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Dynamical Theory of Diffusion.
II. Comparison with Rate Theory and the Impurity Isotope Effect*

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The formalism of the dynamical theory of diffusion is shown to be strictly analogous to that of the reaction-rate theory in the sense that expressions for the jump rate and related quantities can be written in the same form as the corresponding expressions of rate theory. However, the physical meaning of corresponding quantities is different. For example, the role of the saddle-point configuration in rate theory is taken by a dynamical state in the dynamical theory. The reaction coordinate is shown to measure the extent to which lattice reaction forces barring the jump have been overcome by thermal fluctuations. Geometric considerations indicate that for vacancy diffusion, the factor ΔK should have a lower limit on the order of 0.5 in the fcc lattice and an upper limit of the same order for the bcc lattice. In general, ΔK measures the mass dependence of the rms velocity of the system along the jump direction in configuration space. The mass dependence of the isotope effect for impurity diffusion is developed, and a double-isotope-effect experiment involving the simultaneous diffusion of three solute isotopes is proposed to determine impurity correlation factors.

I. INTRODUCTION

In a previous paper,[1] hereafter called I, a general formalism for a consistent dynamical description of the classical diffusion jump process was developed. It is the purpose of the present paper to recast these results in a form that makes their physical meaning more obvious and allows a direct comparison with the predictions of the reaction-rate theory.

In I, we considered a general reaction coordinate $x(t)$ of the form

$$x(t) = \underline{y}(t) \cdot \underline{R}\ , \tag{1.1}$$

where

$$\underline{y}(t) = \sum u_n \hat{\epsilon}_n e^{-i\omega_n t} \tag{1.2}$$

described the thermal motion of the lattice and

$$\underline{R} = \sum A_n \hat{\epsilon}_n \tag{1.3}$$

is a vector in the configuration space of the system, called the reaction vector, whose direction determines the attack frequency (i.e., the average rate at which the system attempts a jump) and whose magnitude sets the energy scale. Fluctuations of $x(t)$ were considered and it was assumed that whenever the projection of $\underline{y}(t)$ onto $\underline{R}$ exceeded R, a jump would take place. The ensemble-average jump rate Γ was found to be of the usual Arrhenius form

$$\Gamma = (\omega_0 / 2\pi)\, e^{-E_m / kT}\ , \tag{1.4}$$

where

$$\omega_0^2 = \langle \underline{R} \,|\, \underline{m}^{-1} \,|\, \underline{R} \rangle / \langle \underline{R} \,|\, \underline{D}^{-1} \,|\, \underline{R} \rangle \tag{1.5}$$

and

$$E_m = \tfrac{1}{2}\, \omega_0^2 \,|\underline{R}\,|^4 / \langle \underline{R} \,|\, \underline{m}^{-1} \,|\, \underline{R} \rangle\ . \tag{1.6}$$

Here $\underline{m}$ and $\underline{D}$ are the mass matrix and dynamic matrix, respectively. If all the atoms of the crystal have the same mass, these expressions simplify to

$$\omega_0^2 = |\underline{R}\,|^2 / \sum \frac{A_n^2}{\omega_n^2} \tag{1.7}$$

and

$$E_m = \tfrac{1}{2}\, m \omega_0^2 \,|\underline{R}\,|^2\ . \tag{1.8}$$

Equations (1.7) and (1.8) show that the problem has effectively been reduced to one of an oscillator of frequency ω_0 vibrating in direction $\underline{R}$ in an N-dimensional harmonic well cut off at the energy E_m.

The energy E_m above is temperature dependent through the elastic constants and so naturally gives rise to an entropylike term in the expression for the jump rate. However, E_m was shown in I to be mass independent, so that the diffusion isotope effect arises only from the mass dependence of ω_0, and does not depend on the migration entropy.

These results are to be compared to those of the absolute reaction-rate formulation of Vineyard.[2] The rate-theory expression for the jump rate has the same form as Eq. (1.4), but the physical interpretation of the quantities involved is somewhat different. If one imagines $(N-1)$-dimensional hyperplanes S_0 and S passing through the equilibrium and saddle-point configurations, respectively, both hyperplanes being normal to the eigenvector of the unstable "mode" at the saddle point, then the attack frequency is given by

$$\omega_0 = \prod^{N} \omega_i \Big/ \prod^{N-1} \Omega_i\ , \tag{1.9}$$

where the $N-1$ Ω_i's are the eigenfrequencies for the system constrained to vibrate in the hyperplane S_0. The activation free energy consists of, besides the height of the potential barrier, an activation entropy term $-T\Delta S$, with ΔS given by

$$e^{\Delta S/k}=\prod^{N-1}\Omega_i\Big/\prod^{N-1}\Omega_i' , \tag{1.10}$$

with Ω_i' being the eigenfrequencies for the system constrained to vibrate in the hyperplane S. The quantity ΔS represents the entropy change involved in reversibly moving the system from S_0 to S.

There are two points to note. First, Eqs. (1.7) and (1.9) appear to portray quite different types of lattice frequency average as appropriate for finding the attack frequency. The second point is that the diffusion isotope effect in rate theory depends on the mass dependence of both the attack frequency and the migration entropy term, while in the dynamical theory it depends only on the attack frequency.

In what follows, we shall show that these and other differences are only apparent. That is, there is a complete formal analogy between the results of the two theories. They are not identical, however, because the analogous quantities do not have the same physical meaning. For example, both theories pick out a special direction in the system configuration space. For rate theory, this direction lies along the unstable "mode" eigenvector, while for the dynamical theory it is the direction of the reaction vector $\underline{R}$. As we shall see, it is possible to think of the dynamical picture in terms of hyperplanes like S and S_0 in just the same way as the reaction-rate theory does. However, the physical meaning of these planes and, in particular, of the analogous "saddle-point" configuration has to be carefully considered. The "saddle point" of the dynamical theory is, in reality, a dynamical state (i.e., displacements and velocities) not far removed from the equilibrium configuration, but dynamically connected to the top of the potential well through the equations of motion.

Section II shows that the attack frequency ω_0 can be written in exactly the form of Eq. (1.9) with the constrained frequencies referring to the system being constrained to a hyperplane normal to the reaction vector $\underline{R}$ through the origin. Section III demonstrates that a hyperplane normal to $\underline{R}$ at its tip plays the role of the saddle-point surface in the dynamical theory. Section IV shows the physical connection between the reaction coordinate and the lattice forces resisting the desired fluctuation. An approximate form for $x(t)$ is derived from geometrical considerations. Section V shows that the diffusion isotope effect has the same form in the two theories. By extending the work of I to the case where the diffusing atom has much different mass than that of the matrix, we derive a general expression for the impurity diffusion isotope effect in terms of the self-diffusion isotope effect involving the same reaction coordinate. This expression shows that the isotope effect does not, in general, merely measure the fraction of energy carried by the diffusing atom in the jump process, although it reduces to this for self-diffusion. Instead, it is a measure of the relative extent to which the phonons can set the various atoms moving along the reaction vector. A double-isotope-effect experiment is proposed that would allow one to unequivocally determine impurity correlation factors for certain systems. Examples of Ca diffusion in NaCl and LiF and of Fe and Ni diffusion in Be are analyzed to demonstrate the magnitude of experimental quantities and uncertainties involved in such experiments. The last section is a discussion of results and conclusions.

II. ATTACK FREQUENCY ω_0

In order to show that the attack frequency of the dynamical theory may be written in the form of Eq. (1.9), let us consider the configuration space hyperplanes[3] S and S_0 shown schematically in Fig. 1. The surface S passes through the tip of $\underline{R}$ and S_0 passes through the origin; both surfaces have $\underline{R}$ as a normal vector. Thus, we may write down the equations for the two hyperplanes in terms of the components of $\underline{R}$ along the normal-mode axes A_n. Arbitrarily taking the component u_1 to be the dependent variable, we can write the equations as

$$S:\ u_1+\sum_2 s_n u_n=\frac{R^2}{A_1} \tag{2.1}$$

and

$$S_0:\ u_1+\sum_2 s_n u_n=0\ , \tag{2.2}$$

where

$$s_n=A_n/A_1\ . \tag{2.3}$$

The equation for S will be used in Sec. III. Here we suppose that the system is constrained to move in the surface S_0, and write down the constrained Lagrangian equations of motion. The unconstrained equations are

$$-\frac{\partial[\frac{1}{2}m\sum_1\omega_i^2u_i^2]}{\partial u_k}=\frac{\partial}{\partial t}\left(\frac{\partial[\frac{1}{2}m\sum_1\dot{u}_i^2]}{\partial\dot{u}_k}\right)\ , \tag{2.4}$$

where the ω_i^2 are the eigenvalues of the unconstrained dynamic matrix. Using the differential form of Eq. (2.2), and assuming harmonic time dependence of frequency Ω, the constrained equations of motion read

$$\omega_k^2u_k-\omega_1^2u_1s_k=\Omega^2(u_k-s_ku_1) \tag{2.5}$$

or

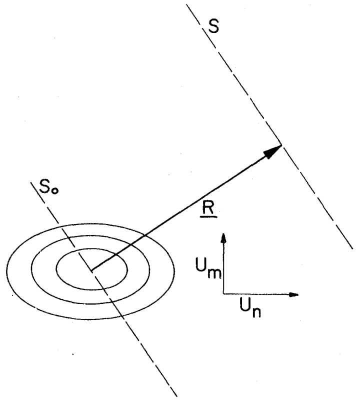

FIG. 1. Schematic drawing of the equipotential surfaces around an equilibrium configuration. The reaction vector $\underline{R}$ and normal surfaces S and S_0 are shown.

$$\frac{u_k}{u_1}=\frac{s_k(\omega_1^2-\Omega^2)}{\omega_k^2-\Omega^2} . \tag{2.6}$$

We may now substitute Eq. (2.6) into (2.2) to find that

$$1=(\omega_1^2-\Omega^2)\sum_2 \frac{s_k^2}{\Omega^2-\omega_k^2} , \tag{2.7}$$

that is,

$$0=\sum_1 \frac{s_k^2}{\Omega^2-\omega_k^2} , \tag{2.8}$$

where $s_1=1$.

Now there is an equation like (2.8) for each of the constrained frequencies Ω_n. That is, the $N-1$ values of Ω_n^2 are just the zeros of the function

$$f(x)=\sum_1 \frac{s_k^2}{x-\omega_k^2} . \tag{2.9}$$

Further, it is obvious from Eq. (2.9) that $f(x)$ has a simple pole at each of the N unconstrained frequencies ω_k^2. This means that $f(x)$ can be written as a rational function with numerator and denominator completely factored. The numerator will consist of $N-1$ factors of type $x-\Omega_k^2$, while the denominator is made up of N factors of type $x-\omega_k^2$. This analysis determines $f(x)$ to within a multiplicative constant which may be found by taking the limit

$$\lim xf(x)=\textstyle\sum_1 s_k^2 \text{ as } x\to\infty . \tag{2.10}$$

Putting all of this together allows us to write

$$f(x)=\sum \frac{s_k^2}{x-\omega_k^2}=\left(\sum s_k^2\right) \prod^{N-1}(x-\Omega_k^2)\Big/\prod^{N}(x-\omega_k^2) . \tag{2.11}$$

The purpose of this exercise is that we may now recast our expression for the attack frequency ω_0, Eq. (1.7), into the form of Eq. (1.9) by evaluating $f(0)$:

$$f(0)=-\sum\frac{s_k^2}{\omega_k^2}=-\left(\sum s_k^2\right)\prod^{N-1}\Omega_k^2\Big/\prod^{N}\omega_k^2 , \tag{2.12}$$

so that

$$\omega_0^2=\frac{\sum A_k^2}{\sum(A_k^2/\omega_k^2)}=\frac{\sum s_k^2}{\sum(s_k^2/\omega_k^2)}=\prod^{N}\omega_k^2\Big/\prod^{N-1}\Omega_k^2 . \tag{2.13}$$

This result shows that the attack frequency of the dynamical theory has exactly the same form as that of the reaction-rate theory. In either case the attack frequency represents the average rate with which the system sets off in a certain configuration space direction, and in either case the frequency can be calculated from the ratio of constrained and free partition functions.[2]

It should be remarked that the physical meaning of ω_0 is that it is the average system velocity along the direction of $\underline{R}$ divided by the average displacement along $\underline{R}$. That is,

$$\omega_0^2=\langle|\dot{\underline{y}}\cdot\underline{R}|^2\rangle/\langle|\underline{y}\cdot\underline{R}|^2\rangle , \tag{2.14}$$

where the brackets indicate thermal averaging. This observation will be of importance in understanding the physical origin of the diffusion isotope effect in Sec. V.

The fact that the two theories give expressions of the same type for the attack frequency does not mean, of course, that the two frequencies so calculated are identical. There would be identity if the direction of $\underline{R}$ and the direction normal to the saddle-point surface were identical, but this is not to be expected. That is, the product of constrained frequencies appearing in the denominator of Eq. (2.13) will be different in the two theories. The nature of the constraining surface in the dynamical theory favors the high-frequency modes in Eq. (1.7) for the reasons discussed in I, while the corresponding surface of the rate theory leads to less weighting of these modes. Thus, one is led to expect a higher attack frequency from the dynamical approach than that found by the rate-theoretic formalism.

III. MIGRATION ENERGY

In I, it was noted that the migration energy E_m of Eq. (1.8) is not the harmonic potential energy at the point $\underline{R}$. Indeed, it was shown that E_m is always less than the energy of the configuration $\underline{R}$. In this section, we shall demonstrate that E_m is precisely the harmonic energy of that configuration on the hyperplane S defined in Sec. II of lowest energy. That is, the hyperplane S plays the role of the saddle-point surface, and it is the configuration of lowest energy on S that sets the rate.

To see the correctness of this assertion, it is only necessary to find the configuration $\underline{r}_m$ of lowest energy, and compare its energy with E_m. Let $\underline{r}_m$ have components u_{km} that minimize the potential energy

$$V=\tfrac{1}{2}m\sum\omega_k^2u_k^2 \tag{3.1}$$

subject to the constraint of Eq. (2.1). Using the differential form of Eq. (2.1), the minimization condition may be written as

$$u_{km}/u_{1m}=s_k\omega_1^2/\omega_k^2\ . \tag{3.2}$$

This last expression may be substituted into Eq. (2.1) to solve for u_{1m}:

$$u_{1m}=\frac{R^2}{A_1}\Big|\sum\frac{s_k^2\,\omega_1^2}{\omega_k^2}\ . \tag{3.3}$$

Thus, from Eqs. (2.1), (2.3), and (3.3) we have that

$$u_{km}=A_k\,\omega_0^2/\omega_k^2\ , \tag{3.4}$$

and the minimum energy from Eq. (3.1) is

$$V_{\min}=\tfrac{1}{2}m\sum\omega_k^2\,u_{km}^2=\tfrac{1}{2}m\,\omega_0^4\sum A_k^2/\omega_k^2=\tfrac{1}{2}m\,\omega_0^2R^2=E_m\ . \tag{3.5}$$

That is, the minimum energy on S is just the migration energy as was claimed.

IV. REACTION COORDINATE $x(t)$

We turn now to an attempt to give a more physical interpretation of the reaction coordinate $x(t)$ and the reaction vector $\underline{\mathrm{R}}$. It is easy to see that $\underline{\mathrm{R}}$ is associated with the lattice reaction force at the configuration $\underline{\mathrm{r}}_m$ corresponding to the saddle point of rate theory. This force is just

$$\underline{\mathrm{F}}(\underline{\mathrm{r}}_m)=-m\sum\omega_k^2u_{km}\hat{\epsilon}_k=-m\,\omega_0^2\sum A_k\hat{\epsilon}_k=-m\,\omega_0^2\underline{\mathrm{R}}\ , \tag{4.1}$$

where the components of $\underline{\mathrm{r}}_m$ and u_{km} are given by Eq. (3.4). Comparison of this expression with that for the migration energy, Eq. (1.8), shows that the effective oscillator analogy of the introduction may be carried over to the "saddle-point" force.

Some insight into the reaction coordinate itself can be found by writing it in terms of $\underline{\mathrm{r}}_m$ instead of $\underline{\mathrm{R}}$. Thus,

$$\begin{aligned}x(t)&=\sum A_ku_ke^{-i\omega_kt}=\omega_0^{-2}\sum u_{km}\omega_k^2u_k\,e^{-i\omega_kt}\\&=-(m\,\omega_0^2)^{-1}\,\underline{\mathrm{r}}_m\cdot\underline{\mathrm{F}}(\underline{\mathrm{y}})\ .\end{aligned} \tag{4.2}$$

From the two above results, it is seen that $x(t)$ may be viewed equivalently as a measure of either the degree to which the thermal displacement $\underline{\mathrm{y}}$ has overcome the reaction force barring the configuration $\underline{\mathrm{r}}_m$ or the degree to which the forces which have been overcome in achieving the thermal displacement are in the direction of $\underline{\mathrm{r}}_m$. Notice that if the displacement $\underline{\mathrm{y}}$ were purely along $\underline{\mathrm{r}}_m$, say,

$$\underline{\mathrm{y}}=\alpha\underline{\mathrm{r}}_m\ , \tag{4.3}$$

then

$$x(t)=\alpha\underline{\mathrm{r}}_m\cdot\underline{\mathrm{R}}=\alpha R^2\ , \tag{4.4}$$

so that the critical displacement would be reached at $x=R^2$. In general, this critical value corresponds to the thermal motion having carried the system to any configuration on the hyperplane S of Sec. II.

It should be remarked that although the configuration $\underline{\mathrm{r}}_m$ plays a role in the dynamical theory analogous to that of the saddle-point configuration in the reaction-rate theory, the two configurations are not physically similar. The configuration $\underline{\mathrm{r}}_m$ corresponds to a dynamical fluctuation in positions and velocities which is dynamically connected with the jump. That is, the equations of motion, with $\underline{\mathrm{r}}_m$ as the initial condition, carry the system through a jump.

In I, we discussed a model calculation for a vacancy jump in a two-dimensional hexagonal lattice. The system was started in the saddle-point dissolution mode with very small velocity and the equation of motion integrated to the bottom of the potential well where the velocities were reversed. The resulting configuration and velocities were used to derive a reaction coordinate. The same information could be used to find the configuration $\underline{\mathrm{r}}_m$ through Eq. (3.4). This analysis yields a configuration very close to the equilibrium configuration; the jumping atom approaches the barrier while the barrier opens up. More precisely, the displacements were

$$x_1=0.0093\ ,\quad x_2=x_3=-0.0026\ ,$$
$$y_2=-y_3=0.0094$$

in units of $\frac{1}{2}a$, with a the lattice constant, and the velocities were

$$v(x_1)=0.1105\ ,\quad v(x_2)=v(x_3)=-0.0046\ ,$$
$$v(y_2)=-v(y_3)=0.0565$$

in units of $\frac{1}{2}a\omega_E$, where ω_E is the Einstein frequency of an atom in the perfect crystal. Here atom 1 is the jumping atom and atoms 2 and 3 form the barrier; x is the jump direction and y the perpendicular direction. The above configuration is far removed from the saddle point $(x_1=\frac{1}{2})$. As discussed in I, it is equivalent to a reaction coordinate proportional to

$$x(t)=x_1-0.432\,(x_2+x_3)+0.802\,(y_2-y_3)\ , \tag{4.5}$$

which clearly shows the importance of the transverse motion.

Actually, it may be possible to make a crude estimate of the reaction coordinate in terms of geometric quantities when the interaction between the jumping atom and the barrier atoms is more important than those with the rest of the lattice. We are looking for a fluctuation that will bring the jumping atom to the center of the barrier with the minimum expenditure of energy. If the rest of the lattice were ignored, this could be accomplished by merely rotating the bonds, i.e., by displacements that bring the jumping atom forward while leaving the jumping-atom–barrier-atom distances unchanged. We will assume that such motion adequately describes the start of a jump, an assumption that becomes more valid as the interactions between barrier atoms and the rest of the lattice become weaker.

Suppose, for example, that the vector $\underline{b}$ separating a barrier atom from the jumping atom has components b_x in the jump direction and b_y normal to this direction. Then infinitesimal displacements δb_x and δb_y leave $|\underline{b}|$ unchanged to first order if

$$\frac{\delta b_x}{\delta b_y} = -\frac{b_y}{b_x} = -\tan\theta \ , \qquad (4.6)$$

where θ is the angle that $\underline{b}$ makes with the jump direction. Equation (4.6) defines a configuration space plane in which such motions lie. The distance from the origin of a point on this plane is measured by

$$-\delta b_x + \tan\theta\, \delta b_y = x_1 - x_b + \tan\theta\, y_b \qquad (4.7)$$

in terms of displacements from equilibrium. Here, the subscripts 1 and b refer to the jumping atom and barrier atom, respectively; x refers to the jump direction and y to the normal direction. We are assuming that only symmetrical compressions and dilations of the barrier enter the reaction coordinate, so that only the outward normal displacement is included in Eq. (4.7).

There is an expression like Eq. (4.7) for each of the N barrier atoms; adding these together gives a reaction coordinate of the form

$$x(t) = x_1 - \frac{1}{N}\sum x_b + \frac{\tan\theta}{N}\sum y_b \ . \qquad (4.8)$$

Equation (4.8) determines the structure of the reaction vector, although not the critical value. Thus the migration energy, Eq. (1.8), remains a parameter. It is sufficient, however, to determine the attack frequency via Eq. (1.7). For example, in the two-dimensional model discussed earlier, Eq. (4.8) predicts the reaction vector

$$\underline{R} \propto \hat{x}_1 - 0.5(\hat{x}_2 + \hat{x}_3) + \tfrac{1}{2}\sqrt{3}\,(\hat{y}_2 - \hat{y}_3) \ , \qquad (4.9)$$

where y is now a Cartesian coordinate. The reaction vector of Eq. (4.9) should be compared to the reaction coordinate of Eq. (4.5) found directly from the equations of motion. Including relaxation reduces the coefficient of the transverse motion to 0.836, the remaining difference between Eqs. (4.5) and (4.9) being due to interactions not included in the above analysis. This reaction vector leads to a value of ω_0 of about half the Einstein frequency for an atom in the perfect crystal.

Equation (4.8) may also be applied to real crystals. The resulting reaction coordinate is identical to Flynn's[4] as far as motion along the jump direction is concerned. It differs in that account is taken of the necessity of transverse barrier atom motion, i.e., that the barrier ring must open up as the jumping atom approaches. If one assumes a Debye spectrum of lattice vibrations, and calculates the summands of Eq. (1.7) to order k^2 as was done by Flynn, one finds his value of $(\frac{3}{5})^{1/2}\,\omega_D$ for the fcc vacancy attack frequency to be reduced by about 10% by the inclusion of transverse barrier motion.

An interesting point regarding the self-diffusion isotope effect in bcc lattices may be made here. Using Eqs. (5.5)–(5.7) of Sec. V which relate the quantity ΔK to the reaction vector $\underline{R}$, the general reaction coordinate of Eq. (4.8) is seen to correspond to a value of ΔK for self-diffusion (and vanishingly small isotopic mass difference) of

$$\Delta K = N/(N + \sec^2\theta) \ . \qquad (4.10)$$

For the bcc vacancy jump, Eq. (4.8) gives a reaction vector

$$\underline{R} \propto \hat{x}_1 - \tfrac{1}{3}\sum \hat{x}_i + \tfrac{1}{3}\sqrt{2}\sum \hat{\rho}_i \ , \qquad (4.11)$$

where ρ_i refers to the outward displacement of barrier atom i. Equation (4.10) gives a value of 0.5 for ΔK. The inclusion of interactions other than those considered would, presumably, increase this value as before. However, the effect of relaxation is the opposite of that in the two-dimensional model or fcc crystals where relaxation decreases $\tan\theta$ in Eq. (4.8), thereby increasing ΔK. For the bcc lattice, calculations[5] show that the triangular barrier to the jumping atom relaxes outward. That is, relaxation increases the coefficient of the transverse displacement, and therefore decreases ΔK. Thus, ΔK is seen to have an upper limit for bcc vacancy diffusion on the order of 0.5, in contrast to the fcc case where the same considerations lead to a lower limit on ΔK.

The above is meant to be no more than a crude qualitative step toward understanding why metals of the same crystal structure have approximately the same isotope effect for self-diffusion, and why this quantity might be lower for bcc metals than for fcc metals.

V. DIFFUSION ISOTOPE EFFECT

In I, assuming $\underline{R}$ to be mass independent, it was shown that the mass dependence of the jump rate arose entirely from ω_0. That is to say, the migration free energy was found to be mass independent in the dynamical theory. It appears that this might be a discrepancy with the rate theory which predicts that the migration entropy may also be mass dependent through the constrained frequencies Ω_i and Ω'_i of the equilibrium and saddle-point surfaces [Eq. (1.10)].

This discrepancy is not real, however. Although the equilibrium hyperplane S_0 is only vaguely defined in Vineyard's rate-theoretic formulation,[2] it seems natural to orient it parallel to the saddle-point surface S. In this case, the ratio of products of frequencies in Eq. (1.10) is just the square root of the ratio of the two constrained dynamic matrices. This ratio is mass independent, as can be seen by writing it in terms of the full dynamic matrices D and D' of the equilibrium and saddle-point configurations, respectively:

$$e^{\Delta S_m/k}=\left(\frac{m'_1[\Omega'_1]^2}{m^*\omega_0^2}\right)^{1/2}\left(\frac{|D|}{|D'|}\right)^{1/2}, \tag{5.1}$$

where $m'_1[\Omega'_1]^2$ is the single negative eigenvalue of D', ω_0 is the attack frequency as before, and m^* is the effective mass associated with the attack frequency. Now the dynamic matrices are mass independent. The two effective masses above refer to the same direction in configuration space and so are identical [see Eq. (3.1) of I]. Finally, the two frequencies above both refer to the same effective mass and so have identical mass dependence. Thus the migration entropy is mass independent if the surfaces S and S_0 are parallel. Also note that since the two frequencies have the same mass dependence, i.e.,

$$\frac{1}{\Omega'_1}\frac{\partial\Omega'_1}{\partial m}=\frac{1}{\omega_0}\frac{\partial\omega_0}{\partial m}, \tag{5.2}$$

the isotope effect as calculated from ω_0 is identical to that calculated from Ω'_1 (the usual rate-theoretic prescription). Once again we see a complete formal analogy between the results of the rate and dynamical theories.

The treatment of the diffusion isotope effect in I was carried out for the case of self-diffusion, i.e., where the diffusing isotopes have nearly the same mass as the host atoms. This situation permitted us to expand in the small mass differences involved. Such an approximation need not be made, however, and avoiding it allows one to gain a more general physical picture of the isotopic dependence of the jump rate.

In Sec. III of I, it was shown that the attack frequency is given by

$$\omega_0^2=\langle\underline{\mathrm{R}}|\underline{\mathrm{m}}^{-1}|\underline{\mathrm{R}}\rangle/\langle\underline{\mathrm{R}}|\underline{\mathrm{D}}^{-1}|\underline{\mathrm{R}}\rangle, \tag{5.3}$$

where $\underline{\mathrm{m}}$ is the mass matrix and $\underline{\mathrm{D}}$ is again the dynamic matrix. It is the numerator of Eq. (5.3) that makes the frequency mass dependent. If we write the reaction vector $\underline{\mathrm{R}}$ in terms of the atom coordinate representation $\hat{x}_\alpha$ rather than the normal-mode representation $\hat{\epsilon}_n$, the effect on the jump frequency of changing the mass of a single atom is easily calculated. If

$$\underline{\mathrm{R}}=\sum A_n\hat{\epsilon}_n=\sum V_\alpha\hat{x}_\alpha,$$

and one substitutes for a host atom of mass m an atom of mass M, the resulting jump frequency is proportional to

$$\Gamma(M)\propto[(M^{-1}-m^{-1})\Delta K_0R^2+\langle\underline{\mathrm{R}}|\underline{\mathrm{m}}_0^{-1}|\underline{\mathrm{R}}\rangle]^{1/2}, \tag{5.4}$$

where $\underline{\mathrm{m}}_0$ is the mass matrix of the perfect lattice. From Eq. (5.4) it is easy to calculate the isotope effect to be expected upon diffusing isotopes of mass M and M':

$$\frac{[\Gamma(M)-\Gamma(M')]/\Gamma(M')}{(M'/M)^{1/2}-1}=\frac{\Delta K_0}{(M'/m)(1-\Delta K_0)+\Delta K_0}\times g(m,M,M'). \tag{5.5}$$

Here

$$\Delta K_0=\langle\underline{\mathrm{R}}|\underline{\Delta}\ \underline{\mathrm{K}}|\underline{\mathrm{R}}\rangle/R^2 \tag{5.6}$$

is the isotope effect one would have for self-diffusion with the same reaction coordinate, and

$$\underline{\Delta K}=|x_1\rangle\langle x_1|+|x_2\rangle\langle x_2|+|x_3\rangle\langle x_3| \tag{5.7}$$

is the projection operator onto the space of the diffusing atom as in I. The factor g in Eq. (5.5) is very nearly unity for all practical cases and will be neglected in the discussion of the next few paragraphs; it will be considered at the end of this discussion.

Equation (5.5) indicates that one should expect a decrease in the isotope effect as the mass of the diffusing atom is increased provided that the reaction coordinate remains the same. This decrease will be the more pronounced the smaller the value of ΔK_0, the rate of change of ΔK with mass being given by

$$\frac{1}{\Delta K}\frac{\partial\Delta K}{\partial(M/m)}\bigg|_{M=m}=-(1-\Delta K_0). \tag{5.8}$$

This result reflects the fact that it is easier for an incoming phonon to set a light atom vibrating with a large amplitude than a heavy one, as will be discussed in more detail below. Thus, one would think, for example, that substitutional impurities in the noble metals[6,7] ($\Delta K_0\sim 0.9$[8,9]), which differ in mass by less than a factor of 2 from the host, would exhibit a value of ΔK different from ΔK_0 by less than about 8%. On the other hand, a substitutional impurity in sodium ($\Delta K_0\sim 0.5$[10]) could have a ΔK significantly different from ΔK_0. The variation of ΔK with the mass of the diffusing atom given by Eq. (5.5) is shown in Fig. 2 for two "typical" values of ΔK_0 to illustrate the above point.

It is also obvious from Eq. (5.5) that, in general, ΔK does not measure the fraction of energy carried by the diffusing atom in the pure jump motion (i.e.,

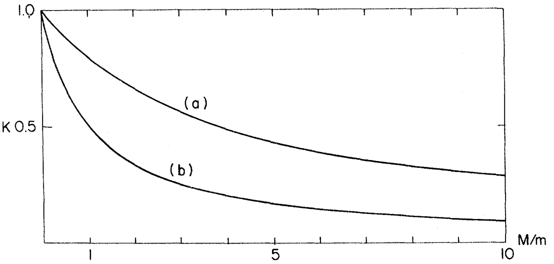

FIG 2. Variation of ΔK with impurity mass M; host mass is m. Curve (a): $\Delta K_0 = 0.8$; curve (b): $\Delta K_0 = 0.5$.

along $\underline{R}$ in the dynamical theory or along the normal to the saddle-point surface in the rate theory), although it reduces to this for self-diffusion. Rather, we must return to Eq. (2.14), where it was shown that the attack frequency depends on the average velocity along direction $\underline{R}$, to see that the physical interpretation of the isotope effect must be in terms of this rms velocity. If we realize that the amplitude of vibration (and therefore the velocity) at a given atom is proportional to the inverse root of the mass, the meaning of Eqs. (5.4) and (5.5) becomes clear. It is a combination of two factors that determines the isotope effect. The first depends on the projection ΔK_0 which measures the extent to which motion of the jumping atom can move the system along $\underline{R}$. This value is then renormalized by the denominator of Eq. (5.5) to account for the fact that heavier (lighter) atoms will have a smaller (larger) influence than that given by the purely geometric quantity ΔK_0.

Finally, we return to the quantity $g(m, M, M')$ of Eq. (5.5). This is a correction factor of very nearly unity and is due to the fact that the difference $M - M'$ is finite rather than infinitesimal. It is given by

$$g(m, M, M') = \left[\left(\frac{M'}{M}\right)^{1/2} + 1\right] \Big/ \left(\frac{[1 + \Delta K_0 (m/M - 1)]^{1/2}}{[1 + \Delta K_0 (m/M' - 1)]^{1/2}} + 1\right), \tag{5.9}$$

and is plotted as a function of m/M' in Fig. 3 for the two values of ΔK_0 used in Fig. 2. We have taken M and M' to differ by 20% in Fig. 3 to exaggerate the effect; it will be smaller in most practical cases.

The expression that we have found for ΔK not only provides an interpretation of the isotope effect for other than self-diffusion; it also can be of help in extracting impurity correlation factors from experiment. We shall give two examples.

The first is the case where one assumes that a substitutional impurity diffuses with nearly the same reaction coordinate as that appropriate to self-diffusion. In such a case, Eq. (5.5) may be applied directly to calculate ΔK and thus find the impurity correlation factor f_i from the quantity $f_i \Delta K$ measured by the usual isotope-effect experiment. Such a treatment would, for example, revise the values estimated by Rothman and Peterson[6] for the correlation factor of Zn in Ag downward by some 5% while not changing those for Zn in Cu.[7]

An experiment that would directly measure ΔK_0 in cases where three isotopes of the impurity may be simultaneously diffused may be feasible in certain systems. This double-isotope experiment would depend on the simultaneous measurement of two concentration ratios to find the ratio of two isotope effects. Suppose isotopes of mass M_a, M_b, and M_c diffuse substitutionally, replacing an atom of mass m. It we start from the usual thin-layer source so that a Gaussian penetration is appropriate, then

$$\ln(c_a/c_b) = (D_a/D_b - 1)(D_a/D_c - 1)^{-1} \ln(c_a/c_c) + \text{small constant}, \tag{5.10}$$

where $c_{a,b,c}$ and $D_{a,b,c}$ are the concentrations and diffusion constants of isotopes a, b, c, respectively. Thus, the slope γ^a_{bc} of the curve $\ln(c_a/c_b)$ vs $\ln(c_a/c_c)$ gives an experimental ratio of two isotope effects. Assuming that the correlation factor f_i is identical for the three isotopes,[11] we have that

$$\Delta K^a_b / \Delta K^a_c = \gamma^a_{bc} [(M_b/M_a)^{1/2} - 1][(M_c/M_a)^{1/2} - 1]^{-1} . \tag{5.11}$$

Here

$$\Delta K^a_b = \frac{\Delta K_0 g(m, M_a, M_b)}{(M_b/m)(1 - \Delta K_0) + \Delta K_0}, \tag{5.12}$$

and similarly for ΔK^a_c. One may thus invert the measured slope to find ΔK_0. To get some idea of the range in values to be expected and the limitations on accuracy inherent in such an experiment it is convenient to consider ΔK_0 as a function of the parameter k defined as follows:

$$k = \frac{\Delta K^a_b}{\Delta K^a_c} \frac{g(m, M_a, M_c)}{g(m, M_a, M_b)} = \frac{M_c(1 - \Delta K_0) + \Delta K_0}{M_b(1 - \Delta K_0) + \Delta K_0} . \tag{5.13}$$

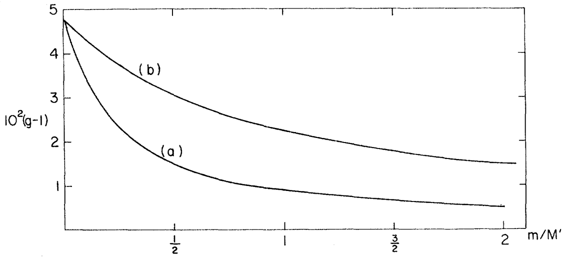

FIG. 3. Correction factor $g(m, M, M')$ as a function of m/M'; $M'/M = 1.2$. Values of ΔK_0 are the same as in Fig. 2.

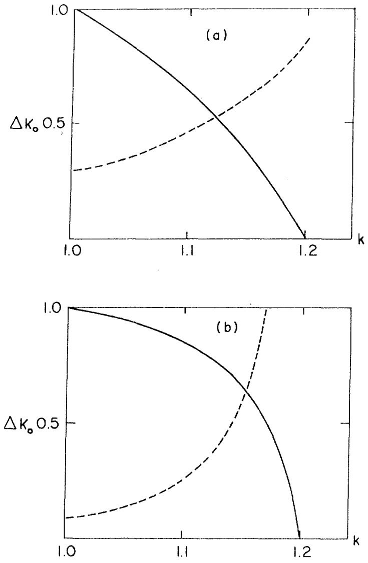

FIG. 4. Variation of ΔK_0 with parameter k in double-isotope experiment described in text. Solid curve is ΔK_0; dashed curve is $-0.1\ \partial\Delta K_0/\partial k$. Curves are for Ca diffusing in (a) NaCl and (b) LiF.

Recalling that the factors g in Eq. (5.13) are nearly unity, we see that k is very nearly the ratio of the two ΔK's and must lie in the range

$$1 \le k \le M_c/M_b \ . \tag{5.14}$$

The uncertainty to be expected in ΔK_0 due to an uncertainty δk in k is given by the derivative

$$\frac{\delta\Delta K_0}{\delta k} = m(M_b - M_c)[k(m - M_b) + M_c - M]^{-2} \ . \tag{5.15}$$

The magnitude of the above quantities is easily calculated for a few favorable examples. One interesting impurity is calcium, because the three naturally occurring isotopes (masses 40, 44, and 48) have a 20% spread in mass. Perhaps the necessary concentration ratios could be measured with the ion-beam mass spectrometer. In Fig. 4 we show ΔK_0 and $\partial\Delta K_0/\partial k$ as a function of k for Ca diffusing in NaCl and LiF. The conversion from the parameter k to the ratio $\Delta K_b^a/\Delta K_c^a$ (the measured quantity) is shown for the LiF case in Fig. 5. Notice that the experimental ratio has a possible range of only about 15%. This tells us something about the accuracy of measurement needed, but the derivatives in Fig. 4 are more revealing. They show that uncertainties in k show up as magnified uncertainties in ΔK_0. In particular, low values of ΔK_0 cannot be determined accurately without great precision in the determination of k. The reason for this can be seen in Fig. 2. Heavy impurities in a material with small ΔK_0 lie on a part of the curve with very small mass dependence.

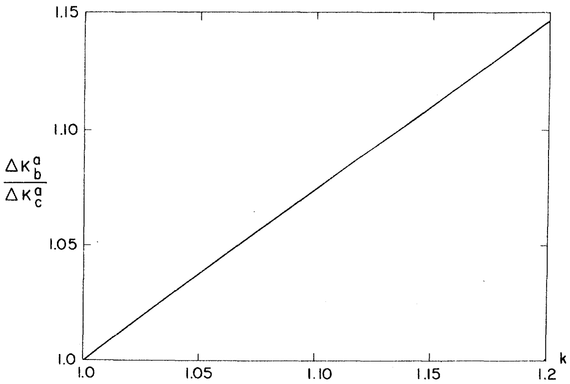

FIG. 5. Conversion from the experimentally measured ratio in double-isotope experiment for Ca in LiF to the parameter k.

Two systems for which double-isotope experiments with radioactive tracers might be carried out are Fe (masses 52, 55, and 59) and Ni (masses 57, 63, and 66) in Be. Curves similar to those of Fig. 4 are shown for these cases in Fig. 6.

The combination of the usual isotope-effect experiment with a double-isotope-effect experiment as outlined above would allow one to unambiguously extract impurity correlation factors if the two concentration ratios could be measured to within 1 or 2%. The proposed experiment is a difficult one, but seems worth attempting because of the new knowledge that could be gained.

VI. DISCUSSION

We have seen from the foregoing that there exists

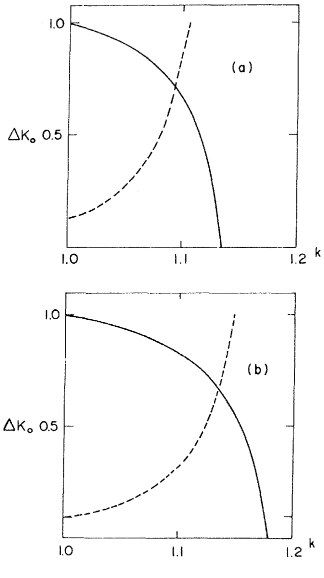

FIG. 6. Variation of ΔK_0 and $-0.1\ \partial\Delta K_0/\partial K$ (dashed curve) for (a) Fe and (b) Ni diffusing in Be.

a complete formal analogy between the rate-theoretic and dynamical expressions for quantities associated with the diffusion jump rate. All other things being equal, one would tend to prefer the rate theory because of its conceptual simplicity and lack of arbitrariness. For example, with a known potential for the interacting atoms, one can in principle calculate all of the quantities that determine the jump rate from the rate theory, while the magnitude of the migration energy remains a parameter in the present form of the dynamical theory. It is because of difficulties that arise in the comparison of rate-theory predictions with experiment, particularly in the case of the diffusion isotope effect as discussed in I, that one feels motivated to attempt alternative descriptions.

One consequence of the formal analogies between the two theories is that certain purely formal analyses can be carried over from one theory to the other, keeping in mind the physical meaning of the quantities involved. For example, the derivation of the attack frequency as a ratio of constrained and free partition functions has been treated by Ebisuzaki *et al.*[12] to show that, except for obvious cases such as H diffusion in metals, quantum effects on the attack frequency will not be very significant. For this reason, a classical description of the diffusion isotope effect should be generally appropriate.

The physical picture that emerges from our analysis of the dynamical description of the jump process is one quite analogous to that of the rate theory, except that the role of the saddle-point configuration is played by a dynamical state which leads to a jump via the dynamics of the system. The real potential is then replaced by an N-dimensional harmonic well cut off at the hyperplane S of Sec. II, and the probability rate of fluctuations that carry the system to S is taken as the jump rate. This replacement will presumably give reasonable results provided that the dynamics of the system can operate long enough after the critical fluctuation has been reached, i.e., that the fluctuation rate is small compared to typical frequencies (a condition also necessary[13] for the validity of the usual rate-theoretic result).

It was found in Sec. IV that the reaction coordinate is a measure of the extent to which thermal fluctuations have overcome the lattice reaction forces barring the dynamical "saddle point." The reaction coordinate is largely determined by the geometry of the lattice, and may be significantly affected by relaxation. It was found that the quantity ΔK has an upper limit greater than 0.5 for vacancy diffusion in the bcc lattice and a lower limit of about the same magnitude for vacancy diffusion in the fcc lattice.

The dependence of ΔK on solute mass for a given reaction coordinate was given in Sec. V. A double-isotope-effect experiment involving the simultaneous diffusion of three isotopes of the solute was proposed that would allow one to unambiguously extract impurity correlation factors in certain favorable cases. ΔK was found to represent, in general, the efficiency with which a fluctuation of the jumping atom leads to motion of the system along the jump direction in configuration space. It reduces to the fraction of energy carried by the jumping atom in the case of self-diffusion.

The dynamical description seems to provide a reasonable account of the self-diffusion isotope effect and of the migration volume,[4] two quantities which the rate theory has been somewhat unsuccessful in explaining. The principal physical assumption is that a certain type of fluctuation (determined largely by geometry) is necessary to initiate a diffusion jump. The required energy of this fluctuation remains a parameter. Although there remain unanswered theoretical questions about the dynamical description, such as whether there exists a unique reaction coordinate, the explanatory power of the model justifies its further development.

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[1] M. D. Feit, Phys. Rev. B 3, 1223 (1971).

[2] G. H. Vineyard, J. Phys. Chem. Solids 3, 121 (1957).

[3] We have chosen to use the same notation for analogous quantities in the two theories. For example, ω_0 is used for the attack frequency in both cases. No confusion should ensue if it is kept in mind which approach is being discussed.

[4] C. P. Flynn, Phys. Rev. 171, 682 (1968).

[5] P. S. Ho, Phys. Rev. B 3, 4035 (1971).

[6] S. J. Rothman and N. L. Peterson, Phys. Rev. 154, 552 (1967).

[7] N. L. Peterson and S. J. Rothman, Phys. Rev. 154, 558 (1967).

[8] S. J. Rothman and N. L. Peterson, Phys. Status Solidi 35, 305 (1969).

[9] S. J. Rothman, N. L. Peterson, and J. T. Robinson, Phys. Status Solidi 39, 635 (1970).

[10] J. N. Mundy, Phys. Rev. B 3, 2431 (1971).

[11] This assumption is likely to be true to within 1% for most systems. See A. D. LeClaire, Phil. Mag. 14, 1271 (1966).

[12] Y. Ebisuzaki, W. J. Kass, and M. O'Keefe, J. Chem. Phys. 46, 1373 (1967).

[13] J. S. Langer, Ann. Phys. (N.Y.) 54, 258 (1969).