Effect of dissipation on the quantum kinetics of phase transitions at low temperatures

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The effect of energy dissipation on the rate of formation of nucleating regions of a stable phase in a metastable liquid is analyzed. At temperatures for which the phase transition occurs by means of macroscopic quantum tunneling the decay probability depends not only on thermodynamic properties but also kinetic characteristics of the system. A new characteristic temperature T_l appears on the temperature dependence of the decay probability when the mean free path of the excitations, $l(T)$, becomes equal to the size of a critical nucleating region. At T_l there is a transition from one temperature dependence, corresponding to energy dissipation in a regime of hydrodynamic viscous flow, to another temperature dependence, in which case the dissipation occurs under Knudsen conditions in the gas of excitations.

1. INTRODUCTION

Much interest has recently been attracted to the analysis of the kinetics of phase transitions at low temperatures, where quantum-mechanical effects can be seen on a macroscopic scale.[1] The transition of a metastable phase into a stable phase occurs through the formation of nuclei of the new phase. At high temperatures the mechanism for the formation of these nucleating regions (we will say simply "nuclei") of the stable phase involves thermal fluctuations. At sufficiently low temperatures, the mechansim instead involves quantum-mechanical fluctuations, which correspond to tunneling through a barrier. Such quantum-mechanical tunneling through a barrier is conveniently described by an approach based on a transformation to an imaginary time and the derivation of solutions with a finite action.[1–3] The approach developed in Ref. 1 has been used widely to analyze specific systems: the solidification of the isotopes ^{3}He and ^{4}He (Ref. 4), the kinetics of the stratification of liquid ^{3}He–^{4}He solutions,[5] the probability for nucleation of the B phase in the A phase of superfluid ^{3}He (Ref. 6), the stability of supercooled liquid hydrogen[7] (H_2), the process by which quantum crystals of helium acquire faceting,[8] and the kinetics of the formation of molecular nuclei in metastable metallic hydrogen.[9]

The analysis of the quantum kinetics of phase transitions which was carried out in Ref. 1 and also that in Refs. 2–9 were based on the assumption that no dissipative processes of any sort occur in the medium. As has recently become clear, however, dissipative processes strongly influence the probability for the decay of a metastable state and reduce the decay rate at zero temperature.[10] In addition, there is a sharp change in the temperature dependence of the decay probability.[11] In the present paper we analyze the effect of the dissipative processes which occur in a medium on the quantum kinetics of phase transitions at low temperatures.

In a macroscopic description of the dynamics of a nucleus of a new phase, one usually distinguishes several macroscopic parameters: the density, the size, etc. That approach corresponds to the assumption that all of the other (unimportant) parameters are related in an unambiguous way to the macroscopic parameters which have been identified. In other words, the times involved in the relaxation to an incomplete equilibrium, by which we mean an equilibrium in terms of only the unimportant parameters or fixed macroscopic variables, are assumed to be much shorter than the times involved in the relaxation of the equilibrium values of the macroscopic parameters which are used to describe the nucleus and its surroundings. In this type of adiabatic "fine tuning" of all of the unimportant parameters, the dynamics in the medium is reversible, i.e., there is no dissipation.

Accordingly, any process which occurs in a medium is reversible only if it occurs at an infinitely low rate, so that the medium, manages to reach equilibrium at any instant. The growth of a nucleus which perturbs the medium is assumed to occur at a low but finite rate, so that the overall system is not in thermodynamic equilibrium at each instant. Consequently, those processes which lead to an equilibrium and whose relaxation times are much longer than the time scale for the growth of a nucleus render the motion irreversible, i.e., lead to dissipation of the total energy of the nucleus.

Two types of processes cause energy dissipation. The first is heat conduction, which arises if there are gradients in the various parts of a medium. The second is viscosity (internal friction), which is manifested in the appearance of irreversible transport of momentum from regions with a relatively high velocity into regions with a relatively low velocity. In the present paper we are concerned only with the dissipative processes of this second kind.

The formation and growth of a nucleus of a new phase in a viscous medium are accompanied by a dissipation of the total energy of the nucleus, i.e., by a transfer of its energy to other degrees of freedom. Such a motion is described by adding to the ordinary potential forces some friction forces which depend linearly on the growth rate of a nucleus and which oppose its growth. The coefficient of friction depends on the dimensions of the nucleus. The effect of energy dissipation on the probability for the formation of a critical-size nucleus by tunneling will be taken into account here by the approach developed in Refs. 10 and 11. In this approach, the description of the energy dissipation reduces to finding an action which is nonlocal in terms of an imaginary time.

2. TUNNELING-ACTIVATION FORMATION OF NUCLEATING REGIONS IN A NORMAL LIQUID

We assume that a metastable phase of density ρ is a normal quantum liquid, in which a solid nucleus of a new phase, of density $\rho + \Delta\rho$, forms. For example, we might be considering the solidification of ^{3}He under pressure. We assume that the liquid and solid phases are quite close to a phase equilibrium and that the critical-size nucleus of the new phase is a macroscopic formation, containing a large number of particles. The appearance of a nucleus of the new phase with small dimensions is unfavorable from the energy standpoint, since the surface energy which arises for the interface of the new metastable phase exceeds the difference between the chemical potentials of the metastable and stable phases.

We assume for simplicity that the thickness of the transition layer between the phases is small in comparison with the size of the nucleus. The potential energy $U(R)$ of a spherical fluctuation of the new phase, of radius R, is then given by

$$U(R) = 4\pi\sigma R^2 (1 - R/R_c). \tag{1}$$

Here σ is the surface tension between the phases, and R_c is the critical size of a nucleus, which is found from the condition $U(R_c) = 0$. The critical size R_c is inversely proportional to the difference between the chemical potentials of the two phases; i.e., it is a measure of the deviation of the system from equilibrium.

We will also ignore the compressibility of the liquid, since in the case of large nuclei the velocity of the boundary is much lower than the velocity of sound, and incorporating compressibility would correspond to incorporating the small contribution $\sim (\dot{R}/c)^2$, where c is the sound velocity. The kinetic energy of a nucleus, expressed in terms of the radius of the nucleus, $R(t)$, and the velocity of its boundary, $\dot{R}(t)$, is then given by the familiar expression[1]

$$K = \frac{1}{2} M(R)\dot{R}^2, \qquad M(R) = 4\pi \frac{(\Delta\rho)^2}{\rho} R^3. \tag{2}$$

The instantaneous velocity field $\mathbf{v}(\mathbf{r})$, which is governed exclusively by the continuity equation, is given in this case by the expression

$$v = \begin{cases} -\dfrac{\Delta\rho}{\rho}\dot{R}\dfrac{R^2}{r^2}, & r > R(t) \\ 0, & r < R(t) \end{cases} \tag{3}$$

It can be seen from (3) that the growth of the nucleus is accompanied by a macroscopic motion $\mathbf{v}(\mathbf{r})$ of the flow of the metastable liquid, which has a nonuniform velocity. This means that different regions of a liquid are moving at different velocities, and some regions of the liquid are moving with respect to others. Correspondingly, dissipative processes occur in the liquid as it relaxes to a complete thermodynamic equilibrium. These dissipative processes stem from the irreversible viscous transport of momentum from regions with a relatively high velocity to regions with a relatively low velocity.

In the absence of dissipation in the medium around the neucleus, the growth of a nucleus is described by the equation of motion

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{R}}\right) - \frac{\partial L}{\partial R} = 0, \tag{4}$$

where L is the Lagrangian of our system,

$$L(\dot{R}, R) = M(R)\dot{R}^2/2 - U(R).$$

The potential energy $U(R)$ is determined by (1).

Because of the viscosity (internal friction) in the metastable region around the nucleus, the medium has a drag, which tends to slow the growth of the nucleus. The energy of the nucleus is dissipated in the process:

$$\frac{dE}{dt} = \frac{d}{dt}\left(\dot{R}\frac{\partial L}{\partial \dot{R}} - L\right) = -\mu(R)\dot{R}^2. \tag{5}$$

The dynamics of the development of a nucleus is described by adding to the right side of the equation of motion (4) an additional "dissipative" drag force F, which is linear in the growth rate and which opposes the growth of the nucleus:

$$F = -\mu(R)\dot{R}.$$

To determine how the coefficient of friction $\mu(R)$ depends on the radius of the nucleus, R, we need to determine the energy dissipation of the nucleus per unit time. We assume that the viscosity coefficient of the liquid phase around a solid nucleus is η_T and depends on the temperature. We will not need the second viscosity coefficient ζ, since the metastable phase is assumed to be incompressible, so we have div $\mathbf{v} = 0$. In general, the coefficient of friction $\mu(R)$ is described by

$$\mu(R) = 16\pi\eta\left(\frac{\Delta\rho}{\rho}\right)^2 Rf\left(\frac{R}{l}\right),$$

$$f(x) = \begin{cases} 1, & x \gg 1 \\ \alpha x, & x \ll 1 \end{cases}. \tag{6}$$

The dimensionless function $f(x)$ is the ratio of the radius of the nucleus to the mean free path of the excitations in the metastable phase, $l(T)$. The number α is of order unity and depends on the nature of the excitations in the metastable phase and their interaction with the surface of the stable phase. Since l increases rapidly with T at low temperatures, as the temperature is varied there may be a transition from one regime in (6) to another, from a hydrodynamic regime with $l(T) \ll R$ at a higher temperature T to a Knudsen regime with $l(T) \gg R$ at a lower T.

The methods used to calculate the coefficient of friction $\mu(R)$ in these two limiting cases are quite different. In the hydrodynamic limit, where the nucleus size R is much greater than the mean free path $l(T)$ (of the excitations in the liquid), we can use the Navier-Stokes equation for an incompressible liquid to find the energy dissipation. The rate of energy dissipation is then given by

$$\frac{dE}{dt} = -16\pi\eta\left(\frac{\Delta\rho}{\rho}\right)^2 R\dot{R}^2, \qquad R \gg l. \tag{7}$$

In this case the drag force F is analogus to the Stokes formula for a sphere.

In the opposite, Knudsen, limit, where the size of the nucleus is much smaller than the mean free path $l(T)$, and the hydrodynamic equations must be abandoned, the energy dissipation is determined with the help of a distribution

function for the excitations in the medium. It is proportional to the surface area of the nucleus:

$$\frac{dE}{dt} = -16\pi\alpha\eta\left(\frac{\Delta\rho}{\rho}\right)^2\frac{R^2}{l}\dot{R}^2, \quad R \ll l. \tag{8}$$

In the case the drag force is no longer dependent on the mean free path $l(T)$, since the viscosity has the behavior $\eta \sim l(T)$. From (7) and (8) we find the form of the function $\mu(R)$ in (6).

We turn now to a quantum-mechanical description of the system. We take the approach pointed out in Refs. 10 and 11 to find the probability for the decay of a metastable state in a system in which there is energy dissipation. The probability for the formation of a nucleus of a new phase is then given to within exponential accuracy by the expression

$$W = \exp(-A), \tag{9}$$

where A is the extreme value of the effective action S_{eff}, specified in terms of an imaginary time:

$$S_{\text{eff}}[R(\tau)] = \int_{-\beta/2}^{\beta/2} d\tau\left[\frac{1}{2}M(R)\dot{R}^2\right.$$

$$\left. + \frac{1}{2}\int_{-\beta/2}^{\beta/2}d\tau'\,\gamma(R_\tau)D(\tau-\tau')\gamma(R_{\tau'})\right], \tag{10}$$

with the periodic boundary conditions $R(-\beta/2) = R(\beta/2)$. Here $\beta = T^{-1}$ is the reciprocal temperature. The first two terms in (10) are the kinetic and potential energies of the system. They are determined unambiguously by the corresponding classical quantities, (2), and (1). The third term arises from the interaction of the collective variable $R(\tau)$ with excitations in the system, which lead in the classical limit to the dissipative term (5). In the limit in which the interaction between the coordinate R and these variables is weak, $D(\tau)$ is the two-particle correlation function of these excitations.[12] The function $D(\tau)$ is an even periodic function with a period of $1/T$:

$$D(\tau) = T\sum_{\omega_n}e^{-i\omega_n\tau}D(\omega_n), \quad \omega_n = 2\pi nT. $$

The function $D(\tau)$ is known[12] to characterize the linear response of the system to an external agent. It can be written as the sum of two terms, one regular and one anomalous:

$$D(\omega_n) = D_{reg}(\omega_n) + D_{an}(\omega_n). \tag{11}$$

The regular term $D_{reg}(\omega_n)$ characterizes the dynamics of the system and can be expanded in squares of the Matsubara frequencies:

$$D_{reg}(\omega_n) = \sum_{k=0}^{\infty}D_{2k}\omega_n^{2k}. \tag{12}$$

The quantities D_0 and D_2 in (12) describe the renormalization of the potential and the mass; they have already been incorporated in the first two terms of the effective action S_{eff} in (10). The quantities D_{2k} with $k \geqslant 2$ in (12) are unimportant, since each term in the series is smaller than the preceding term by a factor of order $(\dot{R}/c)^2$, and the term with D_4 in $(\dot{R}/c)^2$ is already smaller than the term with the kinetic energy of the system.

The anomalous term $D_{an}(\omega_n)$ in (11) characterizes the damping in the system[12] and contains $|\omega_n|$ in addition to ω_n^2 in its expansion. In the limit $(\dot{R}/c)^2 \ll 1$ the leading term in the expansion $D_{an}(\omega_n)$ is

$$D_1(\omega_n) = \eta|\omega_n|, \tag{13}$$

where η is the viscosity of the system.[10,11] This situation corresponds in the τ representation to

$$D_1(\tau) = -\eta\pi T^2\sin^{-2}(\pi T\tau).$$

In the limit of low velocities, $\dot{R} \ll c$, there is accordingly an unambiguous correspondence between the classical problem with dissipation, described by a Lagrangian L and an energy dissipation rate $\dot{E}$ as in (5), and the quantum-mechanical problem, described by an effective action

$$S_{\text{eff}}[R(\tau)] = \int_{-\beta/2}^{\beta/2}d\tau\left\{\frac{1}{2}M(R)\dot{R}^2 + U(R)\right.$$

$$\left. + \frac{\eta}{4\pi}\int_{-\beta/2}^{\beta/2}d\tau'[\gamma(R_\tau)-\gamma(R_{\tau'})]^2\frac{(\pi T)^2}{\sin^2\pi T(\tau-\tau')}\right\}. \tag{14}$$

The quantities γ enter the nonlocal term as a difference between squares, since we have

$$\int_{-\beta/2}^{\beta/2}D_1(\tau)\,d\tau = 0. \tag{15}$$

Equation (15) follows from the circumstance that $D_1(\omega_n)$ in (13) vanishes at zero Matsubara frequency. The quantity $\gamma(R)$ is determined by the classical mobility $\mu(R)$ in accordance with

$$\mu(R) = \eta(\partial\gamma/\partial R)^2. \tag{16}$$

Correspondingly, the functional dependence $\gamma(R)$ is nonlinear in the Knudsen and hydrodynamic limits and is given by

$$\gamma(R) = \begin{cases} 2(\pi\alpha)^{1/2}\dfrac{|\Delta\rho|}{\rho}\dfrac{R^2}{l^{1/2}}, & R \ll l \\[2mm] \dfrac{8\pi^{1/2}}{3}\dfrac{|\Delta\rho|}{\rho}R^{3/2}, & R \gg l \end{cases}. \tag{17}$$

Expressions (17) hold in the case of nucleation in a three-dimensional space. In the general case of a d-dimensional space, expression (6) for the mobility would be replaced by

$$\mu_d(R) = 2(d-1)S_d\eta(\Delta\rho/\rho)^2R^{d-2}f_d(R/l), \tag{6'}$$

which leads to the following expressions for the coefficient γ in the two limiting cases:

$$\gamma_d = \begin{cases} 2[2(d-1)S_d\alpha_d]^{1/2}(|\Delta\rho|/\rho)(d+1)^{-1}R^{(d+1)/2}l^{-1/2}, & R \ll l \\ 2[2(d-1)S_d]^{1/2}(|\Delta\rho|/\rho)d^{-1}R^{d/2}, & R \gg l \end{cases}. \tag{17'}$$

Here S_d is the surface area of a d-dimensional sphere of unit radius. The mass in the d-dimensional space is described by

$$M_d(R) = \frac{S_d}{d-2}\frac{(\Delta\rho)^2}{\rho}R^d. \tag{2'}$$

Expressions (6'), (17'), and (2') can be used (for example)

at $d=2$ to analyze dissipation during the faceting of quantum crystals.[8] In this case we would have

$$M_2(R) = 2\pi \frac{(\Delta\rho)^2}{\rho} R^2 \ln\left(\frac{R}{a}\right),$$

where a is the interatomic distance.

3. CASES OF WEAK AND STRONG DISSIPATION

In the absence of viscosity ($\eta = 0$), the effective action (14) reduces completely to the case of the dissipationless kinetics of the phase transitions which were studied in Ref. 1. It can be seen from (14) that dissipative processes associated with the viscosity, or internal friction, (first) reduce the probability for the tunneling formation of a nucleus by an amount equal to the argument of the exponential function $\sim\mu(R_c)R_c^2$, and (second) cause the argument (A) of the exponential function for the transition probability (9) to become dependent on the temperature, in contrast with the situation in the dissipationless kinetics, where the argument A is completely independent of the temperature in the quantum-mechanical regime.[1]

As in the absence of dissipation, there are in principle two types of trajectories which lead to an extremum of the effective action $S_{eff}[R(\tau)]$ in (14). The first trajectory is a classical trajectory which does not depend on the time τ and which passes through a maximum of the potential energy $U(R)$, given in (1):

$$R(\tau) \equiv R_0 = \tfrac{2}{3}R_c. \tag{18}$$

This trajectory causes the vanishing of both kinetic energy (2), which is proportional to the square of the derivative $\dot{R}(\tau)$, and the dissipative term in the effective action (14). It leads to a classical activation regime with an argument for the exponential function which does not depend on the processes which occur in the medium, being governed exclusively by thermal fluctuations:

$$A(T) = U_0/T, \quad U_0 = \tfrac{4}{27}4\pi\sigma R_c^2, \tag{19}$$

where U_0 is the height of the barrier formed by the potential (1). The second trajectory depends explicitly on the time, and in an analysis of the motion along it is convenient to distinguish between the two characteristic cases of weak and strong dissipation. In the case of weak dissipation, the nonlocal term in (14), which describes dissipation, can be treated as a perturbation. As the trajectory we can take the extremal trajectory which is obtained in the dissipationless regime and which is found from the equation

$$M(R)\dot{R}^2/2 = U(R).$$

This approach leads to the following law of motion along the trajectory:

$$\frac{|\tau(x)|}{\tau_c} = \frac{\pi}{2} - \operatorname{arctg}\left[\left(\frac{x}{1-x}\right)^{1/2}\right] + [x(1-x)]^{1/2},$$
$$x(\tau) = 0, \quad |\tau(x)| > \pi\tau_c/2. \tag{20}$$

Here $x = R/R_c$, and $\tau_c = (|\Delta\rho|/\rho)(\rho R_c^3/2\sigma)^{1/2}$. Substituting $R(\tau)$ according to (20) into (14), we find an extremal action $A(T)$, which can be written in the form

$$A(T) = A_0 + A_1(T). \tag{21}$$

Here A_0 is the value which is found if there is no dissipation in the medium[1]:

$$A_0 = \frac{5\cdot2^{1/2}\pi^2}{16} \frac{|\Delta\rho|}{\rho} (\sigma\rho)^{1/2}R_c^{7/2}. \tag{22}$$

The quantity $A_1(T)$ is determined by the dissipative term in the effective action (14):

$$A_1(T) = \frac{\eta(T)}{4\pi} \int\int_{-\beta/2}^{\beta/2} d\tau\,d\tau' [\gamma(R_\tau) - \gamma(R_{\tau'})]^2 \frac{(\pi T)^2}{\sin^2 \pi T(\tau-\tau')}. \tag{23}$$

The transition from the quantum-mechanical regime (21) to the activation regime (19) occurs at the temperature T_0 determined by the relation

$$A_0 + A_1(T_0) = U_0/T_0. \tag{24}$$

At this point, the argument of the exponential function in the quantum-mechanical regime becomes equal to the argument of the activation exponential function. The temperature T_0 of the transition to the activation regime is lower than that in the dissipationless kinetics by an amount ΔT_0 on the order of $A_1(T_0)/A_0$; the slope of the $A(T)$ curve changes at T_0.

In contrast with problems with a constant mass, in which the time of the motion along the trajectory is infinite,[10] in the problem at hand the extremal trajectory has a finite temporal dimension of $\pi\tau_c$. Since we have $\pi\tau_c T_0 = \tfrac{128}{135} < 1$ according to (20) and (24), expression (23) as a function of the temperature does not depend on the integration limits; i.e., we can write

$$A_1(T) = \frac{\eta(T)}{4\pi} \int\int_{-\pi\tau_c/2}^{\pi\tau_c/2} d\tau\,d\tau' [\gamma(R_\tau) - \gamma(R_{\tau'})]^2 \frac{(\pi T)^2}{\sin^2 \pi T(\tau-\tau')}. \tag{25}$$

In the low-temperature limit $\pi T\tau_c \ll 1$ ($T \ll T_0$), the kernel of the integral in (25) can be expanded:

$$A_1(T) = \eta(T) \int\int_0^{\pi\tau_c/2} d\tau\,d\tau' \frac{[\gamma(R_\tau) - \gamma(R_{\tau'})]^2}{\pi(\tau-\tau')^2}$$
$$+ \frac{1}{3}\eta(T)T^2 \int\int_0^{\pi\tau_c/2} d\tau\,d\tau' [\gamma(R_\tau) - \gamma(R_{\tau'})]^2.$$

The last integral can be evaluated easily; it is

$$2\left\{\frac{\pi\tau_c}{2} \int_0^{R_c} dR\left[\frac{M(R)}{2U(R)}\right]^{1/2}\gamma^2(R) - \left(\int_0^{R_c} dR\left[\frac{M(R)}{2U(R)}\right]^{1/2}\gamma(R)\right)^2\right\}.$$

We introduce the temperature T_l, the temperature at which the mean free path $l(T_l)$ is equal to R_c. In the Knudsen limit, corresponding to temperatures $T \ll T_l$ or $l(T) \gg R_c$, we then have

$$A_1(T) = 4\pi\alpha\left(\frac{\Delta\rho}{\rho}\right)^2 \frac{\eta(T)R_c^4}{l(T)}\left[\frac{J_2}{\pi} + \frac{13}{768}\left(\frac{\pi T\tau_c}{2}\right)^2\right], \tag{26}$$

where

$$J_k = \int\int_0^{\pi/2} d\xi\,d\xi' [(x^k(\xi) - x^k(\xi'))^2/(\xi-\xi')]^2.$$

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Here $\xi = \tau/\tau_c$ is the dimensionless time on the trajectory (20). The quantity J_k is a constant, which depends on none of the physical parameters except the exponent k in expression (17) for $\gamma(R)$. In the Knudsen case we have $k = 2$ and $J_2 = 1.49 \ldots$. In the opposite (hydrodynamic) limit, with $T \gg T_l$ or $l(T) \ll R_c$, we have

$$A_1(T) = \frac{64\pi}{9}\left(\frac{\Delta\rho}{\rho}\right)^2 \eta(T)R_c^3\left[\frac{J_{1/2}}{\pi} + \beta_0(\pi T\tau_c)^2\right],$$

$$\beta_0 = \frac{1}{6}\left(\frac{35\pi^2}{256} - \frac{256}{225}\right) \approx 0.035, \quad J_{1/2} = 3.99\ldots. \quad (27)$$

We turn now to the case of strong dissipation. In this limit the tunneling is determined entirely by the viscous term, and the kinetic energy (2) should be ignored in the effective action. The extremal trajectory is found from the effective action

$$S_{eff}[R(\tau)] = \int_{-\beta/2}^{\beta/2} d\tau\left\{U(R) + \frac{\eta}{4\pi}\int_{-\beta/2}^{\beta/2} d\tau'[\gamma(R_\tau) - \gamma(R_{\tau'})]^2\right.$$

$$\left. \times \frac{(\pi T)^2}{\sin^2\pi T(\tau - \tau')}\right\} \quad (28)$$

with the periodic boundary conditions $R(-\beta/2) = R(\beta/2)$. The argument of the exponential function in (9), $A(T)$, reduces in both the hydrodynamic and Knudsen regimes to a universal function which depends on only a single variable, the temperature in reduced units:

$$A(T) = \eta(T)\gamma^2(R_c)s_k(t). \quad (29)$$

This universal function is related in the following way to the nature of the regime in (17):

$$s_k(t) = \int_{-1/(2t)}^{1/(2t)} d\tau\left[x_\tau^2(1-x_\tau) + \frac{\pi t^2}{4}\int_{-1/(2t)}^{1/(2t)} d\tau'\frac{(x_\tau^k - x_{\tau'}^k)^2}{\sin^2\pi t(\tau - \tau')}\right], \quad (30)$$

where x_τ is the extremal trajectory of functional (30), and k is the exponent in the functional dependence $\gamma(R) \sim R^k$. The reduced temperature t used in (29) is also determined by the particular regime in (17). It is proportional to the ratio of the friction to the height of the potential barrier:

$$t = \frac{1}{27}T\eta\gamma^2(R_c)/U_0. \quad (31)$$

Figure 1 shows $s_k(t)$ as a function of the parameter t for the Knudsen regime ($k = 2$) and the hydrodynamic regime ($k = 3/2$); it is also shown for the case of linear dissipation
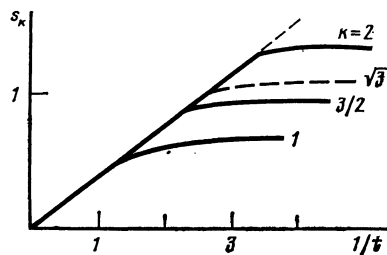

FIG. 1. The reduced effective action s_k versus the dimensionless reciprocal temperature $1/t$. The temperature $t = 4(3/2)^{k-2}/\pi k^2$ is the point of an absolute instability of the classical trajectory.

($k = 1$), in which case an exact solution has been found.[11] At low temperatures ($T < T_l$) there is a Knudsen regime, since the mean free path l increases without bound as $T \to 0$. At temperatures $T \gtrsim T_l$, the regime changes to hydrodynamic. This change occurs if the temperature of the transition to the classical regime satisfies $T_0 \gtrsim T_l$. If, on the other hand, we have $T_0 \lesssim T_l$, then the Knudsen regime persists to the temperature T_0.

In the strong-dissipation regime, the temperature T_0 found by equating the argument of the quantum-mechanical exponential function in (29), $A(T)$, to the argument on the classical trajectory (19), is found from the solution of the equation

$$t_0 s_k(t_0) = \frac{1}{27}, \quad t_0 = \frac{1}{27}T_0\eta\gamma^2(R_c)/U_0. \quad (32)$$

The index here is $k = 2$ if $T_0 < T_l$. For $T_0 > T_l$ we have $k = 3/2$. At large values of $t > t_0$, the classical trajectory (18) is extremal. At $t = t_0$ (this value depends on the index k), there is a transition to the quantum-mechanical trajectory. To study the stability of classical trajectory (18) with respect to small fluctuations, we expand the effective action $S_{eff}(R(\tau))$ around the classical trajectory R_0:

$$R(\tau) = R_0 + x(\tau). \quad (33)$$

We retain terms of up to fourth order in $x(\tau)$:

$$S_{eff} = \beta U_0 + \int_{-\beta/2}^{\beta/2} d\tau\left[\frac{1}{2}M_0\dot{x}^2 + \frac{1}{2}U_0''x^2\right.$$

$$\left. + \frac{1}{2}\gamma_0'^2\int d\tau' x_\tau D(\tau-\tau')x_{\tau'}\right]$$

$$+ \int_{-\beta/2}^{\beta/2} d\tau\left[\frac{1}{2}M_0'x\dot{x}^2 + \frac{1}{6}U_0'''x^3\right.$$

$$\left. + \frac{1}{2}\gamma_0'\gamma_0''\int d\tau' x_\tau^2 D(\tau-\tau')x_{\tau'}\right]$$

$$+ \int_{-\beta/2}^{\beta/2} d\tau\left[\frac{M_0''}{4}x^2\dot{x}^2 + \frac{U^{(IV)}}{24}x^4 + \frac{\gamma_0''^2}{8}\int d\tau' x_\tau^2 D(\tau-\tau')x_{\tau'}^2\right.$$

$$\left. + \frac{\gamma_0'\gamma_0'''}{6}\int d\tau' x_\tau^3 D(\tau-\tau')x_{\tau'}\right].$$

The expansion for $U(R)$ does not contain a term with the first derivative, since the trajectory R_0 passes through a maximum of the potential. For the same reason, we have $U''(R_0) < 0$. We switch to the Fourier representation:

$$x(\tau) = T\sum_{\omega_n} x_n e^{-i\omega_n\tau}, \quad x_n^* = x_{-n}, \quad \omega_n = 2\pi Tn. \quad (34)$$

We can then write

$$S_{eff} = \beta U_0 + \frac{1}{2}\sum_n \alpha_n x_n x_{-n} + \frac{1}{2}\sum_{m,n} B_{mn} x_n x_m x_{-(m+n)}$$

$$+ \frac{1}{2}\sum_{m,n,l} C_{mnl} x_n x_m x_l x_{-(m+n+l)},$$

$$\alpha_n = T(M_0\omega_n^2 + \mu_0|\omega_n| - |U_0''|), \quad \mu_0 = \eta\gamma_0'^2,$$

$$B_{nm} = T^2(-M_0'\omega_n\omega_m + \eta\gamma_0'\gamma_0''|\omega_{n+m}| + U_0'''/3), \quad (35)$$

$$C_{nml} = T^3\left(-\frac{1}{2}M_0''\omega_n\omega_m + \frac{1}{4}\eta\gamma_0''^2|\omega_{n+m}|\right.$$

$$\left. + \frac{1}{3}\eta\gamma_0'\gamma_0'''|\omega_{n+m+l}| + \frac{U_0^{(IV)}}{12}\right).$$

At high temperatures all the coefficients of the quadratic terms, α_n $(n \neq 0)$, are positive. The only exception is $\alpha_0 = - |U_0''| < 0$. As has been shown elsewhere,[3] however, a negative value of α_0 does not imply that the trajectory $R(\tau)$ in (18) is unstable with respect to fluctuations x_0. The fact is that we can assume at a purely formal level that the coefficient $C_{000} = U_0^{(IV)}/12$ is positive in the expansion (35). The term $C_{000}x_0^4 > 0$ then stabilizes the trajectory, since at large values of x_0 we have $\alpha_0 x_0^2 + C_{000}x_0^4 > 0$. To calculate the fluctuational contribution from x_0 it is sufficient to displace the contour of the integration over x_0 into the complex plane, onto the imaginary axis. When we then let C_{000} go to zero, we find that the result is totally independent of C_{000} and is determined by the analytic continuation of the quantities to the imaginary axis.

As the temperature is lowered, the coefficients $\alpha_{\pm 1}$ vanish at $T = T_1$:

$$T_1 = [-\mu_0 + (\mu_0^2 + 4M_0|U_0''|)^{1/2}]/(4\pi M_0), \quad \alpha_{\pm 1}(T_1) = 0. \quad (36)$$

Below the temperature T_1, the classical trajectory (18) becomes absolutely unstable with respect to fluctuations of the mode $x_{\pm 1}$. There are two ways to make a transition from the classical trajectory to the quantum-mechanical regime, continuous and discontinuous. The nature of the transition depends on the sign of the coefficient of $x_{\pm 1}^4$ in expression (35) for the effective action S_{eff}. If this coefficient is positive, the transition will be continuous. If the coefficient is negative, the transition to the quantum-mechanical regime is discontinuous. To find the coefficient of $x_{\pm 1}^4$ at the point $T = T_1$ we need to consider, along with the fluctuations of $x_{\pm 1}$, fluctuations of the modes x_0 and $x_{\pm 2}$. All of the other modes x_n with $|n| \geqslant 3$ contribute in the limit $T \to T_1$ to terms with powers higher than $|x_{\pm 1}|^4$. Near $T = T_1$, the effective action (35) thus takes the form

$$S_{eff} = \beta U_0 + \frac{1}{2}\alpha_0 x_0^2 + \alpha_1|x_1|^2 + \alpha_2|x_2|^2 + B_0|x_1|^2 x_0$$
$$+ B(x_1^2 x_{-2} + x_{-1}^2 x_2) + C|x_1|^4, \quad (37)$$

$$B_0 = 2B_{10} + B_{1,-1}, \quad B = B_{1,-2} + B_{11}/2, \quad C = C_{1,1,-1} + 2C_{-111}.$$

A minimization of (37) with respect to x_0 and $x_{\mp 2}$ leads to an effective action which depends only on the mode $x_{\pm 1}$:

$$S_{eff} = \beta U_0 + \alpha_1|x_1|^2 + D|x_1|^4, \quad D = C - B^2/\alpha_2 - B_0^2/(2\alpha_0). \quad (38)$$

If $D < 0$, the action is absolutely unstable below the temperature $T = T_1$, and the transition occurs discontinuously, with finite (nonzero) components $x_{\pm 1}$. For $D > 0$, the action undergoes a continuous change from the value $x_1 = 0$ to the value $|x_1| = -\alpha_1/(2D) > 0$.

The nature of the transition can be seen easily in two limiting cases. In the dissipationless case, with $D = \frac{7}{12}T^3 U_0''/R_0 < 0$, the transition from the classical activation trajectory to the quantum-mechanical trajectory occurs discontinuously. In the case of strong dissipation we have $D = \frac{1}{2}T^3 U_0''(k^2 - d 3)/R_0^2$, where k is the exponent in the functional dependence $\gamma(R) \sim R^k$ in (17). In the hydrodynamic limit we have $k = 3/2$ and $D > 0$. The transition thus occurs continuously. In the Knudsen case we have $k = 2$ and $D < 0$, and the transition is discontinuous. In this case there is a change in the slope of the $s_2(t)$ curve (Fig. 1). The exponent $k_0 = 3^{1/2}$ is a critical value. For $k < k_0$, the transition from the classical trajectory to the quantum-me-

chanical trajectory is continuous. For $k > k_0$, the $s_k(t)$ curve undergoes a change in slope, and the transition occurs not at the point t_1, determined by $T_1 = |U_0''|/2\pi\mu_0$ in (36) but slightly earlier, at the point $t_0 > t_1$ [see (32)]. Figure 1 shows the curve $s_3^{1/2}(t)$ which separates these two regions of the parameter k.

In the hydrodynamic regime we have $A = U_0/T$ above T_0, and below it we have

$$A = \frac{U_0}{T} - \frac{\pi}{19T\sigma}\left[16\pi\left(\frac{\Delta\rho}{\rho}\right)^2 R_0^2\right]^2 (T_0\eta(T_0) - T\eta(T))^2;$$

i.e., the derivative $\partial A/\partial T$ is continuous, but, as in the case of a linear dissipation,[11] there is a discontinuity in the second derivative, $\partial^2 A/\partial T^2$. As the temperature is lowered, $A(T)$ increases, along with the viscosity of the medium.

4. OVERALL PICTURE OF NUCLEATION IN A SYSTEM WITH DISSIPATION; POSSIBILITY OF OBSERVING IT EXPERIMENTALLY

Figure 2 shows the typical behavior of the formation energy of a stable-phase nucleus of radius R in a homogeneous metastable system. The behavior $U(R)$ at large radii is proportional to the volume of the nucleus and is related to the extent to which the stable phase is preferred energetically to the metastable phase, because of the difference in the chemical potentials of the two phases. At small values of R, the value of $U(R)$ is determined by the surface tension σ which arises at the interface between the two phases. The competition between these two components determines the basic parameters of the potential energy: the barrier height U_0 and the size of a critical nucleus, R_c. At high temperatures, the probability for a transition of the system is proportional to the activation exponential function $\exp(-U_0/T)$, which stems from the finite probability for the system to be in an excited level with an energy U_0 at a high temperature. As the temperature is lowered, the argument of this exponential function, U_0/T increases rapidly, and at T_0 another process becomes predominant: the tunneling of a nucleus from a zero energy level through the barrier. The decay of the metastable system as a result of the quantum-mechanical motion of the nucleus through the barrier differs substantially from the activation decay. In this case the probability for the decay is determined not only by the potential energy but also by the kinetic energy. The argument of the exponential function in this case is equal to the Euclidean action
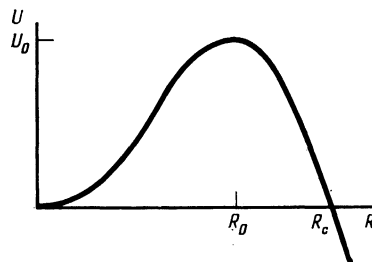
$$S_E = 2\int_0^{R_c} [2M(R)U(R)]^{1/2} dR.$$

FIG.2.

Equating S_E to the arugment of the activation exponential function, we find the characteristic temperature T_0 for a transition from the activation regime to the quantum-mechanical regime.

As the nucleus grows, the energy of its interaction with its surroundings comes into play, in addition to its potential energy and its kinetic energy. The growth of the nucleus causes a nonequilibrium perturbation of the medium. The relaxation of the medium to a homogeneous equilibrium state is accompanied by a dissipation of the energy of the nucleus. This energy dissipation vanishes at a zero growth velocity of the nucleus; along with the kinetic energy, it characterizes the motion of the nucleus through the barrier. Specifically, it retards the transition of the nucleus, i.e., effectively increases the mass of the nucleus. Despite this analogy, the dissipation of energy is fundamentally different from the kinetic energy. The tunneling violates conservation of energy, which is transferred to other degreees of freedom, associated with the medium.

While the probability for a transition in the case of macroscopic quantum-mechanical tunneling in the absence of dissipation is essentially independent of the temperature, tunneling with dissipation depends strongly on the temperature. The reason is that, in contrast with the thermodynamic properties (the density, the surface tension, and the difference betweeen chemical potentials), which characterize the decay in the dissipationless case and which depend only weakly on the temperature as $T \to 0$, the dissipation of energy depends on kinetic properties, in particular, the mean free path of the excitations, $l(T)$, which depends strongly on the temperature and which diverges as $T \to 0$. For Fermi excitations, whose number falls off in proportion to T, we have $l(T) \sim T^{-2}$. For the Bose branches of excitations, the temperature dependence of the mean free path is much stronger. Depending on the particular scattering mechanism, one of several temperature dependences may hold[12,13]: a power law $l(T) \sim T^{-n}$ with a power $n = 5$ or 9, or an exponential law $l(T) \sim e^{\Delta/T}$ ($\Delta \sim \omega_D$, where ω_D is the Debye frequency).

As long as $l(T)$ is not too large ($l < R_c$), we can take the hydrodynamic approach, and the viscosity[12] $\eta \sim \rho v l$ increases with increasing mean free path. As a result, the basic temperature dependence in the argument of the exponential function stems from the dependence $\eta(T)$. In addition to this dependence on T, there is another one, which stems from the particular nature of the extremal trajectory $R(\tau)$: expressions (27) and (29) and Fig. 1 ($k = 3/2$), respectively, in the cases of weak and strong dissipation. At a certain temperature $T_l(R_c)$ the mean free path $l(T)$ becomes equal to R_c, and in the limit $l(T \gg R_c)$ the argument of the exponential function acquires a quantity $\eta/l \sim \rho v$, which does not depend on the mean free path. For various types of excitations, this quantity has very different temperature dependences. For Fermi excitations, ρv is essentially independent of the temperature. For excitations of the Bose type, ρv depends strongly on the temperature and varies with the particular type of dispersion of the excitations. For phonons, for example, we find $\rho v \sim T^4/c^2$. When excitations of several types are involved, ρv has a complicated temperature dependence. The nature of the extremal trajectory also contributes an additional temperature dependence: expressions (26) and (29) and Fig. 1 ($k = 2$), respectively, in the cases of weak and strong dissipation. Consequently, when dissipa-
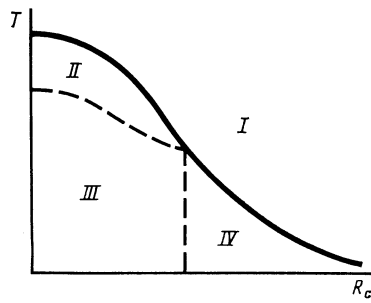

FIG. 3. Phase diagrams of nucleation regimes in the plane of the temperature and the critical size. I—Activation regimes; II—quantum-mechanical, weakly dissipative hydrodynamic limit; III—quantum-mechanical, weakly dissipative Knudsen regime; IV—quantum-mechanical Knudsen regime.

tion is present the argument of the exponential function will have a significant temperature dependence, because of the dependence of η or $\eta/l \sim \rho/v$ on T. In this case there exists a characteristic temperature T_l (at which $l = R_c$), at which a transition occurs from one temperature dependence (which holds in the hydrodynamic regime) to another one (which holds in the Knudsen regime). Figure 3 shows a typical phase diagram of the various decay regimes.

The primary difficulty which arises in planning an experiment to study the kinetics of the decay of a metastable system is the very sharp dependence of the decay probability on the size of the critical nucleus, R_c. Specifically, the probability for nucleation contains, in addition to an exponential function, a large factor which multiplies the exponential function:

$$W_0 = \sim \omega_D V (4\pi R_c^3/3)^{-1}$$

(V is the volume of the system). For a system with $N \sim 10^{21}$ particles, for $\omega_D \sim 10^{13}$ s^{-1}, and for $R_c \sim a$, we would have $W_0 \sim e^{80}$ s^{-1}. If the typical observtion times are to be on the order of a second or an hour, the argument of the exponential function would have to be $A \approx 80$. A deviation by no more than 10% from this value of A would change the characteristic observation time by four orders of magnitude. Here we need to note that the value of A depends nonlinearly on R_c: $A \sim R_c^n$ $n = 2 - 4$). As a result, the tolerable variation in R_c would be no more than 2–3%. A change in R_c by, say, a factor of 1.5 would lead to a catastrophic change in the observation time, in either direction. One way out of this difficulty might be a dynamic (time-dependent) form of the experiment. By gradually increasing the supercooling of the system, we could go from relatively large values of R_c to relatively small values, and at the instant at which the argument A becomes comparable to the factor multiplying the exponential function there would be a transition. In this case we would naturally have $R_c \gg a$, and we would remain in the region within which the theory is applicable at all times. We wish to stress the problem which we have outlined here is not peculiar to quantum-mechanical tunneling. It also occurs in a classical situation. A 10% change in the temperature in the activation regime changes the decay probability by four orders of magnitude. Another possibility for overcoming this difficulty is to use microscopic particles with $N \sim 10^{10}$ atoms to analyze the nucleation process. This approach would soften these functional dependences greatly. The same com-

ments apply to a study of phase transitions on a surface, since in this case the number of nucleation centers is reduced from N to $N^{2/3}$.

Finally, we note that dissipation not only has a strong effect on the coefficient of the exponential function during nucleation but also has a fundamental effect on the coefficient of the exponential function. In the absence of dissipation, this coefficient contains the characteristic oscillation frequency ω_0 in the potential $U(R)$ (Fig. 2). When there is a strong dissipation, ω_0 is replaced by the quantity $\sim \omega_0^2/\eta$, where η is a measure of the damping in the system. While ω_0 does not depend on the temperature, η does, and strongly, because of $l(T)$. Accordingly, even in the region of the activation exponential function there will be a change in the temperature dependence of the nucleation probability because of the coefficient of the exponential function.

We wish to thank Yu. Kagan for many discussions of questions pertaining to the formulation of this problem. We are deeply indebted to K. A. Kikoin, A. N. Kozlov, L. A. Maksimov, N. V. Prokof'ev, and the participants of a seminar on macroscopic quantum-mechanical tunneling led by A. R. Larkin for their interest in this study and for discussion.

APPENDIX

Substituting velocity distribution (3) into the energy-dissipation expression[14]

$$\dot{E} = -\frac{\eta}{2} \int \left(\frac{\partial v_i}{\partial x_k} + \frac{\partial v_k}{\partial x_i} \right)^2 d^3r,$$

we find (7).

As the mean free path l increases, and it becomes comparable to the characteristics radius of the nucleus, R_c, the hydrodynamic equations break down, and we are forced to solve the kinetic equation under certain boundary conditions which characterize the interaction of the gas of excitations with the surface. In the Knudsen limit, in which collisions are rare ($l \gg R_c$), the problem simplifies substantially, since the excitations which have collided with the surface relax in the medium itself, in a process independent of the presence of the nucleus. In this case the rate of energy dissipation can be written in the form $\dot{E} = \oint F v \, df$. The integration here is over the surface of the nucleus, and F is the force associated with the motion of the gas of excitations in the metastable liquid with respect to the nucleus. This force is determined by the momentum flux which is transferred from the gas of excitations to the nucleus, and it is proportional to the magnitude of the velocity: $F_i = \theta_{ik} v_k$. The coefficient θ_{ik} depends only on the properties of the gas of excitations and the nature of the reflections of the excitations from the surface of the nucleus. Under the assumption that the excitations scattered by the solid wall have time to reach a complete thermodynamic equilibrium with the wall, which is moving at a velocity $\dot{R}$, we find $\theta_n = \frac{77}{120} \rho^* v_F$ by analogy with Ref. 13 (θ_n is the normal component of the tensor θ_{ik}). For Fermi excitations we would have $\rho^* = \rho m^*/m$, where m^* is the effective mass, and v_F is the Fermi velocity. For photon branches of the spectrum, the relation for θ_n continues to hold, but ρ^* becomes ρ_n, the density of phonon excitations, and v_F becomes the sound velocity c. Substituting the velocity distribution (3) with $r = R_c$ into these expressions, we find expression (8) for the energy dissipation, where the coefficient α is expressed in terms of the normal component of the tensor θ_{ik} alone, and it depends only on the properties of the gas of excitations and the accommodation coefficient, which reflects the extent to which the collisions of excitations with the nucleus are inelastic. The dissipation rate does not depend on the mean free path l; it is proportional to the quantity $(\Delta \rho/\rho)^2$.

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Translated by Dave Parsons