Breaking of interatomic bond in a solid following adiabatic and sudden action of arbitrary amplitude

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With breaking of an interatomic bond in a solid as an example, the problem is considered of breaking, by a sudden external action, of paired atomic bonds in a medium that can be represented as a common-temperature ensemble of paired bonds. The probability of bond breaking as a function of the binding energy and of the sudden external force is obtained for different initial-temperature regions. The conditions under which the results are valid are discussed and compared with familiar solutions of a similar problem with adiabatic external action. Possible applications of the theory to various physical processes in solids, condensed media, and gases acted upon by external forces are considered. Particular attention is paid to field-emission evaporation of solids and to the theory of disintegration of solids by thermal fluctuations.

§1. INTRODUCTION

Many systems can be approximately described as ensembles of paired bonds with common temperature. The problem of the response of such systems to external action frequently reduces thus to that of the breaking of a paired bond. Some results for the paired potential were obtained in this formulation, to various degrees of approximation, in the theory of field-emission evaporation from surfaces of solids.[1] Development of the corresponding theory of the elementary act of disintegration of solids was also attempted.[2] The same formulation is, in final analysis, the basis of an analysis of atom and ion mobility, of diffusion (see, e.g., Ref. 3), and of similar phenomena induced in condensed bodies by an external field. Chemical reactions, dissociation, ionization and their like in media under external action are also within the scope of this model. All the results obtained so far pertain, however, to the limiting case of an external action that is adiabatic in the sense that $\omega\tau_0 \gg 1$, where ω is the characteristic frequency of the limited motion in the paired potential and τ_0 is the time of application of the external action to the system. The best known case is the thermally activated bond breaking in a medium having a temperature T, and is described by a modified Arrhenius equation for the probability of such a process:

$$P \approx \exp[-(U_0 - Fa)/T] \tag{1}$$

(the symbols are explained in §2 and in Fig. 1).

This paper deals with the inverse limiting case $\omega\tau_0 \ll 1$, corresponding to sudden action on the system. Results for the limiting case $\omega\tau_0 \gg 1$ are cited only to establish clear-cut demarcation lines for the applicability of the model as a whole. Possible applications of the theory developed are considered, including the treatment of the elementary act of disintegration in a solid.

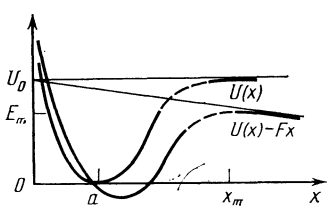

FIG. 1. Paired-bond potential vs relative distance x in the absence of an external action and in a field $V = -F_x$.

§2. INITIAL MODEL AND SCOPE OF ITS VALIDITY

The usual form of the paired (real or pseudo-) potential U that ensures an equilibrium distance a between the basic elements of the system (see, e.g., Ref. 4) is shown in Fig. 1. The limited (finite) motion at $E < U_0$ comprises oscillations about an equilibrium position $x = a$. Regarding the system as an ensemble of different paired bonds, as in the Einstein model,[4] we assign a common frequency ω to all the quanta of these oscillations. The distribution of each bond over the excitation levels E_n as a subsystem relative to the entire ensemble of bonds with temperature T is determined by the Gibbs statistics:

$$P_n = Z^{-1} \exp(-E_n/T) \tag{2}$$

(Z is the partition function). In view of the rapid convergence of the ensuing sums, we can assume for E_n the harmonic approximation

$$E_n \approx \hbar\omega(n+{}^1/_2). \tag{3}$$

We regard the external field as uniform within the chosen microvolume:

$$V(x) \approx -Fx. \tag{4}$$

In a paired-bond potential U perturbed by a field V (see Fig. 1) the excitation levels corresponding directly to unlimited motion are $E_n > E_m$. In addition, the levels $E_n < E_m$ become quasistationary and permit breaking of the bond. In a dense medium, of course, as the distance from the equilibrium position x_m increases the actual form of the paired-bond potential becomes highly sensitive to interactions with surrounding structure elements (to be specific, this will hereafter be referred to as atoms). The potential becomes dependent not only on the distance x_m between the atoms of the bond, but also on the distance from these atoms to their nearest neighbors. There can therefore be no talk of a paired potential in this region (the dashed curves in the figure). It is important, however, that the paired potential be a good approximation in the vicinity of x_m also at $x \gg x_m$, since a noticeable contribution [see, e.g., Eq. (A3a)] to the tunneling probability is made by levels located noticeably below E_m,

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whereas for above-barrier transitions this is immaterial to within exponentially small effects (above-barrier reflection).

The probability of bond breaking in a medium of temperature T by an external field V can be written according to the foregoing, taking (2) into account, in the form

$$P=Z^{-1}\sum_{n,k} w_{nk}D_k \exp\left(-\frac{E_n}{T}\right), \tag{5}$$

where w_{nk} is the probability of the transition, under the action of V, from the level E_n to E_k. The quantity D_k has the meaning of the probability of transition from a level E_k into the region of unlimited motion. Therefore $D_k = 0$ for a stationary level, $D_k = 1$ (neglecting above-barrier reflection) at $E_k > E_m$, and $D_k = D_{0k}$ is the probability of tunneling from a quasistationary level $E_k < E_m$.

In the case of adiabatic perturbation ($\omega\tau_0 \gg 1$) the probability of changing the system state is exponentially small,[5] i.e., $w_{nk} \approx \delta_{nk}$, and Eq. (5) yields

$$P\approx Z^{-1}\sum_{k} D_k \exp\left(-\frac{E_k}{T}\right). \tag{6}$$

In the limit of sudden perturbations ($\omega\tau_0 \ll 1$) this is not the case, and Eq. (5) remains in force. If, however, relaxation of the nonequilibrium distribution over the excitation levels is possible besides the transition to the unlimited-motion region, Eq. (5) is valid either if the time from the instant of the action is

$$t<\tau_R, \tag{7}$$

or if the stronger conditions $\omega\tau_R \gg 1$ and $\omega D_k \tau_R \gg 1$ are met. These are tantamount to assuming that the system decays before it relaxes (τ_R is the characteristic relaxation time). Relaxation is possible, for example, as a result of interaction with the ensemble. In a solid, in particular, this is phonon-phonon interaction.

For condensed media, the adiabaticity and suddenness conditions reduce, recognizing that $\tau_0 \sim a/u$ and $\omega \sim u_s/a$ (u_s and u are the propagation velocities of the sound (or of the elastic wave) and of the action wave) to the stronger inequalities $u \ll u_s$ and $u \gg u_s$. In the first case the rate of application of the external action is much less than the speed of sound, and this case can be regarded as quasistatic. The second case is realized, conversely (if the action is mechanical) when the disintegration is of the shock-wave (explosive) type.

§3. PROBABILITY OF PAIRED-BOND BREAKING IN A MEDIUM

We replace U by a model potential $U = M\omega^2(x-a)^2/2$ at $u < x < 2a$ or $U = U_0 = M\omega^2 a^2/2$ at $x > 2a$, where M is the reduced mass of the bond atoms. When a field V such as (4) is applied we have $E_m = E_0 - 2F_a$, and the corresponding quantum number is, taking (3) into account,

$$k_m=(U_0-Fa)/\hbar\omega+\xi-{}^1/_2, \tag{8}$$

where

$$\xi=F^2/2M\hbar\omega^3 \tag{9}$$

is a dimensionless parameter. At $k < k_m$ the probability D_k is determined by the barrier factor D_{0k} of Ref. 5, which takes here the form

$$D_{0k}\approx\exp\left[-\alpha(\eta k_m-\eta k)^{3/2}\right], \tag{10}$$

where

$$\eta=\hbar\omega/T, \quad \alpha=4(2M)^{1/2}T^{3/2}/3\hbar F$$

and an incorrect factor preceding the exponential in Ref. 5, as well as small corrections to the argument of the exponential, has been omitted.

The value of w_{nk} can be approximated with sufficient accuracy by the probability of the sudden excitation of a harmonic oscillator by an external uniform field (see Ref. 6):

$$w_{kn}=e^{-\xi}\frac{\Gamma(k+1)}{\Gamma(n+1)}\xi^{n-k}|L_k^{n-k}(\xi)|^2, \quad n\geqslant k,$$
$$w_{kn}=e^{-\xi}\frac{\Gamma(n+1)}{\Gamma(k+1)}\xi^{k-n}|L_n^{k-n}(\xi)|^2, \quad k\geqslant n, \tag{11}$$

where $L_k n(\xi)$ are generalized Laguerre polynomials and $\Gamma(k)$ is the gamma function.

If the interaction is weak ($\xi \ll 1$, limit of usual perturbation theory), the probability that the oscillator does not change the initial excitation level is

$$w_{nn}=e^{-\xi}|L_n(\xi)|^2\approx 1.$$

Formally, just as for adiabatic excitation, we get again (6). Physically, however, such a case is not always realized. Samll elastic loads, for example, cannot propagate in a solid faster than the elastic waves, i.e., the condition $u \gg u_s$ is not satisfied.

If, however, $\xi \gg 1$ (as is known from Ref. 5), w_{nn} is exponentially small and the probability of altering the oscillator-excitation level is overwhelmingly large. In the model assumed this circumstance accounts fully for the features of the system response to a fast external action.

Taking (8)–(10) into account we have from (6) in the adiabatic case

$$P=P_t+P_u$$
$$=Z^{-1}e^{-\eta/2}\left\{\sum_{k=0}^{k_m-1}\exp[-\alpha(\eta k_m-\eta k)^{3/2}-\eta k]+\sum_{k=k_m}^{n_m}e^{-\eta k}\right\}, \tag{12}$$

where

$$n_m=\langle U_0/\hbar\omega-{}^1/_2\rangle \gg 1 \tag{13}$$

and the first and second terms describe respectively a tunneling and a thermal-fluctuation (above-barrier) transition.[1)]

If the action is sudden, it follows from (5) that

$$P=P_t+P_u=Z^{-1}e^{-\eta/2}\sum_{n=0}^{n_m}e^{-\eta n}$$
$$\times\left[\sum_{k=0}^{k_m}\exp[-\alpha(\eta k_m-\eta k)^{3/2}]w_{kn}+\sum_{k=k_m}^{n_m}w_{kn}\right], \tag{14}$$

where n and k number the levels of the unperturbed and perturbed potential wells, respectively, and w_{kn} is defined in (11). For the sake of clarity we change the order of summation in (14) representing P_t and P_u in the form

$$P_u=P_{u\uparrow}+P_{u\downarrow}$$
$$=\eta\sum_{k=k_m}^{n_m}\sum_{n=0}^{k}e^{-\eta n}w(k>n)+\eta\sum_{k=k_m}^{n_m}\sum_{n=k}^{n_m}e^{-\eta n}w(k<n), \tag{15}$$

$$P_t = P_{t\uparrow} + P_{t\downarrow}$$

$$= \eta \sum_{k=0}^{k_m} \exp[-\alpha(\eta k_m - \eta k)^{1/2}]$$

$$\times \Big\{ \sum_{n=0}^{k} e^{-\eta n} w(k>n) + \sum_{n=k}^{n_m} e^{-\eta n} w(k<n) \Big\}. \qquad (16)$$

$P_\uparrow$ describes then a transition from lower levels n to levels with higher numbers k, and it is from the latter that the transition into the unlimited motion takes place. Coversely, $P_\downarrow$ corresponds to a transition of the system by "shake-down" to the lower levels k from which it goes into the region $x \gg x_m$.

The results of the calculation of (12), (15) and (16) are given in the Appendix. Here we proceed directly to their interpretation.

§4. "LIFETIME" OF A BOND

To simplify the final expressions, we can regard as satisfied the stronger inequality

$$\hbar\omega/2 \ll Fa \ll 2U_0, \qquad (17)$$

for otherwise the potential barrier is close to vanishing at $F_a \sim U_0$, and the bond breaking will not be diathermal. The condition in the left-hand side of (17) cuts off in turn only the extremely weak loads, with energy on the order of that of the zero-point oscillations. In the upshot we get from (A1), (A3), (A6), and (17) in the adiabatic case, at an estimated bond-breaking probability per unit time τ^{-1} as ωP

$$\tau^{-1} \sim \omega \exp[-(U_0 - Fa)/T], \quad T > T^*, \qquad (18)$$

$$\tau^{-1} \sim \omega \exp\left[-\frac{U_0 - Fa}{T}\right] + \omega_1 \exp\left[-\frac{U_0 - Fa}{T}\left(1 - \frac{1}{3}\frac{T_*^2}{T^2}\right)\right],$$

$$T_* \lesssim T < T^*, \qquad (19)$$

$$\tau^{-1} \sim \omega_2 \exp[-{}^2/_3 (U_0 - Fa)/T_*], \quad T < T_*. \qquad (20)$$

We have introduced here the notation

$$\omega_1 = {}^1/_2 \omega \pi^{1/2} (T^*/T)^{1/2}, \quad \omega_2 = \omega(1 - T/T_*)^{-1},$$
$$T_* = \Theta Fa/4[U_0(U_0 - Fa)]^{1/2}, \quad T^* = Fa(\Theta/U_0)^{1/2}, \qquad (21)$$

where $\Theta \equiv \hbar\omega$.

Expression (18) and the first term in (19) agree with the known classical result (1). At $T > T^*$ the increment from the quantum-mechanical tunneling enters additively into the pre-exponential factor and is small. It becomes noticeable with decreasing temperature; this is why both terms are retained in (19) for the general case. When the temperature is much lower than T^*, however, the second term predominates, i.e., only the tunneling is effective. The argument of the exponential is then a function different from that in (18). Finally, at very low temperatures ($T < T^*$) only below-barrier transitions ar really meaningful. The argument of the exponential in (20) differs therefore radically from that in (18) and is independent of temperature. We emphasize that the quantities T^* and T^*, which demarcate the regions where (18) and (20) are valid, are functions of f_a, U_0, and ω.

We proceed now to the case of sudden action. From (A8) and (A9) we have, allowing for (8)–(10) and (17),

$$\tau_{u\downarrow}^{-1} = \omega P_{u\downarrow} \approx \omega_{u\downarrow}\{1 + S_{u\downarrow}\} \exp[-(U_0 - Fa)/T],$$

$$\tau_{u\uparrow}^{-1} = \omega P_{u\uparrow} \approx \omega_{u\uparrow} \frac{\Theta}{T \ln(1 + \Theta/T)} \left[1 + \frac{\Theta}{T}\right]^{-(U_0 - Fa)/\Theta}.$$

Under the additional condition $T \gg \Theta$ expression (22) is transformed into [see (A10)]

$$\tau_{u\uparrow}^{-1} \approx \omega_{u\uparrow} \exp[-(U_0 - Fa)/T]. \qquad (24)$$

In the temperature range $T^* \ll T \ll T^*$ we have similarly [see (A12)]

$$\tau_{t\downarrow}^{-1} = \omega P_{t\downarrow} \approx \omega_{t\downarrow}(1 + S_{t\downarrow}) \exp\left[-\frac{U_0 - Fa}{T}\left(1 - \frac{1}{3}\frac{T_*^2}{T^2}\right)\right]. \qquad (25)$$

At [see (A13)] $T_* \varphi^{-1}(\Theta/T) \ll T \ll T^* \varphi(\Theta/T)$,

$$\tau_{t\uparrow}^{-1} = \omega P_{t\uparrow} \approx \omega_{t\uparrow} \left[\varphi\left(\frac{\Theta}{T}\right)\right]^{1/2} \left[1 + \frac{\Theta}{T}\right]^{-G},$$

$$G = \frac{U_0 - Fa}{\Theta}\left(1 - \frac{1}{3}\frac{T_*^2}{T^2}\right). \qquad (26)$$

If the condition $T \gg \Theta$ is also satisfied, expression (26) goes over [see (A14)] into

$$\tau_{t\uparrow}^{-1} \approx \omega_{t\uparrow} \exp\left[-\frac{U_0 - Fa}{T}\left(1 - \frac{1}{3}\frac{T_*^2}{T^2}\right)\right], \qquad (27)$$

which is valid at $T_* \ll T \ll T^*$.

The following notation is used in (22)–(27):

$$\omega_{u\downarrow} = \omega \frac{1}{\pi}\frac{T}{Fa}\left(\frac{U_0}{U_0 - Fa}\right)^{1/2},$$

$$\omega_{t\downarrow} = \frac{\omega}{2\pi^{1/2}}\frac{\Theta}{T}\left[\frac{T}{(U_0 - Fa)(1 - T_*^2/T^2)}\right]^{1/2}, \qquad (28)$$

$$\omega_{u\uparrow} = \frac{\omega}{\pi^{1/2}}\left(\frac{\Theta}{T^*}\right)^{1/2}, \quad \omega_{t\uparrow} = \frac{\omega}{2^{1/2}}\left(\frac{\Theta}{T}\right)^{1/2}$$

together with the definition

$$\varphi(x) \equiv x^{-1} \ln(1 + x), \qquad (29)$$

and $S_{u\downarrow}$ and $S_{t\downarrow}$ are written out in full in (A8), (A8a), and (A12).

At low temperatures $T \ll \Theta$ we must use the sum of (A11) and (A15), where $\xi = (1/4)(T^*/\Theta)^3$. This case, obviously, calls for a more detailed investigation.

Analysis of P_u leads to the conclusion that (22) is small compared with (23) in practically all real cases. Thus, the frequency τ_u^{-1} of bond breaking via thermally activated above-barrier transitions is determined by (23) which, even when rewritten in the form

$$\tau_u^{-1} \approx \omega_{u\uparrow} \varphi^{-1}\left(\frac{\Theta}{T}\right) \exp\left[-\frac{U_0 - Fa}{\Theta} \ln\left(1 + \frac{\Theta}{T}\right)\right], \qquad (30)$$

differs substantially (both in the argument of the exponential and in the factor preceding the latter) from (1) and (28). In addition, contrary to (1) and (18), $\omega_{u\uparrow}$ is [see (28)] a function of Fa and T. A transformation to an exponential such as in (1) is formally possible [see (24)] only at extremely high temperatures. Account must be taken here, however, also of the additive contribution of (22). As a result, in contrast to (1) and (18), we obtain a pre-exponential factor [the term

$(1+S_{u\downarrow})$ in (22)] that depends on the external force F and on the initial temperature T, and oscillates (!) at $Fa \ll U_0\Theta/T$.

The situation is similar also for above-barrier transitions, whose number per unit time is determined by (26), i.e.,

$$\tau_t^{-1} \approx \omega_{t\uparrow}\varphi^{1/2}(\Theta/T) \times \exp\left[-\frac{U_0-Fa}{\Theta}\left(1-\frac{1}{3}\frac{T_*^2}{T^2}\right)\ln(1+\Theta/T)\right]. \quad (31)$$

The expression for τ_t^{-1} might contain an exponential of the same form as in the adiabatic case [see (19)] at $T \gg \Theta$. It is then again necessary to take into account as a comparable term, besides expression (25) [or (30)] that goes over into (27), the expression (25) which introduces its own oscillating pre-exponential factor $(1+S_{t\downarrow})$. Physically, however, such a situation is not realized in practice even in extreme cases, for on the one hand the condition $T \gg \Theta$ contradicts the condition $T \ll T^*\varphi(\Theta/T)$ [see (25) and (26)], since it calls for $T \gtrsim T^*$, and on the other hand the quantity τ_t^{-1} introduces at $T \gtrsim T^*$ only a negligibly small correction to the pre-exponential factor in the expression for τ_u^{-1}.

§5. DISCUSSION OF RESULTS AND OF THEIR POSSIBLE APPLICATIONS

Thus, in real cases the lifetime τ of the bond is determined in the case of a sudden action by above-barrier transitions [Eq. (23) or (30)] in the temperature range $T \gtrsim T^*$ or by tunnel transitions [Eq. (26) or (31)] at temperatures

$$T_*\varphi^{-1}(\Theta/T) \ll T < T^*\varphi(\Theta/T).$$

At very low temperatures we have the sum of (A11) and (A15), which is not investigated here in detail.

It can be seen that the transitions are activated not only by the initial temperatures, but also by the sudden "shake up" of the system. The decisive role is played here by the excitation of the system from lower to higher levels. On the whole the results do not reduce to Eq. (1), and the pre-exponential factors (as well as T^* and T^*) are functions of the external acting force. An exponential dependence of τ^{-1} in the form (1) or (18) can occur only if very high temperatures $T \gg \Theta$ are realized. The value of τ^{-1} is then determined by the sum of (22) and (24), with an entirely different pre-exponential factor that gives rise at $Fa \ll U_0\Theta/T$ to oscillations of τ^{-1} as a function of the parameter $Fa/\Theta \gg 1$.

By virtue of the condition (7), Eqs. (23), (30) and (26), (31) describe times $t < \tau_R$ elapsed from the start of the action on the system. Therefore, on the one hand, the condition $\omega\tau_R \gg 1$ must hold if the contribution made to the bond breaking by the processes described by these equations is to be noticeable. On the other hand, the equations that will hold during later instants of time $t > \tau_R$ will be (18)–(20), obtained in the adiabatic limit, except that T must be taken to mean not the initial temperature prior to the action, but the temperature established by relaxation in the perturbed system at the instant $t \sim \tau_R$. The calculation of this temperature calls for a separate study. It follows, however, that when the values of τ obtained from Eqs. (23), (3), (26), and (31) exceed τ_R substantially a wrong impression may be gained that Eqs. (18), (19) and (20) of the adiabatic limiting case are valid also at $\tau_0 \lesssim \omega^{-1}$. These very expressions may be found to hold at $\omega\tau_0 \ll 1$ also for an action that is weak in the sense $\xi \ll 1$, if this case is compatible with the physical character of the acting forces (see §3).

The possible applications of the described model are many— to solids, liquids, diatomic-molecule gases, etc., i.e., to any system that can be represented as an ensemble of paired states with a common temperature. The Appendix contains therefore for Eqs. (12) and (14) all the asymptotic forms that may be needed in actual cases.

Let us apply, for example, the results to field-emission evaporation. Then U_0 is replaced by the activation energy $Q_n(\tilde{F})$ for field evaporation of a surface atom in the form of an n-fold charged ion to which an electric field of intensity $\tilde{F}$ is applied [$Q_n(\tilde{F})$ includes in the case of a metal the additional lowering of the potential by the image forces], and Fa is replaced by $n_e\tilde{F}a$. The quantity τ^{-1} stands then for the rate of field evaporation, and Eqs. (18)–(20) lead to the known expressions of the problem of field–emission evaporation.[1] Equations (23) and (26), on the contrary, give the rate of evaporation for a rapidly applied field $\tilde{F}$ with a rise time $\tau_0 \ll \omega^{-1}$. We treat similarly atom diffusion stimulated by external action, as well as ionic conduction in solids or in condensed media.

All the arguments remain formally in force for external action on gases of diatomic (two-component) molecules, i.e., for phenomena such as dissociation (decomposition) reactions, etc. We must only take T to mean the vibrational temperature of the molecules, τ_R its relaxation, and a the characteristic dimension of the molecules.

We conclude by dwelling briefly on the application of the results to the theory of disintegration of solids by thermal fluctuations. Equation (18) is then analogous to the Zhurkov's longevity criterion[7,8] if we put $Fa \approx \sigma\gamma$, where σ is the stretching stress and γ is the activation volume. Equation (19) differs little from the result of Gilman and Tong,[2] which is more elaborate because of the use of an unjustifiably complicated model. The comparison given in Ref. 2 with the experimental data confirms also the validity of Eq. (19). On the other hand, the disparity between the high-temperature experimental data and Zhurkov's criterion is strong enough to merit a special investigation. From among our present results, the only useful one in this respect is the expression for the temperature $T^*(\sigma\gamma, U_0)$ that demarcates the regions of validity of Eqs. (18) and (19).

Matters are much more complicated when the loading is fast. This case is realized for a solid, as already mentioned, only at $u \gg u_s$, i.e., only for action by shock waves. The ensuing stressed state, however, is the result of the action of the shock-wave front and the usually attendant relaxation wave. Consequently, Eqs. (23) and (26) cannot be compared with the experimental data, since it is necessary to solve first the dynamic problem. It remains to hope that the model, which is fully corroborated by experiment in the adiabatic-loading case, is universal. Hope is raised also by the report of an unexpected (by the authors) experimental confirmation[9] of the validity of Zhurkov's criterion (18) for disintegration of solids by short-duration impact. Within the scope of our present paper, this ties in with a postulated existence of an

exponential relation such as (18) but with a different (not initial) temperature at $t > \tau_R$.

Finally, from the viewpoint of a consistent strength theory, Eqs. (23) and (26) are only the sought bond-breaming microprobabilities in a kinetic equation that describes the statistical nature of disintegration. It is precisely from such an equation that a macroscopic disintegration criterion should be derived.

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APPENDIX

For P_u we have from (12)

$$P_u = e^{-\eta k_m}. \tag{A1}$$

The expressions for P_t from (12) are different in different ranges of the parameters. At

$$^4/_9 (\eta k_m)^{-1} \ll \alpha^2 \ll 1 \tag{A2}$$

the saddle-point method[10] yields

$$P_t \approx \frac{4\sqrt{\pi}}{3\alpha} \exp[-\eta k_0 - \alpha(\eta k_m - \eta k_0)^{3/2}]$$
$$= \frac{4\sqrt{\pi}}{3\alpha} \exp\left[-\eta k_m + \frac{4}{27\alpha^2}\right], \tag{A3}$$

where by virtue of (A2)

$$\eta k_m - \eta k_0 = {}^4/_9 \alpha^2 \gg 1, \tag{A3a}$$

and the fact that the enhanced left-hand inequality in (A2) does not hold rigorously has little effect on the validity of (A3). If

$$^9/_4 \eta k_m \alpha^2 < 1 \tag{A4}$$

and (as can always be assumed)

$$\eta k_m \gg 1, \tag{A5}$$

the Laplace method[10] leads to the different result

$$P_t \approx [1 - {}^3/_2 \alpha (\eta k_m)^{1/2}]^{-1} \exp[-\alpha(\eta k_m)^{3/2}], \tag{A6}$$

which is determined by the region $\Delta k \sim 1/\eta k_m$ near $k = 0$. Under the condition $a^{2/3} \gg 1$ we have

$$P_t \approx {}^2/_3 \Gamma({}^2/_3)\, e^{-\eta k_m}/\alpha^{2/3}. \tag{A7}$$

Here P_t is determined by values of k close to k_m, but by virtue of $\alpha^{2/3} \gg 1$ we have $P_t \ll P_u$, i.e., P_t is of no interest.

For P_u from (15), using the two-dimensional Laplace method[10] and employing in (11) the asymptotic expansions of the generalized Laguerre and gamma functions,[11] we obtain

$$P_{u\downarrow} \approx \frac{1}{2\pi\eta (k_m \xi)^{1/2}} (1 + S_{u\downarrow}) e^{-\eta k_m},$$
$$S_{u\downarrow} = \frac{\eta^2}{\eta^2+\pi^2} \frac{\eta^2}{\eta^2 + 4\xi/k_m} \left\{ \left[1 + \frac{2\pi}{\eta^2} \left(\frac{\xi}{k_m}\right)^{1/2} \right] \right. \tag{A8}$$
$$\left. \times \sin 4(k_m \xi)^{1/2} - \frac{1}{\eta} \left[\pi - 2\left(\frac{\xi}{k_m}\right)^{1/2} \right] \cos 4(k_m \xi)^{1/2} \right\},$$

which is valid at $\eta k_m \gg 1$. For the oscillating term $S_{u\downarrow}$ in (A8) we have in the extreme cases

$$S_{u\downarrow} \approx 0 \quad \text{for} \quad \eta k_m^{1/2} \ll 2\xi^{1/2},$$
$$S_{u\downarrow} \approx \frac{\eta^2}{\eta^2+\pi^2} \left[\sin 4(k_m \xi)^{1/2} - \frac{\pi}{\eta} \cos 4(k_m \xi)^{1/2} \right] \tag{A8a}$$
$$\text{for} \quad \eta k_m^{1/2} \gg 2\xi^{1/2},$$

with $S_{u\downarrow}$ in the upper limiting case having a power-law smallness in terms of the parameter $\eta k_m^{1/2}/2\xi^{1/2}$.

The probability $P_{u\downarrow}$ is similar in character to (A1), since it also describes transitions from states k located below the potential barrier. Here, however, the states k are intermediate and the transitions to them are from upper levels of the potential well. The incompleteness of the analogy is manifest by the appearance in (A8), in contrast to (A1), of a substantial oscillating pre-exponential factor (at $\eta k_m^{1/2} \ll 2\xi^{1/2}$ the oscillations are so rapid that they become integrally averaged).

The probability $P_{u\uparrow}$ has no analog in the case of adiabatic action, since the intermediate state k is arrived at through "ejection" from lower states, including some below the barrier. The difference between the asymptotic form of $P_{u\uparrow}$ and (A1) is therefore more substantial:

$$P_{u\uparrow} \approx \frac{\eta}{(2\pi)^{1/2}(1+\eta)\xi^{1/2}\ln(1+\eta)} (1+S_{u\uparrow})(1+\eta)^{-k_m}, \tag{A9}$$

where

$$S_{u\uparrow} = \frac{\ln^2(1+\eta)}{\pi^2+\ln^2(1+\eta)} \left\{ \sin\left[4\left(\xi \frac{k_m}{1+\eta} \right)^{1/2} - \pi \frac{\eta k_m}{1+\eta} \right] \right.$$
$$\left. - \frac{\pi}{\ln(1+\eta)} \cos\left[4\left(\xi \frac{k_m}{1+\eta} \right)^{1/2} - \pi \frac{\eta k_m}{1+\eta} \right] \right\}$$
$$\times \exp\left\{ -\frac{k_m}{2(1+\eta)^2} \left(\pi + 2\left[\frac{\xi}{k_m}(1+\eta) \right]^{1/2} \right)^2 \right\}.$$

The conditions for the applicability of (A9) are

$$k_m \ln(1+\eta) \gg 1, \quad k_m^{1/2} \gg 1.$$

The oscillating factor $S_{u\uparrow}$ in (A9) is practically always exponentially small.

A form with an exponential similar to that of (A1) is possessed by $P_{u\uparrow}$ only under the additional condition $\eta \ll 1$ (high temperatures):

$$P_{u\uparrow} \approx (2\pi\xi)^{-1/2} (1+S_{u\uparrow}) e^{-\eta k_m}, \tag{A10}$$
$$S_{u\uparrow} \approx \frac{\eta^2}{\pi^2+\eta^2} \left[\sin 4(\xi k_m)^{1/2} - \frac{\pi}{\eta} \cos 4(\xi k_m)^{1/2} \right]$$
$$\times \exp\left\{ -\frac{k_m}{2} \left[\pi + 2\left(\frac{\xi}{k_m} \right)^{1/2} \right]^2 \right\},$$

which in contrast to (A8) has a different pre-exponential factor and an exponentially small $S_{u\uparrow}$.

In the limit of very low temperatures ($\eta \gg 1$) we have

$$P_{u\uparrow} \approx e^{-\xi} \sum_{k=k_m}^{\infty} \frac{\xi^k}{k!} \approx P_u, \tag{A11}$$

i.e., P_u reduces to the probability of ejection by "shakeup" from the ground state $n = 0$ into states $k \geqslant k_m$.

For below-barrier transitions we have

$$P_{t\downarrow} \approx \frac{2}{3\alpha\eta(2k_0\xi)^{1/2}} (1+S_{t\downarrow}) \exp\left\{ -\eta k_m + \frac{4}{27\alpha^2} \right\}, \tag{A12}$$

$$S_{t\downarrow}=\frac{\eta^2}{\eta^2+\pi^2}\left[\sin 4(\xi k_0)^{1/2}-\frac{\pi}{\eta}\cos 4(\xi k_0)^{1/2}\right]$$
$$\times\exp\left(-\frac{16\xi}{9\alpha^2 k_0\eta^2}\right),$$

which is valid under the condition (A2), with k_0 the same as in (A3). Equation (A12) is similar to (A3), which reflects again the partial analogy with the adiabatic transition (transitions from levels $k<n$). The difference lies in the presence of an oscillating factor in (A12).

For tunnel transitions from levels $k>n$ described by $P_{t\uparrow}$ there is no analogy, and at

$$4/9k_m\ln(1+\eta)\ll\alpha^2\eta^3\ln^{-3}(1+\eta)\ll 1$$

we have

$$P_{t\uparrow}\approx\frac{2[2\ln(1+\eta)]^{1/2}}{3\alpha(\xi\eta)^{1/2}(1+\eta)}(1+S_{t\uparrow})(1+\eta)^{-G}, \tag{A13}$$

$$S_{t\uparrow}=\sin\left[4\left(\frac{\tilde{k}_0\xi}{1+\eta}\right)^{1/2}-\pi\frac{\eta\tilde{k}_0}{1+\eta}\right]\exp\left\{-\frac{4\ln(1+\eta)}{9\alpha^2\eta^3\tilde{k}_0(1+\eta)}\right.$$
$$\left.\times\left[2\xi^{1/2}-\pi\eta\left(\frac{\tilde{k}_0}{1+\eta}\right)^{1/2}\right]^2-[2(1+\eta)]^{-1}\left[2\xi^{1/2}+\pi\left(\frac{\tilde{k}_0}{1+\eta}\right)^{1/2}\right]^2\right\},$$

where

$$\tilde{k}_0=k_m-\frac{4}{9\alpha^2\eta^3}\ln^2(1+\eta),\quad G=k_m-\frac{4\ln^2(1+\eta)}{27\alpha^2\eta^3}.$$

The difference between (A13) and (A3) is particularly substantial at $\eta\gtrsim 1$ (low and moderate temperatures), when the level of the initial excitation of the system in accord with the Gibbs distribution is low and for tunneling with a noticeably probable perturbation it is necessary to raise the system from lower to substantially higher levels. At high temperatures ($\eta\ll 1$) the initial perturbation is large and the effective difference $n-k$ is small, therefore (A13) is reduced at $\eta\ll 1$ to a form similar to (A3) and (A12):

$$P_{t\uparrow}\approx\frac{2^{3/2}}{3\alpha\xi^{1/2}}(1+S_{t\uparrow})\exp\left(-\eta k_m+\frac{4}{27\alpha^2}\right), \tag{A14}$$
$$S_{t\uparrow}\approx\sin 4(k_0\xi)^{1/2}\exp\left[-\frac{16\xi}{9\alpha^2 k_0\eta^2}-\frac{1}{2}(2\xi^{1/2}+\pi k_0^{1/2})\right]^2,$$

with $\tilde{k}_0\to k_0$. Since the condition $\alpha^2\gg 4/9\eta k_m$ is then satisfied for $P_{t\uparrow}$, we have $k_0\gg 1$ and the oscillating term in (A14) is exponentially small.

In the case of very low temperatures ($\eta\gg 1$) it follows from (16) that

$$P_t\approx e^{-\xi}\sum_{k=0}^{k_m}\frac{\xi^k}{k!}\exp[-\alpha(\eta k_m-\eta k)^{3/2}], \tag{A15}$$

which corresponds to excitation of an oscillator from the ground state to a level k, followed by tunneling.

[1)]It can be seen from (12) that it is just P_t which is sensitive to the form of the potential, and hence to the model assumed. The argument of the exponential, however, contains two competing terms, one increasing and the other decreasing with k. Therefore P_t is determined by the contribution of the levels in the vicinity of the optimal value $k=k_0$. In the case of negligibly small P_t, the number k_0 is noticeably smaller than k_m [see, e.g., Eq. (A3a)]. Thus the real behavior of the potential at $x\sim x_m$ can introduce only an integrally small error. It is therefore required that the model potential approximate well the eigenfunctions and eigenvalues for relatively low-lying states at $x\sim a$, and also be close to the real potential at $x\gg x_m$. The chosen model potential satisfies these conditions.

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