Rate Theory, Return Jump Catastrophes, and the Center Manifold

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Explicit saddle surfaces and return jump rates are calculated for model crystals; the results establish the validity of rate calculations for atomic jumps in solids. A nonphysical effect, in which isotopic substitution causes a "return jump catastrophe," is resolved by use of an exact momentum-dependent criterion to distinguish successful jumps.

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We describe a theory which permits accurate calculations of jump rates[1] for atomic migration in model solids. Accurate rates have previously been available only from molecular-dynamics simulations.[2] The present analytic methods are generally applicable to processes in which successive jumps are well spaced. Our results include (i) a demonstration that statistical theories of diffusion are widely valid for ordinary solids; and (ii) a method for constructing saddle surfaces for diffusion, including an accurate determination of the saddle surface for diffusion by vacancies in model fcc solids, and an accurate evaluation of the dynamical return-jump frequency. These procedures for calculating absolute jump rates open the path to precise future Monte Carlo determinations both of energies, entropies, and volumes of migration for any chosen interatomic potential, and of the derivatives of these parameters with respect to thermodynamic variables. The latter quantities have been the topic of considerable unresolved discussion. Finally, in an accurate evaluation of the mass dependence of jump rates we encounter an "isotope effect catastrophe" in which clearly nonphysical effects arise from return jumps. The resolution of this problem provides a new conceptual basis for jump theories.

It is widely recognized that statistical treatments of atomic jumps (e.g., rate theory) can predict correct transition rates between configurations, but erroneously assume that randomization occurs between transitions.[1] The present work is based on an *Ansatz* by Flynn and Jacucci (FJ) that, to be nonrandom, successive transitions must occur with very little time delay.[3,4] We analyze the process of vacancy diffusion in model fcc crystals, for which the important nonrandom process is the immediate return jump.[5,6] First we obtain the form of the potential barrier which inhibits jumps, and then determine the shape and potential of the saddle surface; from these we calculate both the total transition rate and the rate of immediate return jumps. The calculations have been performed for several realistic interatomic force laws. In all cases the return-jump fraction is small, $<10\%$ even at high temperature, and less at low temperature. These results establish the validity of the rate-theory approach, and make possible the accurate calculation of jump rates for any chosen model crystal. We describe a specific example before turning to more fundamental issues in what follows.

To construct the required saddle surface we first determine the saddle-point configuration of the crystal for the vacancy jump. This proceeds by damped molecular dynamics and is finally perfected by Taylor expansion in terms of atomic displacements. The expansion then allows a diagonalization of the potential, V, which gives the eigenvalues and eigenvectors. One eigenvalue is negative; its eigenvector points along the jump direction, say ζ, in the $3N$-dimensional configuration space of the model crystal with N atoms. $3N-1$ eigenvectors provide coordinates ξ_i, $i=1, 2, \ldots, 3N-1$, in the saddle *plane*. Our choice of momentum-independent saddle surface is the "watershed" obtained by passing from the saddle point up the maximum gradient. At the saddle point the saddle plane is tangent to the saddle surface but the two do not generally coincide elsewhere. We wish to find the form of the saddle surface. This may be specified by the displacement ζ of the saddle surface perpendicular to the saddle plane, viz. $\zeta=\zeta(\{\xi_i\})$. To proceed further we must determine the form of this relationship.

Since, in retrospect, the deviation of the saddle surface from the plane produces significant but not large effects, it is appropriate to expand ζ in a power series,

$$\zeta = \tfrac{1}{2}\sum_{ij}\alpha_{ij}\xi_i\xi_j + \tfrac{1}{6}\sum_{ijk}\beta_{ijk}\xi_i\xi_j\xi_k + \dots \quad (1)$$

The coefficients α, β, etc., can then be connected with the derivatives $V_i = \partial V/\partial\xi_i$, $V_{ij} = \partial^2 V/\partial\xi_i\partial\xi_j$, etc., of the potential V (writing $\zeta \equiv \xi_0$ for convenience). By definition, $\vec{n}\cdot\nabla V = 0$ on the saddle surface, whose normal is here written $\vec{n}$. When differentiated twice for displacements in the saddle surface and evaluated at the saddle point, this equation yields

$$\alpha_{ij} = V_{0ij}/(V_{ii} + V_{jj} - V_{00}) \quad (2)$$

(noting that $\alpha_{ij} = -\partial n_i/\partial\xi_j = -\partial n_j/\partial\xi_i$ there). Similar expressions can be obtained for β, etc. The power series for ζ may thus be identified from the derivatives of the potential evaluated at the saddle point. In the present calculation it has been sufficient to consider the α_{ij} alone. For the fcc vacancy, symmetry dictates that the eigenvalues ρ_n^{-1} of the quadratic form $\sum_{ij}\alpha_{ij}\xi_i\xi_j$ occur in pairs with equal and opposite values. One then has

$$\zeta = \tfrac{1}{2}\sum_n \rho_n^{-1}(\eta_n^{\,2} - \eta_n'^{\,2}), \quad (3)$$

with the ρ_n principal radii of saddle-surface curvature at the saddle point, and η_n, η_n' the coordinates parallel to the curvatures $\rho_n^{-1}, -\rho_n^{-1}$.

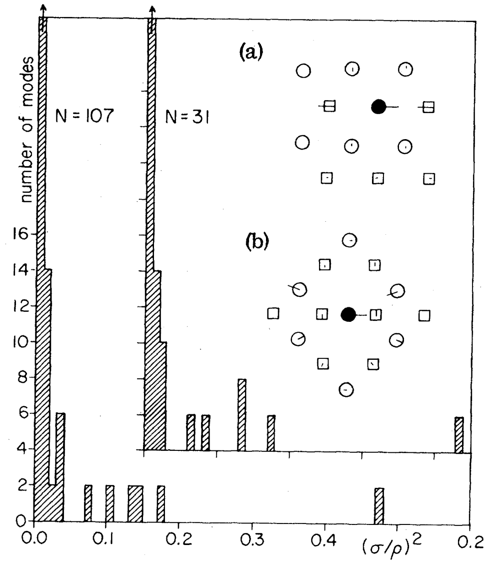

FIG. 1. Distributions of squared principal curvatures of the saddle surface for vacancy jumps in Lennard-Jones 31- and 107-atom cyclically repeating crystals. The atomic displacements in a direction of highest principal curvature are shown projected both (a) in the (110) plane normal to the atomic jump, and (b) in the parallel (100) plane. Circles denote atoms in the central plane, including the jumping atom. Squares denote atoms belonging to the two adjacent planes above and below. The twin directions of identical principal curvature are related by mirror reflection from the (110) plane through the central atom. $\sigma = 3.4$ Å for Ar is the length scale in the Lennard-Jones potential.

We have evaluated coefficients α_{ij} for several model fcc crystals with pair forces corresponding approximately to the cases of Ar, Cu, and Al.[7] From these coefficients we obtain the diagonal curvatures ρ_n^{-1}. Evaluations for crystals having $N = 31$ and $N = 107$ atoms (and with periodic boundary conditions to minimize surface effects) show a behavior which is both remarkable and simple. In most directions of configuration space the saddle surface is essentially flat. Five or six pairs of eigenvalues ρ_n^{-1} are much larger than the remainder, and these are insensitive to N. Figure 1 shows as examples the spectra of ρ_n^{-2} for Ar with $N = 31$ and $N = 107$. We find that the directions with large ρ^{-1} correspond to patterns of atomic displacements which are confined to atoms near the jumping atom. The displacements for the direction of largest curvature of the Ar saddle surface are shown in Fig. 1.

An important application is the evaluation of dynamical return-jump frequencies. As noted by FJ,[3] there is a critical velocity $\dot{s}_c$ at which a representative point moves parallel to a saddle surface of curvature ρ:

$$\dot{s}_c = (\alpha x \rho)^{1/2}, \quad (4)$$

with x the perpendicular distance to the saddle surface (see Ref. 3), and $V = V_0 - \alpha x^2/2$ the second-order variation of the potential along x. Fast return jumps have higher velocities. FJ show that the fraction R'/R of return jumps depends on $\langle\rho^{-2}\rangle$, averaged over all orientations in the saddle surface. For the surface in Eq. (3) this average is

$$R'/R = (2kT/\alpha)\sum_n 1/\rho_n^{\,2}. \quad (5)$$

TABLE I. Upper bound on return jump rates close to the melting point. The values of fcc lattice parameter and temperature were 4.1252, 5.4546, and 3.6963 Å and 933, 80, and 1358 K for Al, Ar, and Cu, respectively.

	$N = 31$	$N = 107$	$N \to \infty$
Al	5.1%	4.6%	4.4%
Ar	3.5%	4.3%	4.6%
Cu	4.0%	...	...

Hence by substitution of the inverse curvatures described above we find the return-jump rates reported in Table I for Ar, Cu, and Al. Our most significant numerical results are, first, that the calculated R'/R depends only weakly on N; and second, that while the return-jump fraction varies significantly among the three cases, it remains well below 10%, even at the melting temperature.

These results have a central importance for the theory of atomic migration in crystals. At all temperatures, only a small fraction of atomic jumps is dynamically eliminated by the subsequent short-time evolution of the system.[8] We thus establish that the rate-theory model is appropriate for ordinary solids. Its incorrect treatment of randomization is often a minor error which can be rectified by an accurate accounting for dynamical return jumps. In future, thermodynamic averages on the actual curved saddle surface, Eq. (3) (obtained for example by Monte Carlo methods), will provide raw jump frequencies. These can be corrected for inevitable return jumps to leave the required frequency of dynamically independent events. Calculations of this type, now in progress in our laboratories, yield absolute jump frequencies correct to within a few percent, which is comparable with the accuracy of the best experiments. It will be possible by these methods to explore the influence of the interatomic potential on the atomic migration rate in model solids, and to compare the model properties with the behavior of real solids.

While the preceding results remain valid in most practical cases, there nevertheless remain circumstances where rate theory breaks down. As pointed out by FJ this happens, for example, for low barriers when return jumps become very numerous. A "return jump catastrophe" occurs, and it is no longer possible to keep track of the configuration to which a particular trajectory belongs. Thus the method fails. We have subsequently realized that a catastrophe can be induced for essentially all interatomic potentials by changing the atomic masses appropriately. This breakdown points to a critical flaw in the conceptual basis of rate theory. We first discuss briefly the symptoms of this breakdown, through the isotope effect in diffusion, and then its cure through the identification of the critical jump condition with the *center manifold* in phase space.

The ratio w'/w of jump rates when the jumping mass is changed from the mass M of lattice atoms to M' may be specified by $w'/w = [1+\kappa(M'-M)/M]^{-1/2}$, where $\kappa = 1$ for an independent classical particle. In the crystal the appropriate effective mass in $w \propto M_\perp^{-1/2}$ is the inertia perpendicular to the saddle surface in configuration space. It is the squared projection of the surface normal onto the subspace of the jumping atom.[5] If the value at the saddle point is κ_0, the thermal average over the surface, Eq. (3), is $\kappa = \kappa_0 - \kappa_T T$. We have evaluated κ_0 and κ_T for our models of Ar, Cu, and Al, with the results given in Table II. The values of κ compare reasonably with experiment, where available.[9,10] κ_0 is lower for the softer metallic structures that relax more around defects. $\kappa_T T$ reduces κ by only one or two percent.

A third contribution κ_R to κ occurs because the return-jump fraction also is isotope dependent.[5] The calculation of this term can be carried out generally for the surface, Eq. (3); the result is $\kappa_R = \lambda R'/R$ with $\lambda \simeq 2$ typically for the curvature modes (see above) in our model crystals. This positive term is about 0.1 at T_m, which gives clearly nonphysical $\kappa > 1$ in some cases. The mass dependence of the return-jump rate which causes κ_R is $R'/R \sim R_0(M_\perp/M)^2$, in which R_0 depends on the state variables but not the atomic masses. This same mass dependence can also cause a return-jump catastrophe. Since $R'/R \sim 0.05$ at T_m for $M = M_\perp$ ($\simeq M'$), a system with $M_\perp$ ($\simeq M'$) $\sim 3M$ has $R'/R \sim 0.5$ at T_m. Multiple crossings of the saddle surface then proliferate and rate theory breaks down. The physical origin of these two effects is easily understood. As $M_\perp$ increases, the corresponding thermal velocity decreases and fewer jumps are caused by motion perpendicular to the saddle surface S. Accordingly, the proportion of jumps induced by motion *locally parallel* to the curved saddle surface S increases, and with it the fraction of *return* jumps

TABLE II. Harmonic and anharmonic isotope-effect factors.

	N	κ_0	$-\kappa_T T_M$	κ
Al	31	0.9229	−0.0188	0.9041
	107	0.9133	−0.0194	0.8939
	255	0.9125	⋯	⋯
	$\to\infty$	0.9124	−0.0196	0.8928
Ar	31	0.9609	−0.0139	0.9470
	107	0.9774	−0.0167	0.9607
	$\to\infty$	0.9789	−0.0178	0.9611
Cu	31	0.9365	−0.0153	0.9212
	107	0.9363	⋯	⋯

caused by the same curvature. Since, as $M_\perp$ becomes large, the system lingers near S, one can see also that more complicated trajectories may become prevalent, which cut S three, four, or more times. Rate theory is then not valid.

The problem has fundamental origins. We have first erected a curved saddle surface to fix the proper potential energy of transitions. Then, in correcting for inherent return jumps within the FJ *Ansatz,* a momentum-dependent jump criterion, Eq. (4), is encountered. The correct definition of a configuration is evidently both position (potential energy) dependent and momentum dependent. Therefore a surface *in phase space* is needed to distinguish separate configurations, and to count transition rates which contain no dynamically inevitable return jumps within the FJ *Ansatz.*

A precise method for separating successful and unsuccessful jumps can be adapted from the literature on invariant mainfolds.[11] In the $6N$-dimensional phase space of a dynamical system, the center manifold is the intersection of two $6N$-1 dimensional surfaces which divide the vector flow field into four regions A, B, C, and D. Of these, the flows in A and C correspond, respectively, to foward and backward jumps which are successful within the FJ *Ansatz,* and those in B and D correspond to unsuccessful jumps. The net forward flow is thus determined by a flow integral over a surface through A extending from the center manifold out to inaccessible regions of phase space. Stokes's theorem transforms this to an integral over the center manifold alone. Our work thus identifies the center manifold as a generalized saddle surface for rate calculations which are correct within the FJ *Ansatz.*

We have made explicit calculations using these ideas for model potentials. Full details will be reported elsewhere. The total jump fluxes so obtained are very close to those determined for the watershed saddle surface. However, all trace of the mass-dependent return-jump catastrophe is eliminated from the isotope effect. The present results therefore appear to provide both a means for calculating accurate jump rates and a more satisfactory conceptual foundation for theories of the jump process.

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[7] The chosen Lennard-Jones potential for Ar, and Morse potentials for Al and Cu, are fitted to the cohesion and compressibility.

[8] We have verified that *delayed* return jumps play no significant role by reproducing Bennett's results (Ref. 2) for the *total* return flux through the saddle *plane.*

[9] N. L. Peterson, in *Diffusion in Solids: Recent Developments,* edited by A. S. Nowick and J. J. Burton (Academic, New York, 1975), Chap. 3. The observed value for Cu is 0.87 ± 0.02.

[10] For Ar, κ is much closer to κ_0 than in Bennett's results (Ref. 2).

[11] R. Abraham and J. E. Marsden, *Foundations of Mechanics* (Benjamin, New York, 1967).