Quantum Kinetics of Phase Transitions at Temperatures Close to Absolute Zero

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At absolute zero, formation of the nuclei of a new phase cannot be due to thermal fluctuations and must be ascribed to a quantum mechanism. It is found that the relevant probabilities can be calculated in the semiclassical approximation. This means that the process of formation of a nucleus reduces to a tunnelling motion of the system along an optimal trajectory in configuration space, through the energy barrier separating the initial metastable state from the state with the real nucleus. In the two opposite limiting cases—close to the phase equilibrium pressure and close to the lability boundary of the initial phase—the critical quantum fluctuations which lead to the formation of a real nucleus are of macroscopic size. The sequence of virtual intermediate states is described macroscopically and is qualitatively different in the two limiting cases. The formulae obtained express the required probabilities in terms of various thermodynamic characteristics of the system.

1. INTRODUCTION. FORMULATION OF THE PROBLEM

A metastable state that is stable with respect to a small change of the internal parameters is necessarily separated from the stable state by some barrier in configuration space. At high temperatures, this barrier can be overcome as a result of the appearance and growth of nuclei of the new phase due to thermal fluctuations. Up to some critical size, growth of the nuclei is an energetically unfavorable process and the free energy of the system at fixed temperature is greater than the free energy of the uniform metastable phase, at least until the first precritical nucleus appears.

At low temperatures, the picture is radically different, as can be seen especially clearly by considering the limiting case T = 0. Now, the appearance and the initial stage of growth of real nuclei are, from purely energetic considerations, impossible. This stage of the phase transformation can be realized only as a result of quantum penetration through the barrier. In practice, we are concerned with the decay of an excited quasistationary state of the system, (the uniform metastable state at T = 0 is this state). The decay will be accompanied by a transition to a spatially nonuniform state, which then undergoes a barrierless evolution to the stable phase. At the moment it appears, the inhomogeneity will itself be localized in a bounded region of space, although such regions will appear at different points of the metastable phase. By assuming them to be independent, we can return to the idea of nuclei, but now the kinetics will be associated with the tunnelling "leakage" of the virtual semiclassical nuclei.

For the problem of the quantum decay of the metastable state through the barrier, the value of the kinetic energy associated with the dynamics of the nucleus in configuration space plays an essential role. In the framework of traditional high-temperature kinetics, the nature of the dynamics is determined entirely by the coefficient of diffusion of the nuclei in space, by their dimensions, and hence by the pre-exponential factor in the magnitude of the rate of the phase transformation. In the quantum case, however, the actual surmounting of the barrier occurs only to the extent that kinetic energy is present, and therefore the value of the latter

has a decisive influence on the magnitude of the exponential itself. It is the kinetic energy that determines the scale of the quantum fluctuations, and thereby also the parameter that must replace the temperature.

In analyzing the dynamics of the nucleation, we encounter two fundamentally different cases. The first is realized in the case when the dynamics have a reversible character, i.e., dissipation is absent. In this case, the coherent nature of the motion is conserved, and this enables us to carry out the analysis in terms of the wavefunction or the transition probability amplitude, using the Schrodinger equation. The second case corresponds to the presence of strong dissipation, and the solution of the problem requires the use of the corresponding quantum kinetic equation. In the present paper, only the first case is considered.

Let the region of phase space corresponding to the various macroscopic phases lie sufficiently far from each other. We assume that the intermediate states corresponding to virtual formation of a nucleus of the new phase are also macroscopic (below, we shall elucidate the conditions for which this is realized). In this case, the whole situation can be described in the semiclassical approximation and in macroscopic terms; for the description, it is sufficient in a number of cases to use a small number of macro-parameters (collective dynamical variables). We shall see that in this case the optimal "trajectory" of the transition in configuration space can also be described in the language of these parameters.

The most detailed macroscopic description of the system at T = 0 can be given by means of the density ρ, the concentrations c of the components and the short-range order parameters (correlation functions) η, the role of which in the case of crystals is played by the parameters of the unit cell and its basis. To describe nonuniform and nonstationary states, for these quantities not only the fields but also the corresponding fluxes must be specified. In most cases, absence of dissipation in the development of the nucleus presupposes that the linear dimensions of the intermediate layer between the phases are large compared with the interatomic spacing, so that this layer can also be described macroscopically.

We shall assume for simplicity that the uniform non-

equilibrium state of the system is completely determined by the value of one of the parameters, with the remaining parameters uniquely related to it. In slow nonstationary processes, the adjustment of the related parameters proceeds adiabatically. For definiteness, we choose the particle density ρ as the single parameter.[1] In practice, this assumption means that the initial metastable phase has zero shear modulus, i.e., is a liquid. Allowance for the shear stresses in the case of a crystalline medium does not change the qualitative picture, but makes the calculations more cumbersome (see below). The free energy (at $T = 0$—simply the energy) of a state specified by a density field ρ can be written in the form

$$F = F\{\rho\} = \int \mathscr{F} dV,$$

where $\mathscr{F}$ is the free energy per unit volume (the free energy density), and the integral is taken over the whole volume of the system. For sufficiently large gradients of ρ, we must take into account the dependence of the free energy $\mathscr{F}$ not only on the local value of the density, but also on the spatial derivatives of ρ:

$$\mathscr{F} = \mathscr{F}(\rho, \nabla\rho,...) = \mathscr{F}(\rho) + \lambda(\nabla\rho)^2 + ...$$

Assuming the total volume of the system to be fixed and taking into account the condition that the number of particles is conserved (ρ_1 is the density of the uniform metastable phase),

$$\int \delta\rho \, dV = \int (\rho - \rho_1) dV = 0, \qquad (1.1)$$

we write the change in the free energy $F\{\rho\} - F\{\rho_1\}$ associated with a density fluctuation $\delta\rho = \rho - \rho_1$ in the form[2]

$$U\{\rho\} = F\{\rho\} - F\{\rho_1\} = \int \{\varphi(\rho,\rho_1) + \lambda(\nabla\rho)^2 + ...\}dV,$$

$$\varphi(\rho,\rho_1) = \mathscr{F}(\rho) - \mathscr{F}(\rho_1) - (\rho - \rho_1)\mathscr{F}'(\rho_1). \qquad (1.2)$$

For ρ close to the equilibrium density in the initial phase, $\varphi(\rho, \rho_1)$ is the elastic compression energy:

$$\varphi(\rho, \rho_1) = K_1(\rho - \rho_1)^2/2\rho_1^2, \qquad (1.3)$$

where K_1 is the isothermal bulk modulus:

$$K_1(\rho_1) = \mathscr{F}''(\rho_1) = \rho_1 \partial p/\partial \rho_1.$$

If $\rho_2 = \rho_2(p)$ is the equilibrium density of the new phase under external pressure p ($\rho_1 = \rho_1(p)$), then taking into account the relation $\partial\mathscr{F}/\partial\rho = \mu$ (μ is the chemical potential), we have

$$\varphi(\rho_2) = \rho_2(\mu_2 - \mu_1), \qquad \mu_i = \mu_i(p).$$

Correspondingly, close to the equilibrium density ρ_2 in the second phase, we shall have

$$\varphi(\rho) = \rho(\mu_2 - \mu_1) + \tfrac{1}{2}K_2(\rho - \rho_2)^2/\rho_2^2. \qquad (1.4)$$

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[1] In reality, the density is an isolated parameter. This is connected with the fact that change in density in a macroscopic region requires displacements of macroscopic masses, while changes in the short-range order require displacements of atoms over distances on the atomic scale. In this case, we can assume that specifying the density within each of the uniform phases implies the equilibrium values of the parameters η.

[2] Writing the energy $U\{\rho\}$ in the form (1.2) makes it unnecessary to take condition (1.1) for any local density fluctuation into account, since a change of $\rho(\infty)$, however small, makes it possible to satisfy this condition without changing $U\{\rho\}$.
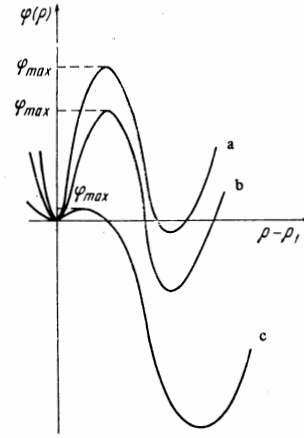
Between ρ_1 and ρ_2 lies the region of lability of the spatially uniform state, in which the thermodynamic inequality $\mathscr{F}''(\rho) = \varphi''(\rho) > 0$ is violated. The boundaries of the lability region are determined by the condition

$$\mathscr{F}''(\rho_c) = \varphi''(\rho_c) = 0 \quad (K = 0). \qquad (1.5)$$

The characteristic form of the function $\varphi(\rho, \rho_1)$ for various cases is depicted in the Figure.

If $\rho_2|\mu_1 - \mu_2| \ll \varphi_{max}$ (curve a), which is always realized, in particular, when the pressure p is sufficiently close to the phase-equilibrium pressure p_0 ($\mu_2(p_0) = \mu_1(p_0)$), then the "critical" nucleus of the new phase must contain a large number of particles in order to compensate for the sharp increase in energy in the intermediate layer. The thickness of the intermediate layer in this case will be small compared with the dimensions of the nucleus. For sufficiently slow migration of the boundary, the equilibrium pattern of the distribution of the quantities in the intermediate layer is displaced together with the boundary, and the latter can be treated as a geometrical surface, the additional energy of this layer being taken into account using the surface tension[3]. The formation of a spherical nucleus of the stable phase, of radius $R(t)$ (which is now the principal collective dynamical variable), corresponds to the optimal sequence of intermediate states. In the limiting case under consideration, the phase boundary is found to move slowly, and so we can neglect the dynamical compressibility of the two phases. As a result, the po-

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[3] In the intermediate layer, where the density and order parameters vary rapidly, the presence of gradient terms in the free energy ensures the existence of a certain equilibrium pattern for the distribution of these quantities, despite the fact that in the intermediate layer there is an interval of ρ (or of η) in which the spatially uniform state is unstable.

In the framework of the customary approximation for equilibrium of the phases ($\varphi(\rho_2) = \rho_2(\mu_2 - \mu_1) = 0$), the equilibrium distribution of the densities in the intermediate layer ($r = R + x$), obtained from the condition that $U\{\rho\}$ be a minimum, is given by the equation

$$\lambda d^2\rho / dx^2 = 2\varphi'(\rho), \qquad \rho|_{x=-\infty} = \rho_2, \qquad \rho|_{x=+\infty} = \rho_1,$$

whence

$$x = \int \sqrt{\lambda/\varphi} \, d\rho.$$

In this case, the surface tension σ is

$$\sigma = \int_{-\infty}^{\infty} \left[\varphi + \lambda \left(\frac{d\rho}{dx} \right)^2 \right] dx = 2\int_{\rho_1}^{\rho_2} \sqrt{\lambda\varphi} \, d\rho.$$

tential energy for a fluctuation of the radius R will have, according to (1.2)–(1.4), the standard form

$$U(R) = AR^2 - BR^3,$$

$$A = 4\pi\sigma, \quad B = \frac{1}{3}(\mu_1 - \mu_2)\rho_2, \quad (1.6)$$

where σ is the surface tension.

The results cited above contained implicitly the assumption that the metastable phase has zero shear modulus κ_1. If this is not the case, it is necessary to take into account the static elastic energy arising in the initial phase and in the nucleus. If we assume that the deformation in the two phases is not great, and make use of the results of the theory of elasticity for spherical occlusion, then we can find an expression for the total elastic energy in the isotropic approximation, which leads to an additional term in (1.6), proportional to R^3 with coefficient

$$B_1 \cong \frac{1}{2}K_2\xi u_{ll}^2 + \kappa_2\xi'\tilde{u}_{ij}^2;$$
$$\xi = \frac{4\kappa_1}{3K_2 + 4\kappa_1}, \quad \xi' = \frac{\kappa_1(9K_1 + 8\kappa_1)}{\kappa_1(9K_1 + 8\kappa_1) + 6\kappa_2(K_1 + 2\kappa_1)}. \quad (1.7)$$

Here, u_{ik} is the uniform deformation tensor that carries phase 1 over into phase 2 at a fixed external pressure p, while $\tilde{u}_{ik}$ is its irreducible part. Allowing for the additional elastic energy reduces to replacing the quantity B in (1.6) by $B' = B - B_1$.[4]

In the case $\rho_2|\mu_1 - \mu_2| \gg \varphi_{max}$ (Curve c in the Figure), when the metastable phase is close to the stability boundary, the presence of the gradient term in (1.2) makes the formation of a stable-phase nucleus, which would have a small radius, unfavorable. On the other hand, an extended virtual fluctuation, but in this case with a small density change (in proportion to the smallness of the ratio $|\rho_c - \rho_1|/|\rho_2 - \rho_1| \ll 1$) sufficient to cancel the small hump in Curve c, turns out to be energetically favorable. The characteristic dimensions of the critical fluctuation are again great compared with the interatomic spacing ($R \to \infty$ as $\rho_1 \to \rho_c$), and the problem has a macroscopic character in this case too, although, of course, no boundary can now exist between the phases, while the nonuniform state arising after the penetration through the barrier does not contain the stable phase even at the core of the inhomogeneity.

To determine the potential energy for the nuclei in this case, we make use of (1.2), assuming that spherically symmetric density fluctuations correspond to the optimal sequence of intermediate states. We take into account that we shall be interested in the density only in an interval, the scale of which is of order $|\rho_1 - \rho_c|$. Then we can expand $\varphi(\rho, \rho_1)$ in a series about ρ_1, keeping the first terms of the expansion:

$$\varphi = \frac{1}{2}\mathscr{F}''(\rho_1)(\rho - \rho_1)^2 + \frac{1}{3!}\mathscr{F}'''(\rho_1)(\rho - \rho_1)^3,$$

or, taking (1.5) into account, we have

$$\varphi(\rho, \rho_1) = -\frac{1}{3!}F'''(\rho_1)[3(\rho_k - \rho_1)(\rho - \rho_1)^2 - (\rho - \rho_1)^3]. \quad (1.8)$$

In this case, the structure of a fluctuation (spatial

and temporal) is determined from the extremum condition for the action, formulated using the functional (1.2) and the corresponding functional for the kinetic energy (see Sec. 4).

In the intermediate case (Curve b in the Figure), when $\rho_2|\mu_1 - \mu_2|$ and φ_{max} are comparable, the "critical" nucleus is of small dimensions and a macroscopic description is no longer possible. Below, only the limiting cases a and c are considered.

2. QUANTUM NUCLEATION NEAR THE PHASE EQUILIBRIUM POINT AT T = 0

Close to the phase-equilibrium point, as was indicated above, the dynamics of the development of an optimal fluctuation correspond to the growth of a spherical nucleus of the new phase. To determine the kinetic energy

$$E_{kin} = \frac{m}{2}\int \rho(r)v^2(r)\,dV$$

it is necessary to know the instantaneous field of the radial speeds v(r) and densities $\rho(r)$ in both phases, expressed in terms of the radius R of the nucleus and $\dot{R}$. Here, it is necessary to take into account that the boundary between the phases is a discontinuity surface, at which the condition

$$\rho_1(R)v_1(R) - \rho_2(R)v_2(R) = (\rho_1(R) - \rho_2(R))\dot{R}. \quad (2.1)$$

is fulfilled.

Let the metastable phase be an ideal incompressible liquid (quantum liquid). In this case, the densities in each phase are constant, and if we take (2.1) and the continuity equation div v = 0 into account, the field of the speeds has the form

$$v = \begin{cases} \frac{(\rho_1 - \rho_2)}{\rho_1}\dot{R}\frac{R^2}{r^2}, & r > R(t) \\ 0, & r < R(t) \end{cases}. \quad (2.2)$$

Hence, for the kinetic energy, we find[5]

$$E_{kin} = 2\pi m\rho_1\left(\frac{\rho_1 - \rho_2}{\rho_1}\right)^2 R^3\dot{R}^2. \quad (2.3)$$

The potential energy in a state with specified R is determined by the relation (1.6).

Neglect of the dynamical compressibility presupposes that $\dot{R}$ is small compared with the speed of sound s. By comparing the kinetic energy (2.3) with the maximum of the potential energy (1.6), we can estimate the maximum rate of the tunneling motion of the boundary

$$\frac{\dot{R}^2}{s^2} \approx \frac{1}{3}\frac{\mu_1 - \mu_2}{ms^2}\frac{\rho_1\rho_2}{(\rho_1 - \rho_2)^2} \ll 1.$$

The requirement that this ratio be small leads in turn to conditions of weak deviation from phase equilibrium.

We introduce the characteristic dimension R_0 of the nucleus from the condition $U(R_0) = 0$:

$$R_0 = A/B. \quad (2.4)$$

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[4]The presence of the elastic energy shifts the pressure at which the spherical nuclei can begin to appear. This pressure is determined from the condition $B' = 0$. We remark that for a certain relation between the parameters, a spherical shape becomes energetically unfavorable.

[5]If the phase transition is associated with change of the parameters η, and the change in density turns out to be weak, the rearrangement kinetic energy, which is associated with the motion of the intermediate layer and which we have ignored until now, acquires a decisive role. In this case, $E_{kin} \propto R^2\dot{R}^2$. The whole of the following treatment can easily be generalized to this case.

We write down the classical Lagrangian of the system under consideration, using the dimensionless coordinate $x = R/R_0$:

$$\mathcal{L}(x, \dot{x}) = \frac{1}{2}M_0 x^3 \dot{x}^2 - ax^2(1-x),\qquad(2.5)$$

$$M_0 = 4\pi m R_0^5 (\rho_1 - \rho_2)^2 / \rho_1, \quad a = 4\pi\sigma R_0^2. \qquad(2.6)$$

The Hamiltonian corresponding to (2.5) takes the form

$$H = P_x^2 / 2M_0 x^3 + U(x), \quad U(x) = ax^2(1-x). \qquad(2.7)$$

Thus, in this approximation, a dynamical description of the system in the transition process can be given by only one principal coordinate (or by the corresponding generalized momentum P_x).

The above should be interpreted more generally, in the sense that at large R_0, by virtue of the slowness of the change in x, the spectrum of the various elementary excitations (including surface waves at the phase boundary and oscillations in the volume) adjusts itself adiabatically to the instantaneous value of x, and actual excitations do not arise in the transition process. As regards the energy of the zero-point vibrations, which depends on the value of x, this is included, naturally, in the definition of the chemical potentials and of the surface energy at $T = 0$. The absence of additional dissipation of energy at the moving boundary itself in the limiting case under consideration is in accordance with the absence of latent heat or change in entropy for infinitely slow motion of the boundary at $T = 0$.

We turn now to the quantum description of the system. The initial state of the system in terms of the dynamical variable x is a metastable "ground" state, i.e., the ground state in the field $U(x)$ when the possibility of a tunnelling transition is ignored. Since x takes only positive values, we must assume that there is a potential wall at $x = 0$.

To determine the energy levels of the metastable system in the semiclassical approximation, we find the vibration frequencies from the solution of the classical problem:

$$\frac{1}{2}M_0 x^3 \dot{x}^2 + ax^2(1-x) = E = \text{const.} \qquad(2.8)$$

Hence,

$$\omega(E) = \pi \sqrt{\frac{2}{M_0}} \bigg/ \int_0^{x(E)} \frac{x^{3/2}\,dx}{[E - ax^2(1-x)]^{1/2}}. \qquad(2.9)$$

For $E \ll \alpha$, the quantity $x(E)$ is equal to $\sqrt{E/\alpha}$ and, performing the integration explicitly, we find

$$\omega(E) = \frac{12\pi^{1/2}}{\Gamma(1/4)}\left(\frac{\alpha}{M_0}\right)^{1/2}\left(\frac{\alpha}{E}\right)^{3/4}. \qquad(2.10)$$

For an approximate estimate of the frequency of the lower level, we put $E = \hbar\omega$. As a result, we obtain

$$\omega_0 = \gamma\frac{\alpha^{2/7}}{M_0^{2/7}\hbar^{3/7}} = \gamma(4\pi)^{3/7}\frac{1}{\hbar}\left(\frac{\hbar^2}{ma_1^2}\right)\left(\frac{\sigma a_1^2}{\hbar^2/ma_1^2}\right)^{3/7}\left|\frac{\rho_1 - \rho_2}{\rho_1}\right|^{-4/7},$$

$$\gamma = [12\pi^{1/2}/\Gamma(1/4)]^{4/7}, \quad a_1^3 = 1/\rho_1. \qquad(2.11)$$

ω_0 gives the frequency of the distinctive "zero-point" vibrations associated with heterophase quantum fluctuations in the uniform metastable phase.

For energies $\omega_0 \ll E \ll \alpha$, using the semiclassical relation (n labels the level)

$$dE_n / dn = \hbar\omega(E_n),$$

we find directly

$$E_n = \hbar\omega_1 n^{4/7}, \quad \omega_1 = \omega_0 (7/4)^{4/7}. \qquad(2.12)$$

The probability of a tunneling transition from level E with formation of one precritical nucleus in unit volume per unit time is given in the semiclassical case by the expression

$$W(E) \cong N_0\omega(E)\exp\left\{-\frac{2}{\hbar}\int_{x_1}^{x_2}|P_x|\,dx\right\}. \qquad(2.13)$$

Here N_0 is the number of virtual centers of formation of the new phase per unit volume. In order of magnitude, N_0 is given by the expression

$$\rho_1 < N_0 \lesssim 1/V_0, \quad V_0 = \frac{4}{3}\pi R_0^3. \qquad(2.14)$$

The momentum P_x, as usual, is determined from the classical Hamiltonian (2.7) with the condition $H = E$. Hence,

$$\int_{x_1(\epsilon)}^{x_2(\epsilon)} |P_x|\,dx = \sqrt{2M_0 a}\,\varphi(\epsilon),$$

$$\varphi(\epsilon) = \int_{x_1(\epsilon)}^{x_2(\epsilon)} x^{3/2}[x^2(1-x) - \epsilon]^{1/2}\,dx, \quad \epsilon = \frac{E}{a}, \qquad(2.15)$$

where $x_1(\epsilon)$ and $x_2(\epsilon)$ are the roots of the equation $x^2(1-x) = \epsilon$.

For the lower level, $\epsilon \approx 0$ and

$$\varphi(0) = 5\pi/128. \qquad(2.16)$$

As a result, for the probability W_0, we have

$$W_0 \cong N_0\omega_0 \exp\left\{-\frac{5\sqrt{2}\,\pi}{64}\left(\frac{M_0 a}{\hbar^2}\right)^{1/2}\right\}$$

$$= N_0\omega_0 \exp\left\{-\frac{5\sqrt{2}\pi^2}{16}\left(\frac{\sigma a_1^2}{\hbar^2/ma_1^2}\right)^{1/2}\frac{|\rho_1 - \rho_2|}{\rho_1}\left(\frac{R_0}{a_1}\right)^{7/2}\right\}. \qquad(2.17)$$

If we represent the exponent in the form (cf. (1.6) and (2.4))

$$U_{max}(R)/T_*, \quad U_{max}(R) = \frac{16}{27}\pi\sigma R_0^2,$$

then for the equivalent quantum "temperature," defining the scale of the quantum fluctuations, we find

$$T_* = \frac{256}{135\sqrt{2}\pi}\frac{\hbar^2}{ma_1^2}\left(\frac{\sigma a_1^2}{\hbar^2/ma_1^2}\right)^{1/2}\frac{\rho_1}{|\rho_1 - \rho_2|}\left(\frac{a_1}{R_0}\right)^{3/2}. \qquad(2.18)$$

It can be seen from this expression that in the case of a large critical nucleus, T_* is small compared with the analogous single-particle characteristic of the quantum vibrations $\hbar^2/ma_1^2$; as the phase-equilibrium point is approached, $T_* \propto R_0^{-3/2}$. Physically, this is connected with the increase of the effective mass of matter set in motion. It is this which also determines the nature of the dependence on the difference between the phase densities.

If the metastable phase is a liquid, then

$$R_0 = 3\sigma/\rho_2(\mu_1 - \mu_2),$$

or, for small deviation from the equilibrium pressure p_0,

$$R_0 = 3\sigma\rho_1/|\rho_2 - \rho_1|p', \quad p' = p - p_0. \qquad(2.19)$$

In the case of cavitation at negative pressure, B in (1.6) is equal to $4\pi|p|/3$ and

$$R_0 = 3\sigma/|p|. \qquad(2.20)$$

(Here, we must put $\rho_2 = 0$ in (2.11), (2.17) and (2.18).)

In the case when the metastable phase is a rigid elastic medium, B in expression (2.4) must be replaced by $B' = B - B_1$, where B_1 corresponds to (1.7).

The condition for the applicability of the formulae obtained is that the nucleus be macroscopic, i.e.,

$$N_1 = V_0 \rho_1 \gg 1,$$

although the result remains valid in order of magnitude for $N_1 \sim 1$ also. Taking into account the dependence of the exponent on N_1 ($\infty N_1^{7/6}$), we are led to think that this condition can be combined with the requirement of a reasonable observation time only for light substances. In this connection, it is interesting to estimate the magnitude of N_1, e.g., in the solidification of He^4 (at $T = 0$), when we choose a pressure p' that corresponds to $W_0 = 1$, i.e., which corresponds to the appearance of one nucleus per sec in 1 cm^3. The corresponding formula has the form

$$N_1^{7/6} = \frac{16}{5\sqrt{2}\,\pi^2} \left(\frac{4\pi}{3}\right)^{7/6} \left(\frac{\hbar^2/ma_1^2}{\sigma a_1^2}\right)^{1/3} \frac{\rho_1}{|\rho_1 - \rho_2|} \ln N_0 \omega_0.$$

Substituting the relevant parameters for He^4, we find $N_1 \sim 500$, i.e., the picture turns out to be reasonably self-consistent.

3. NUCLEATION AT FINITE TEMPERATURES

At non-zero temperatures, a number of competing possibilities of transition arise, associated with the coupling of thermal and quantum fluctuations: a real nucleus of precritical size can arise as a result of a thermal fluctuation and then, by means of a tunnelling transition, can pass through the remaining barrier.

At low temperatures, the system containing the nucleus can be described by means of the complete quantum Hamiltonian $\hat{H}_t$, in which along with the characteristic quantum Hamiltonian $\hat{H}$ of the "coherent" nucleus (obtained from (2.7) by means of the appropriate symmetrization), there are terms $\hat{H}_\xi$ describing the gas of elementary excitations, the spectrum of which is determined by the instantaneous value of the size of the nucleus

$$\hat{H}_t = \hat{H} + \sum_\xi \hat{H}_\xi(x),$$

$$\hat{H} = \frac{1}{2M_0} \frac{1}{x^{3/4}} \hat{P}_x \frac{1}{x^{3/2}} \hat{P}_x \frac{1}{x^{3/4}} + U(x). \qquad (3.1)$$

In this way, we arrive at the previous problem of a tunnelling transition of a heavy semiclassical particle with variable mass. However, now the motion of this particle occurs in a gas of light quasi-particles, which are polarizable by the slowly moving heavy particle.[6] Quasi-particle collisions in the field of the heavy particle lead, naturally, to dissipation of energy.

In the problem, there are two characteristic times: 1) the time of strictly sub-barrier "flight" $t_0 \sim \sqrt{M_0/\alpha}$, and 2) the total transition time $\tau_0 \sim 1/W$. Only those dissipative processes which have time to occur in time t_0 affect the transition probability. If the quasi-particles succeed in thermalizing in this time, then the energy

dissipation that cannot be eliminated will be equal to the heat of transition in the volume of the nucleus.

The question of how the dissipation affects the motion of the boundary of the nucleus requires an additional investigation. Formally, this is manifested, in particular, in the fact that the continuity of the flux of the heat function appears in the hydrodynamic conditions at the phase boundary, while the reversible work of the transition, associated with the kinetic energy of the growing nucleus, is determined by the change $\delta\Phi(x)$ in the thermodynamic potential. However, at low temperatures, the energy of the thermal excitations is small and the change in the thermodynamic potential, like the change in the heat function, is necessarily close to the energy $U(x)$ obtained at $T = 0$, while the entropy and heat of transition are close to zero. Under these conditions, the role of the thermal excitations reduces in practice to their effect on the probability of formation of a real precritical or critical nucleus as a result of thermal fluctuations in the course of the total transition time τ_0. We note that if in this range of temperatures the problem becomes classical, i.e., "over-the-barrier" (see below), then the difficulty disappears completely for the whole range of temperatures.

Using the semiclassical nature of the problem and the condition $T \ll \alpha$, for the transition probability we have

$$W(T) = \sum_n W(E_n) e^{-E_n/T} \Big/ \sum_n e^{-E_n/T}$$

$$\cong \int_{E_0}^{U_{max}} W(E) e^{-E/T} \left(\frac{dE}{dn}\right)^{-1} dE \Big/ \int_{E_0}^{U_{max}} e^{-E/T} \left(\frac{dE}{dn}\right)^{-1} dE$$

$$\cong \frac{\omega_0}{T} \int_0^{U_{max}} \frac{W(E)}{\omega(E)} e^{-E/T} dE. \qquad (3.2)$$

Using the results of the previous section, we have for the total transition probability per unit volume per unit time

$$W(T) = \frac{\alpha \omega_0 N_0}{T} \int_0^{\varepsilon_m} \exp\{-\gamma[\varphi(\varepsilon) + z\varepsilon]\} d\varepsilon;$$

$$\varepsilon = \frac{E}{\alpha}, \quad \varepsilon_m = \frac{U_{max}}{\alpha} = \frac{4}{27}, \quad \gamma = 2\sqrt{\frac{2M_0\alpha}{\hbar^2}}, \quad z = \frac{\alpha}{\gamma T}. \qquad (3.3)$$

Since $\gamma \gg 1$, we can use the method of steepest descents for the integral in (3.3). In practice, this corresponds to choosing the optimal transition path, i.e., the optimal combination of thermal activation and tunnelling "leakage". Let $\tilde{\epsilon} = \tilde{\epsilon}(z)$ be the point at which the function $\chi(\epsilon, z) = \psi(\epsilon) + \epsilon z$ takes its smallest value in the section $0 < \epsilon < \epsilon_m$; then

$$\chi(z) \equiv \chi(\tilde{\epsilon}, z) = \varphi(\tilde{\epsilon}) + z\tilde{\epsilon} = \min\{\varphi(\epsilon) + z\epsilon\}_{0 < \epsilon < \epsilon_m}. \qquad (3.4)$$

Then, for the transition probability (3.3), we have

$$W(T) = \omega_0 N_0 S e^{-\gamma\chi(z)};$$

$$S = \frac{\alpha}{T} \int_0^{\varepsilon_m} \exp\{-\gamma[\chi(\varepsilon, z) - \chi(z)]\} d\varepsilon. \qquad (3.5)$$

To investigate the function χ, we must find the roots of the equation

$$\varphi'(\varepsilon) = -z, \quad \varphi'(\varepsilon) = -\frac{1}{2} \int_{x_1(\varepsilon)}^{x_2(\varepsilon)} \frac{x^{3/2} dx}{[x^2(1-x) - \varepsilon]^{1/2}} \qquad (3.6)$$

and compare the value of $\chi(\epsilon, z)$ corresponding to these

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[6] The Hamiltonian $\Sigma_\xi \hat{H}_\xi(x)$ of the excitations contains not only thermal phonons but also other excitations of the whole nucleus, the frequencies of which are determined by the instantaneous values of x.

roots with the value of this function at the boundaries of the interval

$$\chi(0, z) = \varphi(0), \quad \chi(\epsilon_m, z) = z\epsilon_m.$$

Near the edges of the interval $(0, \epsilon_m)$, we have

$$-\varphi'(\varepsilon) = \begin{cases} \pi/4 & \varepsilon \to 0 \\ 2^{1/2}\pi/3^{3/2}, & \varepsilon \to \varepsilon_m \end{cases};$$
$$\varphi(0) = 5\pi/128, \quad \varphi(\varepsilon_m) = 0. \tag{3.7}$$

Using (3.7), it is easy to find the temperature T_1 at which the solution of Eq. (3.6) corresponds to the upper boundary $\tilde{\epsilon} = \epsilon_m$:

$$T_1 = \alpha/\gamma z_1, \quad z_1 = 2^{1/2}\pi/3^{3/2}. \tag{3.8}$$

Correspondingly, the solution of Eq. (3.6) emerges on to the lower boundary $\epsilon = 0$ at temperature

$$T_0 = \alpha/\gamma z_0, \quad z_0 = \pi/4. \tag{3.9}$$

The temperature behavior of the transition probability depends to an important extent on the relation between $\chi(\epsilon_m, z_1)$ and $\varphi(0)$. If $T_1 > T_0$, and $\chi(\epsilon_m, z_1) < \varphi(0)$, then, beginning at temperature T_0 (in the general case, at temperature T', where $T_1 > T' > T_0$) and up to temperature T_1, the transition takes place as quantum tunnelling of thermally excited nuclei. For $T < T_0$ ($T < T'$), the tunnelling occurs from the lower quantum level, while for $T > T_1$, purely classical thermally activated nucleation takes place. If $\chi(\epsilon_m, z_1) > \varphi(0)$ and $T_1 < T_0$, then in the range of temperatures $0 < T < T_2 = \alpha/\gamma z_2$, where z_2 is determined from the condition $z_2\epsilon_m = \varphi(0)$, a purely quantum transition takes place, with the same exponential as at $T = 0$. At $T = T_2$, the quantum regime of the transition changes discontinuously into the classical regime and the exponent in (3.5) becomes equal to

$$\chi(z) = z\varepsilon_m = \alpha\varepsilon_m/\gamma T, \quad T > T_2. \tag{3.10}$$

For systems described by a Hamiltonian of the form (2.7), the second case is realized. In this case, taking (3.3), (3.7) and (2.6) into account, for the temperature T_2 we find

$$T_2 = T_*, \tag{3.11}$$

where T_* has the value (2.18). It is important to note that T_2 can be extremely small by virtue of the decrease of T_* with increase of the critical size of the nucleus. If T_* is appreciably smaller than the characteristic frequencies of the excitations of our system, then the difficulty referred to at the beginning of the section is completely eliminated.

There is no difficulty in calculating also the additional pre-exponential factor S in (3.5) at $T < T_2$:

$$S = \frac{T_0}{T_0 - T}, \quad T_0 = \frac{4\alpha}{\pi\gamma} = \frac{135}{128}T_*. $$

Near the top of the barrier, the expression (3.5) for S ceases to be valid because of the deviation of the density matrix from its equilibrium value. Therefore, in the region $T > T_2$, the pre-exponential factor must be replaced by its standard classical value.

4. CLASSICAL AND QUANTUM NUCLEATION NEAR THE LABILITY BOUNDARY

As has already been indicated in the Introduction, near the lability boundary it is sufficient to consider only small changes of density, such that $|\rho - \rho_1| \sim |\rho_c - \rho_1| \ll |\rho_2 - \rho_1|$. Therefore, in formula (1.2) for the energy of such a fluctuation, it is sufficient to confine ourselves to the cubic terms in the expansion of $\mathcal{F}(\rho)$ in powers of $\rho - \rho_1$, and this led us to (1.8).

We introduce the dimensionless quantities (for definiteness, $\rho_c > \rho_1$)

$$\xi = \frac{\rho - \rho_1}{\rho_1}, \quad \xi_0 = -\frac{3\mathcal{F}''(\rho_1)}{\rho_1\mathcal{F}'''(\rho_1)} = \frac{3(\rho_\kappa - \rho_1)}{\rho_1} \ll 1. \tag{4.1}$$

Then (1.8) can be rewritten in the form

$$\varphi(\rho) = \mathcal{F}_0[\xi_0\xi^2 - \xi^3], \quad \mathcal{F}_0 = {}^1\!/_6\rho_1{}^3|\mathcal{F}'''(\rho_1)| > 0. \tag{4.2}$$

The quantity ξ_0 is the fundamental small parameter of the problem. In view of its importance, we write the expression for it in terms of other physical characteristics also. Taking into account that $m^{-1}\rho_1\mathcal{F}''(\rho_1) = s_1^2(\rho_1)$, where s_1 is the speed of sound at density ρ_1, we have

$$\xi_0 = {}^1\!/_2\rho_1 s_1{}^2 m/\mathcal{F}_0. \tag{4.3}$$

Finally, from the expansion of the pressure p in powers of $\rho_1 - \rho_c$ near the lability point:

$$|p - p_c| = {}^1\!/_2\rho_c|\mathcal{F}'''(\rho_c)|(\rho_1 - \rho_c)^2 = 3\mathcal{F}_0\xi_0{}^2$$

we obtain

$$\xi_0 = [|p - p_c|/3\mathcal{F}_0]^{1/2}. \tag{4.4}$$

As regards the gradient term in the free-energy density (1.2), by regarding δF as the k-th Fourier-component of the density, it is easy to see that loss of stability of spatially uniform states presupposes[7] $\lambda > 0$. In the opposite case, δF vanishes at a finite value of k. This would correspond to lability with respect to the short-range order. We shall discuss this case specially below.

Thus, the energy $U\{\rho\}$ can be written in the form

$$U\{\rho\} = \mathcal{F}_0\int \{\xi_0\xi^2 - \xi^3 + l^2(\nabla\xi)^2\}dV, \tag{4.5}$$

where $l^2 = \lambda\rho_1^2/\mathcal{F}_0$. Changing to the new variable $\chi = \xi/\xi_c$ and to the dimensionless coordinates

$$\mathbf{x} = \mathbf{r}/R_0, \quad R_0^2 = l^2/\xi_0, \tag{4.6}$$

we obtain

$$U\{\rho\} = U_0\int \{\chi^2 - \chi^3 + (\nabla\chi)^2\}d^3x,$$
$$U_0 = \mathcal{F}_0 R_0{}^3\xi_0{}^3 = \mathcal{F}_0 l^3\xi_0{}^{3/2}. \tag{4.7}$$

To determine the classical thermal-fluctuational probability of formation of a critical nucleus, we must find the minimum height of the energy barrier $U\{\rho\}$, i.e., the saddle point of the functional $U\{\rho\}$:

$$U_{cr} = \min\max U\{\rho\} = U_0\min\max J\{\chi\},$$
$$J\{\chi\} = \int \{\chi^2 - \chi^3 + (\nabla\chi)^2\}d^3x,$$
$$\chi \to 0 \text{ as } x \to \infty. \tag{4.8}$$

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[7] The parameter λ determines the spatial dispersion of the speed of sound. It is not difficult to show that $\omega^2 = k^2(s_1^2 + \rho_1\lambda k^2 + \dots)$.

Since the functional $J\{x\}$ does not contain any dimensional parameters, $J_0 = \min \max J\{\chi\}$ is a numerical constant. The exact value of J_0 is found by substituting into $J(\chi)$ the solution of the equation

$$\Delta\chi = \chi - {}^3/_2\chi^2, \quad \chi|_{x\to\infty} = 0, \qquad (4.9)$$

stemming from the condition $\delta J\{\chi\} = 0$.

It should be noted that such a problem can be solved without difficulty for the one-dimensional case, in which the functional $J_1\{\chi\}$ has the form

$$J_1\{\chi\} = \int_{-\infty}^{\infty} \left\{ \chi^2 - \chi^3 + \left(\frac{d\chi}{dx}\right)^2 \right\} dx, \qquad (4.10)$$

and Eq. (4.9) is transformed into

$$\chi''(x) = \chi(x) - {}^3/_2\chi^2(x), \quad \chi'(0) = \chi(\infty) = 0. \qquad (4.11)$$

The first integral of Eq. (4.11) is

$$\chi'^2 = \chi^2 - \chi^3 \quad \text{for } x > 0$$

or

$$-dx = d\chi / \chi\sqrt{1 - \chi}. \qquad (4.12)$$

Putting (4.12) into (4.10), we obtain

$$J_{10} = 4\int_0^\infty \chi^2(1 - \chi)\,dx = 4\int_0^1 \chi(1 - \chi)^{1/2}\,d\chi = \frac{16}{15}. \qquad (4.13)$$

In the three-dimensional spherically symmetric case,

$$J_0 = J\{\chi\} = 4\pi\int_0^\infty \left\{ \chi^2(1 - \chi) + \left(\frac{\partial\chi}{\partial r}\right)^2 \right\} r^2\,dr,$$

$$\chi'' + 2\chi'/r = \chi - {}^3/_2\chi^2, \quad \chi'(0) = \chi(\infty) = 0. \qquad (4.14)$$

The solution of this equation found on a computer led to the value $J_0 \cong 40$.

Thus, for the probability of thermal-fluctuational formation of a nucleus, we have

$$W \sim \exp\{-J_0\mathcal{F}_0 l^3\xi_0^{3/2} / T\}. \qquad (4.15)$$

Taking (4.4) into account, we obtain

$$-\ln W \sim |p - p_c|^{3/4} l^3 \mathcal{F}_0^{1/4} / T. \qquad (4.16)$$

The characteristic volume of a fluctuational nucleus is $V_0 \sim R_0^3 = l^3\xi_0^{-3/2}$. The length l is of the usual atomic scale ($l \sim a$), and therefore the number of particles in the core of the fluctuation

$$N_1 = V_0 / a^3 \sim (l/a)^3\xi_0^{-3/2} \gg 1,$$

which completely justifies the macroscopic approach. It must be emphasized, however, that whereas N_1 increases without limit as $\xi_0 \to 0$, the energy of the barrier falls away like $\xi_0^{3/2} \sim 1/N_1$.

We now return to the quantum-tunnelling formation of a nucleus at $T \neq 0$. As before, the probability of this process will be

$$W \sim \exp\{-2S_0/\hbar\}, \quad S_0 = |\text{Im } S|, \qquad (4.17)$$

where S is the classical action, taken along the optimal path from the point of entry to the point of exit from under the barrier. To calculate it, it is necessary to construct the Lagrangian of a system for which $U\{\rho\}$ has the meaning of the potential energy. By virtue of the symmetry of the problem and the smallness of the change in density, we can describe the motion of the liquid by means of the displacement field $\mu^*(\mathbf{r})$, i.e.,

we can regard the liquid as an elastic body with zero shear modulus. Then

$$E_{\text{kin}}\{\mathbf{u}^*\} = \frac{1}{2} m \int \rho v^2\,dV = \frac{1}{2} m\rho_1 \int \dot{\mathbf{u}}^{*2}\,dV. \qquad (4.18)$$

The displacements $\mathbf{u}^*(\mathbf{r})$ are connected with ξ by the obvious relation

$$-\xi = \text{div } \mathbf{u}^* = \frac{1}{R_0}\frac{\partial u_i^*}{\partial x_i}. \qquad (4.19)$$

Therefore, introducing the dimensionless vector field $\mathbf{u} = \mathbf{u}^*/R_0\xi_0$, we obtain

$$E_{\text{kin}} = m\rho_1 \frac{R_0^5\xi_0^2}{2}\int \dot{\mathbf{u}}^2\,d^3x,$$

$$\frac{\partial u_i}{\partial x_i} = \frac{1}{r^2}\frac{\partial r^2 u_r}{\partial r} = -\chi, \quad r = |\mathbf{x}|. \qquad (4.20)$$

Finally, introducing the dimensionless time τ:

$$\tau = t / t_0, \quad t_0^2 = m\rho_1 l^2 / \mathcal{F}_0\xi_0^2, \qquad (4.21)$$

we write the Lagrangian of the system in the form

$$L\{\mathbf{u}\} = U_0\mathcal{L}\{\mathbf{u}\}, \qquad (4.22)$$

$$\mathcal{L}\{\mathbf{u}\} = \int \left\{ \frac{1}{2}\left(\frac{\partial\mathbf{u}}{\partial\tau}\right)^2 - \chi^2 + \chi^3 - (\nabla\chi)^2 \right\} d^3x. \qquad (4.23)$$

Correspondingly, for the action $S = S(\tau, \{\mathbf{u}\})$ we obtain

$$S(\tau) = t_0\int_0^\tau L\,d\tau = l^4\xi_0^{5/2}(\mathcal{F}_0\rho_1 m)^{1/2}s(\tau), \qquad (4.24)$$

$$s(\tau) = \int_0^\tau \mathcal{L}\{\mathbf{u}\}\,d\tau.$$

Thus, returning to formula (4.17), we can write

$$S_0 = l^4\xi_0^{5/4}(\mathcal{F}_0\rho_1 m)^{1/2}s_0, \qquad (4.25)$$

$$s_0 = \min\left|\text{Im}\int_0^{\tau_0} \mathcal{L}\{\mathbf{u}\}\,d\tau\right|$$

(the integral s_0 is taken over the complex time along the optimal path from the point of entry to the point of exit from under the barrier). The functional $\mathcal{L}(\mathbf{u})$ does not contain any dimensional parameters, and s_0 is a numerical constant.

For the probability of formation of a nucleus, we have

$$W = A\exp\{-2s_0 l^4(\mathcal{F}_0\rho_1 m)^{1/2}\xi_0^{5/4} /\hbar\}. \qquad (4.26)$$

From the same dimensionality arguments, we can also obtain the order of the pre-exponential factor in (4.26):

$$A \sim 1/R_0^3 t_0 = (\mathcal{F}_0/m\rho_1)^{1/2}\xi_0^{5/2} /l^4.$$

(The form of the pre-exponential factor corresponds to the transition probability per unit time per unit volume.) It is interesting that in quantum and classical transitions, the dependences of the exponent on ξ_0 are found to be essentially different, this dependence being more pronounced in the quantum case ($d \ln W/d \xi_0 \sim \xi_0^{-1/2}$).

The exact calculation of s_0 requires the solution of the extremely complicated equations of motion arising when the Lagrangian $\mathcal{L}(\mathbf{u})$ is varied. We confine ourselves here to an approximate estimation of s_0, choosing for the field of the radial displacements $u(r, \tau)$ or densities $\chi(r, \text{ll})$ a sufficiently simple, but physically reasonable expression, depending on two dynamical dimensionless parameters—"the displacement ampli-

tude" $u = u(\tau)$ and the "fluctuation radius" $X = X(\tau)$. We have

$$u(r, \tau) = uf(z), \quad z = r/X;$$

$$\chi(r, \tau) = \frac{u}{X}\chi(z), \quad \chi(z) = \frac{1}{z^2}\frac{\partial}{\partial z}(z^2 f),$$

where $f(z)$ is a suitably chosen function. Substitution of this field into (4.23) gives the Lagrangian of the dynamical variables u, $\dot{u}$, X and $\dot{X}$. An approximate calculation of s_0 for this Lagrangian (given in the Appendix) gives the value $s_0 \approx 10^2$.

This value is reasonable, if we take into account the magnitude of J_0 found above.

If we introduce the characteristic energy per particle $\mathscr{F}_0 a^3 = \epsilon_0$, the exponent in (4.26) acquires the form

$$2S_0/\hbar = 2s_0(l/a)^4\xi_0^{5/2}(\epsilon_0 ma^2/\hbar^2)^{1/2}.$$

In accordance with (4.4), we have

$$-\ln W \sim 2S_0/\hbar \propto |p - p_c|^{1/4}. \tag{4.27}$$

Naturally, all the formulae obtained presuppose the applicability of the semiclassical approximation, i.e., $2S_0/\hbar \gg 1$, which means that direct use of them in the limit $p \to p_c$ can be only qualitative.

To determine the temperature at which the quantum regime of the transition changes into the classical regime, we equate the exponents of (4.15) and (4.26). This gives

$$T_* = \frac{J_0}{2s_0}\left(\frac{a}{l}\right)\xi_0\left(\epsilon_0\frac{\hbar^2}{ma^2}\right)^{1/2}.$$

To conclude this section, we shall discuss the situation which arises when the first instability appears not with respect to the uniform density, but with respect to the short-range order η. In this case, all the calculations of the potential energy $U = U\{\eta\}$ are performed absolutely identically. The free energy is expanded in powers of $\eta - \eta_1$; as before, $\partial^2\mathscr{F}/\partial\eta^2$ vanishes at the lability boundary η_c and the role of the small parameter ξ_0 is played by the quantity $3(\eta_c - \eta_1)/\eta_1$.

A difference arises only in the estimation of the kinetic energy, since macroscopic displacements are now absent and the speeds v are found to be of order $\xi_0 a/t_0$ (t_0 is the characteristic time). Therefore, scaling arguments give

$$U\{\eta\} \sim R_0^3\xi_0^3\mathscr{F}_0, \quad R_0^2 = l^2/\xi_0,$$

$$E_{\text{кин}} \sim R_0^3\xi_0^2 a^2\rho_1 m/t_0^2, \quad \mathscr{F}_0 = {}^1\!/_6\eta_1{}^3|\mathscr{F}'''(\eta_1)|.$$

From the condition $U \sim E_{\text{kin}}$, we obtain $t_0^2 = a^2\rho_1 m/\xi_0\mathscr{F}_0$ and, consequently, $S_0 \sim l^3 a\xi_0(\rho_1\mathscr{F}_0 m)^{1/2}$. Therefore, the exponent has the form

$$\frac{2S_0}{\hbar} \sim \frac{l^3 a(\rho_1\mathscr{F}_0 m)^{1/2}\xi_0}{\hbar} = \xi_0\left(\frac{l}{a}\right)^3\left(\frac{\epsilon_0 ma^2}{\hbar^2}\right)^{1/2},$$

$$\epsilon_0 = \mathscr{F}_0 a^3, \tag{4.28}$$

i.e., contains ξ_0 in place of $\xi_0^{1/2}$. In addition, now $\partial p/\partial\eta|_{\eta_c} \neq 0$ and, consequently,

$$|p - p_\kappa| \propto |\eta_1 - \eta_\kappa| \propto \xi_0.$$

Therefore, the exponent is found to be linearly dependent on the pressure:

$$-\ln W \sim 2S_0/\hbar \propto |p - p_\kappa|. \tag{4.29}$$

In the classical limit, in which the kinetic energy plays no part, the dependence on ξ_0 remains the same as in the previous case.

The calculational technique used in this Section and the writing of the Lagrangian (4.23) in terms of the displacement field $u(r)$ can be carried over practically whole to the case when nuclei arise in an anisotropic crystal close to the lability boundary, both in the case of a static instability (i.e., an instability with respect to the normal vibrations with $\mathbf{k} = 0$) and in the case of a dynamic instability ($\mathbf{k} \neq 0$). The difference consists in the inclusion of the energy of the shear stresses (1.7) (and in allowing for the anisotropy). If, however, close to the lability point, it is possible to retain only the single quadratic form responsible for the loss of stability, then this change is not a fundamental one and all the results of this Section remain qualitatively valid in this case also[8].

APPENDIX

We shall estimate the magnitude of s_0 by making use of the radial displacement field in the form given in the last Section:

$$u(r, \tau) = u(\tau)f(z), \quad z = r/X(\tau).$$

In this case, in accordance with (4.20), for the density field we have

$$\chi(r, t) = \frac{u(\tau)}{X(\tau)}\chi(z), \quad \chi(z) = \frac{1}{z^2}\frac{d}{dz}(z^2 f(z)),$$

and the Lagrangian $\mathscr{L}(u, X, \dot{u}, \dot{X})$ (4.23) takes the form

$$\mathscr{L} = {}^1\!/_2 M_{11}X^3\dot{u}^2 + M_{12}X^2\dot{u}Xu + {}^1\!/_2 M_{22}Xu^2\dot{X}^2 - U(u, X),$$

$$U(u, X) = A(X)u^2 - Bu^3, \quad A(X) = A_1 X + A_2/X,$$

$$A_1 = 4\pi\int_0^\infty \chi^2(z)z^2\,dz, \quad A_2 = 4\pi\int_0^\infty (\chi'(z))^2 z^2\,dz,$$

$$B = 4\pi\int_0^\infty \chi^3(z)z^2\,dz, \quad M_{11} = 4\pi\int_0^\infty f^2(z)z^2\,dz,$$

$$M_{12} = -4\pi\int_0^\infty f(z)f'(z)z^3\,dz, \quad M_{22} = 4\pi\int_0^\infty f'^2(z)z^4\,dz.$$

The minimum value of the potential energy $U(u, X)$ at arbitrary u is attained for $X_m = \sqrt{A_2/A_1}$ ($A(X_m) = 2\sqrt{A_1 A_2}$), irrespective of the value of u. This means that whereas the "displacement amplitude" $u(t)$ increases from its zero value ($u(t = 0) = 0$), the initial fluctuation radius has a finite magnitude $\sim X_m$. In connection with this, we introduce an additional approximation in the estimation of the action s_0, taking the parameter X to be a constant and determining it from the condition that s_0 be a minimum. In this case, the expression for the Lagrangian is simplified:

$$\mathscr{L} = {}^1\!/_2 M_{11}X^3\dot{u}^2 - U(u, X),$$

$$U(u, X) = A(X)u^2\left(1 - \frac{u}{u_0}\right), \quad u_0 = u_0(X) = \frac{A(X)}{B}.$$

At zero energy, $\mathscr{L} = -2U$ and $\dot{u} = du/d\tau = (-2U/M_{11}X^3)^{1/2}$.

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[8] A similar problem with a specific assumption on the form of the phonon spectrum of the crystal (corresponding to the appearance of the first dynamical instability at $k \neq 0$) has been examined independently by Iordanskiĭ and Finkel'shtein (cf. the paper in this issue).

Accordingly, for the differential of the imaginary time we have

$$d\tau = -i(M_{11}X^3/2U)^{1/2}du.$$

In this case, the action is equal to

$$s(X) = \int_0^{\tau_0} \mathscr{L}\, d\tau = i\int_0^{u_0} \sqrt{2M_{11}X^3U}\, du$$

$$= i\frac{4\sqrt{2}}{15}\sqrt{M_{11}X^3A(X)}\, u_0^2.$$

The extremal value of Im $s(X)$ is attained at $X_0 = \frac{1}{2}X_m = \frac{1}{2}\sqrt{A_2/A_1}$ and is equal to

$$s_0 = \frac{8\sqrt{2}}{15}\left(\frac{5}{4}\right)^{1/2}(M_{11}A_1)^{1/2}\frac{A_2^2}{B^2}.$$

We call attention to the fact that the parameter X has different values at the extremum points of the action and the potential energy.

To determine s_0 numerically, it is necessary to specify the form of $f(z)$ or $\chi(z)$. The simplest natural assumption for the distribution of densities is

$$\chi(z) = \begin{cases} 1 - z^2, & 0 < z < 1 \\ 0, & z > 1 \end{cases}$$

(for $f(z)$, this gives $f = z/3 - z^3/5$ for $0 < z < 1$ and $f = 2/15z^2$ for $z > 1$). In this case, we obtain $s_0 \approx 10^2$. The order of this quantity is not changed by choosing other monotonically decreasing functions $\chi(z)$.

Knowing the Lagrangian $\mathscr{L}(u, \dot{u}, X_0)$, we can find the energy levels and frequencies of the metastable system in the semiclassical approximation, in the same way as was done in Sec. 2. For the lower level, we have

$$\omega_0 = 2\left(\frac{5}{2}\frac{A_2}{M_1}\frac{1}{X_0^4}\right)^{1/2}\left(\frac{\mathscr{F}_0}{m\rho_1^2}\frac{\xi_0^2}{l^2}\right)^{1/2} \approx 10\xi_0\left(\frac{\mathscr{F}_0}{m\rho_1^2 l^2}\right)^{1/2}.$$

This value gives an estimate of the frequency in the pre-exponential factor in (4.26).