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Dynamical theory of migration of an adsorbed atom on solid surfaces*

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A dynamical theory of an adsorbed atom on solid surfaces is developed starting from a Hamiltonian which includes: (1) motion of the adsorbed atom parallel to the surface; (2) the vibration of the adsorbed atom perpendicular to the surface; (3) the lattice vibrations (phonons) of the solid; (4) the coupling between the vibration of the adsorbed atom and its parallel motion; (5) the coupling between the lattice vibrations and the parallel motion of the adsorbed atom; (6) the concerted interaction among the phonons, the vibration, and the parallel motion. Using a canonical transformation, we describe the motion of the adsorbed atom as one of a pseudomolecule formed from the adsorbed atom and the distorted lattice. An equation for the probability of finding the adsorbed atom at a lattice site is derived and the mean square displacement of the motion of the adsorbed atom is calculated. At low temperature, the migration of the adsorbed atom is coherent and the mean square displacement is proportional to the square of time. The adsorbed atom behaves like a free particle with a certain velocity. At high temperature, the migration has diffusional character and the mean square displacement is proportional to time. This is due to the interaction between the parallel motion of the adsorbed atom and phonons as well as to the one between the vibration of the adsorbed atom and phonons. At intermediate temperature, after a certain time, which becomes shorter as the temperature increases, the migration becomes diffusional. The resulting diffusion coefficient consists of two parts: one represents the diffusional character of the migration, and the other its coherent nature. The temperature dependence of the diffusional part is of the Arrhenius type, while that of the coherent part increases as temperature decreases. The coherent part is small when the interaction between the adsorbed atom and the lattice atoms is very strong. Thus the theory gives reasonable trends with respect to the variation of parameters taken into account. Comparison with existing experiments on tungsten and rhodium is briefly made to estimate the order of magnitude of the lattice distortion due to the strong interaction between the adsorbed atom and the lattice atoms.

I. INTRODUCTION

Migration of atoms adsorbed on a crystal lattice is of importance in crystal growth¹ and evaporation, changes of shape of crystal surfaces, particle sintering,² stability of catalyst solid-support systems,³ and kinetics of reactions between chemisorbed species. In addition, the motion of the adsorbed atom is a sensitive probe of the atom-solid interactions and of the dynamics of energy exchange between the atom and the vibrating lattice of the solid.

Previous theories^{2,4} have been based on the assumption that the motion is a random walk of dimensionality d ($d = 1$ or 2) for which the diffusion coefficient is given by

$$D = \lim_{t \rightarrow \infty} \langle R^2 \rangle_t / 2dt. \quad (1.1)$$

Here $\langle R^2 \rangle_t$ is the mean square displacement in the time interval t . Measurements of D are usually interpreted with a model of an activated complex, which gives for the temperature dependence of D the formula

$$D = D_0 \exp(-V/kT); \quad (1.2)$$

V is the energy barrier for a step of the random walk from one site to the neighboring site. Such theories, though useful in systematizing the experimental data, are open to criticism. First, the connection to the dynamics of the migration is not clearly established. A variety of interactions and energy exchange processes may occur between an adsorbed atom and the vibrating atoms of the lattice, which can induce migration of the adsorbed atom, create distortion of the lattice, or increase the amplitude of the vibration of the atom per-

pendicular to the surface, which in turn may facilitate the migration. Therefore it is impossible to describe all of these dynamical aspects by only one parameter such as the energy barrier between sites. Experimental measurements have become possible by field ion microscopy,⁵ and data have been found with puzzling features which cannot be explained in terms of the simple model described above. Existing data are summarized in Table I.⁶⁻¹⁰ Since the faces of Rh(111) and W(110) are the smoothest, and Rh(111) is structurally very similar to W(110), and Rh(331) to W(321), we would expect that the relationship between the activation energies for Rh(111) and Rh(331) is more or less the same as that between the activation energies for W(110) and W(321). However, the corresponding quantities are almost equal for the two faces of tungsten and almost 4 times smaller for Rh(110) as compared to Rh(321). This difference is not likely to be due to possible contribution of correlated migration of pairs to the diffusion although this would usually lower both D_0 and V .⁹ In fact, it is certain that in the case of Rh(111) the migration of only single atoms have been studied.⁵ Thus, attempts to explain these data in a semiquantitative manner in terms of simple energetic models are rather unsuccessful.^{8,10} It is clear that the dynamics of the lattice must play some role in the migration of the adsorbed atom, and this may determine or at least influence the temperature and time dependence of $\langle R^2 \rangle_t$.

Another criticism may be directed against the assumption of the diffusional character of the migration. Although it is to be expected that at long times the mean square displacement is proportional to the time and a proper diffusion coefficient is defined by Eq. (1.1), re-

TABLE I. Experimental data for diffusion coefficients of atoms on surfaces. Values of parameters D_0 and V in the assumed equation for the diffusion coefficient $D = D_0 \exp(-V/kT)$ [Eq. (1.2)] are fitted to experiments. The data for rhodium are from Ref. 10, those for tungsten are from Refs. 6, 7, and 9(b). The symbol d denotes the dimensionality of the motion of the adsorbed atom parallel to the metal surface.

Comment	Plane		$D_0(\text{cm}^2/\text{s})$		$V(\text{kcal/mole})$	
	Tungsten	Rhodium	Tungsten	Rhodium	Tungsten	Rhodium
$d=2$ (Smooth)	(110)	(111)	2.6×10^{-3}	2×10^{-4}	21.2 ± 1.1	3.6 ± 0.5
$d=1$ (Channel)	(211)	(110)	10^{-3}	3×10^{-1}	17.4 ± 1.5	13.9 ± 0.8
	(321)	(331)	3.7×10^{-4}	1×10^{-2}	20.1 ± 1.8	14.8 ± 0.9
Rh(311) has general similarity to W(211)		(331)		2×10^{-3}		12.4 ± 1.2
		(110)		1×10^{-3}		20.2 ± 1.7

cent experiments and quantum mechanical calculations show that this is not the case in a system consisting of small atoms which interact weakly with a solid surface. Important contributions to the migration on the surface come from the *coherent motion*,¹¹ and these may dominate over the contributions of diffusional character. Bretz and Dash¹³ have shown that the specific heat of monolayers of He³ or He⁴ at coverage less than 0.15 and $T \geq 2^\circ\text{K}$, on an exfoliated pyrolytic graphite surface, is that of a two dimensional gas. This result suggests a free motion of the adsorbed atoms and rather weak interaction between helium and surface atoms. Quantum mechanical calculations provide confirmation of this interpretation. In all of these calculations, the interaction energy with the lattice is determined by summing the pairwise Lennard-Jones interactions; the three-dimensional Schrödinger equation is then solved numerically,¹⁴ and the results¹⁵ show that the helium atom on a perfect graphite surface is almost completely delocalized. The zero point energy for He³ (73.5 °K) and He⁴ (66.1 °K) is much larger than the barrier to intersite tunneling (17.2 °K). The bandwidths are large and the band gaps very small. The least probable position along the surface has half the probability of the most probable position. The same high degree of delocalization is computed for helium on the (111) face of xenon.¹⁶ The delocalization of helium depends, of course, on the surface; it is small on Xe(110),^{16,17} large on Kr(100),^{17,18} and practically zero¹⁸ on Ar(100). Low delocalization is calculated for helium on argon-covered copper¹⁹ and on rare-gas-covered graphite.^{20,21} On the basis of these calculations with pairwise potentials, which seem to be adequate,²⁵ one may expect non-diffusional as well as diffusional behavior of the migration; at low temperature, the thermal motion of the lattice atoms of the surface is small and the motion of the adsorbed atom is mainly due to the delocalization of the wavefunction in the periodic potential of the lattice. Therefore one should compute, from first principles, an expression for the mean square displacement $\langle R^2 \rangle_t$, as a function of temperature and time in order to establish criteria for the validity of the two extreme regimes of the migration, the coherent motion and the diffusional motion. Then we may derive an expression for the diffusion coefficient for the diffusional motion. The purpose of this paper is to present such a theory.

We start with a postulated model Hamiltonian which includes the following important aspects of the motion

of the adsorbed atom: The atom is allowed to undergo motion parallel to the surface in the periodic potential of the lattice and to vibrate perpendicular to the surface. These two types of motion are coupled because as the distance from the surface changes owing to the vibration, the strength of the periodic potential, which determines the parallel motion, also changes. Moreover, if the adsorbed atom interacts strongly with the surface atoms, the adsorbed atom distorts the lattice around its position. This distortion of the lattice in turn changes the interaction potential between the adsorbed atom and the surface. We take this strong coupling into account by renormalizing the Hamiltonian. Physically, this amounts to considering the adsorbed atom to form a pseudomolecule with the atoms of the distorted lattice and the pseudomolecule travels on the surface with a renormalized mass. Thus, the distortion of the lattice is included in the motion of the pseudomolecule; the rest of the motion of the lattice atoms is the thermal motion around the distorted lattice positions. This perturbs the motion of the pseudomolecule in the following ways: (a) The pseudomolecule engaged in the coherent motion along the surface randomly gains or losses momentum from or to the thermal motion of the lattice atoms. (b) The interaction between the pseudomolecule and the lattice atom excites and de-excites randomly the vibration of the pseudomolecule perpendicular to the surface. The random occurrence of these interactions is responsible for the diffusional character of the migration. These details of the interaction Hamiltonian are presented in Sec. II. In Sec. III, we use Zwanzig's method²⁶ to derive a differential equation for the probability that the adsorbed atom (or, the pseudomolecule located at a given site at time $t=0$) will be at a site located n steps of the lattice away from the initial site at time t . In Sec. IV we solve this equation and compute the mean square displacement $\langle R^2 \rangle_t$, as a function of time and temperature; we give illustrative numerical calculations to display the characteristics of the motion of the adsorbed atom and the relative importance of various factors contributing to it.

Our main results are as follows: At low temperature, $\langle R^2 \rangle_t$ is proportional to square of the time. The migration is coherent and the adsorbed atom behaves like a free particle with a certain velocity. At high temperature the mean square displacement is proportional to time and a proper diffusion coefficient can be defined from Eq. (1.1). At intermediate temperature,

within a short time, the mean square displacement is proportional to the square of time, that is, the migration is coherent. The coherence breaks down after a certain time, which becomes longer as the temperature is lowered, and the diffusional motion of the adsorbed atom sets in. The diffusion coefficient consists of two parts; one represents the diffusional character of the migration and has a temperature dependence of the Arrhenius type at high temperature. The activation energy is given by the characteristic phonon frequency of the surface and the coupling constants of the interactions between the adsorbed atom and the lattice atoms. The other part of the diffusion coefficient represents the coherent nature of the migration, and it increases as the temperature is lowered. When both parts are of equal importance, the diffusion coefficient becomes a minimum at that temperature. When the coupling between the adsorbed atom and the lattice atoms is weak, as is the case for a rare-gas atom on a rare-gas surface, then both parts contribute to the diffusion coefficient. On the other hand, for strong coupling cases, only the diffusional part is important, which is the case for tungsten and rhodium. Although precise values of parameters in our theory are not known, we may assume some reasonable values for them and compare the theoretical results with experiments. The comparison is made at the end of Sec. IV. We have an order-of-magnitude estimation of the strength of the lattice distortion due to the presence of an adsorbed atom. The theory predicts concave-upward behavior of the Arrhenius curve, which implies a temperature dependence of the activation energy. This may be an explanation for the anomalously low value of the activation energy of Rh(110) surface. The theory also predicts reasonable trends with the variation of the parameters involved. This is discussed in detail in Sec. IV.

II. THE MICROSCOPIC MODEL

The microscopic model used here is given by the Hamiltonian

$$\begin{aligned}
 H = E_0 \sum_n a_n^+ a_n + \hbar \Omega c^+ c + \sum_\lambda \hbar \omega_\lambda b_\lambda^+ b_\lambda + \sum_{n \neq m} J_{nm} a_n^+ a_m \\
 + \sum_{n \neq m} \varphi_{nm} a_n^+ a_m (c + c^+) + \sum_{n\lambda} \hbar \omega_\lambda X_\lambda^n a_n^+ a_n (b_\lambda + b_\lambda^+) \\
 + \sum_{n\lambda} \hbar Y_\lambda^n a_n^+ a_n (c + c^+) (b_\lambda + b_\lambda^+). \quad (2.1)
 \end{aligned}$$

The operators a_n^+ , a_n create or annihilate an adsorbed atom at the lattice site n on the surface, and they can be written $a_n^+ a_m = |n\rangle \langle m|$, where $|m\rangle$ is the site representation of the wavefunction of the motion of the adsorbed atom parallel to the surface in the periodic potential of the lattice. Since we have $\langle n|m\rangle = \delta_{nm}$, the commutation relations for $a_n^+ a_m$ are obvious. The terms $E_0 \sum_n a_n^+ a_n$ and $\sum_{n \neq m} J_{nm} a_n^+ a_m$ produce the parallel motion; $|J_{nm}|^2$ is related to the intersite transition probability from site n to site m due to the coherent motion, and E_0 is the energy of the adsorbed atom on site n in its ground vibrational state. The operators c^+ and c are the creation and the annihilation operators of

the vibration of the adsorbed atom in the direction perpendicular to the surface and the term $\hbar \Omega c^+ c$ represents the energy of the vibration. The symbols b_λ^+ and b_λ denote the creation and the annihilation operators of a phonon of wavenumber λ and frequency ω_λ . For simplicity, the band index is omitted. The term $\sum_\lambda \hbar \omega_\lambda b_\lambda^+ b_\lambda$ represents the energy of the phonons of the lattice; $\sum_{n \neq m} \varphi_{nm} a_n^+ a_m (c + c^+)$ represents the vibration-induced intersite transitions. The terms $\sum_{n \neq m} \hbar \omega_\lambda X_\lambda^n a_n^+ a_n (b_\lambda + b_\lambda^+)$ and $\sum_{n \neq m} \hbar Y_\lambda^n a_n^+ a_n (b_\lambda + b_\lambda^+) (c + c^+)$ are additions to the energy E_0 of the adsorbed atom owing to the fact that the energy is changed by lattice vibrations and concerted vibrations of the adsorbed atom and the lattice, respectively. The coupling constants J_{nm} , φ_{nm} , X_λ^n , Y_λ^n can be calculated if a potential of interaction between adsorbed atom and lattice atoms is chosen and if one solves the Schrödinger equation for the adsorbed atom located at an equilibrium distance from the surface and moving parallel to the surface with the lattice atoms fixed in equilibrium positions.²⁷

In our model Hamiltonian, we neglect phonon-induced intersite transitions and other higher order effects of phonons and vibration of the adsorbed atom since these terms in Eq. (2.1) already form a representative set of those processes likely to be important. The neglected terms can be included at the cost of exceedingly long calculations which make the resulting formulas very complicated. We shall not attempt to show the derivation of the Hamiltonian Eq. (2.1) here, but rather concentrate on studying the character of motion and the dependence of the mean square displacement $\langle R^2 \rangle_t$ on temperature and time.

There is the temptation now to proceed and to use perturbation theory for the computation of $\langle R^2 \rangle_t$. However, the phonons in Eq. (2.1) are those of the lattice, undistorted by the adsorbed atom. In reality, because of the strong interactions between the adsorbed atom and the lattice atoms, the lattice atoms have their equilibrium position shifted towards the adsorbed atom. They form, together with the adsorbed atom, a "pseudomolecule" which persists until the adsorbed atom hops to a new position. When this happens, the previously displaced lattice atoms relax to their normal position and the new neighbors of the adsorbed atoms are displaced to form a new pseudomolecule. The relaxation of the lattice from the distortion and the formation of a new pseudomolecule take place on a time scale of 10^{-12} sec for a strongly adsorbed atom. The estimated time for the hopping of such a chemisorbed atom is much longer than this. Therefore, on this longer time scale, we may consider the migrating species to be the pseudomolecule. If we insist on using in the Hamiltonian the phonons b_λ^+ , b_λ representing the vibration of the undistorted lattice and the motion $a_n^+ a_m$ of the adsorbed atom, then with the phonon-atom interaction being very strong, perturbation theory cannot be used. It is possible, however, to use a canonical transformation^{29,30} to go to new operators B_λ^+ , B_λ , $A_n^+ A_m$, which takes into account the fact that the lattice is distorted around the adsorbed atom and that the pseudomolecule is formed. This transformation changes the center of motion of the lattice atoms to correspond to

this distortion. In other words, the new operators A_n^+ , A_n now represent the creation and the annihilation of the pseudomolecule and B_λ^+ , B_λ the vibrations of lattice atoms around the shifted equilibrium positions. We should further note that because of the coupling between the vibration of the adsorbed atom and the phonons, which is characterized by the coupling constant Y_λ^n in Eq. (2.1), the equilibrium position of the vibration of the adsorbed atom is shifted by the distortion of the lattice. Hence the new operators C^+ , C are also introduced to represent the shifted vibration of the adsorbed atom. The desired transformation is given by

$$Q = e^{-S} q e^S. \quad (2.2)$$

Here Q stands for the transform of the operator q (q may be a_n^+ , a_n , b_λ^+ , b_λ , c , or c^+). The generator of the transformation is defined by

$$S = \alpha(c^+ - c) + \sum_{n\lambda} G_\lambda^n a_n^+ a_n (b_\lambda^+ - b_\lambda), \quad (2.3)$$

where α and G_λ^n are chosen as functions of the coupling constants so that the resulting Hamiltonian is

$$H = \bar{E} \sum_n A_n^+ A_n + \hbar \Omega C^+ C + \sum_\lambda \hbar \omega_\lambda B_\lambda^+ B_\lambda + \sum_{n \neq m} A_n^+ A_m \theta_n \theta_m^+ \\ \times [\tilde{J}_{nm} + \varphi_{nm}(C + C^+)] + \sum_{n \neq m} \hbar Y_\lambda^n A_n^+ A_n (B_\lambda + B_\lambda^+) (C + C^+), \quad (2.4)$$

where the new operator θ_n is introduced:

$$\theta_n = \exp\left(\sum_\lambda G_\lambda^n (B_\lambda^+ - B_\lambda)\right). \quad (2.5)$$

The forms of α and G_λ^n in the canonical transformation are complex, but in the approximation of small dispersion of phonon frequencies, that is, $\omega_\lambda \approx \omega_0$, we may express the coupling constants X_λ^n and Y_λ^n as [see Eq. (2.1)]

$$X_\lambda^n = N^{-1/2} \xi e^{i n \lambda}, \quad Y_\lambda^n = N^{-1/2} \eta e^{i n \lambda}, \quad (2.6)$$

and we have simple expressions for α and G_λ^n ,

$$\alpha = -\frac{2\omega_0 \xi \eta}{\Omega \omega_0 - (2\eta)^2}, \quad (2.7)$$

$$G_\lambda^n = N^{-1/2} g e^{i n \lambda}, \quad (2.8)$$

where

$$g = \frac{\xi \omega_0 \Omega}{\omega_0 \Omega - (2\eta)^2}, \quad (2.9)$$

and N is the number of lattice sites. Note that in Eq. (2.6), the wave number appears only in the phase and not in the modulus of the coupling constants.

The new Hamiltonian Eq. (2.4) represents the following processes: The first term represents the energy of the pseudomolecule at lattice sites, and the energy \bar{E} is given by

$$\bar{E} = E_0 - \xi^2 \hbar \omega_0 \left[\frac{2\omega_0 \Omega}{\omega_0 \Omega - (2\eta)^2} - \left(\frac{\omega_0 \Omega}{\omega_0 \Omega - (2\eta)^2} \right)^2 \right]. \quad (2.10)$$

The change of the energy of the adsorbed atom brought about by the canonical transformation Eq. (2.2) is due to the distortion of the lattice vibrations and to that of the vibration of the adsorbed atom. The second term

and the third term in Eq. (2.4) are the energy of the vibration of the pseudomolecule perpendicular to the surface and that of the lattice vibrations (phonons) around the new equilibrium positions. The migration of the pseudomolecule is induced by the fourth term. The new parameter \tilde{J}_{nm} is given by

$$\tilde{J}_{nm} = J_{nm} - 2\alpha \varphi_{nm}. \quad (2.11)$$

Since we have Eq. (2.5) for θ_n , the amplitude of the probability of transition from the site n to m depends in a nonlinear manner on the phonon operators. This is a consequence of the strong interactions between the adsorbed atom and the lattice atoms. At a later stage, the product $\theta_n \theta_m^+$ will be averaged over the equilibrium ensemble of the phonons, and the resultant expression gives rise to a rate of migration which is temperature dependent. This is not surprising since the motion of the pseudomolecule involves distortion and relaxation of the lattice. The fifth term represents the energy shift of the pseudomolecule at a lattice site due to the concerted vibrations of the pseudomolecule itself and the lattice atoms.

The Hamiltonian Eq. (2.4) is easily diagonalized in two limiting cases: (a) no coupling between the adsorbed atom and phonons ($X_\lambda^n = \varphi_{nm} = Y_\lambda^n = 0$), which corresponds to coherent migration, and (b) no intersite hopping ($J_{nm} = \varphi_{nm} = 0$), which corresponds to zero migration due to the strong binding at a lattice site. As we shall see in the next section, this allows us to define a zeroth order Hamiltonian H_0 and to perform a perturbation calculation which contains both limiting cases.

III. THE DYNAMICS OF SURFACE MIGRATION

With the Hamiltonian derived in the previous section, we can compute, in principle, all the quantities of interest connected with the motion of the adsorbed atom. Of interest to us is the probability that the adsorbed atom which starts at site $n=0$ when $t=0$ reaches the site n at time t . This quantity can be used to compute the mean square displacement, which is measured in experimental studies. The probability is given by

$$P_n(t) = \text{Tr}_S \text{Tr}_B [A_n^+ A_n \rho(t)]. \quad (3.1)$$

Here Tr_B is the trace over the states of the phonons and over the vibrational states of the pseudomolecule. Tr_S is the trace over the states describing the motion of the pseudomolecule parallel to the surface. The density matrix $\rho(t)$ is

$$\rho(t) = e^{-iLt} A_0^+ A_0 \rho_B, \quad (3.2)$$

with

$$\rho_B = e^{-\beta H_B} / Z, \quad (3.3)$$

$$H_B = \hbar \Omega C^+ C + \sum_\lambda \hbar \omega_\lambda B_\lambda^+ B_\lambda, \quad (3.4)$$

and

$$Z = \text{Tr}_B e^{-\beta H_B}. \quad (3.5)$$

Here we imposed the initial condition that the pseudomolecule be at the site $n=0$ and the phonons and the vibration of the pseudomolecule be in thermal equilibrium

at time $t = 0$. The quantity L appearing in Eq. (3.2) is the Liouville operator corresponding to the total Hamiltonian Eq. (2.4). Using the properties of the trace we can rewrite Eq. (3.1) as

$$P_n(t) = \langle n | \text{Tr}_B (e^{-iLt} A_0^* A_0 \rho_B) | n \rangle. \quad (3.6)$$

A differential equation for $P_n(t)$ can be derived by means of Zwanzig's²⁶ projection operator method. We define a reduced density matrix $f(t)$ by

$$\rho_B f(t) = \mathcal{P} (e^{-iLt} A_0^* A_0 \rho_B), \quad (3.7)$$

with the projection operator \mathcal{P} ,

$$\mathcal{P}A = \rho_B \text{Tr}_B A. \quad (3.8)$$

The resulting equation for $f(t)$ is

$$\rho_B \dot{f}(t) = -i\mathcal{P}L f(t) - \int_0^t ds \mathcal{P}L e^{-i(1-\mathcal{P})Ls} (1-\mathcal{P})L \mathcal{P}f(t-s). \quad (3.9)$$

The probability is given by $P_n(t) = f_{nn}(t) = \langle n | f(t) | n \rangle$. It is important to note that for the definition of the probability that the adsorbed atom is at the site n we have used $A_n^* A_n$ rather than $a_n^* a_n$. This is due to our choice of the description in terms of the pseudomolecule formed by the distortion of the lattice.

In order to go further using perturbation theory, we must specify a convenient zeroth order Hamiltonian H_0 and perturbation U . We introduce the definitions

$$H_0 = \bar{E} \sum_n A_n^* A_n + \hbar \Omega C^* C + \sum_\lambda \hbar \omega_\lambda B_\lambda^* B_\lambda + \langle H'_{SB} \rangle, \quad (3.10)$$

$$U = H'_{SB} - \langle H'_{SB} \rangle + H''_{SB}, \quad (3.11)$$

$$H'_{SB} = \sum_{n \neq m} A_n^* A_m \theta_n \theta_m^* \{ \tilde{J}_{nm} + \varphi_{nm} (C + C^*) \}, \quad (3.12)$$

$$H''_{SB} = \sum_{n\lambda} \hbar Y_\lambda^n A_n^* A_n (B_\lambda + B_\lambda^*) (C + C^*). \quad (3.13)$$

The average $\langle \dots \rangle$ is taken over the equilibrium ensemble of the phonons and the vibration of the pseudomolecule. The perturbation U has the property that $\langle U \rangle = 0$, which is useful in dealing with secular terms. Obviously, we have

$$H = H_0 + U, \quad (3.14)$$

$$\langle H'_{SB} \rangle = \sum_{n \neq m} \tilde{J}_{nm} A_n^* A_m \langle \theta_n \theta_m^* \rangle. \quad (3.15)$$

Introducing $H = H_0 + U$ in Eq. (3.9) and performing the algebra, we obtain an equation for the matrix element of $f(t)$,

$$\dot{f}_{im}(t) = -(i/\hbar) \{ \langle H'_{SB} \rangle_{ik} f_{km}(t) - f_{ik}(t) \langle H'_{SB} \rangle_{km} \} - 2\hbar^{-2} \text{Re} \int_0^t ds \{ \langle U_{ip} \bar{U}_{kr}(s) \rangle (e^{i(H'_{SB})s/\hbar})_{pk} (e^{-i(H'_{SB})s/\hbar})_{qm} f_{rq}(t-s) - \langle U_{ip} \bar{U}_{rq}(s) \rangle (e^{i(H'_{SB})s/\hbar})_{pk} (e^{-i(H'_{SB})s/\hbar})_{qm} f_{kr}(t-s) \}. \quad (3.17)$$

Einstein's summation convention is used. The symbol $\bar{U}_{rq}(s)$ represents the r, q matrix element (in the site representation) of the operator U taken in the interaction representation,

$$\bar{U}(s) = e^{iH_B s/\hbar} U e^{-iH_B s/\hbar}. \quad (3.18)$$

The term H_0 incorporates two kinds of contributions. One is H_B [Eq. (3.4)], which gives the evolution of the phonons and the vibration of the pseudomolecule. These phonons and the vibration are assumed to form a heat bath for the motion of the pseudomolecule parallel to the surface. The other is $\bar{E} \sum_n A_n^* A_n + \langle H'_{SB} \rangle$, which gives the parallel motion of the pseudomolecule under the influence of the average interaction with the heat bath. Therefore, this part of the Hamiltonian depends on the temperature of the heat bath. The term U represents the deviation from the average interaction between the hopping of the pseudomolecule and the heat bath, and it is regarded as a fluctuation.

In anticipation of later results, we discuss next the type of contributions to the mean square displacement $\langle R^2 \rangle_t$ brought about by each of these terms, and we introduce a useful nomenclature:

(1) The term $\langle H'_{SB} \rangle$, contained in H_0 and defined by Eq. (3.15), generates the *coherent hopping* of the pseudomolecule in the average periodic potential of the lattice. We expect the temperature dependence of this term to be strong (weak) if the interaction between the adsorbed atom and the lattice atoms is strong (weak).

(2) We call the motion generated by the term

$$U^{(1)} \equiv H'_{SB} - \langle H'_{SB} \rangle = \sum_{n \neq m} \tilde{J}_{nm} A_n^* A_m (\theta_n \theta_m^* - \langle \theta_n \theta_m^* \rangle) + \sum_{n \neq m} \varphi_{nm} A_n^* A_m \theta_n \theta_m^* (C + C^*) \quad (3.16)$$

incoherent hopping. It contains two terms: the first represent intersite hopping induced by a fluctuation of the interaction with the lattice atoms with the fluctuating rate $\tilde{J}_{nm} (\theta_n \theta_m^* - \langle \theta_n \theta_m^* \rangle)$; the second represents intersite hopping induced by a fluctuation of the vibrational state of the pseudomolecule.

(3) Finally, the term $U^{(2)} \equiv H''_{SB}$ generates a contribution to the migration, which we call *incoherent excitation*. It represents change of the energy of the pseudomolecule at a given site due to the fluctuations of the phonon state and the vibrational state. Both incoherent motions, the incoherent hopping and the incoherent excitation, are caused by the fluctuations in the heat bath and contribute to the diffusional character of the migration of the adsorbed atom.

The first term in this formula generates the coherent hopping. It appears because the part $\langle H'_{SB} \rangle$ of H_0 does not commute with the reduced density matrix $f(t)$; hence $\langle H'_{SB} \rangle$ changes the probability $P_n(t) = f_{nn}(t)$ of finding the particle at a given site. The integral term contains contributions from thermal fluctuations, which

are incorporated through the correlation functions of the bath operators in U . This term generates diffusional contributions to the mean square displacement. In computing the kernel we have assumed that in the propagator $e^{-i(1-\phi)Ls}$ in Eq. (3.9) we can neglect U (in L). This is a standard approximation, sometimes referred to as a Born approximation.²⁶

The matrix elements appearing in Eq. (3.17) can be computed to give

$$\begin{aligned} \dot{f}_{im}(t) = & -i(\Theta J/\hbar)\{f_{i+1,m}(t) + f_{i-1,m}(t) - f_{i,m-1}(t) - f_{i,m+1}(t)\} \\ & - 2\{2\gamma_1 f_{im}(t) - \gamma_1 \delta_{im}[f_{m+1,m+1}(t) + f_{m-1,m-1}(t)] \\ & - \gamma_2[\delta_{i,m+1}f_{m,m+1}(t) + \delta_{i,m-1}f_{m,m-1}(t)]\} - \gamma_0(1 - \delta_{im})f_{im}(t) \end{aligned} \quad (3.19)$$

Here we take the nearest neighbor approximation for the hopping rates in that only intersite transitions between nearest neighbor sites are taken into account:

$$\tilde{J}_{nm} = J\delta_{n,m\pm 1}, \quad \varphi_{nm} = \varphi\delta_{n,m\pm 1}. \quad (3.20)$$

Various quantities entering in Eq. (3.19) are given below:

$$\Theta \equiv \langle \theta_n \theta_{n+1}^* \rangle \approx \exp\{-2g^2[\bar{n}(\omega_0) + \frac{1}{2}]\}. \quad (3.21)$$

ω_0 is the characteristic frequency of the phonons, g is given by Eqs. (2.8) and (2.9), and $\bar{n}(\omega_0) = (e^{\beta\hbar\omega_0} - 1)^{-1}$,

$$\gamma_i = (\Theta J/\hbar)^2 \int_0^\infty ds [g_i(s) - 1 + g_i(s)\lambda(s)], \quad i = 1, 2, \quad (3.22)$$

where

$$\lambda(s) = (\varphi/J)^2 \{e^{i\Omega s}[\bar{n}(\Omega) + 1] + e^{-i\Omega s}\bar{n}(\Omega)\}, \quad (3.23)$$

and

$$\begin{aligned} g_i(s) = & \sum_{k=-\infty}^{\infty} I_k(4g^2 e^{-\Delta s} \{\bar{n}(\omega_0)[\bar{n}(\omega_0) + 1]\}^{1/2}) \\ & \times e^{\pm ik\omega_0 s} \left[\frac{\bar{n}(\omega_0) + 1}{\bar{n}(\omega_0)} \right]^{k/2} \quad i = 1, 2. \end{aligned} \quad (3.24)$$

Δ is the dispersion in the density of phonon states which is taken to be a Lorentzian,

$$\rho(\omega) = (\Delta/\pi)[(\omega - \omega_0)^2 + \Delta^2]^{-1}. \quad (3.25)$$

$I_k(Z)$ are modified Bessel functions.³¹ We defined also

$$\gamma_0 = 2(\eta/\Delta)^2 \bar{n}(\Omega)[\bar{n}(\Omega) + 1], \quad (3.26)$$

where $|Y_\lambda^\dagger| = N^{-1/2}\eta$ [Eq. (2.6)]. The calculations needed to arrive at this result are lengthy and are not reproduced here. They are very similar to those performed in exciton theory.³⁰ The three terms in Eq. (3.19) correspond to the coherent hopping of the pseudomolecule, the incoherent hopping, and the incoherent excitation, respectively. The approximations employed in deriving Eqs. (3.19)–(3.26) are as follows:

(a) It is assumed that the correlation function $\langle U_{ip} \bar{U}_{kr}(s) \rangle$ decays very fast as a function of s , so that under the integral appearing in Eq. (3.17) we can use the expression for $e^{i(H'_{SB})s/\hbar}$ valid for small s , $(e^{i(H'_{SB})s/\hbar})_{pk} \approx \delta_{pk}$, and $f_{im}(t-s) \approx f_{im}(t)$ and the upper limit on the time integral can be taken to infinity.

(b) We assume that all cross correlation functions of the type $\langle U_{mn}^{(1)} U_{pr}^{(2)}(s) \rangle$ are zero. Physically, $U^{(1)}$ [Eq.

(3.16)] is responsible for fluctuations in the intersite hopping rate leading to incoherent hopping and $U^{(2)} \equiv H'_{SB}$ [Eq. (3.13)] for fluctuations of the energy at a given site leading to incoherent excitation; the above assumption claims that these two effects are uncorrelated.³²

(c) A simple model is used for phonon dispersion, which consists in choosing the Lorentzian Eq. (3.25) for the phonon state density with a peak at ω_0 , a characteristic phonon frequency.³³ Use of a simpler model of no phonon dispersion leads to divergences on calculation of γ_1 and γ_2 .

(d) We assume only nearest neighbor interactions, which implies that the transitions between other than neighboring sites are negligible.

IV. MEAN SQUARE DISPLACEMENT

In order to find the probability $P_n(t)$ that an adsorbed atom located at site $n=0$ at time $t=0$ will be at site n at time t , we must solve Eq. (3.19); once this is done, the probability is given by $P_n(t) = f_{n0}(t)$ and the mean square displacement can be computed from $\langle R^2 \rangle_t \equiv a^2 \sum_n n^2 P_n(t)$, where a is the lattice spacing. For the limit of high and low temperature this can be accomplished, and the results are presented below. For intermediate temperature we cannot solve the equation for probability; however, if we multiply Eq. (3.19) by n^2 and sum over all values of n , we obtain an equation for $\langle R^2 \rangle_t$ which is solvable.

A. Low temperature limit; coherent hopping

In the limit of very low temperature, Eq. (3.19) is simplified, since γ_0 , γ_1 , and γ_2 are negligible and only the term corresponding to the coherent hopping survives; thus, we obtain

$$\begin{aligned} \hbar \dot{f}_{im}(t) = & -i\Theta J [f_{i+1,m}(t) + f_{i-1,m}(t) \\ & - f_{i,m-1}(t) - f_{i,m+1}(t)]. \end{aligned} \quad (4.1)$$

This equation is easily solved to give, for example, for one-dimensional motion,

$$P_n(t) = [J_n(2\Theta Jt/\hbar)]^2; \quad (4.2)$$

$J_n(Z)$ is the Bessel function of order n . The mean square displacement is

$$\langle R^2 \rangle_t = 2(\Theta J/\hbar)^2 a^2 t^2, \quad (4.3)$$

which has no diffusional character. On the average, the adsorbed atom migrates with a uniform velocity equal to $\sqrt{2}(\Theta J/\hbar)a$. The factor $\tilde{J}_{nm} \equiv J_{nm} - 2\alpha\varphi_{nm} = J\delta_{n,m\pm 1}$ [Eqs. (2.11) and (3.20)] is made up of two terms; J_{nm} characterizes the degree of delocalization of the wavefunction of the motion of the adsorbed atom parallel to the surface in the periodic field of the undistorted lattice. The other term, $\alpha\varphi_{nm}$, appears because the equilibrium position of the vibration of the adsorbed atom is shifted, which thus changes the delocalization strength $J_{nm} \rightarrow \tilde{J}_{nm}$. The factor $\Theta = \langle \theta_n \theta_{n+1}^* \rangle$ [Eq. (3.21)] depends on temperature, and it represents the distortion of the lattice by the adsorbed atom. If the interaction between the adsorbed atom and the lattice is very weak, that is, $|X_\lambda^\dagger| = N^{-1/2}\xi \rightarrow 0$ [Eq. (2.6)], then $|G_\lambda^\dagger| = N^{-1/2}g \rightarrow 0$ and the fac-

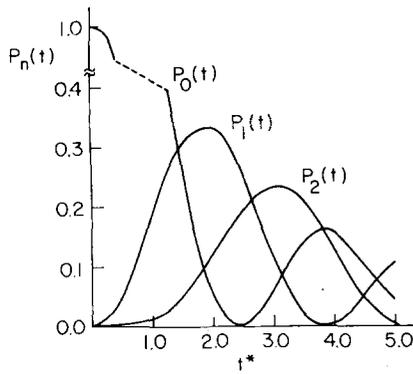


FIG. 1. The time dependence of the probability $P_n(t)$ at very low temperature given by Eq. (4.2). The symbol t^* denotes the time in the unit of $\hbar/2\Theta J$. J is the effective delocalization strength of a pseudomolecule given by Eqs. (2.11) and (3.20). Θ is a temperature dependent function defined in Eq. (3.21).

tor Θ becomes unity. On the other hand, if the interaction between the adsorbed atom and the lattice is extremely strong, then $|G_1^*| = N^{-1/2}g$ becomes large and the factor Θ vanishes and so does the velocity of the coherent migration, so that the adsorbed atom is trapped at the site. It is interesting to note that Θ resembles the Debye-Waller factor. When the temperature is raised, the periodicity of the potential and thus coherence of the hopping are destroyed by the lattice vibration. In fact, as $T \rightarrow \infty$, $\Theta \approx \exp(-2g^2\hbar kT/\hbar\omega_0) \rightarrow 0$, and the velocity of the coherent hopping diminishes. The temperature dependence of the velocity is strongly influenced by the phonon frequency ω_0 ; the smaller the frequency, the faster is the decrease of the velocity with temperature. To illustrate the character of this motion we plot in Fig. 1 the time evolution of the probability $P_n(t)$ of Eq. (4.2). We see that the probability of the adsorbed atom being at site $n=1$ is zero at time $t=0$, reaches a maximum at $t^* = t\hbar/2\Theta J \approx 2$, recedes at $t^* \approx 4$, and grows again at $t^* \approx 5$. This periodic structure illustrates the quantum-wave-like nature of the coherent motion. Because of the reflection and transmission through the potential barrier between the neighboring sites, the probability does not decay monotonically.

B. High temperature limit; incoherent hopping

At very high temperatures, the first term in Eq. (3.19), which represents the coherent hopping of the adsorbed atom, vanishes since $\Theta \rightarrow 0$ in this limit. Hence, Eq. (3.19) reduces to

$$\dot{P}_n(t) = -2\gamma_1[2P_n(t) - P_{n+1}(t) - P_{n-1}(t)], \quad (4.4)$$

with solution in one dimension,

$$P_n(t) = I_n(4\gamma_1 t) \exp(-4\gamma_1 t). \quad (4.5)$$

The mean square displacement is

$$\langle R^2 \rangle_t = 4\gamma_1 a^2 t. \quad (4.6)$$

Comparing Eq. (4.4) to Eqs. (3.17) and (3.19), we see that only the term responsible for the incoherent hopping survives in Eq. (4.4) in the high temperature limit. Hence the incoherent hopping motion has a diffusional character leading to a diffusion coefficient

$$D = 2\gamma_1 a^2. \quad (4.7)$$

The diffusional character of the motion is also reflected in the form of $P_n(t)$ given by Eq. (4.5). The probability $P_n(t)$ is exactly the probability for a symmetrized Poisson process.³⁴ It is interesting to analyze the temperature dependence of the diffusion coefficient in the high temperature limit in order to see if there is behavior as predicted by an activated complex formula. γ_1 in Eq. (4.7) is the sum of two contributions: one, $\gamma_1^{(1)}$, from the fluctuations in the intersite hopping rate caused by the lattice vibrations [the term $g_1(s) - 1$ in Eq. (3.22)], and the other, $\gamma_1^{(2)}$, from the fluctuation in the intersite hopping rate caused by the excitation of the vibrational motion of the adsorbed atom [the term $g_1(s)\lambda(s)$ in Eq. (3.22)]. Using Eqs. (3.21)–(3.24), we obtain for $\gamma_1^{(1)}$,

$$\gamma_1^{(1)} = (J/\hbar)^2 \Delta^{-1} \Theta^2 A(T), \quad (4.8)$$

where

$$A(T) = \int_0^Z du \frac{I_0(u) - 1}{u}, \quad (4.9)$$

with

$$Z = 4g^2 \sqrt{\bar{n}(\omega_0)[\bar{n}(\omega_0) + 1]}. \quad (4.10)$$

At high temperature such that $Z > 5$, $A(T)$ becomes

$$A(T) \approx Z^{-3/2} e^Z [f_0 + f_1(5/Z) + \dots]. \quad (4.11)$$

Here f_0 and f_1, \dots are taken from Ref. 35. At high temperature we see that the temperature dependence of $\gamma_1^{(1)}$ is of the form

$$\gamma_1^{(1)} \sim T^{-3/2} \exp(-E_a/kT), \quad (4.12)$$

with the "activation energy"

$$E_a = g^2 \hbar \omega_0 / 2. \quad (4.13)$$

The other contribution, $\gamma_1^{(2)}$, is

$$\gamma_1^{(2)} = (\varphi/J)(J/\hbar)^2 \Delta^{-1} \Theta^2 B(T), \quad (4.14)$$

where

$$B(T) = \Delta [2\bar{n}(\Omega) + 1] \int_0^\infty ds I_0(Z e^{-\Delta s}) \zeta \cos(\Omega s), \quad (4.15)$$

and $\bar{n}(\Omega)$ is the Bose distribution function. $B(T)$ is a complicated function of the temperature T , the phonon frequency ω_0 , and the ratio of the vibration frequency and the phonon band width Ω/Δ . A crude estimate of $\gamma_1^{(2)}$ for large Ω/Δ limit gives the same type of formula as $\gamma_1^{(1)}$. The meaning of the energy E_a can be established by inspecting Eq. (2.9) for the parameter g and Eq. (2.10) for the renormalized energy of the adsorbed atom. The quantity $g^2 \hbar \omega_0$ is related to the change of energy due to the renormalization, that is, $\bar{E} \approx E_0 - g^2 \hbar \omega_0$ for $\eta^2 \ll \omega_0 \Omega$, in other words, in the limit such that the energy shifts due to the concerted vibrations of the pseudomolecule and the lattice atoms are very small. Therefore the activation energy is about half the energy spent in distorting the lattice on formation of the pseudomolecule. The formula looks as if the vibrations of the lattice promote incoherent hopping by undoing the lattice distortion. One should not, however, take this kind of interpretation very seriously since (a)

the pre-exponential factor has a temperature dependence that would indicate that the customary activated complex formula may not be valid except at extremely high temperature, and (b) at very high temperatures, real surfaces are likely to have defects which invalidate our model. Even at high temperature, if the coupling is very weak, that is, $|X_1^n| = N^{-1/2} \xi \rightarrow 0$, such that $Z < 5$ in Eq. (4.8), a formula for $\gamma_1^{(1)}$ different from Eq. (4.12) results. In this case, Θ may not be negligible and hence the coherent motion contributes to the mean square displacement. We will discuss this case as an intermediate temperature case in the next section.

C. Intermediate temperatures

The case of intermediate temperatures is more complicated and we must solve the complete equation (3.19). Though we could not obtain a formula for the probability $P_n(t)$, it is possible to solve for $\langle R^2 \rangle_t$, and the result for one-dimensional motion is

$$\langle R^2 \rangle_t / a^2 = 4\gamma_1 t + (2J\Theta/\hbar\alpha)^2 (e^{-\alpha t} - 1 + \alpha t). \quad (4.16)$$

Here

$$\alpha = 4\gamma_1 + 2\gamma_2 + \gamma_0. \quad (4.17)$$

At times satisfying $t \gg \alpha^{-1}$, the mean square displacement becomes

$$\langle R^2 \rangle_t / a^2 = [4\gamma_1 t + (2J\Theta/\hbar)^2 / \alpha] t, \quad (4.18)$$

which leads to the diffusion coefficient

$$D = 2a^2[\gamma_1 + (J\Theta/\hbar)^2 / \alpha]. \quad (4.19)$$

Therefore in the case of intermediate temperature the motion acquires diffusional character after a time α^{-1} ; at very low temperature $\gamma_1, \gamma_2, \gamma_0 \rightarrow 0$, and thus the onset of the diffusional motion requires infinite time. Thus, we recover the previous conclusion that at very low temperatures the motion is not diffusional.

Equation (3.19) can also be solved to find $\langle R^2 \rangle_t$ and the diffusion coefficient in the case of two-dimensional motion. For the simple case of nearest neighbor coupling in two perpendicular directions, say x and y , the equations for motion can be solved for $\langle R^2 \rangle_t$ to find

$$\begin{aligned} \langle R^2 \rangle_t = & 4(\gamma_x + \gamma_y)t + (2J_x\Theta/\hbar\alpha_x)^2 (e^{-\alpha_x t} - 1 + \alpha_x t) \\ & + (2J_y\Theta/\hbar\alpha_y)^2 (e^{-\alpha_y t} - 1 + \alpha_y t), \end{aligned} \quad (4.20)$$

where

$$\gamma_i = (J_i\Theta/\hbar)^2 \int_0^\infty ds [g_1(s) - 1 + g_1(s)\lambda_i(s)] \quad i = x, y,$$

$$\gamma'_i = (J_i\Theta/\hbar)^2 \int_0^\infty ds [g_2(s) - 1 + g_2(s)\lambda_i(s)] \quad i = x, y,$$

and

$$\alpha_i = 4(\gamma_x + \gamma_y) + 2\gamma'_i + \gamma_0 \quad i = x, y.$$

$\lambda_i(s)$ can be obtained from Eq. (3.23) by replacing $(\varphi/J)^2$ by $(\varphi_i/J)^2$. Thus the motion in the two directions is decoupled. Note that the qualitative behavior of $\langle R^2 \rangle_t$ is not different in two dimensions from that in one dimension for this model. Therefore we will analyze the formulas Eqs. (4.16)–(4.19) for the one-dimensional motion only.

The first term in the expression of the diffusion coefficient Eq. (4.19) is the one which appears in the case of high temperature limit, discussed in Sec. B. Hence, this term corresponds to the diffusional character of the migration. On the other hand, the second term represents the coherent character of the migration. To see this, we examine the behavior of the mean square displacement within a time in which the coherence persists, that is, $t < \alpha^{-1}$. Equation (4.16) gives

$$\frac{\langle R^2 \rangle_t}{a^2} = 4\gamma_1 t + 2(J\Theta/\hbar)^2 t^2 + \dots \quad (4.21)$$

for $\alpha t < 1$. The first term on the rhs represents the diffusional character of the migration, and the second one is just the form of the mean square displacement at low temperature limit, given in Eq. (4.3), thus representing the coherent migration.

For the convenience of numerical calculation, we introduce the following notations:

$$\frac{D}{2a^2(J/\hbar)^2/\Delta} = D_1 + D_2, \quad (4.22)$$

$$D_1 = \Theta^2 [A(T) + (\varphi/J)^2 B(T)], \quad (4.23)$$

$$D_2 = (\Delta/J)^2 \Theta^2 \{6\Theta^2 [A(T) + (\varphi/J)^2 B(T)] + C(T)\}^{-1}. \quad (4.24)$$

Here $A(T)$ and $B(T)$ are the same as given in Eqs. (4.9) and (4.15). The function $C(T)$ is given by

$$C(T) = 2(\eta/J)^2 \bar{n}(\Omega) [\bar{n}(\Omega) + 1]. \quad (4.25)$$

D_1 and D_2 represent the diffusional character of the migration and the coherent one, respectively. One should keep in mind that the functions $A(T)$, $B(T)$, and $C(T)$ are connected to various processes in the migration: $\Theta^2 A(T)$ corresponds to the phonon-induced fluctuations in the hopping rate, $\Theta^2 B(T)$ to the vibration-induced fluctuations in the hopping rate, and $C(T)$ to incoherent excitations. The quantities $\gamma_1^{(1)}$, $\gamma_1^{(2)}$, and γ_0 are proportional to $A(T)$, $B(T)$, and $C(T)$, respectively. We see the following trends: The contribution of the phonon-induced incoherent hopping [$\Theta^2 A(T)$] to the diffusional part D_1 is increased, at a given temperature, if ω_0 is decreased, which means a more flexible lattice. The contribution of the vibration induced incoherent hopping [$\Theta^2 B(T)$] to the diffusion coefficient at a given temperature increases with φ/J , Δ/Ω , and $kT/\hbar\Omega$. The first is the intersite hopping rate φ due to vibration, expressed in units of the rate of coherent intersite hopping J . The second is the ratio between the phonon bandwidth Δ and the frequency of the vibration of the adsorbed atom Ω ; the broader the band, the easier it is to transfer energy from lattice to the adsorbed atom; when Ω is small, the binding of the adsorbed atom to the surface is weak and one expects a high mobility. The term of the incoherent excitations $C(T)$ grows with Ω^{-1} and η/J . If Ω^{-1} is large, the vibration of the adsorbed atom is more easily excitable. When η/J is large, the strong on-site excitation destroys the coherence of the hopping, hence the contribution of the coherent part D_2 to the diffusion coefficient decreases.

More explicit dependence of the diffusion coefficient on temperature and other parameters can be obtained by analyzing the functions in Eqs. (4.22)–(4.24) numerically.

ically. We show below the numerical results of the following two cases.

(a) Weak coupling case, such that $Z \equiv 4g^2\sqrt{\bar{n}(\omega_0)}[\bar{n}(\omega_0)+1] < 3.75$ holds.

First note that since the Bose distributions $\bar{n}(\omega_0)$ is an increasing function of the temperature, the results to be shown below are valid for a wide range of values of g^2 at low temperature. On the other hand, if the temperature is high, g^2 should be small. In this case we have polynomial forms for $A(T)$ and $B(T)$,

$$A(T) \approx \sum_{k=1}^6 [a_k/(2k-1)](Z/3.75)^{2k}, \quad (4.26)$$

$$B(T) \approx \sum_{k=1}^6 a_k(Z/3.75)^{2k} 2k [2\bar{n}(\Omega)+1] [(2k)^2 + (\Omega/\Delta)^2]^{-1}. \quad (4.27)$$

The numbers a_n are taken from Ref. 36. In Figs. 2 and 3, we give some representative graphs to illustrate the temperature dependence of the diffusional part D_1 and the coherent part D_2 of the diffusion coefficient. D_1 in Fig. 2 satisfies, in a wide range of temperature, the activation energy law, $D_1 \sim \exp(-\hbar\omega_0/kT)$. The coherent part D_2 has quite different temperature dependence from that of D_1 ; at low temperature it is $D_2 \sim \exp(\hbar\omega_0/kT)$, which brings about deviations from the temperature dependence of the diffusion coefficient, required by the activated complex theory. The resulting plots of the

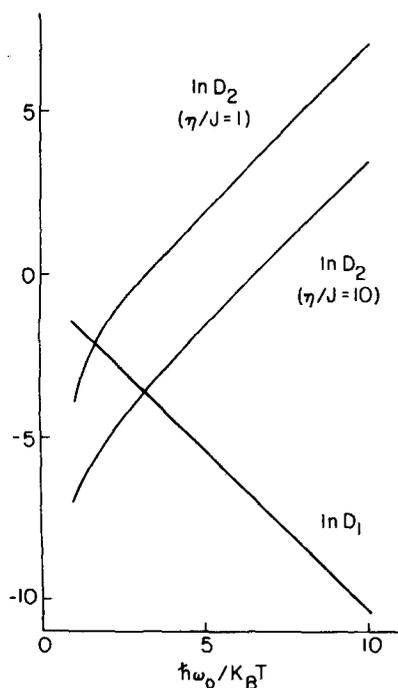


FIG. 2. Logarithmic plots of the two contributions, D_1 and D_2 , to the diffusion coefficient, defined in Eqs. (4.23) and (4.24), as functions of $\hbar\omega_0/kT$. D_1 and D_2 are scaled by $2\alpha^2(J/\hbar)^2/\Delta$ as shown in Eq. (4.22). D_1 represents the diffusional character of the migration, D_2 the coherent character of the migration. Values of the parameters are chosen as follows: $\Omega/\Delta = 13.9$, $\Omega = \omega_0$, $\Delta = J/\hbar$, $\varphi/J = 5.47$, and $g = 0.8$ (weak coupling). Two curves of D_2 for $\eta/J = 1$ and $\eta/J = 10$ show that the migration of the adsorbed atom is less coherent (small D_2) when the incoherent excitation is enhanced (large η/J).

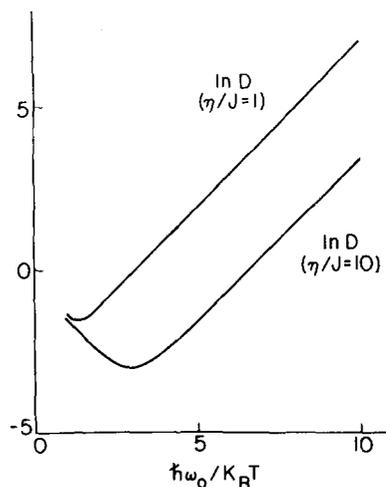


FIG. 3. Logarithmic plots of the diffusion coefficient as a function of $\hbar\omega_0/kT$. The diffusion coefficient in Eq. (4.22) is the sum of two terms D_1 and D_2 , shown in Fig. 2. Values of the parameters are chosen the same as those for the plots in Fig. 2 (weak coupling). At higher temperature D_1 dominates D_2 and an activated complex formula is valid. At lower temperature, D_2 becomes important and the temperature dependence becomes different from the one given by the activated complex theory. As (η/J) increases, that is, as the incoherent excitation dominates the coherent hopping, the temperature dependence of D becomes the activated complex theory type.

diffusion coefficient in Fig. 3 have a minimum at the temperature at which the two contributions D_1 and D_2 to D [Eq. (4.22)] are of equal importance. As the ratio η/J increases, the temperature dependence of D becomes more like the prediction of the activated complex theory, because the incoherent excitations at lattice sites destroy the coherence of the hopping. This type of phenomenon as shown in Figs. 2 and 3 is expected for adsorbed atoms weakly interacting with solid surfaces, such as discussed in the Introduction. For example, the interaction of an adsorbed He and the surface of solid Kr should be very weak. On the other hand, the Debye temperature of the bulk solid Kr is 72°K ,³⁷ and we may expect the surface phonon frequency to be even smaller. Therefore, if we want to observe the predicted increase of D vs $1/T$, then we must make measurements at temperatures much below the Debye temperature.

(b) Strong coupling case such that $Z \equiv 4g^2\sqrt{\bar{n}(\omega_0)}[\bar{n}(\omega_0)+1] > 5$.

In this case we may neglect the contribution of the coherent motion D_2 to the diffusion coefficient; that is, the pseudomolecule is trapped at a lattice site because of the strong coupling with the lattice atoms, and the coherent motion is immediately broken. Hence, this case is just the case of high temperature limit, discussed previously, in which the incoherent hopping is the main mechanism of the migration. In fact, the condition $Z > 5$ may also be satisfied by $\hbar\omega_0/kT \ll 1$. Of course, if g^2 is extremely large, the pseudomolecule remains at the lattice site as indicated by $D \rightarrow 0$ as $g^2 \rightarrow \infty$. As shown in Eq. (4.23), the diffusional part of

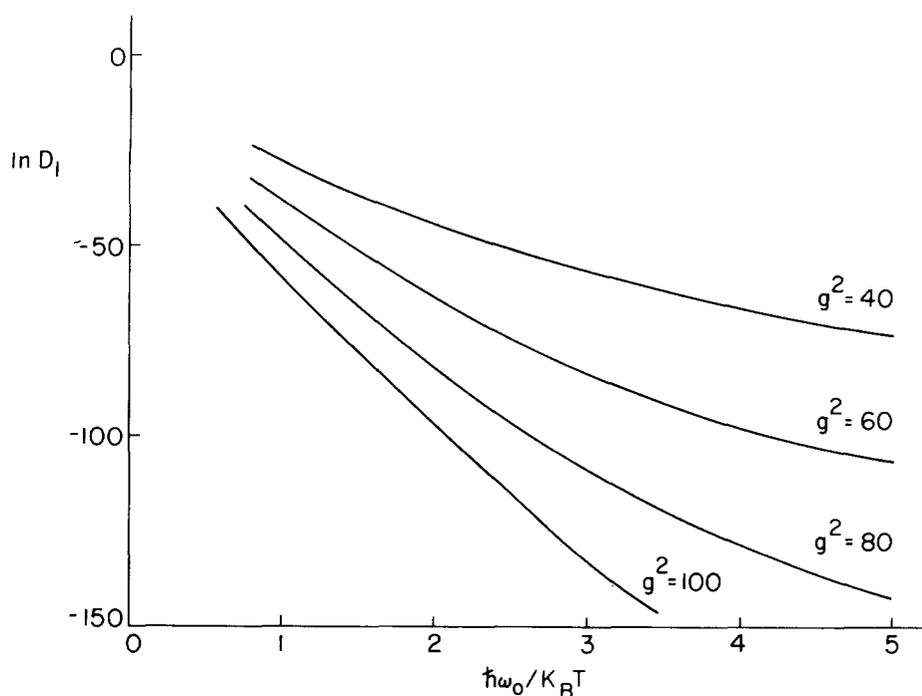


FIG. 4. Logarithmic plots of the diffusion coefficient D_1 given in Eq. (4.28) as a function of $\hbar\omega_0/kT$ for various values of the coupling constant g^2 (strong coupling case). ω_0 is the characteristic frequency of phonons. $\ln D_1$ is a concave-up function of $\hbar\omega_0/kT$, and the tangent, which is proportional to the activation energy, is a decreasing function of $\hbar\omega_0/kT$.

the diffusion coefficient D_1 consists of two parts: one is proportional to $\Theta^2 A(T)$, representing phonon-induced fluctuation of intersite hopping; the other, $\Theta^2 B(T)$, represents vibration-induced intersite hopping. Assuming that the former part is larger than the latter, we may calculate the temperature dependence of D_1 ,

$$D_1 \propto \Theta^2 A(T), \quad (4.28)$$

using the formula Eq. (4.11). The assumption is valid if the coupling between the vibration and the hopping is small or if the frequency of the vibration Ω is very large compared to the phonon bandwidth Δ . The resulting temperature dependence of D_1 is shown in Fig. 4. The logarithm of D_1 is a concave-up function of $\hbar\omega_0/kT$ and it is approximately linear only in a limited range of variation of $\hbar\omega_0/kT$. This implies that the activation energy V in Eq. (1.2) is an increasing function of temperature.

The migration of a tungsten atom on tungsten surfaces and that of a rhodium atom on rhodium surfaces are classified into this strong coupling case. Although we have no precise data for the phonon frequencies ω_0 and for the coupling constants X_λ^n , Y_λ^n of those surfaces, we may use some appropriate values for them and compare the experimental results of the activation energies with our calculations. Usually, surface phonon frequencies are smaller than the bulk phonon frequencies³⁶ and the data for the bulk phonon frequencies are available.³⁷ We assume that characteristic frequencies ω_0 of various surfaces of tungsten to be 200–300 °K and compare the D vs $1/T$ curves in Fig. 4 with the experimental data. It seems that curves with the choice of the parameter g^2 in the range $80 < g^2 < 90$ fit the experimental data for the migration of a tungsten atom on tungsten surfaces. For the case of rhodium, similar comparisons give the estimation of the parameter g^2 , which turns out to be $60 < g^2 < 80$. The large value of $g \lesssim 9$ is

surprising at first sight. However, the shift of the equilibrium position of a tungsten lattice atom at the site of the adsorbed atom is $\approx 2g\sqrt{\hbar/2m\omega_0}$, which is $\approx 0.4 \text{ \AA}$ for $g \approx 9$. On the other hand, the lattice constant of tungsten crystal is $\approx 3 \text{ \AA}$. Therefore, the shift of the equilibrium position is $\lesssim 10\%$ of the lattice constant. However, this estimation does not include the effect of phonon dispersion. In reality, the shift of the equilibrium position of a lattice atom is shared among neighboring lattice atoms; thus the resulting shift of the equilibrium position is smaller than the estimation above.

The anomalously small value of the activation energy of the Rh(110) surface, which we discussed in the Introduction, may be explained by the concave-up behavior of the Arrhenius curves shown in Fig. 4. That is, the observed activation energy depends on the temperature range of the measurement. However, the anomaly in the activation energy may be due to other effects as well: to more complex interactions with the surface atoms and to phonon dispersion, which are not completely included in our treatment.

V. SUMMARY AND DISCUSSIONS

In this paper we have discussed dynamical aspects of the surface migration of an adsorbed atom. The adsorbed atom may interact strongly with the atoms of the solid surface, thus forming a pseudomolecule together with the atoms of the distorted lattice. The motion of the pseudomolecule is described by the use of the canonical transformation [Eq. (2.2)]. Through this transformation, and subsequent thermal average procedure, the coherent migration of the quasimolecule acquires temperature dependence. Further, the coherent migration is coupled with the vibrational motion perpendicular to the surface and with the thermal motion of the lattice atoms. These couplings give the diffusional character

to the motion of the adsorbed atom. Deviations from the temperature dependence of an activated complex theory for the diffusion coefficient have been pointed out in the previous sections: (a) At low temperature and for relatively weak coupling between the adsorbed atom and the solid surface, the coherent nature of the migration dominates the diffusional character. The Arrhenius plot then becomes V shaped as in Fig. 3. This may occur in the case of migration of a rare-gas atom on the solid surface of rare gases. (b) For strong coupling cases, such as a tungsten atom on tungsten surfaces and a rhodium atom on rhodium surfaces, the diffusional character dominates the coherence of the migration. However, as we have seen, the Arrhenius plot is not simply linear and the resulting activation energy calculated from the linear approximation depends on the temperature range in which we make experiments. The formula Eq. (4.8) with Eq. (4.11) relates the diffusion coefficient to the coupling constants of the interactions between the adsorbed atom and the lattice vibrations and to the characteristic frequency of the lattice vibrations. We made an attempt to compare the theory with existing experimental results. Although there exist no precise data for the parameters in our theory, we assumed reasonable values for them. The theoretical Arrhenius curves with the choice of $60 < g^2 < 90$ seem to fit the experimental ones for Rh and W. The large values of g^2 seem to be due to the fact that those atoms are chemisorbed³⁹ on the solid surface. As seen from Eq. (2.9), the large value of g is related to the strong coupling between the adsorbed atom and the lattice atoms, $|X_\lambda^n| = N^{-1/2} \xi \rightarrow \infty$. However, the parameter g can be large when the coupling constant $|Y_\lambda^n| = N^{-1/2} \eta$ in the Hamiltonian Eq. (2.1) is large; that is, the shift of the energy of the adsorbed atom at a site due to the coupling between its vibration and the lattice vibrations is large. In fact, if $2\eta \lesssim \sqrt{\omega_0 \Omega}$ in Eq. (2.9), g becomes very large. Of course in such a case the last term in the Hamiltonian Eq. (2.4) should not be treated as a perturbation. Rather we should introduce another canonical transformation which renormalizes the frequencies of phonons and vibration of the pseudomolecule as well as the energy of the pseudomolecule at a lattice site.

The qualitative picture of our model, that is, the pseudomolecule approach, is consistent with recent quantum mechanical studies of the chemisorptive bond³⁹ in many systems. The dynamical description can be tested by various experimental approaches. The measurement of the mean square displacement as a function of temperature has already been mentioned. For adsorbates and surfaces of different chemical composition, it may be possible to measure the effect of diffusion on the line shape of optical or infrared absorption of the adsorbate, especially if there is more than one site for adsorption. The nature of the transport between inequivalent sites would then effect the line shape in much the same way that triplet exciton diffusion effects ESR line shapes.⁴⁰ However, for adsorbates which are chemically identical to the surface (e.g., W on W), such an approach would be impossible. The contribution that the diffusion of the adsorbate will make to the

line shape of ESCA or photoelectron spectroscopy is unknown at the present time.

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