Tunneling in an anharmonic liquid

Yu. I. Dakhnovskiĭ and V. V. Nefedova

Institute of Chemical Physics, USSR Academy of Sciences

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We consider quantum-mechanical tunneling of particles in a liquid. We obtain a single-instanton approximation for the tunneling rate in an arbitrary potential, when the motion of the molecules of the medium is classical. An interaction of the particle with the medium is specified by an arbitrary, generally non-bilinear function of the coordinates of the particle and of the medium. Particle tunneling in a "two-parabola" potential that interacts bilinearly with the medium is considered by way of example. The medium is described by a fourth-degree anharmonic potential. It is shown that, depending on the sign of the anharmonicity parameter, the tunneling rate is increased or decreased by many orders of magnitude.

1. INTRODUCTION

Tunneling is one of the main phenomena that prove the quantum-mechanical laws of motion of macroscopic particles. Interest in this phenomenon has increased considerably in the last decade in view of a new possibility of theoretically describing instantons on the basis of an ideal gas.[1-3] The lifetime of the metastable state was calculated for many different phenomena: tunneling of a macroscopic superconducting flux in a Josephson junction,[4-8] tunneling in a metal and the heavy-fermion problem,[9-11] the theory of chemical reactions,[12-14] crystal-growth dynamics,[15] electron or exciton self-trapping,[16,17] and the general theory of tunneling of a particle that interacts with a harmonic medium.[18-22] In all these papers (and the list is far from complete) it was assumed that the tunneling particle interacts with a harmonic medium. The number of tunneling processes in a liquid, however, is large. They include chemical tunneling reactions with transport of one or two protons (or hydrogen atoms) in various solvents.[23-30] Tunneling of a particle in a high-temperature harmonic medium with bilinear coupling of the particle and medium coordinates was considered in Refs. 31 and 32, where the transport rate was obtained for an arbitrary tunneling potential. However, a liquid can not always be represented as a set of harmonic oscillations (except for polar modes in the linear-response approximation[32]). Moreover, it is frequently impossible to separate in an anharmonic medium even the modes of the anharmonic oscillations. When a molecule of the medium is far from the tunneling center, farther than the tunneling length, the interaction potential of the particle with the medium no longer has the usual bilinear form. In fact, a molecule in the immediate vicinity of the tunnel system is close-by, and the particle interaction potential cannot be expanded in quadratic terms (bilinear interaction). It is necessary to use the complete function of the interaction term. The question of which is the stronger interaction, that with the remote continuum or with the nearest surrounding, depends on the specific tunnel system.

In this paper we consider all these question for a classical liquid, i.e., when all the oscillations (even the anharmonic) satisfy the condition

$$\omega_\alpha\beta\ll 1, \tag{1}$$

where ω_α are the characteristic oscillation frequencies of the medium molecules and $\beta = \hbar/kT$ is the reciprocal temperature. We assume hereafter that tunneling in a one-dimensional potential $V(q)$ is well described either in the one-instanton or in the quasiclassical approximation. Moreover, the tunneling transport of a particle interacting with a medium will also be considered in the one-instanton approximation. In this approximation the tunneling probability Γ is characterized by the instanton action S_B:

$$\Gamma=A\exp(-S_B/\hbar), \tag{2}$$

where A is the factor preceding the exponential. We are interested only in the quasiclassical exponential function, i.e., the quantity S_B and will postpone the calculation of A to the future.

We describe liquids by a potential $U(\mathbf{Q}_\alpha)$, which we assume known, say from quantum mechanical calculations. The vector $\mathbf{Q} = (Q_1,\ldots,Q_N)$ is the coordinate vector of all the degrees of freedom of the molecules of the medium. As already noted, the potential $U(\mathbf{Q})$ cannot always be represented in the form $U(\mathbf{Q}) = \Sigma_\alpha U_\alpha(Q_\alpha)$, i.e., as a sum over all modes. The formalism for the calculation of the single-instanton action will be described later. In Sec. 3 we consider an example with a very simple tunnel potential—the "two-parabola potential." The interaction potential is chosen to be bilinear. The medium is regarded as anharmonic, divided into modes with a fourth-degree anharmonic potential. The instanton action is determined numerically and we find its dependences on the coupling to the medium, on the temperature, and on the anharmonicity parameter.

2. THE FORMALISM

We choose the quasiclassical action of the tunnel system in the medium to be of the form

$$S_E=\int_{\beta/2}^{\beta/2} dt\left[\frac{M\dot{q}^2}{2}+V(q)-F(q,\mathbf{Q})+\sum_\alpha\frac{m_\alpha\dot{Q}_\alpha{}^2}{2}+U(\mathbf{Q})\right], \tag{3}$$

where m_α is the mass of the molecule of the medium, M is the mass of the particle, and $F(q, \mathbf{Q})$ is the potential of the interaction of the particle and the solvent molecule. The potential surface of a high-temperature medium depends not on the

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trajectory $\mathbf{Q}(t)$, but on the time-independent position $\mathbf{Q}$. Integration over the kinetic energy of the medium yields the coefficient of the exponential. We can then rewrite (3) in the form

$$S_E=\int_{\beta/2}^{\beta/2} dt\left[\frac{M\dot{q}^2}{2}+V(q)-F(q,\mathbf{Q})\right]+U(\mathbf{Q})\beta. \tag{4}$$

Since the characteristic time of motion in a quantum degree of freedom is much shorter than that of motion in a classical one, the tunneling can be regarded as ordinary one-dimensional tunneling in a static field of a fluid with configuration $\mathbf{Q}$. In the one-instanton approximation the tunneling probability is determined by the trajectory (instanton) from the following equation of motion:

$$\delta S/\delta q=0, \tag{5a}$$

or

$$-M\ddot{q}+\frac{\partial V}{\partial q}-\frac{\partial F(q,\mathbf{Q})}{\partial q}=0. \tag{5b}$$

This equation can be easily solve by introducing the integral of motion—the "energy"

$$E=-\frac{M\dot{q}^2}{2}+V(q)-F(q,\mathbf{Q})=0. \tag{6}$$

Since $dE/dt=0$, a trajectory described by Eq. (5b) can be found to be

$$t_E=\int_{q_A}^{q} dq\left[\frac{2}{M}(V(q)-F(q,\mathbf{Q})-E)\right]^{-1/2}. \tag{7a}$$

The condition for the periodicity of the trajectory $q(t)$ having a period β takes the form

$$\beta=2\int_{q_A}^{q_B} dq\left[\frac{2}{M}(V(q)-F(q,\mathbf{Q})-E)\right]^{-1/2}, \tag{7b}$$

where q_A and q_B are turning points obtained from the condition that the deominator of the integrand be zero. Note the last equation determines the particle "energy" at a fixed temperature β. The instanton action is obtained by substituting the trajectories (7a) and (7b) in expression (4) for the action:

$$S_B[\mathbf{Q}]=2\int_{q_A}^{q_B} dq\{2M[(V(q)-F(q,\mathbf{Q})-E(\mathbf{Q})]\}^{-1/2}+E(\mathbf{Q})\beta+U(\mathbf{Q})\beta. \tag{8}$$

The largest contribution to the tunneling probability is made by a trajectory with configuration of the molecules of the medium; this configuration is obtained from the equations

$$\partial S_B[\mathbf{Q}]/\partial Q_\alpha|_{Q_\alpha=Q_{\alpha\,\min}}=0,\quad \alpha=1,\ldots,N. \tag{9}$$

Such a configuration determines the smallest of all the actions $S_B[\mathbf{Q}]$.

Equations (7)–(9) thus determine the action of a particle tunneling in a potential $V(q)$, with arbitrary interaction $F(q,\mathbf{Q})$ with the medium described by an arbitrary energy surface $U(\mathbf{Q})$ in which, as mentioned in the Introduction, the modes need not be separated. In the general case these transcendental equations cannot be solved analytically, but must be solved numerically.

3. INFLUENCE OF THE ANHARMONICITY OF THE MEDIUM ON THE TUNNELING RATE

Consider tunneling in a specific potential—the "two parabola" potential:

$$V(q)=\frac{M^2\omega_0}{2}q^2\theta(q_0-q)+\left[\frac{M\omega_0^2}{2}(q-q_0)^2-\Delta I\right]\theta(q-q_0). \tag{10}$$

Here ω_0 is the frequency of the oscillations in the well, and $\Delta I=\frac{1}{2}M\omega_0^2(q_1^2-q_0^2)$ is the energy difference between the initial and final positions (see Fig. 1).

We choose the ineraction energy to be that of the usual bilinear interaction

$$F(q,\mathbf{Q})=q\sum_\alpha C_\alpha Q_\alpha. \tag{11}$$

The potential energy of the medium is an anharmonic oscillator of fourth degree (we neglect the interaction between the modes):

$$U(\mathbf{Q})=\sum_\alpha\left(\frac{m_\alpha\omega_\alpha^2Q_\alpha^2}{2}+\frac{a_\alpha Q_\alpha^4}{4}\right). \tag{12}$$

The parameter a_α can be either positive or negative. The instanton action takes then the form

$$S_B[Q_\alpha]=\frac{M\omega_0(q_1+q_0)^2}{2}[1-\alpha-x+(\alpha+x)\ln(\alpha+x)]-\frac{M\omega_0^2}{8}(q_0+q_1)^2x\beta\mp\sum_\alpha\left(\frac{m_\alpha\omega_\alpha^2Q_\alpha^2}{2}+\frac{a_\alpha Q_\alpha^4}{4}\right)\beta. \tag{13}$$

It was assumed in the derivation of (13) that the tunneling takes place at zero temperature, i.e., $\omega_0\beta\gg1$, whereas the opposite inequality $\omega_0\beta\ll1$ holds for the oscillators of the medium. The latter inequality is well satisfied at room temperature in the case of charge transport in a polar solvent, where the frequencies of the polar oscillations are of the order of 10 cm^{-1}.

We have introduced in (13) the dimensionless parameter

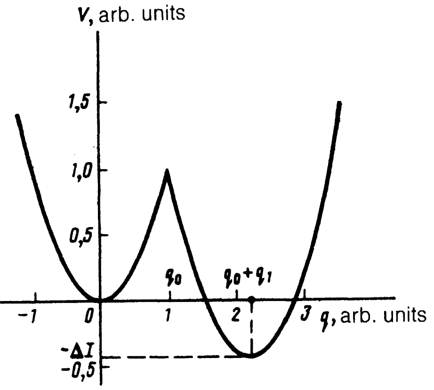

FIG. 1. Tunneling potential $V(q)$; 0 and q_0+q_1 are the equilibrium positions of the particle in the wells of the initial and final states; q_0—barrier position; ΔI—difference between the energies in the final and initial states.

$$x=2\sum_{\alpha}C_{\alpha}Q_{\alpha}/M\omega_0^2(q_0+q_1). \tag{14}$$

The tunneling energy E_0 is equal to

$$E_0={}^1/_8M\omega_0^2(q_0+q_1)^2x^2. \tag{15}$$

The potential-asymmetry parameter α is given by

$$\alpha=(q_1-q_0)/(q_1+q_0). \tag{16}$$

The optimal configuration determined by the general equation (9) is obtained in a specific case from the condition

$$a_{\alpha}Q_{\alpha}^3+m_{\alpha}\omega_{\alpha}^2Q_{\alpha}={}^1/_2C_{\alpha}(q_1+q_0)\,[x-(2/\omega_0\beta)\ln(\alpha+x)\,]. \tag{17}$$

This equation for $Q_{\alpha}(x)$ can be solved. Substituting $Q_{\alpha}(x)$ in the definition (14), we obtain the parameter x that determines $Q_{\alpha\,\min}$ via expression (17). This entire procedure leads to a complicated transcendental equation for x, which can be solved only numerically. The procedure in this case is the following: we assume that in the tunnel process the strongest interaction is that with the immediate environment, i.e., interaction with six molecules equidistant from the metastable system. We assume that the coupling constant C_{α}, the oscillation frequencies ω_{α}, and the mass m_{α} are independent of the index α. Then

$$Q=M\omega_0^2(q_0+q_1)x/12C. \tag{18}$$

Equation (17) can be rewritten in the form

$$\tilde{a}x^3+x(1-B)B=-(2B^2/\omega_0\beta)\ \ln\ (\alpha+x), \tag{19}$$

which contains the dimensionless parameter

$$\tilde{a}=a(q_0+q_1)^2M\omega_0^2/12m\omega^2. \tag{20}$$

We also introduce a parameter B indicative of the interaction of the particle with the medium:

$$B=\sum_{\alpha}\frac{C_{\alpha}^2}{m_{\alpha}\omega_{\alpha}^2}\Big/ M\omega_0^2. \tag{21}$$

In a polar solvent, according to Ref. 30,

$$B=E_c/E_q, \tag{22}$$

where E_c is the energy of relaxation (reorganization) of the polar medium. In the linear-response approximation this energy is given by[33]

$$E_c=\frac{1}{8\pi^2}\sum_{\mathbf{k}}|\Delta\mathbf{D}_{\mathbf{k}}|^2\int_{-\infty}^{\infty}\frac{d\omega}{\omega}\frac{\operatorname{Im}\varepsilon(\mathbf{k},\omega)}{|\varepsilon(\mathbf{k},\omega)|^2}, \tag{23}$$

$\Delta\mathbf{D}_{\mathbf{k}}$ is the difference between the induction vectors in the final and initial states, $\varepsilon(\mathbf{k},\omega)$ is the complex dielectric constant of the liquid, and

$$E_q={}^1/_2M\omega_0^2(q_0+q_1)^2 \tag{24}$$

is the energy of the relaxation along the tunnel coordinate.

Solving (19) numerically and substituting the solution in expression (13) for the action we obtain the one-instanton action for different values of the parameter.

Figure 2 shows how the normalized negative increment to the action S_1/S_0 depends on the coupling parameter B. We define S_1 as

$$S_B/S_0=1-S_1/S_0, \tag{25}$$

where S_0 is the action due to tunneling through a one-dimensional barrier if there is no interaction with the medium. Consequently S_1 is the increment that results from the interaction with the liquid:

$$S_0=M\omega_0(q_0+q_1)^2[1-\alpha+\alpha\ln\alpha]. \tag{26}$$

It is seen from Fig. 2 that S_1/S_0 increases as a function of B at various values of the anharmonicity parameter a. An increase of S_1/S_0 leads to a decrease of S_B/S_0, i.e., to an increase of the tunneling constant, as noted in Refs. 34–36. This increase is due to the lowering of the tunneling barrier by the interaction with the medium. The barrier lowering, however, is accompanied by an increase of the potential energy of the liquid on account of the shift of the equilibrium position. The optimal configuration is determined by Eq. (19).

It is important to study the influence of the anharmonicity of the medium on the value of the one-instanton action. For $B=0.75$ and $\omega_0\beta=15$ (this value of the frequency ω_0 corresponds to the oscillation frequency 3000 cm^{-1} of the C—H bond) Fig. 3 shows the dependence of S_1/S_0 on a. It can be seen that for negative a the ratio S_1/S_0 becomes quite large, owing to the effective decrease of the solvent-molecule oscillation frequencies. For $a>0$ the frequencies become harder; this leads to deeper tunneling and decreases the transport-rate constant.

An important characteristic of tunneling is the dependence on the temperature. In studies of tunnel processes in a liquid the temperature must not be varied strongly, since the solvent can undergo a phase transition into a solid or a gas. The parameter $\omega_0\beta$ can therefore be changed significantly by changing the frequency ω_0; for the C—N bond, for example, $\omega_0=1000$ cm^{-1} ($\omega_0\beta=5$). Figure 4 shows the temperature dependence of S_1/S_0. When the temperature T is raised ($\omega_0\beta$ is decreased) S_1/S_0 decreases, i.e., the tunneling velocity increases. Note that the polarity of the medium B influences considerably the value of S_1/S_0 at different temperatures. The greatest influence occurs at high temperatures, as shown in Fig. 5.

4. CONCLUSIONS

We have considered tunneling, in a potential $V(q)$, by a particle related to a liquid by an arbitrary function $F(q,\mathbf{Q})$ in

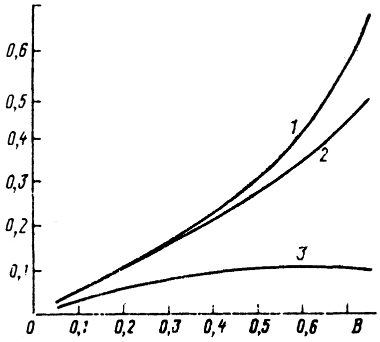

FIG. 2. Plots of S_1/S_0 vs the interaction parameter B at $\omega_0\beta=15$, $\alpha=0.1$, $a=-0.2$ (curve *1*), $a=0$ (*2*), $a=3$ (*3*).

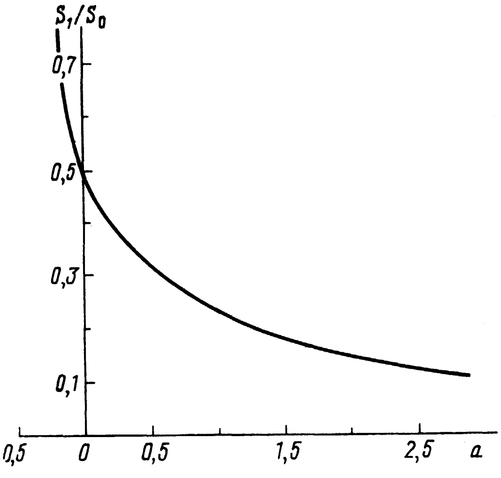

FIG. 3. S_1/S_0 as a function of the liquid anharmonicity parameter a at $B = 0.75$, $\omega_0\beta = 15$, $\alpha = 0.1$.

a potential $V(q)$. The liquid is described by an arbitrary surface potential energy $U(\mathbf{Q})$. All the molecule motions in the liquid are classical.

We obtained the one-instanton action, determined by a system of transcendental equations that can be solved numerically. Our aim here was to investigate the influence of the anharmonicity of the oscillations of the molecules of the medium on the transition rate. We chose for this purpose the simplest tunneling-potential model—the "two-parabola" potential. The particle is bilinearly coupled with the coordinates of the medium, and the potential energy of the material-particle oscillations is a fourth-degree parabola.

We have shown that a positive value of the anharmonicity parameter a leads to a decrease of S_1/S_0—to a negative addition to the action, i.e., to a decrease of the tunneling speed. The probability of the tunnel transition increases for a negative anharmonicity ($a < 0$) (see Fig. 3). This is due to the effective "softening" of the oscillations of the medium. In fact, if the interaction of the particle with the medium is strong enough the one-dimensional tunneling barrier is effectively lowered while the potential energy of the solvent is increased by the shift of the equilibrium position of its molecules. Such a potential energy will be smaller the lower the frequency of the oscillators of the medium.

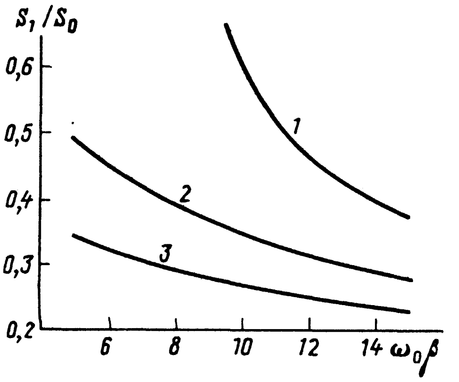

FIG. 4. Temperature dependence of S_1/S_0 at $B = 0.75$, $\alpha = 0.1$, $a = -0.5$ (curve *1*), $a = 0$ (*2*), $a = 0.5$ (*3*).

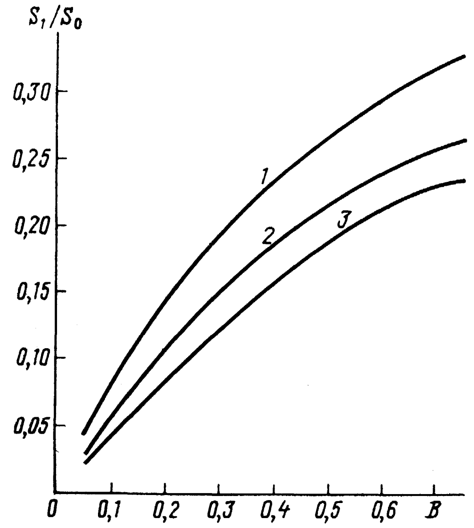

FIG. 5. Dependence of S_1/S_0 on the coupling parameter B for different values of the temperature: *1*—$\omega_0\beta = 5$; *2*—$\omega_0\beta = 10$; *3*—$\omega_0\beta = 15$; $\alpha = 0.1$; $a_\alpha = 1$.

We investigated the influence of the coupling to the medium on the value of S_1/S_0. According to Fig. 2, S_1/S_0 increases as a function of the binding parameter B (which determines the polarity of polar solvents). This dependence is stronger for a negative anharmonicity parameter a than for a positive one. The effects considered are strong, since $S_B/\hbar = 25$–40. According to Fig. 2, at $a = 3$ we have $S_1/\hbar = 2.8$–4.5, while for $a = -0.2$ we have $S_1/\hbar = 20$–30, which alters the tunneling constant by many orders of magnitude.

We investigated the temperature dependence of the negative increment to the action S_1/S_0 (Figs. 4 and 5). It can be seen that at high temperatures (smaller $\omega_0\beta$) S_1/S_0 increases and the tunneling is facilitated. The calculations were made for different values of the anharmonicity parameters. It is shown in Fig. 4 that failure to allow for the anharmonicity of the medium leads to an appreciable overestimate ($a > 0$) or underestimate ($a < 0$) of the transport velocity.

The considered anharmonicity effects are particularly important for the calculation of the tunneling rate of a particle interacting strongly with the nearest environment, where the potential energy of the molecules of the first coordinate sphere cannot be regarded as harmonic.

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