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# Dynamical corrections to rate theory

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We discuss the corrections required to incorporate into a rate-theoretic description of diffusion the dynamical processes which cause diffusion jumps to occur prior to the randomization of the system in its new configuration. A calculation is carried through in detail for the case of immediate return jumps which occur prior to randomization. The results establish that rate theory gives correct predictions at sufficiently low temperatures in classical systems. We also discuss the limit in which the coupling between the migrating particle and the lattice is progressively weakened, as in some known cases of surface diffusion. The available evidence favors a description in which dynamical events are broken by frequent, totally randomizing collisions.

## I. INTRODUCTION

Within the limitations of classical statistical mechanics the treatment known as "rate theory" provides essentially exact prediction for the frequency with which a system makes transitions from one configuration to another. One need only know the masses $M_i$ of the $N$ interacting particles and their potential energy of interaction $V(\vec{r}_i \cdots \vec{r}_N)$ as a function of their coordinates $\vec{r}_i$, together with the specification $T,p$ of the temperature and pressure bath with which the ensemble equilibrates.[1] These serve to define precisely the probability with which a point representing the coordinates of all particles in the system is expected to pass between two arbitrarily connected neighboring configurations, thereby providing a determination of the transition rate between them.

This transition rate is ordinarily incorporated into simple models of behavior to describe bulk properties of systems.[1] In the case of vacancy diffusion in solids, for example, the transition rate defines "vacancy jump frequency." It is presumed that a specific vacancy jump is not influenced by any memory of an earlier jump except, of course, in the obvious way that the sequence of earlier jumps determines which configuration the system occupies. Unfortunately the assumption that successive vacancy jumps are uncorrelated is not always justified, and the prediction of the theory then falls into error.

The way is which the future behavior of a complex system is determined by past events is not very well understood at present. A classical system is, of course, entirely deterministic; its future is fully specified by the position it occupies in its phase space at any instant of the past. In a complex system, however, the future trajectories associated with neighboring initial positions in phase space are found to depart from each other quite radically after a long trajectory.[2] Any specific randomizing perturbation, such as interaction with the ambient photon field, for example, can therefore make the long-time behavior truly stochastic.

Insofar as this problem of memory influences the validity of rate theory, the only significant question is how long the memory of prior events lasts. If, for example, successive vacancy jumps occur after a period so long that all memory of former jumps is effectively lost, then current procedures that presume this randomization always occurs are valid. If dynamical consequences of earlier jumps remain important, however, their effects must be determined and appropriate corrections introduced into the theory.

Our purpose in this paper is to propose a specific method to deal with the system memory, and thereby, for the first time, to correct rate-theory predictions for dynamical effects. The basis for our proposal is derived from observations on com-

 

puter dynamical investigations of the behavior in systems of particle size $N \gtrsim 100$ for which increases of $N$ have only minor effects. Clear evidence appears to be available to establish that the memory can be extremely short, significantly less, in fact, than the shortest vibrational period of any particle, and that dynamical consequences of earlier behavior are negligible beyond this time. Corrections for dynamical behavior need be made only for cases in which successive events are separated by a time interval shorter than this brief memory.

In what follows we first discuss the evidence which justifies our proposal. In Sec. III we then apply this method to an example which has been a longstanding problem in diffusion—that of the dynamical return jump. Finally, we make some more speculative comments in Sec. IV about a certain regime of behavior in which the dynamical events of interest here play an increasingly strong role in determining the diffusive evolution of the system. This relates to the eventual loss of any useful role for rate theory as the randomization process progressively weakens.

## II. COMPUTER SIMULATION

Computer simulations which display the cooperative dynamics of many-particle systems can give vivid insight into the system behavior. An early example by Bennett[3] drew attention to a peculiarity of the vacancy jump process in solids. Bennett's analysis showed that, in many trajectories that result in a completed jump, the system appears to cross a (somewhat arbitrarily defined) critical jump condition several times before the jump is completed. This feature has been reproduced in a number of subsequent examinations of jump dynamics.[4] The behavior led one of us to suggest that the multiple crossings resulted from dynamical correlation effects, together with a less than optimum definition of the condition for jump completion.[5] An important feature of the observations is that multiple crossings take place during only a brief period. This makes it appear very likely that dynamical effects can be significant in the short time regime, but gives no indication about the long time randomization of the system.

Much clearer and more specific information has come available recently through molecular dynamics investigations of vacancy diffusion in Al and Na by Da Fano and Jacucci.[6] These calculations clearly show *multiple* jump processes occurring at high temperature such that the vacancy may be displaced through two or more near-neighbor steps in the course of one complex dynamical event. Caution must be exercised in dealing with multiple events in small systems where, of course, such processes may occur as artifacts attributable to the boundary conditions. In the examples of interest here this is almost certainly not the case. In the first place, a cell length of 12 atoms was employed, so that two atoms moving in the cell remain a fractionally small number. In addition, however, the observed processes proved insensitive to the cell size employed in the simulation, so that it appears unlikely that boundary conditions could have been involved in the occurrence of the multiple jumps. We therefore proceed under the assumption that these events are characteristic of large equilibrating crystals. Analogous processes have, in any event, been clearly identified in hard-disk and hard-sphere crystal simulations.[7]

The analysis of multiple events in Ref. 6 is particularly useful because it allows one to deduce coarse features of both the long- and short-time characteristics of the system memory. An example is given in Fig. 1. The figure shows for two-particle processes the distribution of time lapses from the occurrence of the first jump until the second particle was observed to jump. The definition of jump instants used for this purpose was only approximate,[6] but was certainly serviceable in

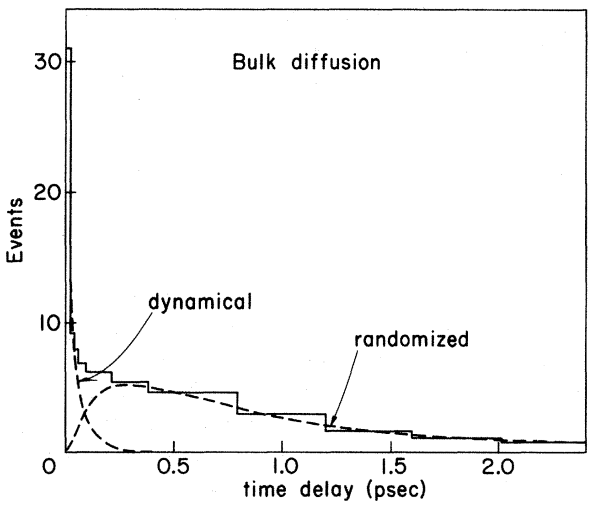


FIG. 1. Time delay between successive jumps of a vacancy, according to DaFano and Jacucci (Ref. 6). The figure indicates by broken lines the separation of double events into the exponential long-time behavior of the randomized system and the short-time behavior due to dynamical correlations.

the present application.

Figure 1 shows that the evolution subsequent to the first jump falls clearly into two regimes. These have been emphasized by broken lines drawn in the figure. At very short times there is an unusually large density corresponding to events in which two jumps occur within a period $\lesssim 5\times 10^{-14}$ sec, and mainly $\lesssim 2\times 10^{-14}$ sec. We emphasize that this extremely short time interval corresponds to only $\sim 10\%$ of the Debye period. It is the time required for an Al atom to move $\sim 1$ Å at thermal speeds of $2\times 10^{5}$ cm/sec. There appears to be no reasonable doubt that for processes in this short-time peak the second event is a direct dynamical consequence of the first. The system moves through two successive jump conditions without randomization.

The second important feature of the distribution is that the processes occuring later than about $5\times 10^{-14}$ sec all conform exceptionally well to the exponential decay which is fitted to the long-time tail in the figure (broken line). The exponential decay is, of course, characteristic of a system which has lost its memory and hence, through the time invariance of its decay probability, necessarily follows an exponential decay.

Taken together these two results indicate quite strongly that the system is essentially randomized within a small fraction of a Debye period. Apparently a single interatomic collision in the excited complex can serve to randomize the events. Consequently, the time evolution breaks into two very well-separated regimes: (i) a short-time regime of $\lesssim 5\times 10^{-14}$ sec in which dynamical events may be dominant, and (ii) a long-time regime for $t \gtrsim 5\times 10^{-14}$ sec in which randomization is sensibly complete and in which the exponential decay signals the applicability of rate theory. Provided that the mean jump time in the randomized system is very much longer than $5\times 10^{-14}$ sec, the dynamical and random processes can thus be located independently.

Under the conditions of the computer simulation these characteristics do not vary significantly with temperature, although the proportions of processes represented by dynamical and randomized categories of behavior do, of course, change. It is easy to understand that dynamical processes can never extend over intervals longer than $\sim 10^{-13}$ sec. As the temperature is lowered, the durations of the rate-theory decay must become still more protracted, and therefore the clear separation between dynamical and randomized events never breaks down for the typical bulk system under discussion here. In point of fact, the chosen model example is rather extreme in that the vacancy dwell time is only $\sim 10^{-12}$ sec at high temperatures, which is unusually short. It seems probable that since this clear separation of dynamical and random events holds even under these extreme circumstances, it will prevail rather generally for all jump processes in bulk solids.

While the existence of the separation is itself of some consequence, the causes are also of specific interest. As mentioned above, dynamical processes can hardly last longer than the time to cross several cells at thermal velocities, and therefore are limited to the time scale of $10^{-13}$ sec or less. On the other hand, the evidence of Fig. 1 suggests that thermalization for the remaining trajectories sets in rapidly with the first significant atom-atom collisions in the excited complex. This again requires a time of a fraction of a Debye period, which is $2\times 10^{-13}$ sec for Al. Provided, then, that the mean jump time is very much longer than a fraction of a Debye period, it follows that the two regimes must necessarily appear distinct.

## III. RETURN JUMPS

Given the reasons why rate-theoretic predictions break down due to dynamical correlations among successive jumps, the question remains how best to use this understanding to correct the errors in rate-theory predictions. We shall show here how the dynamical processes may be predicted in specific cases. The results of the calculations may then be used to correct the basic predictions of diffusion coefficients from rate theory, which hold only when each event is followed by a total loss of dynamical memory.

The example we choose is the return jump, to which attention has been drawn in earlier work.[3–6] We shall treat the problem in terms of mass weighted coordinates $\vec{s}_i = \vec{r}_i\sqrt{M_i}$, with the corresponding potential energy function $V(\vec{s}_1 \cdots \vec{s}_N)$. As always the two relevant configurations $A$ and $B$ between which jumps take place correspond to minima of $V$ separated by a surface $S$ which is the locus of points on the potential ridge separating $A$ from $B$. It cannot be expected in general that $S$ is planar. Therefore trajectories with high speed (and hence little curvature) moving almost parallel to $S$ may possibly cut $S$ twice (see Fig. 2) thereby giving rise to return jumps.[5] Our purpose is to derive an

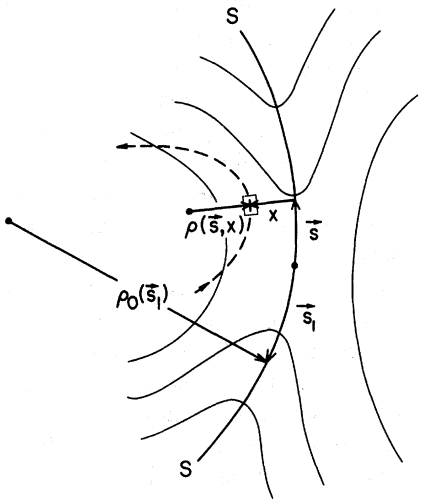


FIG. 2. Schematic representation of a curved saddle surface and the potential energy at neighboring points. The location of a volume element at $x,\vec{s}$ is indicated, together with a trajectory which is parallel to $S$ inside the volume element. Return jumps occur when the radius of curvature $\rho(\vec{s},x)$ of the trajectory is greater than the radius of curvature $\rho_o(\vec{s})$ of the saddle surface at the same value of $\vec{s}$, so that the trajectory cuts $S$ twice.

analytical expression for the return jump frequency. The answer will, of course, depend on geometrical properties of $S$ which to the best of our knowledge have not yet been calculated for any model system. Numerical conclusions must therefore await future results. However, the principles involved in this correction of rate theory can already be conveyed accurately, and this is our intent in what follows.

Suppose that the distribution function may be written $P(d\vec{s}/dt,\dot{x})P(\vec{s},x)$, with separable and normalized velocity and space factors. The rate $R$ at which representative points pass from $A$ to $B$ is then

$$R=\frac{1}{u}\int_S d\vec{s}\int_{-\infty}^{\infty} d\left[\frac{d\vec{s}}{dt}\right] \times\int_0^{\infty} d\dot{x}\,\dot{x}P\left[\frac{d\vec{s}}{dt},\dot{x}\right]P(\vec{s},0)\,. \tag{1}$$

Here, for simplicity of notation we employ $\vec{s}$ to span the $3N-1$ dimensions in $S$, and $x$ as the perpendicular to $S$; $u$ is the unit distance.

The rate at which return jumps occur may be calculated directly under a simplifying assumption valid near $T=0$. We need to identify the behavior of trajectories almost parallel with $S$, and with $x$ small, which may therefore cross $S$ twice as specified above. Each such trajectory accounts for two jump events in rate theory which are, in fact, immediately cancelled by subsequent dynamical processes. The factor of two arises from the two possible directions along the path.

Consider a trajectory with velocity $\dot{s}_{||}$ passing through the volume element at $\vec{s},x$ of size $d\vec{s}_{\perp}dx\,d(d\vec{s}/dt)d\dot{x}$ in phase space (we have here made the factorization $d\vec{s}=d\vec{s}_{\perp}ds_{||}$ with respect to the direction of the chosen trajectory). Sufficiently close to the saddle surface we can write the potential at $\vec{s},x$ as $V=V_0(\vec{s})-\frac{1}{2}\alpha(\vec{s})x^2$ because $S$ is a maximum of $V$ along $x$. Clearly, the trajectory has a radius of curvature $\rho(s_{||},\vec{s},x)$ given by the usual expression,

$$\dot{s}_{||}^2/\rho(s_{||},\vec{s},x)=\alpha(\vec{s})x\,, \tag{2}$$

with $\rho(s_{||},\vec{s},x)$ the curvature of the trajectory at $\vec{s},x$ in the direction parallel to $s_{||}$. The trajectory will cut the surface $S$ twice if $\rho(s_{||},\vec{s},x)>\rho_0(s_{||},\vec{s})$, with $\rho_0$ the analogous radius curvature of $S$. Consequently, trajectories parallel to $S$ at $\vec{s},x$ will produce return jumps if

$$\dot{s}_{||}^2\geq\dot{s}_m^2=\rho_0(s_{||},\vec{s})\alpha(\vec{s})x\,, \tag{3}$$

with $\dot{s}_m$ the minimum velocity at $\vec{s},x$ along $s_{||}$ for which return jumps are possible.

As $\rho_0$ passes through $\infty$ to negative values all return jumps cease within the present approximation. The formulas that follow concern only positive $\rho$, negative values being regarded as $+\infty$. The present formulation neglects changes of $\dot{s}_{||}$ caused by $(\nabla V)_S\neq 0$, which produce changes in the predictions that, from symmetry, must be of second order in $\nabla_S V$ (and hence in $T$). Also, the present treatment presumes that $V$ varies quadratically with $x$ within an energy $\sim k_B T$ of its value of $x=0$, and that no more than two crossings occur. All these approximations are valid for $T\to 0$, and all can be improved upon when $V(\vec{s},x)$ is known explicitly, if necessary by direct computer dynamics methods.

In keeping with the discussion of Sec. II we treat all such double intersections as trajectories which have been included erroneously in the calculation of the rate-theory jump rate $R$. We shall calculate the total rate $R'$ at which these trajectories eliminate completed jumps, and employ $R'/R$ as the fraction of the rate theory jumps which correspond to false events. The true jump rate is $R-R'$.

Returning to the volume element at $\vec{s},x$ we can write the rate of return jumps through this volume as

$$dR' = \frac{2}{u} P\left[\frac{d\vec{s}}{dt},0\right] P(\vec{s},s)\dot{s}_{||} d\vec{s}\, d\vec{s}_{\perp} d\dot{x} \quad (\dot{s}_{||} > \dot{s}_m) . \tag{4}$$

However, from geometrical considerations alone it is clear that $d\dot{x} = \dot{s}_{||} ds_{||}/\rho_{||}$ (see Fig. 2), with $\rho_{||} \equiv \rho(s_{||},\vec{s},x)$, and so we can finally write

$$\frac{R'}{R} = \frac{2\int d\vec{s} \int_{\dot{s}_m}^{\infty} d\left[\frac{d\vec{s}}{dt}\right] \int_0^{\infty} dx (\dot{s}_{||}^2/\rho_{||}) P(\dot{s},0) P(\vec{s},x)}{\int_S d\vec{s} \int_{-\infty}^{\infty} d\left[\frac{d\vec{s}}{dt}\right] \int_0^{\infty} d\dot{x}\, \dot{x} P\left[\frac{d\vec{s}}{dt},x\right] P(\vec{s},0)} . \tag{5}$$

The integrals over $\vec{s}$ can be performed in part by writing $d(d\vec{s}/dt) = \dot{s}_{||}^{3N-1} ds_{||} d\Omega$, with $d\Omega$ an angular element in the space of $S$, whence the thermal average containing $e^{-\beta \dot{s}^2/2} d\vec{s}$ becomes a $\delta$ function of width $(3N-1)^{-1/2}$ centered on $\dot{s}_{||}^2 = (3N-1)k_B T$. Consequently the $s_{||}$ integral has the value $(3N-1)k_B T/\rho_{||}$ for $x < (3N-1)k_B T/\alpha\rho_{||}$ and is otherwise zero. For small $x$ the variation of $V$ with $x$ may be neglected and the $x$ integral therefore amounts to a multiplication by $(3N-1)k_B T/\alpha\rho_{||}$. The remaining integrals are trivial; one thus finds

$$\frac{R'}{R} = \frac{2(3N-1)^2 k_B T}{\langle \alpha\rho^2 \rangle_{\text{av}}} , \tag{6}$$

in which

$$\frac{1}{\langle \alpha\rho^2 \rangle_{\text{av}}} = \left\langle \frac{1}{\alpha(\vec{s})\rho^2(\Omega,\vec{s})} \right\rangle_{\Omega,S} \tag{7}$$

has the quantity $(\alpha\rho^2)^{-1}$ thermally averaged over all the surface $S$ and over all directions contained in $S$.

The physical meaning of this result is easily understood. The expected kinetic energy is such that $\dot{s}^2/2 = 3Nk_B T/2$, of which, however, only $k_B T/2$ is associated with average motion along $x$. Trajectories are therefore expected to cross $S$ at an angle $\sim(3N)^{-1/2}$ and thus to penetrate a distance $\bar{x}$ given by

$$(\rho/\sqrt{3N})^2 \simeq 2\rho\bar{x}$$

or

$$\bar{x} < \rho/6N \tag{8}$$

below a surface $S$ of (positive) curvature $\rho$. But the radius of the trajectory is $\rho' = \dot{s}_{||}^2/\alpha x'$ and the trajectory is therefore trapped unless

$$x' < \dot{s}^2/\alpha\rho < 3Nk_B T/\alpha\rho . \tag{9}$$

Equation (8) and (9) show that the ratio of untrapped to trapped trajectories is

$$\frac{R'}{R} \sim \frac{x'}{\bar{x}} \sim \frac{18N^2 k_B T}{\alpha\rho^2} , \tag{10}$$

which agrees with Eq. (6) within a trivial numerical factor.

Equation (6) determines the frequency of dynamically inevitable return jumps, which occur in addition to the appropriate random fraction of return jumps predicted by rate theory. The identification of dynamical events evidently does converge, because they are confined to small $x$. This is the first time rate theory has been extended in this manner. The presence of the factor $T$ in Eq. (6) establishes in a definitive way that rate theory gives correct predictions in all classical systems at sufficiently low temperatures, provided that the system memory behaves as assumed.

The analytical expression for the return jump rate obviously depends on the geometry of $S$. Its numerical magnitude cannot be estimated accurately at present for real crystals, although return jumps are certainly observed in dynamical simulations of high temperature experiments.[3,4] An illustrative calculation carried through in the Appendix for a very simple model system suggests that return jumps may not be catastrophically numerous, even at the melting point, in most real materials. Calculations on more realistic models, now in progress in our laboratories, have been undertaken to resolve these questions in a definitive way.

## IV. MULTIPLE JUMPS AND THE LIMIT OF WEAK COUPLING

In certain instances the diffusion jump is coupled rather weakly to the lattice. This is notably the case for superionic conductors,[8] and in some types of diffusion that occur on smooth crystal surfaces.[9,10] In both cases the "activation energy" of the diffusion process is small. Also important is the fact that successive jumps may often take place without intervening randomization. These are events involving strong dynamical correlations. In what follows we discuss the way these processes may be treated as the coupling is progressively weakened.

Multiple jumps that occur when the mobile particle and the lattice remain strongly coupled can be treated by the methods employed in Sec. III. Instead of the trajectory recutting the same saddle surface, as in return jumps, it simply cuts two or more surfaces corresponding to successive jumps. Figure 3 shows, by way of example, six atomic sites unoccupied by atoms labeled 1—5, the fifth site being vacant. A sketch of the correponding crystal energy as a function of the coordinates $x_2, x_3, x_4$ of atoms 2, 3, and 4 is also given in Fig. 3. Saddle surfaces for the successive jumps of atoms 4, 3, and 2 are indicated as $S_4, S_3, S_2$. Dynamical trajectories for the single jump of atom 4, the double jump of atoms 4 and 3, and the triple jump of atoms 4, 3, and 2 together are indicated schematically be successively longer arrows in Fig. 3.

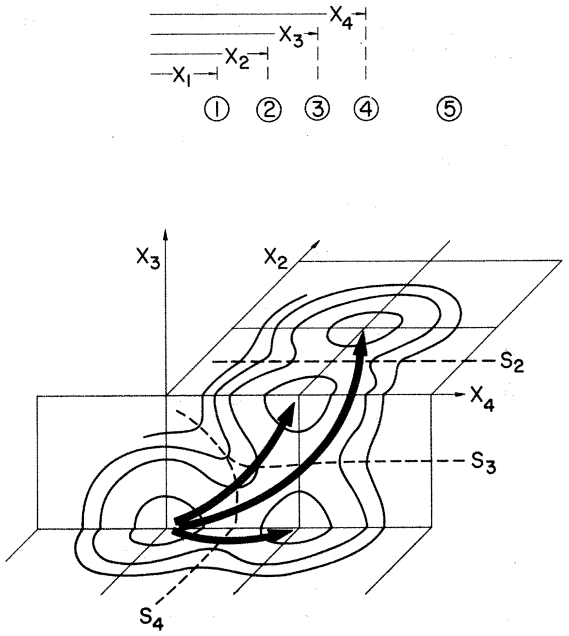


FIG. 3. The upper figure shows a row of atoms with a vacant site. The lower figure indicates schematically the potential energy contour for motion of atoms 2, 3, and 4, and the saddle surfaces $S_4, S_3, S_2$ for successive jumps of atoms 4, 3, and 2 into the vacancy. Progressivity longer heavy arrows indicate the jump of atom 4 from the initial configuration, the double jump of atoms 4 and 3, and the triple jump of atoms 4, 3, and 2 in a single dynamical event. It is possible in principle to calculate the rate at which multiple events occur as explained in the text, and hence to correct errors in the rate theory predictions. The possibility exists that single saddle surfaces can merge, over some areas as indicated for $S_4$ and $S_3$.

Computer simulation experiments[6] show that the hopping transition may be separated into the two categories of randomized and direct processes, as detailed in Sec. II. The frequency of direct processes can be calculated from a knowledge of the potential energy of the system as a function of configuration (and, of course, the saddle surfaces derived therefrom) in a manner directly analogous to that employed in Sec. III for double cutting of a single surface. One need only find the thermal expectation rate of trajectories which cut the relevant surfaces in direct succession. These in turn provide the required corrections to the single jump rate-theory prediction.

Interesting questions of principle arise as the coupling is weakened until the representative point moves almost freely among configurations. An excellent example is the case in which a surface adatom slides almost freely on a relatively smooth, close-packed surface.[9] Computer simulations[10] show that, at temperatures above those relevent to mainly near-neighbor hopping, there is a regime in which the diffusing particle rarely confines itself to a near-neighbor jump alone. A variety of multi-neighbor jumps and other extended, curved, flights occurs instead. No conceptionally simple method for describing diffusive motion in this latter regime has previously been put forward. One-dimensional models employing ideas about a periodic one-dimensional potential and "friction," through Kramers's methods and the Langevin equation, have been used[11] to examine motion and identify a "breakaway" regime in strong fields. This is quite analogous to treatment of dislocation breakaway through pinning obstacles by Granato and co-

workers.[12]

It seems possible that the entropic factors associated with the high dimensionality of the real crystal problem may confine the relevance of the one-dimensional treatment to the quasi-one-dimensional motions of dislocations. It is not clearly applicable to adatom diffusion. Self-trapping of the mobile particle depends on cooperative motion of other atoms, and the efficiency of trapping is determined as much by the volume of configuration space available for trapping as by the depth of the trap. In complete conformity with this observation, computer simulations of surface diffusion in the weakly coupled regime exhibit a remarkable similarity to the ordinary hopping regime of strong coupling.[10] Figure 4 shows an example. The correlations between motion into successive configurations once more separate into a direct, dynamically correlated part and a randomized exponential decay. The proportions and time scales of events are, of course, rebalanced, but the physical distinction remains clear. Of greatest significance here is the fact that the mobile particle does repeatedly trap, randomize, and subsequently conform to an exponential, rate-theory-like escape probability.

We suggest here that this protracted trapping, followed by temporally brief flights, provides the appropriate conceptual simplification through which the diffusion may be calculated and specified. A prediction of the diffusion coefficient reduces to a calculation of the (rate-theory) detrapping time, and of the thermal expectation of the spectrum of random flights that the system takes between trapping events. Taken together these two properties determine the rate of which the mean square displacement changes.

Note that the consequences of this model may differ radically from those of friction models. In particular, if the cross section of trapping varies only weakly with particle energy, it is to be expected that the regime of breakaway field-induced motion is suppressed until the applied fields are large enough to cause direct detrapping.

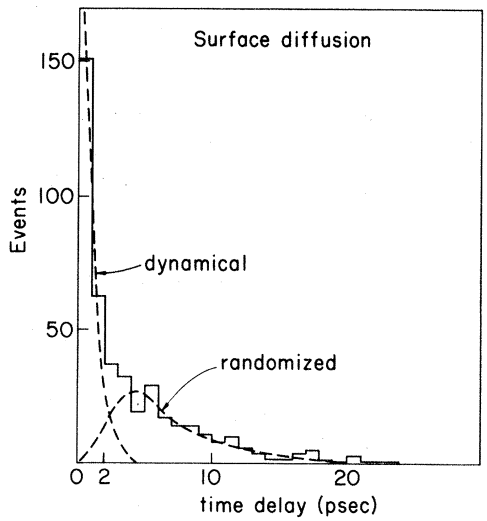


FIG. 4. Time delay between successive jumps of an adatom on a smooth surface according to de Lorenzi *et al.* (Ref. 10). Note the quantitative similarity to Fig. 1, despite the prevalence of multiple jumps in the adatom case. The existence of an exponential decay characteristic of randomization is the most significant aspect of this result.

## ACKNOWLEDGMENT

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## APPENDIX

To aid intuition and add concrete example to the theory we present here a simple model and calculate explicitly the shape of the saddle surface and the effect of this shape on the isotrope effect and the return jump rate. The model, shown in Fig. 5(a), is two dimensional and purely harmonic. It has two "atoms," 1 and 2, fixed by harmonic

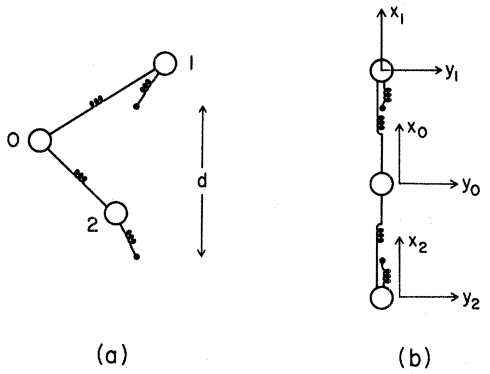


FIG. 5. The three-particle jump model employed in the Appendix is shown in (a). The saddle-point configuration and the coordinates used in the calculation are shown in (b).

springs to sites separated by a distance $d$, and a third, mobile "atom" labeled 0 connected to the other two by harmonic springs of unstretched length $d$. All particles have the same mass $M=1$ and all springs have the same force constant $k=1$. When the system is thermally excited the third atom can make transition to the opposite side of the other two. This thermal process is analyzed here.

The saddle point $s$ is easily found to have atoms 1 and 2 located respectively at $\pm 3d/4$ from atom 0 [see Fig. 5(b)]. In terms of coordinates $x_i$, $y_i$ of displacements from this configuration the potential energy $V$ is given by

$$2V=\left[x_1+\frac{d}{4}\right]^2+y_1^2+\left[x_2-\frac{d}{4}\right]^2+y_2^2+\left\{\left[\left[x_1-x_0+\frac{3d}{4}\right]^2+(y_1-y_0)^2\right]^{1/2}-d\right\}^2$$
$$+\left\{\left[\left[x_2-x_0-\frac{3d}{4}\right]^2+(y_2-y_0)^2\right]^{1/2}-d\right\}^2 . \tag{A1}$$

The orthonormal modes and eigenfrequencies about $s$ are

$$\eta_0=(a/\sqrt{2})(y_1+y_2)-(1-a^2)^{1/2}y_0 , \quad \omega_0^2=-\sqrt{2/3} ,$$
$$\eta_1=(1/\sqrt{2})(1-a^2)^{1/2}(y_1+y_2)+ay_0 , \quad \omega_1^2=\sqrt{2/3} ,$$
$$\eta_2=(1/\sqrt{2})(y_1-y_2) , \quad \omega_2^2=\tfrac{2}{3} , \tag{A2}$$
$$\eta_3=\tfrac{1}{2}(x_1+x_2)-(1/\sqrt{2})x_0 , \quad \omega_3^2=2[1+(1/\sqrt{2})] ,$$
$$\eta_4=\tfrac{1}{2}(x_1+x_2)+(1/\sqrt{2})x_0 , \quad \omega_4^2=2[1-(1/\sqrt{2})] ,$$
$$\eta_5=(1/\sqrt{2})(x_1-x_2) , \quad \omega_5^2=2 ,$$

with $a^2=(1-\sqrt{2/3})/2$. Mode $\eta_0$ is the jump mode; its directional cosine squared with respect to the axis $\eta_0$ gives the isotope effect factor for $T=0$ as

$$\kappa=1-a^2=\tfrac{1}{2}(1+\sqrt{2/3})=0.908248\ldots$$

for the jump process. The motion energy is

$$E_m=d^2/8 .$$

The shape of the saddle surface may be obtained with respect to the saddle plane $\eta_0=0$ by substituting the reciprocal equations $y_i=\sum_j \alpha_{ij}\eta_j$ of Eqs. (A2) into the potential energy given by Eq. (A1), expanding the function about $\eta_0=0$, and finally determining $\eta_0=-(\partial V/\partial\eta_0)_0/(\partial^2 V/\partial\eta_0^2)_0$. One finds to lowest order the saddle surface

$$\eta_0=\frac{d^3}{2}(\tfrac{3}{2})^{1/2}\{X_1^{-1}(\alpha_{20}-\alpha_{00})[\alpha_{12}\eta_2+(\alpha_{21}-\alpha_{01})\eta_1]^3+X_2^{-1}(\alpha_{10}-\alpha_{00})[\alpha_{22}\eta_2+(\alpha_{11}-\alpha_{01})\eta_1]^3\} , \tag{A3}$$

with

$$X_1=(x_1-x_0+3d/4)^3$$

and

$$X_2=(x_0-x_2+3d/4)^3$$

both reducing to $(3d/4)^2$ in this first approximation. Terms quadratic in the $\eta_i$ vanish, as required by the asymmetry of the jump in this simple example, to leave only cubic and higher terms.

In this same approximation of the inverse radius of saddle-surface curvature

$$\rho_i^{-1}=(\partial^2\eta_0/\partial\eta_i^2)_S/[1+(\partial\eta_0/\partial\eta_i)_S^2]^{3/2}$$

reduces to $(\partial^2\eta_0/\partial\eta_i^2)_S$. An evaluation of the coefficients $\alpha_{ij}$ and a thermal average over $\eta_1$ and $\eta_2$ with the Boltzmann weight

$$\exp[-\tfrac{1}{2}(\omega_1^2\eta_1^2+\omega_2^2\eta_2^2)/k_BT]$$

then provides the desired return jump rate in terms of the $\alpha_{ij}$. The relevant coefficients are

$$\alpha_{00}=-(1-a^2)^{1/2}=-\alpha_{11}=-\alpha_{21}\ ,$$
$$\alpha_{01}=a=\sqrt{2}\alpha_{10}=\sqrt{2}\alpha_{20}\ , \tag{A4}$$
$$\alpha_{12}=-\alpha_{22}=1,\alpha_{02}=0\ .$$

By means of a numerical evaluation of the final analytical result the fraction is finally obtained from $\langle(\omega_0^2\rho^2)^{-1}\rangle$ in the form

$$R'/R=4.63(k_BT/E_m)^2\ . \tag{A5}$$

Note that the dimensionality factor $3N-1$ in Eq. (6) must be taken as 5 rather than 8 because motion is permitted in only two space dimensions.

It is equally easy to find the temperature dependence of the isotope effect factor $\kappa=\langle\cos^2\theta\rangle$, with $\theta$ the angle between $y_0$ and $\eta_0$.[15] A very direct calculation leads to the result

$$\kappa=0.908-0.133(k_BT/E_m)\ . \tag{A6}$$

The results obtained from this simple model are interesting and somewhat reassuring. The cubic curvature of the surface with $\eta_1$ is mild over the range of thermal excursion even at high temperatures. Many simple solids melt at a temperature $T_m$ such that $E_m/k_BT_m\simeq 6$. Equation (A6) then indicates that $\kappa$ is changed by the coupling to this single mode by only a few percent between $T=0$ and $T=T_m$. It is not clear at present whether this is fortuitously small, but the indication is that very large changes of $\kappa$ with $T$ are not to be expected, in agreement with the experimental facts for real crystals.

In keeping with the mild isotope effects indicated by Eqs. (A6), Eq. (A5) suggests that most real systems do not come close to the condition of a return jump catastrophe. At low temperature such that $E_m/k_BT\gtrsim 10$, less than 5% of all jumps in our simple model system suffer dynamically inevitable return jumps after brief crossings of the saddlesurface; these occur even with the optimal choice of surface geometry, and none of the return processes would occur if, instead, the barrier actually contained a planar saddlesurface. In this regime the Vineyard theory clearly makes physical sense, and can be corrected in this simple way for dynamical memory. Even at the typical melting point $T_m\simeq E_m/6k_B$ the fraction of these return jumps only rises to about 13%. For this simple model, then, conventional rate theory appears to hold rather well at all reasonable temperatures for an optimum choice of the saddle surface separating the two configurations.

It is not, of course, assured that rate theory proves equally successful in real solids; the outcome must await detailed calculations for realistic models. A change by a factor of 10 in the coefficient of $T^2$ in Eq. (A6), or a factor of 3 reduction of $E_m$, each lead to a catastrophe in which trajectories with return jumps predominate, even for an optimal choice of surface separating the two configurations, and to a regime in which many trajectories cross the surface several times. In this latter regime the usefulness of rate theory is greatly reduced. The calculation in Refs. 3 and 4 shows signs of such behavior in computer simulations. It now appears very likely that this happens most widely in nature for cases such as alkali metals and superionic conductors which have $k_BT/E_m$ small. Detailed calculations now in progress will reveal the extent to which these phenomena do occur in solid materials.


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