phase transitions in the framework of statistical mechanics one frequently employs model Hamiltonians in the construction of which simplifications are made, only those interactions that lead to the phase transition being preserved, while the remainder are deliberately suppressed. Thus, in the theory of superconductivity the point of departure is the BBCS model (27), in which the interaction is due to the Fröhlich electron-phonon mechanism.[26] The Coulomb repulsion of the electrons is usually omitted. The model problem with the Hamiltonian (27) admits, as is well known, an exact (as $N\rightarrow\infty$) solution describing a phase transition between pure phase states.[101] If to this model problem we apply the principle of extending the spaces and the mixing principle, the exact solution is not changed—the phases still remain pure. The result will be different if the Coulomb repulsion of the electrons is included, even in the simplest approximation.[21] It can be shown that the behavior of the thermodynamic variables and the occurrence of the heterophase state depend strongly on the relationship between the effective pairing due to the Fröhlich attraction mechanism and the Coulomb repulsion.[21,22]

In the example given, the Fröhlich interaction leads to a phase transition, to the occurrence of the ordered state of Cooper pairs, while the Coulomb repulsion hinders such ordering, competing with it. We note that if the model (27) with the Coulomb interaction is treated without allowance for the possible extension of the state space, it can be shown that the presence of Coulomb repulsion leads to a decrease in the effective attraction.[26]

An analogous competition between the interactions occurs in other physical systems. For example, to describe ferromagnetic ordering one usually employs the Heisenberg model (25), retaining in the Hamiltonian only the so-called exchange interaction $J_{ff'}$ associated with the Coulomb interaction of the electrons of neighboring sites,

$$\Phi(\mathbf{r}, \mathbf{r}') = \frac{e^2}{|\mathbf{r}-\mathbf{r}'|}$$

and determined by a matrix element of the form[22,122]

$$J_{ff} = \langle f, f' \mid \Phi(\mathbf{r}, \mathbf{r}') \mid f, f' \rangle,$$

where $|f\rangle$ are Wannier functions. On the transition to the quasispin formalism in the construction of the Heisenberg model from the polar model of a metal,[122] the Hamiltonian must contain in addition to this term a C-number term of the form

$$\left.\begin{aligned} \frac{1}{2}A &= \frac{1}{2}\sum_{ff'}\left\{L_{ff'} - \frac{1}{2}J_{ff'}\right\};\\ L_{ff'} &= \langle f, f' | \Phi(\mathbf{r}, \mathbf{r}') | f', f \rangle, \end{aligned}\right\} \qquad (40)$$

which takes into account the presence of the "direct" repulsion of the electrons, which competes with the ordering exchange interaction. When phase transitions are considered in the framework of the usual approaches, this term is omitted, it being assumed that it merely renormalizes the ground-state energy.[105] On the extension of the state space and mixing, the presence of this term leads, as we shall see below, to the appearance of heterophase states and makes it possible to explain some features in the thermodynamic behavior of magnets (see Refs. 17, 20, 22, 46, 123, and 124).

In models of nuclei based on the pairing hypothesis,[59] the existence of disordering is in the first place evidently due to the fact that the system is finite.

In heterophase multiquark systems, there is competition between the attraction at large distances and the repulsion of bags, which behave like hard spheres.[8]

Thus, the study of the problem of the heterophase state requires not only extension of the state spaces and mixing of the phases but also a modification of the models in order to take into account not only the ordering interactions but also the disordering ones that compete with them.

We now consider models of specific physical systems.

9. MODELS OF HETEROPHASE STATES

In this section, as examples, we consider models of heterophase states for ferromagnets, superconductors, and multiquark formations in nuclear matter. We shall follow our studies in Refs. 7, 20–22, 38, 46, 118, 123, and 124. We can describe similarly heterophase states in other systems, in particular, in crystals (Refs. 14–16, 18, 19, and 114), antiferromagnets,[125] and ferroelectrics,[126,127] including such states in metastable substances.[128,129]

We begin with the model of a heterophase ferromagnet. In the previous section, we pointed out that the standard Heisenberg Hamiltonian (25) must be augmented by the term (40). Then the original SU(2) invariance is naturally conserved. In accordance with the extension principle, we define the Hamiltonian on the space

$$\mathscr{H} = \mathscr{H}_{\mathbf{e}} \otimes \mathscr{H}_0,$$

where $\mathscr{H}_{\mathbf{e}}$ is the space of states with distinguished direction **e** in the three-dimensional space of quasispin variables that corresponds to the ferromagnetic phase, and $\mathscr{H}_0$ is the space of disordered states that corresponds to the paramagnetic phase.

Further, having representations S_{fi} of the quasispin variables on each of the factor spaces, we can construct corresponding representations of the Heisenberg Hamiltonian:

$$H_i = \frac{1}{2}\sum_{ff'}\left(L_{ff'} - \frac{1}{2}J_{ff'}\right)\hat{1}_i - \sum_{ff'} J_{ff'}\mathbf{S}_{fi}\mathbf{S}_{f'i}. \qquad (41)$$

Here, each summation Σ_f must obviously be applied only to the sites $f \in V_i$ that belong to the regions of phase i, and the values of the coordinates that occur in V_i must vary in their dependence on the time. Taking into account the principle of phase mixing (see Sec. 7), we can represent the total Hamiltonian of the heterophase ferromagnet in the form[17]

$$H = \bigoplus_i H_i;$$

$$H_i = (w_i^2 A/2 - w_i\mu_i)\,\hat{1}_i - w_i^2\sum_{ff'} J_{ff'}\mathbf{S}_{fi}\mathbf{S}_{f'i}, \qquad (42)$$

where μ_i is the chemical potential of the corresponding phase, and w_i is the phase concentration.

The problem with the model Hamiltonian (42) can now be investigated by any of the well-known methods of the quantum theory of magnetism. However, to emphasize the fundamental difference that arises in the description of the heterophase state, we shall here use the simplest mean-field approximation. We emphasize that the mean-field method leads to a result which is exact in the limit $N \to \infty$ in the case of a so-called long-range interaction, when

$$(\forall f, f')J_{ff'} > 0, \ \lim_{N\to\infty} J_{ff'} = 0, \ \lim_{N\to\infty} J < \infty,$$

$$J = \sum_g J_g, \quad g = |\mathbf{f} - \mathbf{f}'|.$$

In this case, the original Hamiltonian (42) is equivalent to the approximating Hamiltonian

$$H^{\text{app}} = \bigoplus_i H_i^{\text{app}};$$

$$H_i^{\text{app}} = (w_i^2 A/2 - w_i\mu_i)\,\hat{1}_i - w_i^2\sum_{ff'} J_{ff'}(2\mathbf{S}_{fi} - \langle \mathbf{S}_i \rangle)\langle \mathbf{S}_i \rangle \qquad (43)$$

in the sense that they determine equal values of the thermodynamic potentials.[20] Here, $<S_i>$ is the average spin in the ith phase, whose value does not depend on f by virtue of the translational invariance on the lattice. It is clear that for the paramagnetic phase $<S_p> = 0$, whereas for the ferromagnetic phase $<S_F>$ can be nonzero.

In the standard manner, we obtain for the ferromagnetic mean spin the equation[4)]

$$\langle S_F\rangle = \frac{1}{2}\,\mathrm{th}\,(Jw^2\langle S_F\rangle/\Theta), \tag{44}$$

where w denotes w_F, and $<S_F>$ is the modulus of the mean spin. From the condition (36) in conjunction with the normalization condition

$$w_F + w_p = 1$$

(see Sec. 2) we obtain the expression

$$w\ (\equiv w_F) = A - J\,\langle S_p\rangle^2/2\,(A - J\sum_i \langle S_i\rangle^2).$$

Taking into account the equation $<S_p> = 0$, we obtain from this

$$w = A/2\,(A - J\,\langle S_F\rangle^2). \tag{45}$$

It is readily seen that the relations (44) and (45) comprise a closed system of equations, the solutions of which determine the possible thermodynamic states of the system.

For the total free energy per spin, we have

$$\overline{F} = \overline{F}_F + \overline{F}_p = A\,(w^2 - w + 1/2) + w^2J\,\langle S_F\rangle^2 - \Theta\ln\,[4\,\mathrm{ch}\,(w^2J\,\langle S_F\rangle/\Theta)]. \tag{46}$$

We can now investigate the question of the realization of any particular phase state. Here, investigating the possible solutions of the system (44), (45), we must also take into account the solutions corresponding to pure phases, i.e., with $w\equiv 0$ (paramagnet) and with $w\equiv 1$ (pure ferromagnet).

We note that the nature of the solutions depends qualitatively on the relationship between the coupling constants J and A, i.e., on the contributions due to the exchange interaction and the direct interaction competing with it. We consider the following situations.

1) $A\geqslant 3J/2$. In this case, a phase transition of the second kind takes place in the system at the critical point

$$\Theta_c = J/8 \tag{47}$$

(Fig. 4). At the same time, the ferromagnetic state (state with $<S_F> \neq 0$) contains below Θ_c and right down to zero temperature a macroscopic fraction of the paramagnetic state, whose concentration is determined by the quantity $1-w$. In other words, below Θ_c there is a heterophase state, an equilibrium mixture of the ferromagnetic and paramagnetic phases.

Above Θ_c, the state with zero mean magnetization (paramagnet) is advantageous, but in it, however, $w = 1/2$ (Fig. 4c). In other words, half of the particles still belong to the ferromagnetic phase, although there is no long-range order. Such a result can be interpreted as the manifestation of short-range order above Θ_c.

2) $J/2 < A < 3J/2$. The phase transition between two heterophase states (ferromagnet with nucleation centers of the paramagnetic phase and paramagnet with ferromagnetic nucleation centers of short-range order type) is a transition of the first kind and is realized at a temperature $\Theta_{tr} > \Theta_c$ (Fig. 5). As the value of A is decreased, the transition temperature increases. The temperature Θ_{tr} is determined by the equation

$$A\,\langle S_F\rangle_{\mathrm{tr}} + J\,\langle S_F\rangle^3_{\mathrm{tr}} + A\,\frac{\ln\,(1 - 4\,\langle S_F\rangle^2_{\mathrm{tr}})}{\mathrm{Ar\,th}\,2\,\langle S_F\rangle_{\mathrm{tr}}} = 0;$$

$$\Theta_{\mathrm{tr}} = \frac{JA^2\,\langle S_F\rangle_{\mathrm{tr}}}{4\,(A - J\,\langle S_F\rangle^2_{\mathrm{tr}})^2\,\mathrm{Ar\,th}\,2\,\langle S_F\rangle_{\mathrm{tr}}}\,.$$

Above Θ_{tr} it is possible to have a magnetic state which exists up to the temperature $\tilde{\Theta}$ of absolute loss of stability, which is determined by the conditions

$$\frac{\partial w}{\partial\Theta} = \infty, \quad \frac{\partial\,\langle S_F\rangle}{\partial\Theta} = \infty \quad (\Theta = \tilde{\Theta}).$$

Such behavior corresponds to the possibility of temperature hysteresis (curve 6).

3) $0\leqslant A\leqslant J/2$. The phase transition is also a transition of the first kind. At a finite temperature $\Theta_n \leqslant \Theta_{tr}$ the parameter w reaches a value equal to unity. In other words, below Θ_n a pure ferromagnetic state is realized. At this point, which can be interpreted as the nucleation temperature, there are singularities of the mean spin and concentration (Fig. 6). At $A = J/2$, $\Theta_n = 0$. For A/J equal to a root of the equation

$$\frac{1}{2}\,\frac{A}{J} = \frac{\sqrt{A/2J}}{\mathrm{Arth}\,\sqrt{2A/J}}\,\ln\,\mathrm{ch}\,\mathrm{Arth}\,\sqrt{2A/J},$$

the nucleation temperature reaches the value

$$\Theta_n = \Theta_{\mathrm{tr}} = \sqrt{AJ/2}/\mathrm{Arth}\,\sqrt{2A/J}.$$

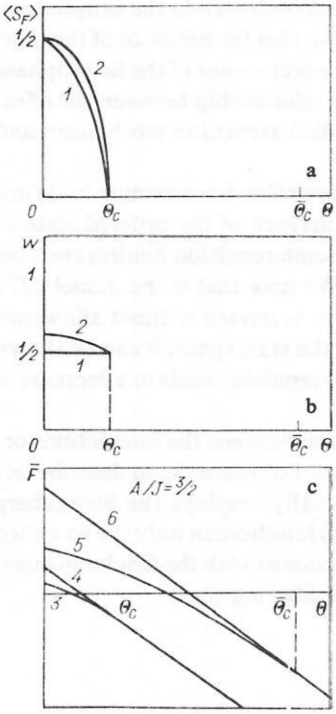

FIG. 4. Temperature dependence of the mean spin (a), the ferromagnetic concentration (b), and the free energy (c) of a heterophase ferromagnet for $A\geqslant 3J/2$: 1) $A\rightarrow +\infty$; 2) $A/J = 3/2$; 3) heterophase state; 4) $w\equiv 1/2$, $\langle S_F\rangle\equiv 0$; 5) ordinary solution ($w = 1$); 6) $w\equiv 0$, $\langle S_F\rangle\equiv 0$.

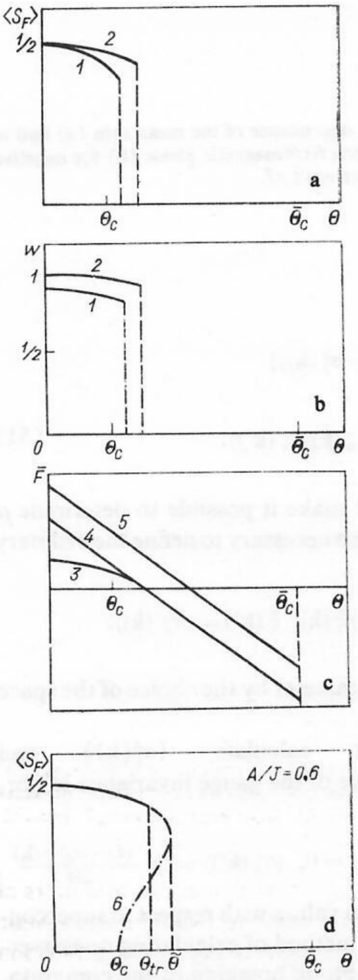

FIG. 5. Temperature dependence of the order parameters and of the free energy in the case $J/2 < A < 3J/2$: 1) $A/J = 0.8$; 2) $A/J = 0.6$; 3) heterophase solution; 4) $w \equiv 1/2, \langle S_F \rangle \equiv 0$; 5) $w \equiv 0$, $\langle S_F \rangle \equiv 0$; 6) unstable solution.

In other words, for such A/J the nucleation point coincides with the phase-transition point, and the ferromagnetic phase is pure. With further decrease in A/J, the transition temperature continues to increase, reaching at $A = 0$ the value

$$\overline{\Theta}_c = J/2,$$

which corresponds to the phase-transition point in the ordinary Heisenberg model calculated by the mean-field method. At $A = 0$, the phase transition again becomes a transition of the second kind between pure phases.

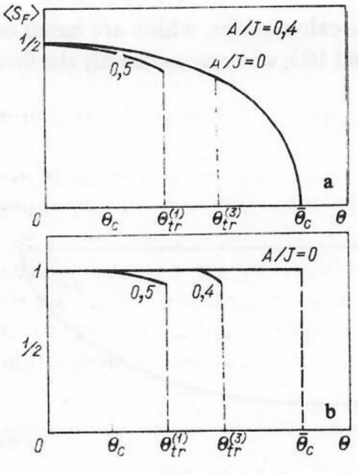

FIG. 6. Temperature dependence of the order parameters for $0 < A \leqslant J/2$.

Thus, this extension of the Heisenberg model includes not only heterophase solutions but also the ordinary situation.

4) $A < 0$. In this case, there exists a solution corresponding to a phase transition of the second kind at the point Θ_c (47) to the heterophase state. However, in contrast to case 1, the ferromagnetic concentration w here decreases with decreasing temperature, whereas the mean spin increases (Fig. 7). This is an equilibrium but unstable solution, since

$$\partial^2 \overline{F} / \partial w^2 < 0.$$

The corresponding state of the system can only be metastable. Stable in this case is the solution corresponding to pure phases and a transition of the second kind at the point $\overline{\Theta}_c$.

Our treatment permits the conclusion that the phase concentration w of the heterophase system is indeed an additional order parameter whose variation is associated with a further specific phase transition, which takes place at the nucleation point. We noted above the presence of singularities of the two order parameters at this point. We now consider the behavior of the other thermodynamic variables.

The magnetization of the heterophase system must obviously be determined by the relation

$$M = \langle S_F \rangle w \tag{48}$$

(the mean spin multiplied by the probability of finding it in the system). In other words, the magnetization is here not simply an order parameter but a product of two order parameters. The temperature dependence of M for different values of $\nu = A/J$ is shown in Fig. 8. For $A/J > 1/2$, the magnetization of the ground state does not reach the saturation magnetization, and this is something that, as we already said in Sec. 1, is observed in certain ferromagnets.

For $A < 0$, the growth of the mean spin with decreasing temperature and simultaneous decrease of the ferromagnetic concentration w can lead to the appearance of a wide maximum of the magnetization (48) (Fig. 8), something that is also observed in a number of partly ordered ferro- and antiferromagnets.[43–46]

At the nucleation point Θ_n, the magnetization (48) has a singularity.

The entropy of the heterophase system is determined by

$$\overline{S} = \ln\left[4\,\mathrm{ch}\,\frac{Jw^2\sigma}{2\Theta}\right] - \frac{Jw^2\sigma^2}{2} \quad (\sigma \equiv 2\langle S_F \rangle).$$

Its temperature dependence for different A/J is shown in Fig. 9.

The specific heat $C_B = 0$ in zero external field is

$$C_B = \frac{4A^{1}J^2\sigma^2(1-\sigma)^2}{\Theta(4A - J\sigma^2)\left[\Theta(4A - J\sigma^2)^3 - 2JA^2(1-\sigma^2)(4A + 3J\sigma^2)\right]}$$

(Fig. 10). It is readily seen that at the nucleation point there is an additional jump in the specific heat. Such a picture is observed, for example, in the compound $CdCr_2S_4$.[130]

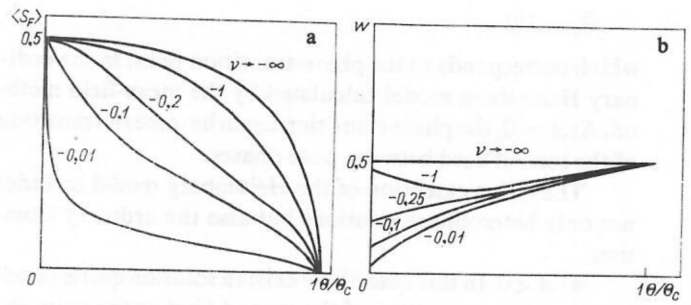

FIG. 7. Temperature dependence of the mean spin (a) and of the concentration of the ferromagnetic phase (b) for negative values of the parameter $\nu\equiv A/J$.

We now consider a further example—a model of a heterophase superconductor.[21,22] In the previous section, it was pointed out that application of the principle of extension of the spaces and mixing to the standard BBCS model does not lead to the description of a stable heterophase state. We shall show that this is indeed the case. For simplicity, we use the quasispin formulation of the problem.[107,108] Then with allowance for what was said above the Hamiltonian of the system can be represented in the form[21]

$$\left.\begin{aligned} &H=\bigoplus_i H_i;\\ &H_i=\frac{w_i}{2}\sum_k \varepsilon(\mathbf{k})\{\hat{1}-\sigma_i^z(\mathbf{k})\}-\frac{w_i^2}{2V}\sum_{k,k'}J(\mathbf{k},\mathbf{k}')\,\sigma_i^-(\mathbf{k})\,\sigma_i^-(\mathbf{k}'),\end{aligned}\right\} \tag{49}$$

where $\varepsilon(\mathbf{k})=k^2/2m\text{-}\mu$, $J(\cdot)$ is the kernel of the effective two-body interaction, and $\sigma_i^{\cdot\cdot}$ is the representation of the Pauli operators for phase i. The structure of the spaces corresponding to the phases i was considered in Sec. 5.

In the usual manner, we define the thermodynamic potential

$$\Omega=\Omega_s+\Omega_n;\quad \Omega_i\equiv-\Theta\ln\operatorname*{Sp}_{(i)}e^{-H_i/\Theta}.$$

Bearing in mind that

$$w_i=\frac{\partial\Omega_i}{\partial\mu}\Big/\frac{\partial\Omega}{\partial\mu}\ (i=s,\ n),$$

and differentiating formally, we find

$$w_i=w_i\sum_k\{\langle\sigma_i^z(\mathbf{k})\rangle-1\}/\sum_i w_i\sum_k\{\langle\sigma_i^z(\mathbf{k})\rangle-1\}. \tag{50}$$

The condition of minimality of the free energy [see (36)] has the form

$$\frac{1}{V}\sum_{kk'}J(\mathbf{k},\mathbf{k}')\{\langle\sigma_s^-(\mathbf{k})\,\sigma_s^+(\mathbf{k}')\rangle+\langle\sigma_n^-(\mathbf{k})\,\sigma_n^+(\mathbf{k}')\rangle\}$$

$$=\frac{1}{2}\sum_k\varepsilon(\mathbf{k})\{\langle\sigma_n^z(\mathbf{k})-\sigma_s^z(\mathbf{k})\rangle\}$$

$$+\frac{1}{V}\sum_{kk'}J(\mathbf{k},\mathbf{k}')\langle\sigma_n^-(\mathbf{k})\,\sigma_n^+(\mathbf{k}')\rangle. \tag{51}$$

Equations (50) and (51) make it possible to determine μ and w_s. In addition, it is also necessary to define the ordinary order parameter (gap)

$$\Delta(\mathbf{k})=\frac{1}{V}\sum_{k'}J(\mathbf{k},\mathbf{k}')\,\xi(\mathbf{k});\ \xi(\mathbf{k}')=\langle\sigma_s^{\mp}(\mathbf{k})\rangle.$$

Note that $\xi(\mathbf{k})$ is a real parameter by the choice of the space $\mathscr{H}_s$ as $\mathscr{H}(\varphi=0)$.

Thus, we must calculate $\langle\sigma_i^z(\mathbf{k})\rangle$ and $\langle\sigma_z^-(\mathbf{k})\sigma_i^+(\mathbf{k}')\rangle$. By virtue of the gauge invariance of normal states,

$$\langle\sigma_n^+(\mathbf{k})\rangle=0,\quad\langle\sigma_n^-(\mathbf{k})\,\sigma_n^+(\mathbf{k}')\rangle=0,\quad\langle\sigma_n^z(\mathbf{k}')\rangle=\operatorname{th}\frac{(1-w_s)\,\varepsilon(\mathbf{k})}{2\Theta}.$$

To determine the mean values with respect to superconducting states, we use the method of calculating quasiaverages associated with asymptotic breaking of the commutation relations (see Sec. 5). We introduce the operator constructions

$$\gamma^-(\mathbf{k})=u^2(\mathbf{k})\,\sigma_s^-(\mathbf{k})-v^2(\mathbf{k})\,L^2\sigma_s^+(\mathbf{k})+2u(\mathbf{k})\,v(\mathbf{k})\,L\sigma_s^z(\mathbf{k});$$
$$\gamma^+(\mathbf{k})=u^2(\mathbf{k})\,\sigma_s^+(\mathbf{k})-v^2(\mathbf{k})\,\sigma_s^-(\mathbf{k})\,L^2+2u(\mathbf{k})\,v(\mathbf{k})\,\sigma_s^z(\mathbf{k})\,L,$$

where $L=(1/V)\Sigma_k\boldsymbol{\sigma}(\mathbf{k})\hat{\mathbf{1}}_x/(1/V)\Sigma_k\xi(\mathbf{k})$ and the transformation coefficients satisfy the conditions

$$u^2(\mathbf{k})+v^2(\mathbf{k})=1;$$
$$u^2(\mathbf{k})-v^2\mathbf{k}=\frac{w_s\varepsilon(\mathbf{k})}{E(\mathbf{k})};\quad E(\mathbf{k})=\sqrt{\varepsilon^2(\mathbf{k})\,w_s^2+\Delta^2w_s^4}.$$

Omitting the cumbersome calculations, which are based on the method of Refs. 102 and 103, we reproduce only the final result:

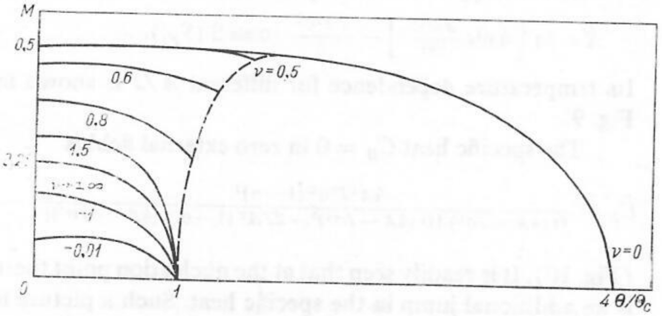

FIG. 8. Temperature dependence of the specific magnetization.

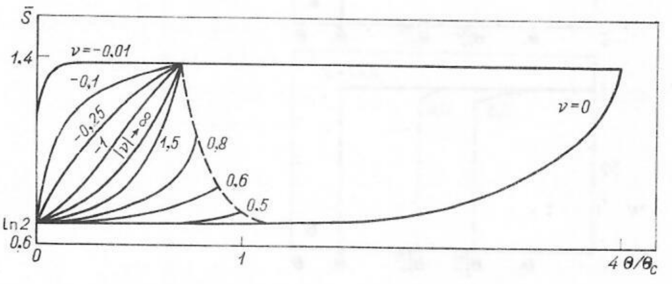

FIG. 9. Temperature dependence of the specific entropy for different values of the parameter ν.

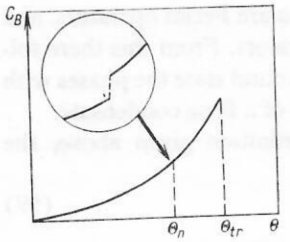

FIG. 10. Behavior of the specific heat of the system at the nucleation point.

$$\langle \sigma_s^z(\mathbf{k})\rangle = \frac{w_s \varepsilon(\mathbf{k})}{E(\mathbf{k})} \operatorname{th} \frac{E(\mathbf{k})}{2\Theta};$$

$$\langle \sigma_s^{\pm}(\mathbf{k})\rangle = \frac{w_s^2 \Delta(\mathbf{k})}{2E(\mathbf{k})} \operatorname{th} \frac{E(\mathbf{k})}{2\Theta};$$

$$\langle \sigma_s^-(\mathbf{k})\,\sigma_s^+(\mathbf{k})\rangle = \frac{1}{2}\left\{1 - \frac{w_s \varepsilon(\mathbf{k})}{E(\mathbf{k})} \operatorname{th} \frac{E(\mathbf{k})}{2\Theta}\right\}.$$

The relations (50) and (51) and the equation for the gap can now be represented in the form

$$w_s = \frac{w_s \sum\limits_k \left\{1 - w_s \frac{\varepsilon(\mathbf{k})}{E(\mathbf{k})} \operatorname{th} \frac{E(\mathbf{k})}{2\Theta}\right\}}{w_s \sum\limits_k \left\{1 - w_s \frac{\varepsilon(\mathbf{k})}{E(\mathbf{k})} \operatorname{th} \frac{E(\mathbf{k})}{2\Theta}\right\} + (1-w_s)\sum\limits_k \left(1 - \operatorname{th} \frac{(1-w_s)\varepsilon(\mathbf{k})}{2\Theta}\right)};$$

$$w_s = \frac{w_s}{2V} \sum_k \left\{1 - \frac{w_s \varepsilon(\mathbf{k})}{E(\mathbf{k})} \operatorname{th} \frac{E(\mathbf{k})}{2\Theta}\right\}; \qquad (52)$$

$$\Delta(\mathbf{k}) = \frac{1}{V} \sum_{k'} \frac{w_s^2 J(\mathbf{k}, \mathbf{k}')\,\Delta(\mathbf{k}')}{E(\mathbf{k}')} \operatorname{th} \frac{E(\mathbf{k}')}{2\Theta}.$$

The system (52) admits three sets of solutions characterized by the value of the parameter w_s, namely:

a) $w_s \equiv 0$;

b) $w_s \equiv 1$;

c) $w_s \not\equiv 0, 1$.

In the first case, $\Delta(\mathbf{k}) \equiv 0$ for all temperatures, i.e., there is no superconducting component in the system. As is well known,[26] such a solution is unstable at sufficiently low temperatures. Case (b) corresponds to the purely superconducting state. In this case, the equation for the gap in (52) goes over into the standard equation of BBCS theory.

We now consider case (c). As $\Delta \to 0$, we obtain from the first equation in (52)

$$(1-w_c) \sum_k \left\{1 - \operatorname{th} \frac{(1-w_c)\varepsilon(\mathbf{k})}{2\tilde{\Theta}_c}\right\} = w_c \sum_k \left\{1 - \operatorname{th} \frac{w_c \varepsilon(\mathbf{k})}{2\tilde{\Theta}_c}\right\},$$

where $\tilde{\Theta}_c$ is the critical temperature, and w_c is the critical value of the superconducting concentration. Obviously, $w_c = 1/2$. Therefore, in the Bardeen approximation, when[27]

$$J(\mathbf{k}, \mathbf{k}') = \begin{cases} J = \text{const} & |\varepsilon(\mathbf{k})| \leqslant \hbar\omega_0, \\ 0 & |\varepsilon(\mathbf{k})| > \hbar\omega_0, \end{cases}$$

we have for $\tilde{\Theta}_c$

$$\tilde{\Theta}_c = \frac{2e^C}{\pi} w_c \hbar\omega_0 e^{-1/J\rho_0 w_c}. \qquad (53)$$

Here, $C = 0.5772$ is Euler's constant, and $\rho_0 = mk_0/2\pi^2\hbar^3$ is the density of states on the Fermi surface, with

$$\sqrt{2m(\mu - \hbar\omega_0)} < k_0 < \sqrt{2m(\mu + \hbar\omega_0)}, \quad \mu > \hbar\omega_0.$$

Hence

$$\tilde{\Theta}_c = 0.567\hbar\omega_0 e^{-2/J\rho_0},$$

a value that is significantly lower than the critical temperature in the standard theory[26,27]: $\Theta_c = 1.134\hbar\omega_0 \times \exp(-1/J\rho_0)$. Note that the exact formula (53) agrees well with the phenomenological result established in Ref. 131.

We now consider the energy of the ground state in the model (49). Going over to integration over **k** and to the limit $\Theta \to 0$, we obtain

$$E_0 = \frac{V}{2\pi^2\hbar^3}(1-w_0)\left(\frac{1}{2m}\frac{k_0^5}{5} - \frac{k_0^3}{3}\mu_0\right) + \mu_0 N$$
$$+ \frac{Vw_0}{2\pi^2\hbar^3}\left(\frac{k_+^5 + k_-^5}{10m} - \frac{k_+^5 + k_-^3}{3}\mu_0\right) - V\rho_0 w_0 \hbar\omega_0 \sqrt{(\hbar\omega_0)^2 + \Delta_0^2 w_0^2},$$

where $k_0 = \sqrt{2m\mu_0}$. We consider E_0 as a function of w_0. It is readily seen that E_0 decreases with increasing w_0, reaching its smallest value at $w_0 = 1$. Thus, the ground state corresponding to case (c) is unstable.

In the previous section, we have already said that the stability of the heterophase state is determined by the Coulomb interaction. The contribution of this interaction to (49) is described by the term[26]

$$H_i^c = \frac{1}{2V} \sum_{q \neq 0} w_i^2 U(\mathbf{q})\,\rho_i^+(\mathbf{q})\,\rho_i(\mathbf{q}),$$

where $U(\mathbf{q}) = 4\pi e^2/q^2$ and the operator $\rho_i(\mathbf{q})$ describes the Fourier transform of the spatial density of the electrons of the corresponding phase.

We now consider the qualitative changes to which the inclusion of the Coulomb term must lead. The condition of equality of the chemical potentials can be now represented in the form

$$2w_s \sum_i \langle Q_i - I_i\rangle = \langle T_n - T_s\rangle + 2\langle Q_n - T_n\rangle, \qquad (54)$$

where

$$T_i = \frac{1}{2} \sum_k \varepsilon(\mathbf{k})\,\langle 1 - \sigma_i^z(\mathbf{k})\rangle;$$

$$I_i = \frac{1}{2V} \sum_{kk'} J(\mathbf{k}, \mathbf{k}')\,\langle \sigma_i^-(\mathbf{k})\,\sigma_i^+(\mathbf{k}')\rangle;$$

$$Q_i = \frac{1}{2V} \sum_q U(\mathbf{q})\,\langle \rho_i^+(\mathbf{q})\,\rho_i(\mathbf{q})\rangle.$$

Since the mean values in (54) are functions of the temperature, this relation can be used to determine the nucleation point Θ_n corresponding to the condition $w_s(\Theta_n) = 1$. Obviously,

$$2\{Q_s(\Theta_n) - I_s(\Theta_n)\} = T_n(\Theta_n) - T_s(\Theta_n). \qquad (55)$$

At the point Θ_n there must be a singularity of the order parameter (the gap) and, evidently, a jump in the specific heat (cf. the ferromagnetic case). It can be seen from (55) that the value of Θ_n depends on the relationship between the Coulomb repulsion and the effective pairing of the electrons.

The heterophase state will be stable in the low-temperature phase when

$$2\sum_i (Q_i - I_i) + T'_s - T'_n + 2w_s \sum_i (Q'_i - I'_i) \geqslant 2(Q'_n - T'_n), \tag{56}$$

where $X'_i \equiv dX_i/dw_s$. The investigation of the relation (56) is a very complicated mathematical problem and, unfortunately, can be done only by the approximate methods hitherto developed for problems with the Coulomb interaction. Since we are interested in the first place in the qualitative result, we use the roughest approximation and replace the energy of the Coulomb interaction per electron by the constant quantity $1/2Q$.[21,22] Then instead of (56) we have in the ground state

$$2Q - \frac{1}{4} Q^2 v \rho_0 w_0^2 - \Delta_0 \frac{v}{J} \geqslant 0, \tag{57}$$

where v is the specific volume. It is clear that Q can always be chosen in such a way as to satisfy the inequality (57). Thus, inclusion of the Coulomb interaction does indeed lead to stabilization of the heterophase state even at $\Theta = 0$.

In the two previous examples, the phase concentration w_i was introduced directly into the Hamiltonian by means of a renormalization of the type (39). Below, we consider an example in which w_i is calculated in a different way. We investigate a six-quark admixture in a nucleon system.[8]

We assume that nuclear matter is a system of interacting quarks, the interaction leading to the formation of quasiparticle excitations characterized by bound states of three, six, etc., quarks. From this point of view, the nucleon is a quasiparticle excitation. In the general case, the different states of the quark matter in which we are interested are characterized by the parameter n, the number of quarks that form a bound cluster (a particle). For $n = 3$, we shall speak of the nucleon phase, for $n = 6$ the six-quark phase, etc. The parameter n characterizes the method of ordering of the quarks in the clusters, i.e., the method of organizing the given phase state of quark matter. Therefore, n can be regarded as a certain order parameter.

In accordance with what was said above, a state space $\mathscr{H}_n$ must correspond to each value $n = 3, 6, 9, \ldots$, the states with different values of n being mutually orthogonal.

It is obvious that if we were to include absolutely all the properties of the real quark system, this would lead to an improbable complication of the mathematical formulation of the problem; moreover, at the present time the confinement mechanism is not yet fully clear. It is therefore expedient to consider a "simplified" model that makes it possible to take into account the most important features of the system associated with the phenomenon under investigation.[8]

Our main assumption is that there exist n-quark clusters and that they can be described in accordance with bag theory.[132,133] Then the representation of the total Hamiltonian for the nth phase can be written in the form

$$H_n = \sum_k \left(\sqrt{k^2 + M_n^2} - \mu_n\right) a_n^+(\mathbf{k})\, a_n(\mathbf{k}) + \Phi_n. \tag{58}$$

Here, $\mathbf{k}$ is the momentum of the bag, M_n is its mass, μ_n is the chemical potential of the nth phase, $a_n^+(\mathbf{k})$ and $a_n(\mathbf{k})$ are the operators of creation and annihilation of a cluster (bag) of n quarks with momentum $\mathbf{k}$, and Φ_n is the operator of the interaction energy of bags of the given species. It is clear that for $n = 3$ the nine operators a^+, a are Fermi operators, and for $n = 6$, 12 they are Bose operators. From this there follows the conclusion that in the ground state the phases with $n = 6$ and $n = 12$ are in the state of a Bose condensate.

In accordance with the definition given above, the phase concentration is

$$w_n = \frac{n}{N} \sum_k \langle a_n^+(\mathbf{k})\, a_n(\mathbf{k}) \rangle. \tag{59}$$

For simplicity, we restrict the treatment to just two phases with $n = 3$ and $n = 6$ (nucleons and quark sextets) and assume that the interaction is a contact interaction of hard spheres. We shall regard the nucleon phase as a collection of bags with the quantum numbers of the nucleons and mass

$$M_3 = \frac{3x_0 - z_0 + \alpha_c \Delta_3}{R_3} + BV_3, \tag{60}$$

which is determined in the standard theory.[134–136] Here, V_3 is the volume of a spherical bag of radius R_3, x_0/R_3 is the kinetic energy of a quark in the bag, $-z_0/R_3$ is the energy of the zero-point modes of the field in the bag, the term $\alpha_c \Delta_3$ takes into account the energy of one-gluon exchange, and the parameter B determines the pressure in the bag.

In its turn, the six-quark phase represents a collection of bags with mass[136]

$$M_6 = \frac{6x_0 - z_0 + \alpha_c \Delta_6}{R_6} + BV_6. \tag{61}$$

We restrict the treatment to six-quark bags with the quantum numbers of the deuteron and volume V_6. Of course, in giving up a dynamical treatment of the interacting quarks and bags, we rule out the possibility of investigating the microscopic mechanism of formation of the quark sextets from the nucleons. However, the assumption of the existence of the two phases and their description by means of the representation of a gas of bags makes it possible, in a certain sense, to take into account effectively the existence of such a mechanism and to study the problem of which phase state is thermodynamically advantageous for given external conditions.

In accordance with what was said above, we assume that the operators (58) realize representations of the "true" quark Hamiltonian on the state spaces $\mathscr{H}_3$ and $\mathscr{H}_6$ with corresponding symmetry properties, and $\mathscr{H}_3 \cap \mathscr{H}_6 = \varnothing$. The thermodynamic potential of such a system is

$$\Omega \equiv -\Theta \ln \underset{(\mathscr{H})}{\mathrm{Sp}}\, e^{-H/\Theta} = \Omega_3 + \Omega_6;$$

$$\Omega_i \equiv -\Theta \ln \underset{(\mathscr{H}_i)}{\mathrm{Sp}}\, e^{-H_i/\Theta}, \quad i = 3, 6.$$

Suppose that in a system of volume V there are N quarks. We shall assume that, interacting with one another, the bags behave as hard spheres, each with volume v_i. It is clear that such bags will move not in the complete volume V but only in a certain "free" part, the magnitude of which can be determined as

$$V' = v - \frac{w}{3} N v_3 - \frac{1 - w}{6} N v_6,$$

where

$$w = N_3/N$$

is the parameter that determines the concentration of the hadronic phase (N_3 is the number of quarks in bags that form the nucleon subsystem). It is obvious that in this case the concentration of the six-quark phase is $1 - w$, since $N_3 + N_6 = N$. There is here a direct analogy with a van der Waals gas, whose equation of state also contains a parameter that takes into account the impossibility of the penetration of hard spheres into each other.

We now investigate the behavior of the thermodynamic functions of the system in the ground state, i.e., for $\Theta = 0$. First of all, we make the standard transition from summation over $(\mathbf{k}, s)$ in the Fermi system to integration:

$$\sum_{k,\, s} \ldots \to g \frac{V'}{(2\pi)^3} \int d^3\mathbf{k} \ldots = g \frac{V'}{2\pi^2} \int_0^{k_F} dk\, k^2 \ldots,$$

where the Fermi momentum k_F is determined from the condition

$$\sqrt{k_F^2 + M_3^2} = \mu_3.$$

In addition, for the number of nucleons in the system we have

$$\frac{N_3}{3} \equiv \lim_{\Theta \to 0} \sum_{k,\, s} \left\{ \exp \frac{-(\sqrt{k^2 + M_3^2} - \mu_3)}{\Theta} + 1 \right\}^{-1}$$

$$= g_3 \frac{V'}{2\pi^2} \int_0^{k_F} dk\, k^2 = \frac{g_3 V'}{6\pi^2} k_F^3, \text{ where } g_3 = 2(2s+1) = 4.$$

From this we obtain

$$k_F = \left(\frac{\pi^2}{2} \frac{N_3}{V'} \right)^{1/3}.$$

From the definition of the thermodynamic potential Ω_3 we have at $\Theta = 0$

$$\Omega_3 = \sum_{k,\, s} (\sqrt{k^2 + M_3^2} - \mu_3) = \frac{g_3 V'}{2\pi^2} \int_0^{k_F} dk\, k^2 (\sqrt{k^2 + M_3^2} - \mu_3)$$

$$= \frac{g_3 V'}{16\pi^2} \Big[k_F (2k_F^2 + M_3^2) \sqrt{k_F^2 + M_3^2} - M_3^4 \ln \frac{k_F + \sqrt{k_F^2 + M_3^2}}{M_3} \Big] - \frac{g_3 V'}{6\pi^2} k_F^3 \mu_3.$$

With regard to the six-quark subsystem with the Hamiltonian, it, as we said above, is at $\Theta = 0$ in the state of a Bose condensate with $\mu_6 = M_6$ and $\Omega_6 = 0$.

In practice, instead of the thermodynamic potential Ω, which is a function of V and μ, it is more convenient to use the free energy $F = \Omega + \mu N$, which is a function of V and N. Then the total free energy is

$$F = F_3 - F_6,$$

where

$$F_3 = \frac{V'}{4\pi^2} \Big[k_F (2k_F^2 + M_3^2) \sqrt{k_F^2 + M_3^2} - M_3^4 \ln \frac{k_F + \sqrt{k_F^2 + M_3^2}}{M_3} \Big]$$

and

$$F_6 = \frac{N - N_3}{6} M_6.$$

Since, strictly speaking, quark matter must be characterized by very large values of V and N $(V \to \infty, N \to \infty)$, it is meaningful to consider the free-energy density in the system, i.e., the free energy per quark:

$$f \equiv \frac{F}{N} = \frac{F_3 + F_6}{N} = f_3 + f_6.$$

It can be regarded as a function of the variables v' and w, where

$$v' = V'/N.$$

As is well known, the most stable state of the system is the one in which the free energy is minimal. In our case, the free parameter with respect to which the function $f(v', w)$ must be minimized is the concentration w of the hadronic component, which is related to the concentration w_6 of the six-quark component by $w_6 = 1 - w$. From the minimization condition,

$$\frac{1}{4\pi^2} \frac{k_F}{w} v' \left[1 - \frac{w}{3v'} \left(\frac{v_6}{2} - v_3 \right) \right] \Big[(6k_F^2 + M_3^2) \sqrt{k_F^2 + M_3^2} + \frac{(2k_F^2 + M_3^2) k_F^2 - M_3^4}{\sqrt{k_F^2 + M_3^2}} \Big] + \frac{f_3}{v'} \left(\frac{v_6}{2} - v_3 \right) - \frac{M_6}{2} = 0, \tag{62}$$

where

$$k_F = \left(\frac{\pi^2}{2} \frac{w}{v'} \right)^{1/3}. \tag{63}$$

The system of equations (62), (63) makes it possible to determine the concentration w of the hadronic component as a function of the bag parameters and the variable v', which is related to the density of the system by

$$\rho = \frac{w (M_3 - M_6/2) + M_6/2}{3v' + w v_3 + \frac{1 - w}{2} v_6}. \tag{64}$$

We now turn to the direct calculation of the concentration w as a function of the parameters of the system and the investigation of phase transitions. To this end, we choose the numerical values of the parameters in (60) and (61) in accordance with standard bag theory[134–136]: $x_0 = 2.04$, $\alpha_c = 0.55$, $B^{1/4} = 146$ MeV, $\Delta_3 = 1.44$, $\Delta_6 \approx 0.48$. The value of the volume v_3 corresponds to the core volume determined from data on nucleon-nucleon scattering. In this case, the value of v_6 can be determined by using the well-known relationship in bag theory between the radii of the proton and the six-quark object[135]

$$R_6^3 / R_3^3 = M_6 / M_3.$$

It is now possible to determine the free-energy density and the concentration w as functions of the density ρ of the system. Figure 11 gives the result of calculating the dependence $w(\rho)$ in accordance with the expression (64). The value of ρ is measured in units of the normal nuclear density:

$$\rho = m\rho_0,$$

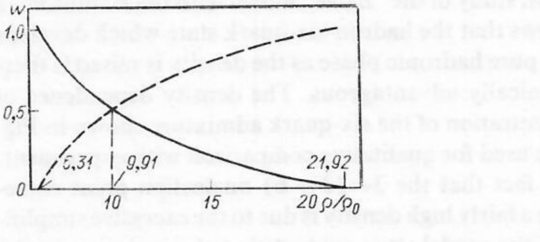

FIG. 11. Dependence of the concentrations of the nucleon and six-quark components on the density in the system. The continuous curve corresponds to the nucleon phase, and the broken curve to the six-quark phase.

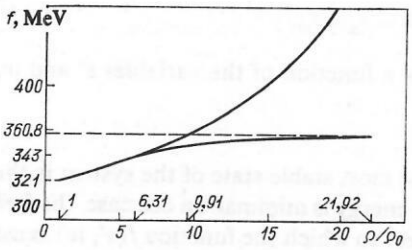

FIG. 12. Behavior of the specific free energies of the phase states of the system when its density is varied.

where m is the scale value and $\rho_0 = 1.23 \times 10^9\ |\mathrm{MeV}|^4$. It is readily seen that for variation of ρ from ρ_0 to $6.31\rho_0$ the parameter w has the value unity, $w(\rho) = 1$, this corresponding to a pure hadronic phase. At densities $\rho \geqslant 6.31\rho_0$, a six-quark component occurs in the system. With further increase in the density, more and more quarks go over from the hadronic to the six-quark phase. At $\rho \geqslant 21.92\rho_0$, no hadrons at all remain in the system, $w(\rho) = 0$, this corresponding to a pure six-quark phase. Thus, for $6.31\rho_0 \leqslant \rho \leqslant 211.92\,\rho_0$ there can be a heterophase state in the system, i.e., an equilibrium mixture of the nucleon and six-quark phase components.

To show that the heterophase state is thermodynamically advantageous, we consider the behavior of the free-energy density $f[\rho, w(\rho)]$ and the free-energy densities f_3 and f_6 of the pure phases, respectively. The results of such calculations are given in Fig. 12. As can be seen from Fig. 12, in the region $6.31\rho_0 < \rho < 21.92\,\rho_0$ the free-energy density corresponding to the heterophase state (thick continuous curve) has the smallest value, whereas for $\rho_0 \leqslant \rho \leqslant 6.31\rho_0$ the free-energy density of the hadronic phase (thin continuous curve) is minimal, while for $\rho > 21.92\rho_0$ that of the six-quark phase (broken curve) is minimal. Thus, there is in the system initially a pure hadronic phase, which at the density $\rho = \rho_{c1} \equiv 6.31\rho_0$ goes over into an equilibrium mixture of hadrons and six-quark objects, and, finally, when $\rho \geqslant \rho_{c2} \equiv 21.92\rho_0$ there is a pure six-quark phase (f_6 is minimal). The densities ρ_{c1} and ρ_{c2} correspond to phase-transition points of nucleation type (in other words, at these points nucleation centers of the competing phase state appear). In the model considered, these transitions are of the first kind, since at them the function $\partial f / \partial v'$ has a singularity. The phase transition of the first kind between the pure hadronic and six-quark phases at $\rho_c = 9.91\rho_0$ is not realized in stable equilibrium of the system (the corresponding free-energy density of the pure phases is greater than for the heterophase state).

Thus, study of the "naive" model with the Hamiltonian (58) shows that the hadron-six-quark state which develops from the pure hadronic phase as the density is raised is thermodynamically advantageous. The density dependence of the concentration of the six-quark admixture shown in Fig. 11 can be used for qualitative comparison with experiment.

The fact that the $3 \leftrightarrow (3 + 6)$ nucleation point corresponds to a fairly high density is due to the excessive simplification of the model. It is evident that the inclusion in the scheme of nuclear forces, for example, by going over to the "little bag" model,[133] will reduce the value of ρ_{c1}. An analogous result can be obtained in the model at nonzero temperature. In addition, an important simplification of the model is the assumption that the volumes of the bags are constant.

In reality, the bags cannot be hard spheres but are rather something like soap bubbles with a volume that depends on the external conditions. Allowance for the compressibility of the bags must also affect the critical densities ρ_{c1} and ρ_{c2}.

It is very interesting that the nucleation point ρ_{c2} lies appreciably above the point of the transition between the pure phases. Thus, the presence of the heterophase state leads to a delaying of the transition to the pure six-quark phase. The same may apply to the other, heavier multiquark states. In other words, the presence of the heterophase states can shift the point of transition to the pure phase of freely moving quarks to significantly higher densities. It must be emphasized that in a system with constant density in which the temperature is raised the existence of the heterophase states can also lead to a delaying of the transition to the phase of a pure quark-gluon plasma, i.e., the currently accepted temperature $T \sim 200$ MeV of this transition may be strongly underestimated. We note that our results can be used to calculate structure functions. The structure function for the heterophase mixture can be defined as

$$f = wf_3 + (1 - w) f_6,$$

where f_n are the structure functions for the pure phases, defined in the standard manner. We emphasize that by virtue of (14) the function f is a function of the density. This last circumstance opens up the possibility of investigating the so-called A dependences.[137]

10. CONCLUSIONS

We give a brief review of our study of the various approaches to the description of the dynamical and equilibrium properties of heterophase states in physical systems.

The description of the behavior of nucleation centers of one phase in another over short times is based primarily on the use of phenomenological kinetic equations and computer simulation using molecular dynamics and Monte Carlo methods. Particularly promising is the approach associated with study of the dynamics of quasisolitons, the application of which, however, is complicated by the absence of results in the three-dimensional case, which corresponds to the majority of real systems.

Bogolyubov's concept of quasiaverages, the basis of the modern theory of phase transitions, makes it possible to regard equilibrium heterophase states as macroscopic states with different symmetries. An important part here is played by the principle of extending the state spaces, the introduction of which is obvious from the mathematical point of view. The mixing principle has a more hypothetical nature; its justification is intimately related to the investigation of the process of establishment of equilibrium in a microscopic dynamical system and may constitute an independent problem of ergodic theory. The principle of the competition of interactions has a clear physical meaning and makes it possible to establish the true reason for the occurrence of heterophase states.

We emphasize that the approach presented here to the study of the equilibrium properties of heterophase states is essentially a method of constructing microscopic models of such states and has a certain universality. The principles formulated above can be applied to objects of different physical natures; the necessary calculations can be based on known methods and approximations, since improvement of the agreement with the experimental results is associated here in the first place with extension of the model and not perfection of the calculations.

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[1] Superconducting (condensate) electrons cannot transport heat.

[2] We are grateful to L. A. Aslanov for discussing the problems of the x-ray–neutron experiment.

[3] The authors are most grateful to A. Navrotsek for the possibility of seeing the model described above in action.

[4] *Translator's Note.* The Russian notation for the trigonometric, inverse trigonometric, hyperbolic functions, etc., is retained here and throughout the article in the displayed equations.

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