Effect of Quantum Fluctuations on the Lifetimes of Metastable States in Solids

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Quantum transitions from the metastable state of a crystal close to the lability point are considered. A simple model is studied in which allowance is made for only anharmonicity of third order. This permits one to carry out a microscopic analysis and to derive the relevant formula for the lifetime.

IN connection with the development of high-pressure techniques and the possibility of obtaining different modifications of the same substance, it is of interest to calculate the lifetime of different metastable states of a solid. At sufficiently low temperatures, besides the classical transition to a stable state as a result of thermodynamic fluctuations, there can occur a quantum transition of the sub-barrier tunneling type. Such a mechanism may turn out to be significant for the determination of the lifetime of the metastable states of light substances such as hydrogen or helium, for in this case, owing to the small mass of the atoms, the quantum fluctuations are the largest.

I. Lifshitz and Yu. Kagan[1] considered macroscopically the theory of quantum transitions from a metastable state for two limiting cases. The first case, which is realized near equilibrium points, is connected with the formation of a macroscopically large spherical nucleus of a stable phase, separated by a thin surface layer from the metastable isotropic medium. In the second case, which also pertains to an isotropic medium, the transition from a state near the lability point is considered. It is assumed that the nucleation is connected with long-wave fluctuations of the density and can be considered in the continual approximation. We investigate in the present paper a quantum transition from a metastable state of a solid close to the lability point, with allowance for the real crystal structure. Unlike the cases considered in[1], this transition is connected with the behavior of the phonon spectrum at finite momenta, and can therefore not be investigated macroscopically.

The probability of an ordinary thermodynamic transition is determined by the probability of occurrence of the minimal necessary fluctuation—the "critical nucleus." Analogously, in the quantum case, the time of transition is determined by the probability of tunneling into definite regions of the configuration space of the body with lower potential energy, regions corresponding to localized changes of the metastable-phase structure. The subsequent development of such nuclei is quite rapid, and we shall not be interested in the succeeding processes that bring the body to the final stable state. Thus, the calculation of the transition time reduces to a determination of the asymptotic form of the wave function in configuration space far from the local minimum of the potential energy corresponding to the metastable state. This asymptotic form determines the probability flux in a region with lower potential energy.

Since the analysis is carried out in a space with a very large number of dimensions, equal to the number of degrees of freedom of the macroscopic body ($N \sim 10^{25}$), there are considerable differences from the case of a small number of dimensions. The characteristic square of the region of the configuration space, within which the wave function is mainly concentrated, turns out to be unusually large, on the order of Nq_0^2 (q_0 is the average amplitude of the zero-point oscillations for each degree of freedom). It is therefore necessary to investigate the structure of the potential energy and the form of the wave function in a very wide region of radius $\sim N^{1/2}q_0$. In addition, whereas the total energy of the zero-point oscillations $E_0 \sim N\omega_d/2$ is unusually large (ω_d is the Debye frequency in the metastable phase; we use a system of units with $\hbar = 1$), the energy of the barrier separating the metastable minimum from the states with lower potential energy, corresponding to localized nuclei, is entirely independent of N. Therefore the energy of the zero-point oscillations exceeds the heights of these barriers by many times. This problem thus differs greatly from the usual one-dimensional case, and consequently it is necessary to exclude first the larger and "ineffective" part of the total energy of the zero-point oscillations.

We consider the transition from a metastable state close to the lability point. The proximity of the metastable state to the lability point usually denotes that the transition is determined by the lower terms of the expansion of the potential energy in powers of the displacements. The existence of such a situation can be indicated by deep dips in the phonon spectrum or by a small value of the sound velocity of one of the acoustic branches in some direction. We shall consider below the simplest transition of this type, when the long-wave deformations can be neglected.

1. DESCRIPTION OF MODEL

We consider a situation in which there exist three vectors $\mathbf{K}_1$, $\mathbf{K}_2$, and $\mathbf{K}_3$, in the vicinity of which the frequency of a certain branch s_0 of the phonon spectrum has a sharp dip, with the sum $\mathbf{K}_1 + \mathbf{K}_2 + \mathbf{K}_3$ equal to one of the reciprocal-lattice vectors. We shall show that in this case the phase under consideration is metastable and the lifetime is determined by a corresponding anharmonicity of third order.

In order for the existence of three such vectors not to be a random coincidence, we assume that the crystal has a threefold symmetry axis and that in the vicinity of

a certain vector $\mathbf{K}_1$, which is perpendicular to the symmetry axis, the minimum value of the square of the frequency ω^2_{min} of the branch s_0 is small compared with the square of the characteristic frequency ω_0^2 outside the dip, the latter being of the order of the Debye frequency. Then, owing to the symmetry, there exist two more vectors, $\mathbf{K}_2$ and $\mathbf{K}_3$, which make up together with $\mathbf{K}_1$ a regular triangle, on which a dip of the phonon spectrum is also produced. In addition, from the existence of one triod of vectors there follows automatically the existence of another triod, $-\mathbf{K}_1, -\mathbf{K}_2, -\mathbf{K}_3$, with the same properties.

We introduce the symbol $\Omega_1^{(+)}$ for the region near the vector $\mathbf{K}_1$, such that $\omega^2(\mathbf{k}) \leq 2\omega^2_{min}$ if $\mathbf{k} \in \Omega_1^{(+)}$. The analogous regions near the vectors $\mathbf{K}_2$, $\mathbf{K}_3$, $-\mathbf{K}_1$, $-\mathbf{K}_2$, and $-\mathbf{K}_3$ will be denoted respectively by $\Omega_2^{(+)}$, $\Omega_3^{(+)}$, $\Omega_1^{(-)}$, $\Omega_2^{(-)}$, and $\Omega_3^{(-)}$. We shall use normal coordinates[2] connected with the displacements of the lattice atoms by the formulas

$$Q(\mathbf{k},s)=\frac{1}{\sqrt{N}}\sum_{\varkappa,l,\alpha}\left(\frac{M_\varkappa}{M}\right)^{1/2} e_\alpha(\varkappa|-\mathbf{k},s)U_\alpha(l,\varkappa)e^{-i\mathbf{k}\mathbf{x}(l)},$$
$$\mathbf{U}(l,\varkappa)=\frac{1}{\sqrt{N}}\left(\frac{M}{M_\varkappa}\right)^{1/2}\sum_{\mathbf{k},s} Q(\mathbf{k},s)\mathbf{e}(\varkappa|\mathbf{k},s)e^{i\mathbf{k}\mathbf{x}(l)}; \quad (1.1)$$

here κ numbers the sites in the unit cell, and l numbers the unit cell; $\mathbf{U}(l, \kappa)$ is the displacement of site κ in the l-th cell; $\mathbf{e}(\kappa|\mathbf{k}, s)$ is a unit vector of s-th polarization with wave vector $\mathbf{k}$ for the sites κ; M_κ is the mass of the atom located at the site κ; N is the number of unit cells in the crystal; $\mathbf{x}(l)$ is the radius vector of the l-th cell; M is the mass of one of the atoms.

In terms of the variables $Q(\mathbf{k}, s)$, the potential energy is given by[2]

$$u=\frac{1}{2}\sum_{s,\mathbf{k}} M\omega_s^2(\mathbf{k})Q(\mathbf{k},s)Q(-\mathbf{k},s)$$
$$+\frac{1}{3!}\frac{1}{\sqrt{N}}\sum_{\substack{\mathbf{k},\mathbf{k}',\mathbf{k}''\\ s,s_1,s_2}}\Phi(\mathbf{k},s;\mathbf{k}',s_1;\mathbf{k}'',s_2)Q(\mathbf{k},s)Q(\mathbf{k}',s_1)Q(\mathbf{k}'',s_2) \quad (1.2)$$
$$\times\Delta(\mathbf{k}+\mathbf{k}'+\mathbf{k}'')+\ldots;$$

Here $\Delta(\mathbf{P}) = 1$ if $\mathbf{P}$ is a reciprocal-lattice vector, and equals zero in the opposite case; the vectors $\mathbf{k}$, $\mathbf{k}'$, and $\mathbf{k}''$ belong to the Wigner-Seitz unit cell. The coefficients $\Phi(\mathbf{k}, s; \mathbf{k}', s_1; \mathbf{k}'', s_2)$ are expressed in a well known fashion in terms of the third-order derivatives of the potential energy with respect to the displacements $U_\alpha(l, \kappa)$, with $\Delta(\mathbf{k}+\mathbf{k}'+\mathbf{k}'')\Phi(\mathbf{k}, s; \mathbf{k}', s_1; \mathbf{k}'', s_2)$ symmetrical with respect to the indices $(\mathbf{k}, s)$, $(\mathbf{k}', s_1)$, and $(\mathbf{k}'', s_2)$. Since the displacements and the potential energy are real, we get

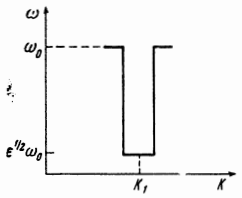
$$Q(\mathbf{k}, s) = Q^*(-\mathbf{k}, s), \quad (1.3)$$

$$\Phi(-\mathbf{k}, s; -\mathbf{k}', s_1; -\mathbf{k}'', s_2)=\Phi^*(\mathbf{k}, s; \mathbf{k}', s_1; \mathbf{k}'', s_2). \quad (1.4)$$

Assuming that the function $\Phi(\mathbf{k}, s_0; \mathbf{k}', s_0, \mathbf{k}'', s_0)$ varies little in the vicinity of the dips, we put

$$\Phi(\mathbf{k}, s_0; \mathbf{k}', s_0; \mathbf{k}'', s_0)=\lambda e^{\pm i\varphi}\omega_0^2 M/a$$
$$\text{for}\quad \mathbf{k}\in\Omega_1^{(\pm)},\quad \mathbf{k}'\in\Omega_2^{(\pm)},\quad \mathbf{k}''\in\Omega_3^{(\pm)}, \quad (1.5)$$

where a is the atomic distance (the lattice constant) and λ is a dimensionless coefficient. We assume that the dip in the phonon spectrum is due to random circumstances and not to common causes such as the existence of an indifferent equilibrium. Therefore



$\Phi(\mathbf{k}, s_0; \mathbf{k}', s_0, \mathbf{k}'', s_0)$ has in the region of the dips the usual atomic order of magnitude and accordingly $\lambda \sim 1$ (it is assumed that the symmetry of the crystal does not require that λ vanish).

Let us show that in the space of the normal coordinates there is a region, close to the origin, where the values of the potential energy become negative. To this end we construct the deformation out of only those $Q(\mathbf{k}, s)$, which correspond to the dip in the phonon spectrum. We put $Q(\mathbf{k}, s_0) = Q^{(+)}$ for $\mathbf{k} \in \Omega_i^{(+)}$ and $Q(\mathbf{k}, s_0) = Q^{(-)}$ for $\mathbf{k} \in \Omega_i^{(-)}$, where

$$Q^{(\pm)} = -e^{\mp i\varphi/3}\frac{1}{N^{1/2}}\frac{\Omega_B}{\Omega_1}\frac{a}{\lambda}A, \quad (1.6)$$

and $Q(\mathbf{k}, s) = 0$ in all the remaining cases (here Ω_1 is the volume of one of the regions $\Omega_i^{(\pm)}$, and Ω_B is the volume of the Brillouin zone). With increasing A, the sum of the harmonic part of the potential energy and of the anharmonicities of third order first increases, and then decreases and becomes negative at $A_c \sim \omega^2_{min}/\omega_0^2 \ll 1$. It is easy to verify that at such A the anharmonicities of higher orders are small compared with the considered terms, with a parameter

$$\varepsilon = \omega^2_{min}/\omega_0^2 \ll 1. \quad (1.7)$$

The constructed deformation $Q(\mathbf{k}, s)$ corresponds to a displacement of the group of atoms forming the nucleus localized near the origin, and the number of these atoms is $N_n \approx \Omega_B/\Omega_1$.

Thus, in our case the barrier separating the local minimum at the origin from the more convenient states is formed only by the harmonic terms and by the third-order anharmonicities. We obtain the probability of the quantum transition for this case, and confine ourselves to a simplified situation when the dip can be regarded as abrupt and the phonon frequency inside the dip equal to a constant value $\epsilon^{1/2}\omega_0$ (see the figure). Such a simplification is justified since, as shown above, only normal coordinates with wave vectors near the bottom of the dip were significant in the formation of favored states. We shall henceforth assume the regions $\Omega_i^{(\pm)}$ to coincide with the regions where $\omega^2_{s_0}(\mathbf{k}) = \epsilon\omega_0^2$, and assume that these regions are located at finite distances away from the boundaries of the Wigner-Seitz cell.

2. STRUCTURE OF POTENTIAL ENERGY IN MULTIDIMENSIONAL SPACE

It is possible to fall into the region of negative potential energy via a saddle point defined by the equation $\partial u/\partial Q(\mathbf{k}, s) = 0$. Retaining in u only the harmonic terms and the anharmonicities of third order, we obtain

$$\frac{\partial u}{\partial Q(-\mathbf{k},s)} = M\omega_s^2(\mathbf{k})Q(\mathbf{k},s) \quad (2.1)$$
$$+\frac{1}{2\sqrt{N}}\sum_{\mathbf{k}',\mathbf{k}'',s_1,s_2}\Delta(-\mathbf{k}+\mathbf{k}'+\mathbf{k}'')\Phi(-\mathbf{k},s;\mathbf{k}',s_1;\mathbf{k}'',s_2)Q(\mathbf{k}',s_1)Q(\mathbf{k}'',s_2)=0,$$

where Q(k, s) satisfy the relation (1.3).

We consider first those equations of the system (2.1) which are obtained by differentiating the potential energy with respect to the normal coordinates corresponding to the dip in the phonon spectrum. We set the remaining coordinates equal to zero in these equations. We introduce

$$b_i^{(\pm)}(\mathbf{k}) = Q(\mathbf{k}, s)\frac{\lambda}{\varepsilon a}N^{1/2}e^{\pm i\varphi/3}\frac{\Omega_1}{\Omega_B}, \tag{2.2}$$

where each of the pair of indices +, i and −i, denote respectively that $\mathbf{k} \in \Omega_i^{(+)}$, $s = s_0$ or $\mathbf{k} \in \Omega_i^{(-)}$, $s = s_0$. Using expression (1.5) for $\Phi(\mathbf{k}, s_0; \mathbf{k}', s_0; \mathbf{k}'', s_0)$ and changing over in (2.1) from sums to integrals, we obtain an integral equation for the quantities b:

$$b_i^{(\pm)}(\mathbf{k}) = -\frac{1}{\Omega_1}\int b_2^{(\mp)}(\mathbf{k}')\, b_3^{(\mp)}(\mathbf{k}-\mathbf{k}')\, d^3\mathbf{k}' \tag{2.3}$$

and the equations obtained by cyclic permutation of (1, 2, 3), with $b_i^{(+)} = (b_i^{(-)}(-\mathbf{k}))^*$, owing to the requirement that the displacements (1.3) be real. Equations (2.3) do not contain any small parameters and can be solved only numerically. An order-of-magnitude estimate of the solution leads to $|b| \approx 1$, and consequently to $|Q(\mathbf{k}, s_0)| \sim (\Omega_B/\Omega_1)N^{-1/2}\epsilon a/\lambda$.

Substituting the solutions of the system (2.3) in the right-hand side of (2.1) for values of k and s not corresponding to the dip, we obtain the first approximation for the values of Q(k, s) lying outside the dip. In this case Q(k, s) turned out to be different from zero only for values of k that can be represented in the form of a sum $\mathbf{k}' + \mathbf{k}'' = \mathbf{k}$, where $\mathbf{k}', \mathbf{k}'' \in \Omega_i^{(\pm)}$. In order of magnitude, we have in these regions

$$|Q(\mathbf{k}, s)| \approx \varepsilon^2\Omega_B a/\Omega_1\lambda N^{1/2}.$$

Let us examine in somewhat greater detail the first approximation for the acoustic coordinates Q(p, s) corresponding to a certain small homogeneous deformation inside the nucleus, since a somewhat different estimate is obtained for them. Using (2.1), we obtain for Q(p, s) with $|\mathbf{p}| \sim \Omega_1^{1/3}$

$$Q(\mathbf{p}, s) = \frac{\varepsilon^2 a^2\omega_0^2}{2\lambda^2 c_s^2|\mathbf{p}|}\left(\frac{\Omega_B}{\Omega_1}\right)^2\frac{1}{N^{1/2}\Omega_B}\int \lambda_{ss_0}\left(\frac{\mathbf{p}}{|\mathbf{p}|}, \mathbf{k}\right) b(\mathbf{k})\, b(\mathbf{p}-\mathbf{k})\, d^3\mathbf{k}. \tag{2.4}$$

By introducing an effective interaction coefficient λ_{ss_0} we have taken into account here the fact that the anharmonic interaction with the acoustic phonon is proportional to its momentum; c_s is the speed of sound. Although the quantities Q(p, s) diverge at small p, this divergence, however, is immaterial for quantities that are integral with respect to p. Let us estimate, for example, the contribution of the acoustic coordinates to the square of the distance to the saddle point:

$$R_{ak}^2 = \sum |Q(\mathbf{p}, s)|^2 \sim \varepsilon^4\left(\frac{\Omega_B}{\Omega_1}\right)^2\frac{1}{\Omega_B}\int_{\Omega_1}\frac{d^3\mathbf{p}}{p^2} \sim \varepsilon^4 a^2\left(\frac{\Omega_B}{\Omega_1}\right)^{5/3}.$$

The contribution of the normal coordinates in the region of the dip to the square of the distance to the same point is of the order of

$$\varepsilon^2 a^2\Omega_B/\Omega_1 \approx R_{ak}^2/\varepsilon^2(\Omega_B/\Omega_1)^{2/3}.$$

We shall henceforth assume that the nucleus corresponding to the solution of Eq. (2.1) is not very large, so that $\epsilon^2(\Omega_B/\Omega_1)^{2/3} \approx \epsilon^2 N_n^{2/3} \ll 1$, and we shall therefore neglect the contribution of the acoustic coordinates both in the distance to the saddle point and in the other integral quantities.

Integrating further, we verify that in the remaining region the Q(k, s) are proportional to still higher powers of the small parameter ϵ, and that refinements of the solution in the regions inside the dip and the regions adjacent to them do not change the obtained estimate. Thus, the first approximation, in which only Q(k, s) for k and s lying inside the dip are taken into account, gives a good approximation to the true solution in the entire unit cell.

We denote by $Q_\mu(\mathbf{k}, s)$ that solution of (2.1) which corresponds to a certain solution $b_\mu(\mathbf{k})$ of the system (2.3). Each $Q_\mu(\mathbf{k}, s)$ corresponds to one of the saddle points of the function u in configuration space. In order to clarify the form of the potential energy, let us determine the minima of u on the sphere

$$R^2 = \sum_{\mathbf{k},s} Q(\mathbf{k}, s)Q(-\mathbf{k}, s).$$

Using the Lagrange method, we introduce the function $u_R = u - \frac{1}{2}\alpha MR^2$ and seek its minima, after which we determine α from the condition that R^2 be constant. Since u_R differs from u only in the quadratic terms, the equations that determine the minima of u_R will coincide with (2.1), except that $\omega_s^2(\mathbf{k})$ is replaced by $\omega_s^2(\mathbf{k}) - \alpha$. If we assume our approximation of the phonon spectrum and confine ourselves only to Q(k, s) in the region of the frequency dip, then we readily see, by introducing $\epsilon(R) = [\omega_{\min}^2 - \alpha(R)]/\omega_0^2$ instead of ϵ from (1.7), that the equations obtained for the quantity $c(\mathbf{k}) = [\epsilon/\epsilon(R)]b(\mathbf{k})$ coincide with (2.3). Therefore the positions of the minima of u on the sphere R^2 = const are determined by the intersections of the straight lines

$$Q(\mathbf{k}, s) = \frac{\varepsilon(R)}{\varepsilon}Q_\mu(\mathbf{k}, s)$$

with this sphere. It follows therefore that these straight lines will be the steepest-descent lines from the corresponding saddle points. The saddle point itself corresponds to $\alpha = 0$; if $\alpha > 0$, then we descend to a minimum corresponding to a metastable state, and if $\alpha < 0$ we move towards an unlimited decrease of u. u vanishes at a certain $\alpha \sim -\epsilon\omega_0^2$ and remains negative from there on.

Equation (2.3) does not contain complex coefficients and has a real solution with $b^{(+)}(\mathbf{k}) = b^{(-)}(-\mathbf{k})$. It can be shown that the absolute minimum of the potential energy on the sphere R^2 = const lies on the straight descent line corresponding to the real solution of (2.3). We denote this solution by $b_0(\mathbf{k})$; it is then easy to see that

$$\tilde{b}_i^{(+)}(\mathbf{k}) = b_{0i}^{(+)}(\mathbf{k})e^{\pm 2\pi i/3}, \quad \tilde{b}_i^{(-)}(\mathbf{k}) = b_{0i}^{(-)}(\mathbf{k})e^{\mp 2\pi i/3} \tag{2.5a}$$

will also be solutions. In addition

$$\tilde{\tilde{b}}_1^{(\pm)}(\mathbf{k}) = b_{01}^{(\pm)}(\mathbf{k}), \quad \tilde{\tilde{b}}_2^{(\pm)}(\mathbf{k}) = b_{02}^{(\pm)}(\mathbf{k})e^{\pm 2\pi i/3}, \quad \tilde{\tilde{b}}_3^{(\pm)}(\mathbf{k}) = b_{03}^{(\pm)}(\mathbf{k})e^{\mp 2\pi i/3} \tag{2.5b}$$

together with the different permutations of (1, 2, 3) obtained from them, form an additional six solutions. The potential energy is the same along the descent lines corresponding to each of these nine solutions Q_ν, $\nu = 0, \ldots, 8$. Any of the solutions Q_ν corresponds to a certain displacement localized near the origin, of the group of lattice sites of the crystal, and the number of

these sights $N_n \approx \Omega_B/\Omega_1$. Such a formation can be called the critical nucleus.

The potential energy (1.2) does not change when $Q(\mathbf{k}, s)$ is replaced by $Q_l(\mathbf{k}, s) = e^{i\mathbf{k}\cdot\mathbf{x}(l)}Q(\mathbf{k}, s)$, if $\mathbf{x}(l)$ is any period of the Bravais lattice of the crystal. Thus, for each Q_ν there are N solutions $Q_{\nu,l}(\mathbf{k})$ with identical potential energy, corresponding to nuclei shifted by $\mathbf{x}(l)$. If $\mathbf{x}$ is an arbitrary vector, then the quantities $Q_\nu(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{x}}$ will not correspond, strictly speaking, to saddle points. They determine a certain three-dimensional hypersurface on a sphere of radius R_0:

$$R_0^2 = \sum |Q_0(\mathbf{k}, s)|^2 \sim \varepsilon^2 a^2 N, \tag{2.6}$$

(we took into account here (2.2) and the fact that in order of magnitude $|b_0(\mathbf{k})| \approx 1$), on which the potential energy $u(Q_\nu(\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{x}})$, has minima at the points corresponding to $\mathbf{x} = \mathbf{x}(l)$. However, if we confine ourselves only to momenta $\mathbf{k} \in \Omega_i^{(\pm)}$, then the potential energy will not depend at all on $\mathbf{x}$, and consequently the barrier between these minima is of the order of $\epsilon^2 u(Q_\nu)$ or even lower.

Let us estimate the distances between the saddle points:

$$|\Delta R|^2 = \sum |Q_{\nu'}(\mathbf{k}, s) - Q_{00}(\mathbf{k}, s)|^2$$

$$= \sum 2|Q_0(\mathbf{k}, s)|^2\{1 - \cos[\chi_0(\mathbf{k}) - \chi_{\nu'}(\mathbf{k})]\},$$

where $\chi_\nu^l(\mathbf{k})$ is the phase of $Q_{\nu,l}(\mathbf{k}, s)$, and $\chi_0(\mathbf{k})$ is the phase of the solution $Q_{00}(\mathbf{k})$ corresponding to a real $b_0(\mathbf{k})$. The phase difference is $\chi_\nu^l(\mathbf{k}) - \chi_0(\mathbf{k}) = \mathbf{k}\cdot\mathbf{x}(l) + \Delta_\nu\chi(\mathbf{k})$, where according to (2.5) the quantities $\Delta_\nu\chi(\mathbf{k})$ take on the values $\pm 2\pi/3$. We shall assume, for concreteness, that there is no $\mathbf{x}(l)$ for which $\mathbf{K}_i \cdot \mathbf{x}(l) \pm 2\pi/3 = 2\pi m$ and simultaneously $|\mathbf{x}(l)|\Delta k \ll 1$, where Δk is the linear dimension of the region Ω_1. If these conditions are satisfied, then $|\Delta R|^2 \sim R_0^2$. By assumption, R_0^2 is large in comparison with the square of the amplitude of the zero-point oscillations, for otherwise the lifetime of the metastable state would be of atomic order.

Owing to the large value of $|\Delta R|$, two limiting cases are possible: weak penetrability of the barriers between different saddle points, when the barriers can be regarded as large, and conversely, complete penetrability of the barrier between the saddle points with different values of $\mathbf{x}(l)$ and with identical ν, when the barrier can be neglected. It is clear that the case of low barrier penetrability between the saddle points should lead to large lifetimes of the metastable state, owing to the decrease of the volume through which the tunneling can occur. We shall consider this case in detail and then indicate how the lifetime is altered by increasing the volume through which the tunneling takes place in the case of a completely penetrable barrier.

3. CALCULATION OF TRANSITION PROBABILITY

For a given structure of the potential energy, the tunneling will occur independently along each straight descent line from the saddle points. In the vicinity of the descent line, the potential energy u can be expanded in powers of the transverse coordinates, and this expression will have a positive quadratic form (otherwise one could find a saddle point with a lower energy).

We shall consider the descent line from $Q_{00}(\mathbf{k}, s)$. On the descent line we introduce the energy $v(r) = u(rQ_{00}(\mathbf{k}, s)/R_0)$, where r is the distance on this straight line:

$$v(r) = \frac{1}{2}\varepsilon^3 M\omega_0^2 \frac{a^2}{\lambda^2}\frac{r^2}{R_0^2}\frac{\Omega_B}{\Omega_1^2}\int b_0(\mathbf{k})\,b_0(-\mathbf{k})\,d^3\mathbf{k}$$
$$+\frac{1}{3!}\varepsilon^3 M\omega_0^2 \frac{a^2}{\lambda^2}\frac{r^3}{R_0^3}\frac{\Omega_B}{\Omega_1^3}\int b_0(-\mathbf{k}-\mathbf{k}_1)\,b_0(\mathbf{k})\,b_0(\mathbf{k}_1)\,d^3\mathbf{k}\,d^3\mathbf{k}_1. \tag{3.1}$$

Assuming

$$q(\mathbf{k}, s) = Q(\mathbf{k}, s) - Q_{00}(\mathbf{k}, s)\frac{1}{R_0^2}\sum Q(\mathbf{k}', s)Q_{00}(-\mathbf{k}', s),$$
$$q(-\mathbf{k}, s) = Q(-\mathbf{k}, s) - Q_{00}(-\mathbf{k}, s)\frac{1}{R_0^2}\sum Q(-\mathbf{k}', s)Q_{00}(\mathbf{k}', s), \tag{3.2}$$

we represent u in the form $u = v(r) + w_r q(\mathbf{k}, s))$, where

$$w_r = \frac{1}{2}\sum M\omega_s^2(\mathbf{k})\,q(\mathbf{k}, s)\,q(-\mathbf{k}, s)$$
$$+\frac{1}{2}\frac{1}{\sqrt{N}}\frac{r}{R_0}\sum \Phi(\mathbf{k}, s_0; \mathbf{k}', s_1; \mathbf{k}'', s_2)\Delta(\mathbf{k}+\mathbf{k}'+\mathbf{k}'') \tag{3.3}$$
$$\times q(\mathbf{k}', s_1)\,q(\mathbf{k}'', s_2)\,Q_{00}(\mathbf{k}, s_0),$$

with $q(\mathbf{k}, s)$ perpendicular to the descent line:

$$\sum q(\mathbf{k}, s)\,Q_{00}(-\mathbf{k}, s) = 0.$$

In this expression we did not use the model expression (1.5) for $\Phi(\mathbf{k}, s_0; \mathbf{k}', s_1; \mathbf{k}'', s_2)$, bearing it in mind that $Q(\mathbf{k}, s_0)$ interacts in the region of the dip with all the $Q(\mathbf{k}, s)$, and recognized that there should be no terms linear in $q(\mathbf{k}, s)$.

Among the eigenvectors of the quadratic form (3.3) there are vectors corresponding to the scattering of the phonons by the nucleus, and, in addition, vectors corresponding to localized oscillations in the nucleus itself. As shown by I. Lifshitz[3], the number of such local oscillations does not exceed $N_n\gamma$, where N_n is the number of displaced atoms and γ the number of end points of the phonon spectrum without the nucleus. It is easy to see that the shift of the squares of the local oscillations from the boundaries of the initial spectrum has an average order of magnitude $\epsilon\omega_0^2$. As to the influence of the anharmonic term in (3.3) on the quadratic-form eigenvectors corresponding to the continuous spectrum, each of them changes on the average by not more than $1/N$, and contributes quantities independent of N to the different additive expressions[3]. In particular, it can be stated that the change of the energy of the corresponding zero-point oscillations is of the order of $N_n\epsilon^{1/2}\omega_0$. Thus, on the average, all the corrections to w_r, due to the anharmonicity, do not depend on N and their order of magnitude is

$$w_r - w_0 \sim N_n\varepsilon^{1/2}\omega_0 \sim N_n\varepsilon\omega_0^2 M q_0^2,$$

where $q_0^2 = \langle|Q(\mathbf{k}, s)Q(-\mathbf{k}, s)|\rangle$ is the square of the amplitude of the zero-point oscillations, calculated in the harmonic approximation for $\mathbf{k}$ lying in the region of the dip (w_0 denotes the quadratic form (3.3) without the anharmonic terms).

We are considering a classical crystal and assume therefore that when the critical nucleus is produced the average displacement of the particles ϵa is much larger than the amplitude of the zero-point oscillations. Since in accordance with (3.1) the barrier is given by

$$v_b = v(R_0) = u(Q_{00}(\mathbf{k}, s)) \sim N_n\varepsilon M\omega_0^2(\varepsilon a)^2,$$

it follows that

$$(w_r - w_0)/v_b \sim q_0^2/(\varepsilon a)^2 \ll 1. \quad (3.4)$$

The conclusion that the deviation of w_r from w_0 for a classical crystal is small on the average can be arrived at in a non-rigorous fashion by using somewhat more elementary considerations and estimating the relative volume in the form of a sphere of radius $N^{1/2}q_0$, in which $w_r - w_0$ takes on a value larger than a certain number. It turns out that for values larger than $N_n\epsilon\omega_0^2 M q_0^2$, this volume is exponentially small.

To determine the transition probability it is necessary to solve the Schrödinger equation

$$(\hat{T} + u)\psi = (E_0 + \delta E)\psi, \quad (3.5)$$

where $\hat{T}$ is the kinetic-energy operator and has the form of a multi-dimensional Laplace operator in terms of real normal coordinates; E_0 is the energy of the zero-point oscillations, calculated in the harmonic approximation for the metastable structure; δE is the correction due to the anharmonicity. The imaginary part of δE gives the frequency of interest to us, of the transitions to a state with lower energy. The appearance of an imaginary part in the energy, just as in the one-dimensional case, is connected with the form of the boundary condition (see[4,5]) in the region beyond the barrier, where there should be only an outgoing wave. This leads to the presence of a current, in terms of which Im δE is indeed expressed if we use the conservation law

$$\frac{\partial}{\partial t}\int \psi\psi^* dV = 2\,\mathrm{Im}\,\delta E \int \psi\psi^* dV = -\int \mathbf{j}\, d\mathbf{S}. \quad (3.6)$$

Integration over the volume can be assumed to be carried out, in the first approximation, over the region where the wave function of the ground state for the metastable structure is concentrated and where the harmonic approximation can be used. As to the surface integral, it is evaluated in the classically inaccessible region beyond the barrier (it should be borne in mind that all the integrations are multidimensional and occur in the configuration space of the crystal). The integration surface in (3.6) is conveniently chosen to be a hyperplane perpendicular to the line of descent from the saddle point. The radius of the integration region in this hyperplane is of the order of

$$q_\perp = \left(\sum \langle |Q(\mathbf{k}, s)Q(-\mathbf{k}, s)| \rangle\right)^{1/2} \sim N^{1/2}q_0 \gg R_0,$$

where R_0 is the length of the path along the descent line to the saddle point. Thus, to calculate the imaginary increment to the energy it is necessary to find the asymptotic value of the wave function at large r in a hyperplane perpendicular to the descent line.

When calculating the asymptotic value we can neglect, in accord with (3.4), the difference between w_r and w_0, and put $u = v(r) + w_0(q(\mathbf{k}, s))$. Then, in the cylinder of interest to us around the descent line, we obtain the equation

$$(\hat{T}_r + \hat{T}_q)\psi + [v(r) + w_0(q(\mathbf{k}, s))]\psi = E\psi \quad (3.7)$$

(we have taken the descent line as one of the coordinate axes). This equation can be solved by separating the variables, assuming that $\psi = \phi(\mathbf{r})\varphi_0(q(\mathbf{k}, s))$, where φ_0 is the wave function of the ground state in terms of the transverse coordinates $q(\mathbf{k}, s)$. In the quasiclassical approximation we have

$$\phi(r) = \frac{A}{v^{1/4}(r)} \exp\left\{-\int_0^r [2Mv(r)]^{1/2} dr\right\}.$$

The constant A should be obtained from the condition of continuity with the solution of Eq. (3.7) in the classically accessible region, i.e., in the region of small r, where $v(r) = \frac{1}{2}\epsilon\omega_0^2 M r^2$. Omitting the intermediate steps, we present the answer for Im E[4,5]:

$$\mathrm{Im}\,E \sim 9N\varepsilon^{1/2}\omega_0 \exp\left\{-2\int_0^{r_1} [2Mv(r)]^{1/2} dr\right\}. \quad (3.8)$$

In this formula we have taken into account the contribution made to the current by all 9N descent lines. The quantity $r_1 \sim R_0$ was determined from the condition $v(r_1) = 0$. The argument of the exponential, according to (3.1), is of the order of

$$[v(R_0)M]^{1/2}R_0 \sim N_n\omega_0 M a^2 \varepsilon^{5/2}.$$

Expression (3.8) for the transition probability does not take into account the change of the potential energy in directions transverse to the descent line with changing r. This change determines the effective volume of the hypersurface along which the tunneling takes place. Although the relative contribution of such terms in the argument of the exponential is of the order of $(w_r - w_0)/v_b \sim q_0^2/(\epsilon a)^2$, the corresponding exponential can be much larger than unity. An approximate estimate of this exponential is given in the Appendix. We note that if we have a quantum rather than a classical crystal, then the factors connected with the change in the form of the potential energy in the transverse hyperplane will be of the same order as the "main" exponential.

Formula (3.8) corresponds to the case of small barrier penetrability between the straight descent lines (see Sec. 2). As already noted in Sec. 2, to calculate the transition probability in the case of total penetrability of the barrier it is necessary to find the increase of the effective volume through which the tunneling takes place. The volume of the three-dimensional hypersurface specified by the quantities $Q_{\nu\mathbf{X}} = Q_\nu e^{i\mathbf{k}\cdot\mathbf{x}}$, in which the energy u can be regarded as constant, is determined by integrating the square root of the Gram determinant (see, for example,[6]) for the N-dimensional vectors

$$X(\mathbf{k}, s) = \frac{\partial Q_{\nu\mathbf{x}}(\mathbf{k}, s)}{\partial x}, \quad Y(\mathbf{k}, s) = \frac{\partial Q_{\nu\mathbf{x}}(\mathbf{k}, s)}{\partial y}, \quad Z(\mathbf{k}, s) = \frac{\partial Q_{\nu\mathbf{x}}(\mathbf{k}, s)}{\partial z}.$$

The integration is carried out with respect to dV = dxdydz in the volume of the entire crystal. Using (2.6), we can easily obtain an estimate for the volume of this hypersurface:

$$V_h \sim 9|\mathbf{K}_t|^2\Omega_t^{1/2}Na^3R_0^3 \sim 9(\varepsilon a)^3 N N_n^{7/6}.$$

In the case of an inpenetrable barrier, a volume on the order of q_0^3 near each of the descent lines interacts effectively on this hypersurface during the tunneling, owing to the zero-point oscillations. Consequently, the total effective volume taken into account in the derivation of formula (3.8) was of the order of $9Nq_0^3$.

Thus, in the case of a fully penetrable barrier, an additional factor $(\epsilon a/q_0)^3 N_n^{7/6} \gg 1$ appears in the lifetime estimate given by (3.8). The result shows that it is

generally incorrect to express the factor proportional to the volume in the form N/N_n. However, this very difference is insignificant, owing to the difficulty in calculating exactly the entire pre-exponential factor.

4. CONCLUSION

The result enables us to draw certain conclusions concerning the influence of quantum fluctuations on the destruction of the metastable states.

If the destruction were to be connected with the classical thermodynamic fluctuations, then we would have for the transition frequency $1/\tau \propto N \exp(-v_b/T)$. According to (3.8), the probabilities of the classical and quantum transitions become equal when

$$(v_b/R_0^2M)^{1/2}/T \sim \varepsilon^{1/2}\omega_0/T \sim 1.$$

The simplicity of the model analyzed in the present paper is connected with the fact that the descent line from the saddle point is straight. We note that motion along a straight line corresponds to a fixed dimension of the nucleus. In the general case, such a descent line is a curve and there are no grounds for stating that the tunneling will occur near this curve. As we have seen with the model as an example, the energy connected with the zero-point oscillations is eliminated from the problem. In the general case we can therefore find the tunneling path by putting E = 0 in the Schrödinger equation (3.5), and finding the wave function in the classical approximation in the form e^{-S}, with S given by the Hamilton-Jacobi equation (with u replaced by $-u$)

$$(\nabla S)^2/2M = u.$$

At the origin, which corresponds to the metastable state, S = 0. Solving this equation in the usual manner, we obtain its characteristics:

$$\frac{dx_i}{v_i} = M\frac{dv_i}{\partial u/\partial x_i} = dt$$

and the trajectories $x_i(t)$, with only the trajectories grown from the origin being of interest to us (here x_i denote coordinates in configuration space). These trajectories reach ultimately caustics beyond which they cannot penetrate.

Among these trajectories there are singular points which reach the hypersurface u = 0 at points where the caustic is that hypersurface, and on which the action is minimal. For the analyzed model, such trajectories coincided with the straight descent lines. If this singular trajectory is not too strongly bent in configuration space, all the statements made in the present paper concerning the form of the wave function in the perpendicular hyperplane should remain in force for this trajectory. For a classical crystal this makes it possible to separate the variables approximately, with accuracy $(q_0/a)^2$, eliminate the zero-point oscillation energy, and write the answer in the form

$$\operatorname{Im} E \sim N\exp\left\{-2\int_0^L [2Mu(l)]^{1/2}dl\right\},$$

where the integration is along the classical trajectory and L is the length of the trajectory to the point where $u(l) = 0$ (we have omitted the pre-exponential factor here). Taking into account the Maupertuis least-action principle, this formula can be used to estimate the transition probability.

In conclusion we note the following. The foregoing analysis can be transferred with practically no change to the case when the frequency of any branch of the optical oscillations has a dip at a zero wave vector, provided the symmetry of the crystal does not call for the vanishing of the corresponding third-order anharmonicity.

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APPENDIX

Let us calculate approximately the change in the form of the wave function in the transverse hyperplane as a function of r. We separate the eigenvectors of the quadratic w_r into vectors $\eta_i(r)$ corresponding to high frequencies with $\omega_i^2 \sim \omega_0^2$, and vectors $\xi_j(r)$ corresponding to low frequencies with $\omega_j^2 \sim \epsilon\omega_0^2$. The degrees of freedom corresponding to the high frequencies will be taken into account in the adiabatic approximation. The slow frequencies will be assumed to be approximately the same, so that their square is $\omega_j^2 = \epsilon\omega_0^2 + \epsilon\delta\omega^2(r)/N_i$, where $N_i \sim N/N_n$ is the number of slow frequencies. At r = 0 this approximation is exact. The quantity $\delta\omega^2(r) \sim \omega_0^2$ can be obtained by averaging the truly slow frequencies.

We assume that the subspaces of the vectors $\eta_i(r)$ and $\xi_j(r)$ do not depend on r. We can then seek the wave function in the form

$$\psi = \phi_r(\eta)\frac{A(\rho,r)}{\tilde{u}^{1/4}(r)}\exp\left(-\frac{\rho^2}{4q_0^2}\right)\exp\left\{-\int[2M\tilde{u}(r)]^{1/2}dr\right\} \quad (A.1)$$

where $\rho^2 = \sum\xi_j^2$; $\phi_r(\eta)$ is the wave function of the ground state with respect to the coordinates η_i in the adiabatic approximation; $\tilde{u} = v(r) = \delta E_0(r)$ is the effective potential energy, which takes into account the adiabatic change of the energy of the zero-point oscillations of the fast frequencies, $\delta E_0 = \sum[\omega_i(r) - \omega_i(0)]$; $A(\rho, r)$ is assumed to be a slow function of its arguments. We have used the assumed asymmetry with respect to rotations in the hyperplane of the slow coordinates, assuming the wave function to depend only on ρ.

Substituting (A.1) in the Schrödinger equation and recognizing that the number of slow coordinates is exceedingly large, we obtain accurate to terms $\sim 1/N_l$

$$(2\tilde{u}M)^{1/2}\frac{\partial A}{\partial r} + \frac{\partial A}{2\partial\rho}\frac{\rho}{q_0^2} - \frac{N_i}{2\rho}\frac{\partial A}{\partial\rho} + \frac{\varepsilon\delta\omega^2(r)}{2N_i}\rho^2AM^2 = 0. \quad (A.2)$$

Here, as is usually done in the quasiclassical approach, we have neglected the quantity $\partial^2A/\partial r^2$. This equation can be integrated in quadratures. Without stopping on the intermediate steps, we present the final answer for Im δE in such an approximation:

$$\operatorname{Im}\delta E \sim 9N\omega_0\varepsilon^{1/2}\exp\left\{-2\int_0^r(2Mv)^{1/2}dr)\right\} \quad (A.3)$$

$$\times\exp\left\{-2M^{1/2}\int_0^r\frac{\delta E_0(r)+\varepsilon^{1/2}\delta\omega^2(r)/4\omega_0}{(2v)^{1/2}}dr\right\}.$$

An exact calculation of the pre-exponential factor is extremely difficult owing to the dispersion of the slow frequencies. We see that the corrections to the argument of the exponential of (3.8) have a relative order of magnitude $q_0^2/(\epsilon a)^2 \ll 1$, as was assumed in the derivation of (3.8).

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