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EQUILIBRIUM NUCLEATION – A NEW TYPE OF PHASE TRANSITION

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The nonequilibrium dynamical process of nucleation from a metastable state is quite often investigated both theoretically and experimentally. We can mention in this connection several experiments concerning the study of supercooled and superheated states near the superconducting transition [1-4] and of supercooled liquides near the crystalization point [5]. There is a number of theoretical works dealing with the kinetics of nucleation [6-8] as well as with the connected problems of spinodal decomposition [9,10] and of quasilocal metastable states [11].

There exists also another problem of describing fluctuational nuclei of competing phases in equilibrium systems. The presence of such heterophase inclusions has been clearly demonstrated in very different experiments. For instance, there are paraelectric fluctuations in ferroelectrics HCl, DCl and apparently in $RbKF_3$ [12]. It has been found, recording photoemission spectra, that Ni below and above T_C consists of magnetic and nonmagnetic components [13]. The neutron coherent inelastic-scattering technique has been used to prove the existence of spin waves in Fe and Ni above T_C [14,15], which means that in the paramagnetic region there are some quasimagnetic clusters due to a short-range magnetic order. In several materials, e.g., in $Pd_2MnIn_{1-x}Sb_x$ and $Pd_2MnIn_{1-x}Sn_x$ ferromagnetic and antiferromagnetic phases coexist [16]. The coexistence of superconductive and normal-conductive components can explain an unusual behaviour of $(SN)_x$, $TaSe_3$ and $NbSe_3$ [17].

An equilibrium microscopic theory of heterophase systems has been developed in refs. [18-20]. This approach has been applied for describing crystals with dissociative lattices and for constructing the theory of melting and crystallization [21-23]. The heterophase model of a ferromagnet [24-26] and a superconductor [27] has also been advanced. In the frame of this theory fluctuational nuclei of competing phases appear in the system when they are thermodynamically profitable, and if not the system is in a pure phase. The point separating these two states can be called the nucleation point. The behaviour of system near such a point was not yet studied in detail.

The aim of the present paper is just an investigation of this phenomenon of equilibrium nucleation. We discuss here the physical reasons causing the profitability of heterophase fluctuations, and we show that the nucleation is a special kind of phase transition. Some possibilities of experimental observation of this effect are also pointed out.

In order to compare the heterophase approach with the usual phase-transition theory let us first remind the basic theses of the latter one:

i) a system having a phase transition is described by the Hamiltonian H with the symmetry group G, so that the ground state of the system is macroscopically degenerated (in the thermodynamic limit);

ii) a spontaneous symmetry breaking is occurring at the transition point; the ordered phase corresponding to the symmetry group $G_1 \subset G$;

iii) phase state of a system can be described by an order parameter, which is a macroscopic quantity possessing the symmetry properties of this system;

iiii) the spontaneous break of symmetry occurs simultaneously in the whole volume of the system, affecting all its particles.

These propositions can be easily illustrated by a number of models known. We should only mention that there are several models exibiting phase transitions between phases without long-range order or between a disordered phase and a phase with a hidden symmetry [28].

As we have emphasized above, real physical systems are not generally speaking pure but they can contain more than one phase. It is evident that this contradicts to the thesis iiii). An equilibrium heterophase state of a system will be called later on the mixed phase. It is very important that this mixed phase can exist in a quite wide region of temperatures, comparing with a narrow critical region, where homophase fluctuations should be taken into account.

What is more for describing the mixed phase the thesis iii) is also unsufficient. Let us consider for illustration an isotropic ferromagnet, the usual order parameter of which is the mean spin per particle $\vec{\xi} = \langle \frac{1}{N} \sum_f \vec{S}_f \rangle$, enumerating the lattice sites. In the paramagnetic phase the symmetry group of the system is SU(2) and $\vec{\xi} = 0$, while in the ferromagnetic phase the symmetry group is U(1) and $\vec{\xi} \neq 0$. Consequently, the order parameter $\vec{\xi}$ can only distinguish between the phases with different symmetries, but for the mixed phase when there is a mixture of ferromagnetic and paramagnetic phases, we need to add another macroscopic parameter [18] defining the relative concentrations (probabilities) of the phases $w_i = N_i / N$ $(w_1 + w_2 = 1)$. N_i being the number of particles in the i-th phase. In this way, in order to describe the two-phase ferro-paramagnetic mixture we need to introduce two order parameters: the mean spin $\vec{\xi}$ and the probability of one of phases, for instance $w \equiv w_1$. The probability of the second phase is $w_2 = 1 - w$. The additional order parameter w (or w_2) characterises the phase state of the system,

since in the pure ferromagnetic state $w = 1$ $(w_2 = 0)$, in the mixed state $w < 1$ $(w_2 > 0)$, and in the pure paramagnetic phase $w = 0$ $(w_2 = 1)$. It is clear that two nucleation points should exist, the corresponding temperatures can be called the nucleation temperatures Θ_n and Θ_n'. The first one Θ_n is the temperature at which paramagnetic nuclei appear in the pure ferromagnetic phase. The second one Θ_n' is the temperature at which ferromagnetic nuclei appear in the pure paramagnetic phase. Thus the mixed phase exists in the temperature region $\Theta_n < \Theta < \Theta_n'$, where the two order parameters defining this phase should be nontrivial: $\vec{\xi} \neq 0$, $w_2 \neq 0$. The equations $\vec{\xi} = 0$ and $w_2 = 0$ can be exploited as the equations for boundary temperatures Θ_n' and Θ_n, respectively. As far as there are phase changes at the nucleation points, these points should be regarded as the points of phase transitions. The right boundary of the stable mixed phase being defined by the equation $\vec{\xi} = 0$ corresponds to a usual phase transition. We have to concentrate here on the consideration of the nucleation point Θ_n, where $w_2 \simeq 0$. Let us study the peculiarities of thermodynamic characteristics near this point using the isotropic model of a heterophase ferromagnet [24-26]. The Hamiltonian of such a model is a direct sum

$$H = H_1 \oplus H_2 \tag{1}$$

of Hamiltonians

$$H_i = \frac{1}{2} N A w_i^2 \hat{1}_i - w_i^2 \sum_{fg} J(f-g) \vec{S}_{fi} \vec{S}_{gi} , \tag{2}$$

where $A = Q - J/2$, $J \equiv \sum_f J(f)$, Q is an effective direct interaction. The Hamiltonian H_1 is defined on the space $\mathfrak{F}_1$, which is constructed of wave functions invariant with respect to transformations from the group U(1) that is $\mathfrak{F}_1$ is the space of ferromagnetic states. The Hamiltonian H_2 is defined on the paramagnetic space $\mathfrak{F}_2$, which is the space of SU(2) symmetric states. Therefore, the Hamiltonian (1) acts in the space $\mathfrak{F}_1 \otimes \mathfrak{F}_2$. The free energy of a heterophase system is

$$F = F_1 + F_2 , \quad F_i = -\frac{\Theta}{N} \ln \mathrm{Tr}\, e^{-H_i/\Theta} .$$

The condition of phase equilibrium (identical to the equality of chemical potentials) can be written in the form

$$\frac{\partial F}{\partial w} = 0 , \quad w \equiv w_1 . \tag{3}$$

which gives $(2w-1)A - \frac{2}{N} w \sum_i \sum_{fg} J(f-g) \langle \vec{S}_{fi} \vec{S}_{gi} \rangle +$

$$+ \frac{2}{N} \sum_{fg} J(f-g) \langle \vec{S}_{f2} \vec{S}_{g2} \rangle = 0 .$$

Generally speaking, the onset of nucleation can be of either continuous or discontinuous type. In the first case $w_2(\Theta_n)=0$, and $w(\Theta_n)=1$, which yields

$$\frac{2}{N}\sum_{fg} J(f-g)\langle \vec{S}_{f1}\vec{S}_{g1}\rangle = A\,, \quad (\Theta=\Theta_n)\,.$$

This shows that the existence of the nucleation point depends on the value of the parameter A, or in other words, depends on the relation between the direct and exchange interactions in the system.

A calculation of the correlation functions $\langle \vec{S}_{fi}\vec{S}_{gi}\rangle$ can be produced by different methods. When the nucleation point Θ_n is not too near to the critical temperature, one can use the mean-field approximation, which corresponds to an exact solution if $J(\cdot)$ is the Kac potential /26/. In this approximation two order parameters, w and $\xi=|\vec{\xi}|$, must be defined from the two equations

$$2w(A-J\xi^2)=A\,, \quad 2\xi=\tanh(Jw^2\xi/\Theta)\,; \tag{4}$$

the spin is taken to be one half. A numerical analyses of these equations makes it certain, that the nucleation point Θ_n lies in the stable region only for $A_0 \le A \le 0{,}5J$ ($A_0 \cong 0{,}4907J$), being the solution of the equation

$$\frac{3A_0}{J}+\frac{(2A_0/J)^{1/2}\,\ln(1-2A_0/J)}{2\,\mathrm{Arth}\,(2A_0/J)^{1/2}}=0\,.$$

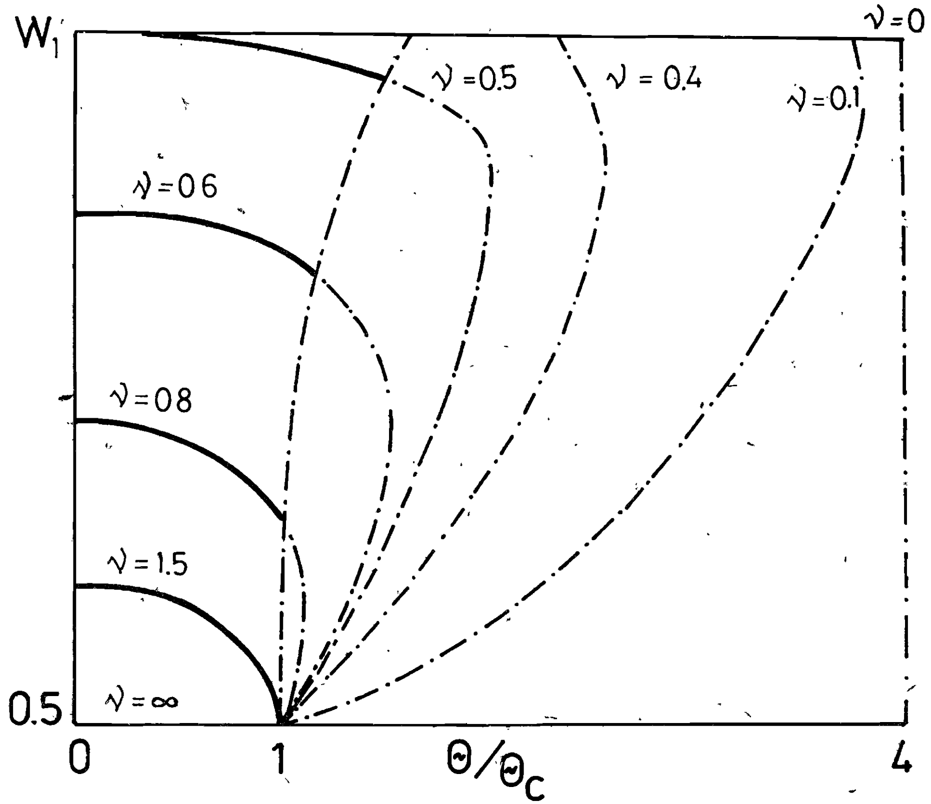
When $A=A_0$, the nucleation point coincides with the first-order transition point from the ferromagnetic to the paramagnetic phase. If $A<A_0$, the nucleation point shifts to the metastable region of the overheated mixed state (see the figure). When $A=0{,}5J$, then $\Theta_n=0$. Finally, if $A>0{,}5J$ there is no nucleation in the system, which is always in the mixed state, even at zero temperature.

It is interesting to examine analytical asymptotic behaviour of thermodynamic functions near the nucleation point, for which we have

$$\Theta_n=\sqrt{\frac{AJ}{2}}\Big/\mathrm{Arth}\sqrt{\frac{2A}{J}}\,, \quad \xi_n=\sqrt{\frac{A}{2J}}\,. \tag{5}$$

Introducing the relative temperatures

$$\epsilon_n=\frac{\Theta-\Theta_n}{\Theta_n}=\frac{T-T_n}{T_n}\,, \quad T_n=\frac{\Theta_n}{j}=\frac{\xi_n}{\mathrm{Arth}\,(2\xi_n)}\,, \quad T\equiv\frac{\Theta}{j}\,,$$



Ferromagnetic phase concentration versus temperature for different values of $\nu\equiv A/j$. *The dashed lines correspond to metastable and unstable solutions. The dotted line is the line of the first-order phase-transition points.*

and expanding the probability of the paramagnetic phase in a power series in ϵ_n, we get

$$w_2 \sim B_+\epsilon_n\,, \tag{6}$$

where $B_+=\dfrac{2(1-4\xi_n^2)}{\dfrac{2\Theta_n}{J}-5(1-4\xi_n^2)}$.

In complete analogy with critical indices describing the behaviour of thermodynamic functions near the critical point we can introduce nucleation indices describing these functions near the nucleation point. Eq.(6) allows us to define the nucleation index for the order parameter w_2 in the right vicinity of the nucleation point $\varkappa_+ = \lim_{\epsilon_n \to +0} (\ln w_2 / \ln \epsilon_n) = 1$. To the left of Θ_n the order parameter $w_2 = 0$; the left nucleation index κ_-, defined analogously to κ_+, is $\kappa_- = 0$. Thus, the probability w_2 is characterized by different nucleation indices on the left and on the right of the nucleation point. At this point $w_2(\Theta)$ has a fracture (see the figure).

The mean spin to the right of Θ_n has the asymptote

$$\xi \sim \xi_n (1 - B_+ \epsilon_n). \tag{7}$$

According to (6) and (7) the magnetization becomes

$$M \equiv w \xi \sim \xi_n (1 - 2 B_+ \epsilon_n). \tag{8}$$

The asymptotic expressions (7) and (8) describe the so-called weak singularity with the nucleation index

$$\beta_+ = \lim_{\epsilon_n \to +0} (\ln M / \ln \epsilon_n) = 0.$$

To the left of Θ_n

$$M \equiv \xi \sim \xi_n (1 - B_- \epsilon_n), \tag{9}$$

where $B_- = \dfrac{1 - 4\xi_n^2}{2T_n - (1 - 4\xi_n^2)}$.

So, the singularity is also weak: $\beta_- = 0$. The functions $\xi(\Theta)$ and $M(\Theta)$ are continuous at Θ_n, although they have fractures there, because $\lim_{\epsilon_n \to +0} \dfrac{\partial M}{\partial \epsilon_n} \neq \lim_{\epsilon_n \to -0} \dfrac{\partial M}{\partial \epsilon_n}$.

The specific heat $C = -\Theta \partial^2 F / \partial \Theta^2$ has a loap at Θ_n.

In the vicinity of the nucleation point

$$C \sim C_\pm (1 - D_\pm \epsilon_n); \tag{10}$$

here the sign plus corresponds to $\Theta > \Theta_n$, the sign minus to $\Theta < \Theta_n$ and the following notations are used:

$$C_+ = \xi_n B_+, \quad C_- = 2\xi_n B_-, \quad D_+ = \frac{B_+}{\xi_n} \left[\frac{4T_n - 1 - 4\xi_n^2}{1 - 4\xi_n^2} + \frac{2(6T_n + 3 - 32\xi_n^2)}{2T - 5(1 - 4\xi_n^2)} \right],$$

$$D_- = B_- \left[\frac{8\xi_n^2}{2T_n - (1 - 4\xi_n^2)} - \frac{2T_n + 1 - 12\xi_n^2}{1 - 4\xi_n^2} \right].$$

The magnitude of the specific-heat leap is $\Delta C = C_+ - C_- = 4\xi_n B_+ B_-$. The relative value of the leap is $2\Delta C/(C_+ + C_-) \lesssim 0.1$. The existence of this leap is very important, since it gives the possibility for an experimental investigation of the nucleation phenomenon. In some materials there exist unexplained leaps in the specific heat. This was reported for instance to take place in $CdCr_2S_4$ in the vicinity of the first-order transition point /29/. We think that such leaps could be connected with the process of nucleation.

In the example considered above of the heterophases ferromagnet with long-range forces the transition from the pure ferromagnetic phase to the mixed one was continuous. Because the difference between the phases disappears at the nucleation point, the latter plays a role of a critical point. However, it is also possible to suppose that for some other models the order parameter w_2 can have a break at the nucleation point, corresponding to a discontinuous phase transition. Another exotic possibility is when the free energy is not analytic on the manifold of nonzero measure /30/, when w_2 could be also nonanalytic on this manifold, and in the place of a nucleation point a nucleation region should appear.

In conclusion let us emphasize the main points:

1. The existence of the mixed phase is due to a competition between interactions of an ordering and disordering nature. In the case of the heterophase ferromagnet (1)-(3) these are the exchange and direct interactions respectively. For the model of a heterophase superconductor /27/ these are the Fröhlich and Coulomb interactions.

2. The mixed phase, consisting of two macroscopic states with different symmetries, needs and additional order parameter w_1 (or $w_2 = 1 - w_1$), which characterizes the relative concentrations of pure phases.

3. The nucleation point, being a special type of phase transitions, permits the definition of nucleation indices. The specific heat at this point has a break, which can be observed in experiments.

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Равновесная нуклеация - новый вид фазового перехода

В рамках равновесной теории изучен переход между чистой низкотемпературной фазой и смешанным состоянием, состоящим из упомянутой фазы и макроскопической доли высокотемпературной фазы. Такое изменение состояния может рассматриваться как фазовый переход специального типа. Особенности термодинамических характеристик вблизи точки нуклеации и физические причины, обусловливающие этот переход, обсуждаются на примере простой магнитной модели.

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Equilibrium Nucleation - a New Type of Phase Transition

In the framework of an equilibrium theory the transition between a low-temperature pure phase and a mixture of the pure phase mentioned and a macroscopic fraction of a high-temperature phase is investigated. Peculiarities of thermodynamic characteristics near the nucleation point are discussed.

The investigation has been performed at the Laboratory of Theoretical Physics, JINR.

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