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Escape of Particles over a Dynamic Barrier

E. H. Rezayi and H. Suhl
Institute for Pure and Applied Physical Sciences, University of California, San Diego, La Jolla, California 92093
(Received 27 May 1980)

A particular example of impurity diffusion in a solid is calculated and it is noted that the usual assumptions for Brownian-motion theory are invalid in this case.

PACS numbers: 66.30.Dn, 05.40.+j

Of the multitude of processes in physics and chemistry that involve activated escape of a "particle" over a barrier (chemical reactions, dynamics of certain spin-glass models, diffusion, superionic conductors, etc.) only those are adequately understood that involve a clear separation of time scales of "particle" and "heat-bath" motion. The effect of the heat bath is then represented by a friction coefficient. According to Kramers,[1] when this friction coefficient lies in a certain range, the so-called absolute-rate theory (ART) applies, and in this range, the escape rate is practically independent of the value of the friction, i.e., independent of the dynamics of the particle-bath interaction. Purely statistical arguments then give the escape rate. The term "particle," in general, refers to the representative point in the multidimensional configuration space of a many-particle system. Vinyard's[2] theory of impurity diffusion in a crystalline solid is an example of ART (at each step of the diffusion process the crystal configuration is assumed entirely relaxed). The rate is then the forward current per particle over the saddle point of the energy hypersurface. However, the rate of motion of the host and impurity atoms are not significantly different; thus the preconditions for Kramers' theory in general and ART in particular are not met, at least not insofar as the host acts as heat bath. Nor will they be met in the important case of a chemical reaction on the surface of an insulator. It is to be emphasized that there are at present no reliable theories in the absence of the particular separation of time scales mentioned above. However, in one particular case, namely that of an impurity bound in a lattice in such a way so as to give rise to a well-defined local mode, it is possible to calculate an approximate diffusion rate of the impurity without Langevin-Fokker-Planck assumptions.

Escape over the barrier here corresponds to mode instability and the escape rate is the average number of times per second that instability conditions are met. The anharmonicity causes instability in three ways: (i) Impinging phonons occasionally excite the mode to an amplitude it cannot stably sustain. (ii) The incident phonons modulate the effective local mode frequency, occasionally turning it imaginary. (iii) Parametric excitation by incident phonons.

Processes (ii) and (iii) combined dominate the rate. They are related to an effect proposed by

Kornblit, Pelleg, and Rabinovitch.[3] Occasionally a local fluctuation pulls some nearest neighbors of the impurity far enough apart to permit it to move through.

We treat the host crystal within the harmonic approximation, but allow the impurity to interact with its nearest neighbors with a harmonic force large enough to yield a local mode, plus a repulsive anharmonic part dominant at large displacement (in the absence of a well-defined local mode, the problem is more difficult). For conciseness, we take the mass of the impurity atom equal to that of host atoms.[4] An advantage of this model is that it permits actual evaluation of Vinyard's formula for comparison.

In the continuum approximation the Lagrangian density of this model is

$$\mathcal{L}(x)=\tfrac{1}{2}(\partial\varphi/\partial t)^2-\tfrac{1}{2}c^2(\nabla\varphi)^2 -\tfrac{1}{2}\epsilon\delta(\vec{x})(\nabla\varphi)^2+\tfrac{1}{4}b\delta(\vec{x})(\nabla\varphi)^4, \quad (1)$$

where c is the speed of sound and $\varphi(\vec{x})$ is the field of the atomic displacements from their equilibrium positions. For simplicity φ is taken to be a scaler, ϵ is the excess force constant, and $\delta(\vec{x})$ is the Dirac δ function. The quartic term simulates the actually prevailing anharmonicity sufficiently well to permit discussion of the rate. Whenever appropriate we have used the Debye model for the phonon spectrum.

The normal modes for the bilinear part of the Lagrangian ($b=0$) are

$$\varphi_p(\vec{x})=\frac{1}{V}\sum_{\vec{q}}\frac{i\vec{q}\cdot\hat{n}\exp(-i\vec{q}\cdot\vec{x})}{\omega_0^2(\vec{q})-\omega_p^2}, \quad (2)$$

V is the volume and $\omega_0(\vec{q})=c|\vec{q}|$ is the unperturbed phonon frequency for wave vector q, and $\hat{n}$ is an arbitrary unit vector. The continuum frequencies ω_n and the local mode frequency ω_l are determined from the eigenvalue condition

$$-\frac{\epsilon}{3V}\sum_{\vec{q}}\frac{q^2}{\omega_0^2(\vec{q})-\omega_p^2}=1. \quad (3)$$

This equation gives rise to $M<N$ distinct modes. $N/3$ is the total number of particles. The remaining $N-M$ modes have vanishing gradient at the origin and are, therefore, unaffected by the impurity.[5] Hereafter we neglect all such solutions. The set $\{\varphi_p(\vec{x})\}$ is therefore not a complete set. The wave functions $\varphi_p(\vec{x})$ are, however, orthogonal,

$$\int d^3x\,\varphi_p(\vec{x})\varphi_{p'}^*(\vec{x})=M_p\delta_{p,p'}, \quad (4)$$

with

$$M_p=\frac{1}{3V}\sum_{\vec{q}}\frac{q^2}{[\omega_0^2(q)-\omega_p^2]^2}, \quad (5)$$

which, with the help of the eigenvalue condition, can also be written as

$$M_p^{-1}=\epsilon^2 d\omega_p^2/d\epsilon. \quad (6)$$

The nontrivial solutions of the full Langranian can be expanded as[6]

$$\varphi(\vec{x},t)=\textstyle\sum_p\chi_p(t)\varphi_p(\vec{x}),\quad p=1,\ldots,M; \quad (7)$$

the expansion coefficients $\chi_p(t)$ satisfy the equation

$$M_p\frac{d^2\chi_p(t)}{dt^2}+M_p\omega_p^2\chi_p(t)-\frac{b}{\epsilon^4}\Big(\sum_{p'}\chi_{p'}(t)\Big)^3=0, \quad (8)$$

where $p,p'=1,\ldots,M$ refer to any mode (local or otherwise).

The familiar methods by which the nonlinear terms lead to damped quasilinear modes are not of interest here. We postulate that the rate to be found is the mean reciprocal time interval needed by the local mode to change from small amplitude behavior over to an unstable exponential growth. This crossover is due to coupling to the continuum modes, whose motion is only affected negligibly by that of the local mode.

The equation of motion for the local mode is

$$d^2\chi_l/dt^2+[\omega_l^2-3b_lf_1(t)]\chi_l -3b_lf_0(t)\chi_l^2-b_l\chi_l^3=b_lf_2(t), \quad (9)$$

where

$$b_l=b/\epsilon^4M_l,$$
$$f_k(t)=\Big(\sum_{i\neq l}\chi_i(t)\Big)^{k+1},\quad k=0,1,1. \quad (10)$$

The root-mean-square frequency spectra (in three dimensions) of $f_k(t)$ are shown in Fig. 1. The interesting feature is that there is concentration of the weight under nonoverlapping well-defined peaks, implying that they can be regarded as sums of slowly (superscript s) and rapidly (superscript r) varying functions of time, $f_k(t)=f_k^s+f_k^r$ with negligible overlap between f_k^s and f_k^r. As the dimensionality increases the peaks of these functions shift towards their limiting values (Fig. 1), and their spectra narrow.

The physical effects of the various time-dependent terms for the local mode, taken separately, are as follows:

(a) The slowly varying part of $f_1(t)$ (see Fig. 1)

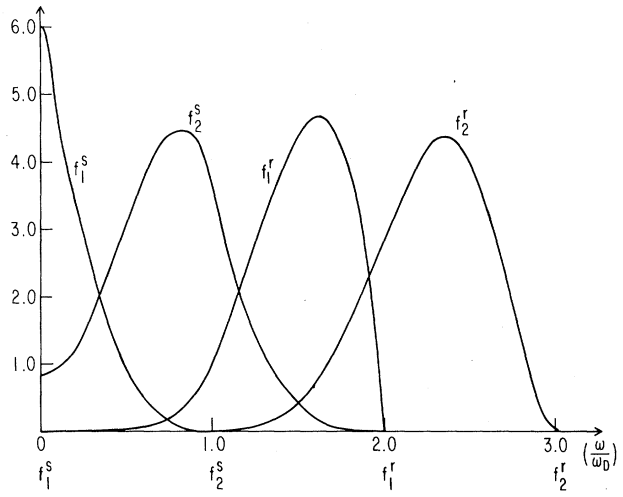

FIG. 1. f_0 has the usual Debye spectrum (not shown). The spectral density of f_1 and f_2 are in arbitrary unrelated units. The labeled points are the limiting peak positions for infinite dimensionality.

modulates the curvature of the harmonic well, occasionally turning it into a nonbounding potential.

(b) The fast part of $f_1(t)$ can be written as $[\exp(i\omega_b t)g(t) + \text{c.c.}]$, where $g(t)$ is a relatively slowly varying function of t, and ω_b $(= 1.680\omega_D)$ is the peak frequency of the spectrum of f_1^r. $g(t)$, treated adiabatically, will occasionally destabilize $\chi_l(t)$ according to Mathieu's equation.

(c) $f_0(t)$ may be written $[\exp(i\omega_D t)h(t) + \text{c.c.}]$, with $h(t)$ relatively slowly varying; occasionally $h(t)$ is big enough to destroy the barrier.

(d) The slow part of $f_2(t)$ can be studied by standard nonlinear-oscillator theory, combined with an adiabatic assumption for $f_2(t)$. Again χ_l occasionally becomes unstable.

(e) The fast part of f_2 treated similarly does not yield an instability for $\omega_l \lesssim 2.4\omega_D$ (for large ω_l see below).

We calculate the mean rates of occurrence of these processes,[7]

$$\lim_{T\to\infty}(2T)^{-1}\int_{-T}^{T}dt\,[\textstyle\sum_i \delta(t-t_i)],$$

where t_i are the critical times, by converting the time average to an ensemble average. We neglect correlation between all these processes except (a) and (b). This is obviously justified if any one of these rates is reasonably faster than the others.

With the rates written as

$$\nu\exp[-h/kT], \tag{11}$$

for each of the cases (a)–(d), we obtain[8]

$$\nu_a = \omega_D\left[\frac{2h_0(1+\bar\epsilon)^3\gamma_l^2\Gamma}{3kT\lambda_l^3}\right]^{1/2},$$

$$h_a = h_0\left(\frac{4}{3}\frac{\bar\epsilon+1}{\lambda_l}\right); \tag{12}$$

$$\nu_{b+a} = \tfrac{2}{3}\left[1-\left(\frac{\omega_b}{2\omega_l}\right)^2\right]^{1/2}\nu_a,$$

$$h_{b+a} = \tfrac{2}{3}\left[1-\left(\frac{\omega_b}{2\omega_l}\right)^2\right]h_a; \tag{13}$$

$$\nu_d = \left[1-\left(\frac{\omega_d}{\omega_l}\right)^2\right]^{1/2}\nu_a,\quad h_d = \left[1-\left(\frac{\omega_d}{\omega_l}\right)^2\right]h_a; \tag{14}$$

where $h_0 = \epsilon^2/4b$, $\bar\epsilon = n\epsilon/c2$, $\bar\omega_i = \omega_i/\omega_D$, $\gamma_l = d\ln\bar\omega_l^2/d\ln\bar\epsilon$, $\beta_i = d\bar\omega_i^2/d\bar\epsilon$,

$$\Gamma = \sum_{i,\,j\neq l}\beta_i\beta_j(1/\bar\omega_i - 1/\bar\omega_j)^2,\quad \lambda_l = \gamma_l[\bar\epsilon - \gamma_l(\bar\epsilon+1)],$$

$n = N/V$ is the total mode density, and $\bar\omega_b = 1.680$ and $\bar\omega_d = 0.8571$ are the peak spectral frequencies of the functions f_1^r and f_2^r (Fig. 1), respectively. For reference, we also show process (a) alone. It is interesting to compare our results to that of Vinyard's (ART), which for our model is given by

$$\nu_v = \omega_D(\eta^2/2)^{1/2}/2\pi,\quad h_v = h_0(1+\bar\epsilon)^2/\bar\epsilon^2, \tag{15}$$

where η^2 is the unique real solution of

$$\sum_{i=1}^{M}\frac{\beta_i}{\bar\omega_i^2+\eta^2} = \frac{1}{3(\bar\epsilon+1)}. \tag{16}$$

To show differences in our various rates as well as the difference from that of Vinyard's, we have plotted h_a/h_0, h_{b+a}/h_0, h_d/h_0, and h_v/h_0 in Fig. 2. Thus our highest rate [processes (b) and (a) combined] is lower than ART. The amount that ART differs from our rate grows as ϵ becomes large; in this regime our picture of diffusion is most reliable. Figure 2 clearly shows that ART overestimates the rate by a very large factor.

To bring the results to an even sharper focus we finally consider the extreme case $\omega_l \gg \omega_D$ when the entire harmonic potential (not just its slow part) occasionally becomes nonbonding, and we obtain

$$\nu_\infty = \omega_D\left(\frac{\bar\epsilon(1+\bar\epsilon)\gamma_l(\frac{3}{5}-\beta_l)}{\pi\lambda_l}\right)^{1/2},\quad h_\infty = h_a/2; \tag{17}$$

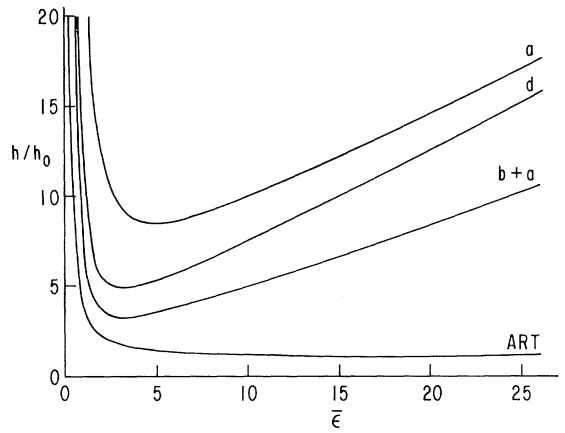

FIG. 2. The barrier of ART is finite at $\epsilon = 0$. All the other barriers grow faster than ϵ^{-2} resulting in divergent barrier heights.

for large ϵ, we have the analytic forms

$$\nu_\infty \cong 0.1637\omega_D, \quad h_\infty \cong 0.2593\bar{\epsilon}h_0, \tag{18}$$

$$\nu_v \cong 0.3162\bar{\epsilon}^{1/2}\omega_D, \quad h_v \cong h_0. \tag{19}$$

We conclude with a few comments. Our results are only valid for $\bar{\epsilon} > 2$ ($\omega_l > 1.1\omega_D$); in fact, our barriers diverge as $\epsilon \to 0$. This unphysical result is the consequence of the local mode becoming less localized which involves very many of the host atoms. The total strain energy associated with the local mode becomes correspondingly large and the barrier correspondingly high. Presumably this difficulty would be avoided with a more realsitic "periodic" local interaction for the impurity because of the possibility of the system snapping into a contiguous equilibrium configuration. A more detailed version of this work will be published elsewhere.

This work was supported by the National Science Foundation under Grant No. DMR77-24957.

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[6]We leave out all but the p waves in the expansion of $\varphi(\vec{x}, t)$; other partial waves do not couple to each other or to the p waves through the anharmonic terms.

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[8]It is convenient to combine the cases (a) and (c), the resulting rate may be obtained from Eq. (12). One needs to change γ_l and λ_l by the substitution

$$\gamma_l^{-1} \to \gamma_l^{-1}\left\{1 - (8\bar{\omega}_l^2)^{-1} + \frac{9kT\gamma_l^2}{h_0} \times \left[\left(1 - (8\bar{\omega}_l^2)^{-1} + \frac{9kT}{h_0}\gamma_l^2\right)^2 + (4\bar{\omega}_l^2)^{-1} - 1\right]^{1/2}\right\}.$$