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Analytical Mechanics of Atomic Migration Including Nonadiabatic Effects*

Wilbur Franklin and William Graddick†
Physics Department, Kent State University, Kent, Ohio 44240

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A theoretical analysis of the analytical mechanics of atomic migration in many-body condensed systems is given together with numerical calculations for Cu. In order to simplify the many-body problem, a realistic Morse-type potential is designed for metals for nuclear motions orthogonal to the migration direction. Then the well-developed classical theory of three-body chemical reactions is utilized. The vibrational energy for motions during a migration event is derived including nonadiabatic terms. The resonances are isolated, in part, between the localized mode frequency ω_1 leading to migration and another mode ω which is representative of the remaining defect lattice modes. The frequency ω is allowed to vary along the migration path. The resonances obtained in the equilibrium configuration (EC) are given by $2\omega_0 = n\omega_1$, where ω_0 is ω in the EC and n is an integer. More complicated resonance relations are obtained for the saddle-point configuration (SPC) and for an arbitrary point between the EC and SPC. The jump time is derived, and a numerical evaluation for Cu yields a value $\approx 2\times10^{-13}$ sec for the time between the EC and SPC at 888 °C. The jump time is found not to be strongly dependent on the ratio of force constants in the EC and SPC. For impurity diffusion a set of values of the impurity force constants at which resonance occurs is derived. For Cu, this is given by $\phi_{0r}(\mathrm{Cu}) \approx 6.5\times10^3 n^2$ dyn/cm, where n is the order of the resonance.

I. INTRODUCTION

In two preceding papers[1,2] concerning the anharmonic theory of atomic migration, the jump frequency was determined utilizing equilibrium statistical mechanics. No consideration was given in those papers to nonequilibrium terms or to the amount of energy transferred between vibrational modes. The purpose of the work reported in this paper is to study the energy transfer between the localized mode which leads to migration and another mode which is representative of the remaining modes of the system. Previous work dealing with this interaction includes the study of irreversible effects by Rice and Frisch[3] and the development of the localized migration mode in terms of curvilinear coordinates by Weiner.[4]

In a recent series of papers, Marcus and coworkers[5-10] have explored the analytical mechanics of three-body reaction kinetics in generalized coordinates. For the three-body system the interchange of energy between the kinetic energy, which leads to the reaction, and the vibrational mode orthogonal to the reaction direction was obtained with reasonable ease. When diffusion in an N-body system is considered, the exchange of energy between the migration mode and other modes is found to be almost identical in its principal features to the corresponding theory of three-body chemical reactions. This correspondence is especially clear when the similarities are noted between the results of Weiner's[4] many-body theory of diffusion and of the classical three-body analytical mechanics of Marcus.[6] The formalism on which this paper is based is derived from the classical theory developed in I.

Atomic migration in a three-dimensional N-body system can be described in terms of the superposition of harmonic phonons and the anharmonic interaction of localized and band modes, such that the components of these modes which give rise to displacements of the diffusing species in the migration direction contribute to diffusion. In the work reported here a potential, for vibrations orthogonal to the migration direction, is developed with the explicit purpose of adapting the migration mechanics of an N-body system to the more amenable theory of three-body analytical mechanics as represented in I. Utilizing this potential, a relation for the energy transfer between the migration mode and other modes during a diffusion event is derived together with the resonances in this energy transfer. In addition, the jump time is calculated and an expression obtained for the activation energy of migration including vibrational terms.

The theory presented here complements, in part, the new approach to the theory of diffusion initiated by Weiner[4] in that it extends Weiner's theory to include more general potentials and obtains further results useful in diffusion theory and experimental work. The assumption was made by Weiner that the band modes were harmonic and that their frequencies remained constant during a migration event. The latter assumption is not made here and the former is adopted only after estimating the effects of quartic anharmonic terms.

One of the major results of the theory is the derivation of the resonances of the migration mode ω_1 with another mode ω which is representative of the defect modes localized about the migrating atom. The frequency ω is allowed to vary between ω_0, the frequency at the equilibrium configuration (EC), and ω_s^*, that at the saddle-point configuration (SPC). It is shown for Cu self-diffusion that if ω_0 represents one of the band mode frequencies, then $\omega_0 \neq \frac{1}{2} n\omega_1$, but that resonances can be predicted for impurities in Cu for a set of values of the impurity force constant. In a material in which there are resonances between ω_1 and existing band modes, the artificial excitation of the resonance frequency by external nonthermal means could, perhaps, stimulate a diffusion event more than a nonresonance frequency, provided the wave vector is properly directed.. Ultrasonic frequencies have been used to alter diffusion rates by moving dislocations,[11] but these frequencies are too low (the wavelengths are too long) to affect diffusion directly by phonon interaction. However, acoustic or optic phonons having short wavelengths formed by the anharmonic decay of $\vec{k}=0$ transverse optic phonons[12,13] stimulated by external means, such as an infrared source, should affect the diffusion rate[14] most significantly at the resonance frequencies. For the reasons mentioned here, as well as others, it is deemed important to derive the resonances for the diffusion process and to understand the jump time and vibrational terms in the activation energy.

II. POTENTIALS

In order to adapt I to solid-state diffusion, a two-part potential is developed for an atom migrating in a three-dimensional crystal. This potential consists of a trigonometric function for the migration direction and a three-body Morse-type potential for motions perpendicular to the diffusion directions The latter potential is provided with adjustable parameters designed to account for the change in force constants and internuclear distances as the atom migrates. The potentials and generalized coordinate system which are utilized circumvent a divergence which is encountered in the activation energy for migration when a perturbation expansion is made about the EC.[1]

The system of interest in diffusion events, is an atom, or group of adjacent atoms, which experiences large excursions along a direction in coordinate space leading to migration. Excursions leading to critical displacements which do not culminate in a diffusion event, or reach the saddle point, can be considered just as easily as those which do. However, only migration events will be considered here.

A curve in coordinate space, which may represent the space-averaged locus of a vibrating system, is called C (see Fig. 1). The distance traveled along or parallel to this path by the center of mass of the oscillating system, starting at the EC, is called s. The EC is the static potential-energy (PE) minimum of the system, whereas the SPC is defined as the maximum in the static PE for the minimum PE path between two EC's. The shortest perpendicular distance from the center of mass of the migrating system to C is called x. The localized mode frequency ω_1 for the attainment of the SPC is defined as π/t_s^*, where t_s^* is the time for the system to travel the oscillating path between the EC and the SPC. It is questionable that ω_1 can be called a frequency since the localized mode leading to migration is short-lived and shows a significant time development with respect to a sampling time of, for example, one "period" or so if interaction with other modes is strong. However, ω_1 will be called a frequency here and resonances in terms of ω_1 will be derived.

Following I the reaction path is defined as the path in coordinate space corresponding to the path of minimum PE for the system traveling through the SPC. The reaction coordinate, on the other hand, is defined as the locus of points that the vibrationally averaged system follows. For a system as highly symmetrical as vacancy diffusion in a cubic lattice the reaction path and reaction coordinate coincide on the average.

The PE, V, for migration in a three-dimensional

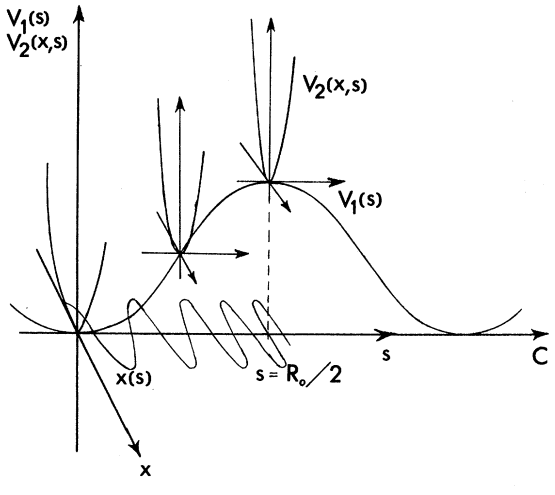

FIG. 1. PE for migration V separated into two parts, $V_1(s)$ and $V_2(x,s)$, which are given by (3) and (4), respectively. The zero of $V_2(x,s)$ lies on $V_1(s)$ for each value of s. The function $x(s)$, which is given by (18), is shown for a frequency ω which depends on s. C is displayed as a straight line, but it could have any desired curvature, and $x_0=0$ so that $x(s)$ is centered on C.

system in a condensed state is separated into two parts as follows:

$$V = V_1(s) + V_2(x, s), \tag{1}$$

where $V_1(s)$ is the PE on C at a distance s from the EC. $V_2(x, s)$ is the PE for the migrating system located away from C a perpendicular distance x with a zero at s on the reaction path. Therefore, $V(0, s) = 0$ for all s when C is the reaction path. Figure 1 portrays $V_1(s)$ and $V_2(x, s)$ for the case when C is a straight line. A definition of the reaction path is the path for which $\partial V/\partial x = 0$. The reaction coordinate is defined as the locus of points $x_0 = x_0(s)$ defined by the minimum in an effective potential given by

$$V_3(x, s) = V_1(s) + V_2(x, s) + p_s^2\,[2\mu(1+\kappa x)^2], \tag{2}$$

where p_s is the momentum tangent to C at s, μ is the effective mass of the migrating system, and κ is the curvature of C at s. In most of what follows C is chosen to be the reaction path.

Let the potential along the migration direction be

$$V_1(s) = \tfrac{1}{2}V_1(R_0/2)[1 - \cos(2\pi s/R_0)], \tag{3}$$

where R_0 is the nearest-neighbor distance and $R_0/2$ is the distance between the EC and the SPC in the vacancy mechanism, for example. Let $V_2(x, s)$ be a Morse-type pseudopotential for a three-body linear chain with fixed ends except that the distance between the ends depends on s. It represents the two halves of the crystal, with a dividing plane through C (assuming the atom to move along C) perpendicular to x at s, as two sources (represented as atoms) on either side of the diffusing atom. This representation neglects angular dependence for angles around C. The potential is given by

$$\begin{aligned} V_2(x, s) &= [V_0 - V_1(R_0/2)b]\,(\cosh 2x/\chi - 2\cosh x/\chi + 1) \\ &= [V_0 - V_1(R_0/2)b]\,[(x/\chi)^2 + 7/12\,(x/\chi)^4 + \cdots\,], \end{aligned} \tag{4}$$

where V_0 is the binding energy and $V_1(R_0/2)$ is the static potential difference between the EC and SPC. In order to account, in a simple manner, for the change in V_2 with s, a term consisting of a constant times $b = \sin(\pi s/R_0)$ was added to each of the three constants in the Morse potential. The quantity x in (4)[15] is given by $r - r_0 + \sigma b$ and $\chi = a - \beta b$ so that

$$x/\chi = (r - r_0 + \sigma b)/(a - \beta b), \tag{5}$$

where r_0, σ, a, and β are constants with dimension of length. The equilibrium distance in the EC ($b = 0$) between the migrating atom and either artificial source is r_0 and in the SPC ($b = 1$) is $r_0 - \sigma$. Noting that $\partial^2 V_2/\partial x^2 = \partial^2 V_2/\partial r^2$, the constants a and β are evaluated utilizing the harmonic force constants of the EC, SPC, and points in between, which are denoted, respectively, by ϕ_0, ϕ_s^*, and $\phi(s)$:

$$\frac{\partial^2 V_2(r_0, 0)}{\partial r^2} = \phi_0 = \frac{2V_0}{a^2} = \mu\omega_0^2, \tag{6}$$

$$\frac{\partial^2 V_2(r_0 - \sigma,\, R_0/2)}{\partial r^2} = \phi_s^* = \frac{2[V_0 - V_1(R_0/2)]}{(a-\beta)^2} = \mu\omega_s^{2*}, \tag{7}$$

$$\frac{\partial^2 V_2(r_0 - \sigma b,\, s)}{\partial r^2} = \phi(s) = \frac{2[V_0 - b(s)V_1(s)]}{[a - \beta b(s)]^2} = \mu\omega^2. \tag{8}$$

From (6) $a = (2V_0/\phi_0)^{1/2}$ and from (7) $\beta = a - \{2[V_0 - V_1(R_0/2]/\phi_s^*\}^{1/2}$.

Physically, the quantity σb in V_2 brings the EC of the sources, which lie in a line perpendicular to C and moving with s, closer together as s increases while βb reflects the increased or decreased slope of the potential (depending on the sign) as s increases. It should be noted that $V_2(x, s) = 0$ when $x = 0$ as required. In a free surface, half of the potential is missing and the surface potential is a Morse potential with adjustable constants:

$$V_2^s(x, s) = \tfrac{1}{2}\,[V_0 - V_1(R_0/2)b\,](e^{-2x/\chi} - 2e^{-x/\chi} + 2). \tag{9}$$

Then $V_2^s(\infty, 0) = V_0$ and $V_2^s(\infty,\, R_0/2) = V_0 - V_1(R_0/2)$ as expected for the potential in a surface.

III. VIBRATIONAL ENERGY AND ITS RESONANCES

In this section the vibrational energy E_{vib} will be formulated for motions orthogonal to C and resonances in E_{vib} will be derived. Nonadiabatic motions of the migrating system are treated; energy transfer between the migration mode ω_1 and an orthogonal vibration mode $\omega = \omega(s)$ is considered. The frequency ω is not necessarily a band mode, but may be localized. It may or may not resonate with ω_1 and with existing or modified band modes. Its value in the EC is given in our simple representation by $\omega_0 = a^{-1}(2V_0/\mu)^{1/2}$ and it depends on the distance s and on time since $s = s(t)$.

An expression for E_{vib} has been derived in I for chemical reactions in three-body systems which is directly applicable to diffusion in condensed systems when only two modes are considered. The initial state ($t = 0$) of the system considered here is the EC of a condensed N-body system in which a single migrating atom is assumed for a simple mechanism such as the vacancy mechanism. The migrating atom is assumed to have an initial velocity $\dot{s}_i$ in the migration direction which is sufficient for the system to attain the SPC and have a vibrational energy $E_{\rm Vib}$ there. The velocity in the migration direction $\dot{s}$ is assumed to vanish in the SPC, which results in the vanishing of x_0 there. At the SPC $E_{\rm Vib}$ is the sum of potential and kinetic parts. If the quartic anharmonic term of the expanded form of the potential energy given by (4) is included, we obtain, using (8),

$$E_{\rm Vib}=\frac{\mu}{2}\left((\dot{x}-\dot{x}_0)^2+\omega^2x^2+\frac{7\omega^2x^4}{12(a-\beta b)^2}\right)_{s^*}. \tag{10}$$

Adopting the transformation $x-x_0=(\omega_0/\omega)^{1/2}y$, (10) becomes

$$E_{\rm Vib}=\frac{\mu}{2}\left[\frac{\omega_0}{\omega}\dot{y}^2-\frac{\omega_0\dot{\omega}y\dot{y}}{\omega^2}+\left(\frac{\omega_0\dot{\omega}^2}{4\omega^3}+\omega\omega_0\right)y^2 + \frac{7\omega_0y^4}{12(a-\beta b)^2}\right]_{s^*}. \tag{11}$$

The equation of motion obtained in I is given by

$$\frac{d^2y}{d\tau^2}+\omega_0^2y=-\left(\frac{\omega_0}{\omega}\right)^{3/2}\ddot{x}_0-\left(\frac{\omega_0}{\omega}\right)^{3/2}y\,\frac{d^2}{dt^2}\left(\frac{\omega_0}{\omega}\right)^{1/2} \tag{12a}$$

and the integral equation solution is

$$y=\frac{C}{(\omega_0)^{1/2}}\sin(\omega_0\tau+\delta)+\frac{1}{\omega_0}\int_0^{\tau}\sin\omega_0(\tau-\tau')F(\tau')\,d\tau', \tag{12b}$$

where $\sin\omega_0(\tau-\tau')$ is Green's function and the reduced time τ is given by

$$\tau=\int_0^t(\omega/\omega_0)\,dt', \tag{13}$$

where the initial time $t_0=0$ corresponds to the EC and $\omega=\omega(t)$. Utilizing (12) in (11) the harmonic oscillator approximation for $E_{\rm Vib}$ at the SPC is

$$E_{\rm Vib}=\frac{J_0\omega_s^*}{2\pi}+\left(\frac{J_0\mu\omega_{s^*}^2}{\omega_0\pi}\right)^{1/2}\times\int_0^{\tau}\cos(\omega_0\tau'+\delta)F(\tau')\,d\tau' +\frac{\mu}{2}\,\frac{\omega_{s^*}}{\omega_0}\left|\int_0^{\tau}\exp(i\omega_0\tau')F(\tau')\,d\tau'\right|^2, \tag{14}$$

where J_0 is the action variable and

$$F(\tau)=(x-x_0)\frac{d^2}{d\tau^2}\left(\frac{\omega}{\omega_0}\right)^{1/2}-\left(\frac{\omega_0}{\omega}\right)^{3/2}\ddot{x}_0. \tag{15}$$

Equations (12)–(15) are the same as those in I except that the lower limit of integration is zero instead of $-\infty$. This lower limit is more suitable for diffusion since x and ω vary with time for $t<0$, whereas they did not for three-body chemical reactions so that, in that case, $F(\tau)=0$ for $\tau<0$. It is possible to set the lower limit at zero and obtain (14), since $\dot{\omega}_{s^*}=0$ as shown below. Before doing this, however, some definitions and simplifications in notation will be made.

The velocity in the migration direction is assumed to have the form

$$\dot{s}=\tfrac{1}{2}\dot{s}_i(\cos\omega_1t+1) \tag{16}$$

and

$$s=\tfrac{1}{2}(\dot{s}_i/\omega_1)(\sin\omega_1t+\omega_1t). \tag{17}$$

The time dependence of x is assumed to be given by

$$x=x_i\cos\omega t. \tag{18}$$

Using s in ω given by (8)

$$\omega=\omega_0\epsilon/\eta, \tag{19}$$

where

$$\epsilon=\left(1-\frac{V_1(R_0/2)}{V_0}\sin\zeta\right)^{1/2}, \tag{20}$$

$$\eta=1-(\beta/a)\sin\zeta, \tag{21}$$

and

$$\zeta=\gamma(\sin\omega_1t+\omega_1t), \tag{22}$$

where $\gamma=\pi\dot{s}_i/2R_0\omega_1=\frac{1}{2}$ since the average velocity between $t=0$ and $t=t_{s^*}$ is $\bar{\dot{s}}=\frac{1}{2}\dot{s}_i=R_0/2t_{s^*}=R_0\omega_1/2\pi$, assuming $\dot{s}=0$ at the SPC. The time derivatives of ω are

$$\dot{\omega}=\omega\omega_1\Psi(\Delta-\Lambda)\cos\zeta, \tag{23}$$

$$\ddot{\omega}=\frac{\dot{\omega}^2}{\omega}-\omega_1\dot{\omega}\left[\frac{\Psi}{2}\tan\zeta+\frac{1}{\Psi}\sin\omega_1t-\frac{\Psi}{2}\left(\frac{\Delta^2-2\Lambda^2}{\Delta-\Lambda}\right)\cos\zeta\right], \tag{24}$$

where $\Psi=\cos\omega_1t+1$, $\Delta=\beta/\eta a$, $\Lambda=V_1/2V_0\epsilon^2$, and $V_1=V_1(R_0/2)$. In the SPC $\dot{\omega}_{s^*}=\ddot{\omega}_{s^*}=0$ and at $t=0$

$$\dot{\omega}(t=0)=\omega_0\omega_1\left(\frac{\beta}{a}-\frac{V_1}{2V_0}\right), \tag{25}$$

$$\ddot{\omega}(t=0)=\omega_0\omega_1^2\left(\frac{2\beta^2}{a^2}-\frac{\beta V_1}{aV_0}-\frac{V_1^2}{4V_0^2}\right). \tag{26}$$

The integrals in (14) can be converted to integrals over t utilizing $d\tau/dt=\omega/\omega_0$ since

$$\frac{d^2}{d\tau^2}\left(\frac{\omega}{\omega_0}\right)^{1/2}=\frac{\omega_0^{3/2}}{2\omega^{5/2}}\left(\frac{5}{2\omega}\dot{\omega}^2-\ddot{\omega}\right), \tag{27}$$

TABLE I. Numerical evaluation of the reduced time τ for Cu given by (13) using the frequency ω given by (19)–(21). The ratio $V_1/V_0=0.282$ and selected values of β/a were assumed.

β/a	0.3	0.4	0.5	0.6
τ_s*/t_s*	1.15	1.29	1.46	1.72

if $\cos(\omega_0\tau+\delta)\simeq\cos(\omega_0 t+\delta)$ and $\exp(i\omega_0\tau)\simeq\exp(i\omega_0 t)$. Numerical integration of (13) using (19)–(21) gives values of τ at the SPC such that $1.15\leq\tau_s*/t_s*\leq 1.72$ for $V_1/V_0=0.282$ (representative for Cu) for values of β/a between 0.3 and 0.6 as shown in Table I. The ratio β/a, which appears in the Morse-like potential, can be related to the force constant ratio ϕ_0/ϕ_s* by combining the relations for a and β given following (8). The result is

$$\beta/a=1-[\phi_0/\phi_s*(1-V_1/V_0)]^{1/2}. \tag{28}$$

Since V_1, which is approximately the activation energy for migration, V_0, ϕ_0, and a are known for most materials, β depends on the unknown SPC force constant. In Table II, V_1/V_0 is chosen as $\frac{1}{3}$ and β/a given for selected values of ϕ_0/ϕ_s*. For realistic choices of ϕ_0/ϕ_s*, the deviation of τ_{s*} from t_{s*} is not negligible but τ_s*/t_s* is certainly less than 2. Since our interest lies principally in the resonances in E_{vib} rather than in its absolute value, the approximation was made that τ could be replaced by t in the cosine and exponent terms in (14).

Utilizing (27) in the first term of $F(\tau)$ in the first integral of (14), we obtain

$$I=\int_0^\tau \cos(\omega_0\tau'+\delta)\,(x-x_0)\frac{d^2}{d\tau^2}\left(\frac{\omega}{\omega_0}\right)^{1/2}d\tau'$$

$$=\frac{x_i}{2\omega_0}\int_0^{t_s*}\left(\frac{\eta}{\epsilon}\right)^{3/2}\cos(\omega_0 t'+\delta)$$

$$\times\cos\omega t\left(\frac{5}{2\omega}\,\dot{\omega}^2-\ddot{\omega}\right)dt'\;. \tag{29}$$

This integral was evaluated approximately using (23) and (24) and the first two terms of binomial expansions of η, ϵ, and Ψ. The integrand, when written out with trigonometric identities, contained a few hundred separate sine and cosine terms but these were derived with reasonable ease since most differed only by signs in the angles. A typical group of terms, selected at random, is given by $\sin[\zeta\pm(\omega_0 t+\delta)\pm\omega t\pm\omega_1 t\pm 2\zeta]$ in which $\zeta=\zeta(t)$ and $\omega=\omega(t)$. The general form which the separate integrals take when η and ϵ in ω are expanded and the first two terms in each retained is given by

$$\int_0^{t_s*}\begin{matrix}\sin\\ \cos\end{matrix}[c_0+c_1t+c_2\sin\omega_1 t+c_3\sin\zeta+c_4\sin^2\zeta]\,dt\,. \tag{30}$$

The integration of (30) yields

$$-\begin{matrix}\cos\\ \sin\end{matrix}[\cdots]\Big/\frac{d}{dt}[\cdots]\Bigg|_0^{t_s*}$$

$$\pm\int_0^{t_s*}\left\{\begin{matrix}\cos\\ \sin\end{matrix}[\cdots]\frac{d^2}{dt^2}[\cdots]\Big/\left(\frac{d}{dt}[\cdots]\right)^2\right\}dt, \tag{31}$$

where $[\cdots]$ denotes the brackets in (30). Repeated integration by parts of (30) yields terms which have odd powers of

$$\frac{d}{dt}[\cdots]\Bigg|_0^{t_s*}$$

in their denominators. Therefore, the resonances are given by

$$\frac{d}{dt}[\cdots]\Bigg|_0^{t_s*}=0\,.$$

The final result for the limit $t=0$ for the resonances in (29) is given by

$$2\omega_0=n\omega_1,\quad n=1,2,\ldots,8\;. \tag{32}$$

Higher-order approximations in the binomial expansions of η and ϵ lead to higher values for the integer n in (32). A result similar to (32) was obtained when $\exp(i\omega_0 t)$ replaced $\cos(\omega_0 t+\delta)$ in (29) except that the integer n was found to be $n=1, 2, \ldots, 6$.

For the integration limit $t=t_{s*}$ the infinities are given by

$$c_1\omega_1+c_2\omega_0+c_3\omega_s*=0, \tag{33}$$

where the constants c_i are simple numerical constants and $\omega_s*=\omega_0(1-V_1/V_0)^{1/2}/(1-\beta/a)$. If a time between 0 and t_{s*} is considered, without reconsidering the initial assumptions leading to (29), the infinities are given by

$$a_1\omega_0+(a_2+\tfrac{1}{2}a_3\Psi)\,\omega_1+a_4(\omega+\dot{\omega}t)=0, \tag{34}$$

where a_i are numerical constants. The variability of ω with s during a migration event is made manifest by the presence of ω_{s*} in (33) and of ω and $\dot{\omega}$ in (34).

TABLE II. Values of β/a obtained from (28) assuming $V_1/V_0=0.3$ for selected values of ϕ_0/ϕ_s*.

ϕ_0/ϕ_s*	0.25	0.50	0.75	1.00
β/a	0.58	0.41	0.28	0.16

When the second term in $F(\tau)$ is used in the integrals of (14) a relation considerably more complicated to evaluate than (29) is obtained. This term was not worked out, therefore, because of its complexity and since it would probably yield resonances similar to those given by (32)–(34) anyway.

IV. JUMP TIME

The jump time given by Marcus in I for the case $x_0 = 0$ is

$$t = \mu^{1/2} \int_0^{s^*} ds \left\{2[\alpha - J_0\omega/2\pi - V_1(s)]\right\}^{-1/2}, \qquad (35)$$

where α is the total energy of the migrating system and J_0 is the action variable. In an N-body system, which is considered here, energy is imparted to α from modes other than ω [4,6] so that the square brackets in (35) can be positive, thus giving real times. If (3) is used for $V_1(s)$ in (35) and if ω is expanded and truncated at the $\sin^2$ term, then

$$t = \mu^{1/2} \int_0^{s^*} ds \left[2\alpha - \frac{J_0\omega_0}{\pi}\left(1 + \lambda \sin\frac{\pi s}{R_0}\right) + \left(\frac{J_0\omega_0\xi}{\pi} - 2V_1\right)\sin^2\frac{\pi s}{R_0}\right]^{-1/2}, \qquad (36)$$

where $\lambda = V_1/2V_0 - \beta/a$ and $\xi = \beta^2/a^2 - V_1^2/8V_0^2 - \beta V_1/2aV_0$. The simple harmonic approximation can be made for J_0 without significant error in t. Then $J_0 = 2\pi\langle E\rangle(\mu/\phi_0)^{1/2}$, where $\langle E\rangle$ is the average energy of the oscillator in the EC at temperature T, $J_0\omega_0/\pi = 2\langle E\rangle$, and

$$t = \left(\frac{\mu}{2}\right)^{1/2} \int_0^{s^*} ds \left[\alpha - \langle E\rangle\left(1 - \lambda \sin\frac{\pi s}{R_0}\right) + (\langle E\rangle\xi - V_1)\sin^2\frac{\pi s}{R_0}\right]^{-1/2}. \qquad (37)$$

A reality condition for t is given by

$$\alpha > \langle E\rangle\left(1 - \lambda \sin\frac{\pi s}{R_0}\right) - (\langle E\rangle\xi - V_1)\sin^2\frac{\pi s}{R_0}. \qquad (38)$$

TABLE III. Numerical evaluation of the jump time for Cu self-diffusion by a vacancy mechanism. Parameters in (37).

m	1.055×10^{-22} g
V_1	1.00 eV
V_0	3.55 eV
$\langle E\rangle$	0.10 eV
R_0	2.5564×10^{-8} cm

TABLE IV. Jump time $t_s{}^*$ for motion between the EC and SPC in the adiabatic approximation for selected values of β/a.

β/a	0.3	0.4	0.5	0.6
$t_{s^*}\times10^{13}$ sec	2.100	2.045	2.034	1.986

In (37) μ, a, V_0, and V_1 are known for most materials, whereas β can be estimated and α given arbitrary values satisfying (38).

The jump time was evaluated numerically for Cu self-diffusion for the vacancy mechanism assuming four arbitrary values of β/a. A temperature of 1161 °K, corresponding to $\frac{1}{10}$ eV, was assumed and the known quantities in (37) are listed in Table III. The jump times for the four values of β/a are given in Table IV and were approximately 2×10^{-13} sec. Doubling the ratio of β/a from 0.3 to 0.6 resulted in only a 0.6% decrease in t_{s^*} which shows that t_{s^*} is only weakly dependent on variations in the saddle-point force constant. t_{s^*} was more strongly dependent on α; a 5% increase in α resulted in a 30% decrease in t_{s^*}. From Table IV it is concluded that $t_{s^*} \approx 2\times10^{-13}$ sec for Cu self-diffusion by a vacancy mechanism under the stated assumptions when the condition (38) is just satisfied for $s = \frac{1}{2}R_0$ [α in Table IV was chosen for computation purposes to be 0.625×10^{-3} eV greater than the right-hand side of (38)].

V. DISCUSSION

The resonances obtained for the vibrational energy in the EC are given by $2\omega_0 = n\omega_1$, where $n = 1, 2, \ldots, 8$ for the approximations made. Weiner[4] obtained a single resonance at $\omega_0 = 2\omega_1$ under the assumption of constant ω during a migration event. The set of resonances obtained in our study, rather than a single resonance, stemmed from the dependence of ω on s and t. In addition, when the system is not in the EC, the resonance equation is modified by the dependence of ω on s as shown by (33) for $s = s^*$ and (34) for $0 < s < s^*$.

The vibrational energy can be incorporated within the activation energy for migration by

$$E_m = V_1(R_0/2) + E_{\text{vib}} - J_0\omega_0/2\pi, \qquad (39)$$

where $V_1(R_0/2)$ represents the static potential difference between the EC and SPC, E_{vib} is the vibrational energy in the SPC, and $J_0\omega_0/2\pi$ that in the EC. If E_{vib} consists of only the first term in (14) $J_0\omega_{s^*}/2\pi$, then the difference in the vibrational energy between the EC and SPC is $J_0(\omega_{s^*} - \omega_0)/2\pi$ in (39). This situation is considered as the adiabatic approximation, following I, and the other terms in E_{vib} as the nonadiabatic corrections. An adiabatic transition in this sense means, classically, that ω_1 has sufficient energy at the EC for the system to attain the SPC without the addition of further energy and with concurrent change in ω from ω_0 to ω_{s^*}. The reason that equilibrium transition rate theory has worked so well is apparently that nonadiabatic corrections for a single migration motion between the EC and SPC are small. In quantum-mechanical terms, the nonadiabatic terms correspond to the asymmetrical Goldstone diagrams of nonequilibrium statistical mechanics. The energy transfer must necessarily be anharmonic but only the nonequilibrium diagrams would contribute. Since the derivation of the resonances by means of analytical mechanics was both approximate and tedious [over 900 separate resonance equations were obtained from (29)], the method appears to be no less complicated than the N-body nonequilibrium statistical mechanics of the migration process. If the latter calculation were made, following the anharmonic quantum-mechanical formalism of Franklin,[2] a comparison could be made between the results of a many-body theory, and the approach taken here. A calculation of the saddle-point potential would be of substantial value in obtaining numerical estimates for both of these theoretical approaches.

From the EC resonance equation (32) the dependence of resonances on impurity force constants at the EC was derived. From (6), (32), and the relation $\omega_1 = \pi/t_{s^*}$ we obtain

$$\omega_0 = (\phi_0/m)^{1/2} = (n/2)\,\omega_1 = n\pi/2t_{s^*}\,, \tag{40}$$

from which the resonance force constants are given by

$$\phi_{0r}(n) = m\ (n\pi/2t_{s^*})^2 \tag{41}$$

for the nth resonance at equilibrium. For Cu, $t_{s^*} \approx 2\times10^{-13}$ sec, as shown in Table IV so that $\phi_{0r}(\mathrm{Cu}) \approx 6.5\times10^3\, n^2$ dyn/cm. For pure Cu the Debye frequency is $\omega_D = 4.4\times10^{13}$ sec^{-1} so that $\omega_D = 2.8\omega_1$. Therefore, the Debye frequency does not satisfy the resonance condition given by (40). However, the modes of certain impurities might satisfy the resonance condition if the ratio m/t_{s^*} satisfied (41) for some value of n. Since (37) shows that $t_{s^*} \propto m^{1/2}$, ϕ_{0r} is essentially mass independent. However, there is a quadratic dependence on the resonance number n in (41).

From (37) a jump time of $\approx 2\times10^{-13}$ sec was obtained for pure Cu which gives $\omega_1 = \pi/t_{s^*} = 1.57 \times10^{13}$ sec^{-1}. This frequency corresponds to 0.065 eV which means that approximately 15 phonons of this energy are required to attain a migration energy of 1 eV. When the interaction of ω_1 with another frequency ω of the defect lattice is considered in cases where one of the resonance conditions given by (32)-(34) is not satisfied, another phonon ω' (or phonons) enters the picture. Then, in the EC, the energy conservation relation, given by $\omega = \frac{1}{2}n\omega_1 + m\omega'$ where m is an integer, must be satisfied. Similar relations are obtained when the system is not in the EC.

In summary, diffusion in an N-body condensed system was considered by simplifying the potentials so that the analytical mechanics become tractable. The vibrational energy and the resonances between ω and ω_1 were derived. The jump time was evaluated in the adiabatic approximation, which probably has negligible error, and was approximately 2×10^{-13} sec for pure Cu. The methods developed here could be utilized for liquids and liquid crystals as well as solids for both translational and rotational diffusion.

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†Present address: Bell Telephone Laboratories, Columbus, Ohio.

[1] W. M. Franklin, J. Phys. Chem. Solids 28, 829 (1967).

[2] W. M. Franklin, Phys. Rev. 180, 682 (1969).

[3] S. A. Rice and H. L. Frisch, J. Chem. Phys. 32, 1026 (1960).

[4] J. H. Weiner, Phys. Rev. 152, 597 (1960).

[5] R. A. Marcus, J. Chem. Phys. 45, 4493 (1966).

[6] R. A. Marcus, J. Chem. Phys. 45, 4500 (1966); denoted by I hereafter.

[7] R. A. Marcus, J. Chem. Phys. 49, 2610 (1968).

[8] R. A. Marcus, J. Chem. Phys. 49, 2617 (1968).

[9] S. Wu and R. A. Marcus (private communication).

[10] M. Attermeyer and R. A. Marcus, J. Chem. Phys. 52, 393 (1970).

[11] G. A. Hayes and J. C. Shyne, IEEE Trans. Sonics Ultrasonics SU-16, 68 (1970).

[12] P. G. Klemens, Phys. Rev. 148, 845 (1966).

[13] L. A. Vredevoe, Phys. Rev. 140, A930 (1965).

[14] W. M. Franklin, Bull. Am. Phys. Soc. 14, 800 (1969).

[15] The x given here corresponds to that in I, except that it is defined here for diffusion in an N-body system in which the force constant changes with s.