

COHERENT AND DIFFUSIONAL MOTION OF A CHEMISORBED ATOM**H. METIU***The James Franck Institute, University of Chicago, Chicago, Illinois 60637, USA*

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Experiments indicate that there are two extreme types of motion of an atom on a solid surface. One is characterized by an average velocity and has a mean square displacement proportional to the square of the time (we call this coherent). The other (called purely diffusional) is characterized by a diffusion coefficient and has a mean square displacement proportional to time. We present a simple stochastic model to explain the microscopic origin of these two extreme types of motion. In the case in which both types of motion coexist, the motion becomes diffusional for times longer than an intrinsic time depending on the intensity of the thermal fluctuations of the atom-lattice coupling.

1. Introduction

Recent work with the field ion microscope [1] has made it possible to observe the motion of a single chemisorbed atom on a crystal face without defects. These observations allow the computation of a diffusion coefficient given by the formula:

$$D = \langle R^2(t) \rangle / 2dt, \quad (1)$$

where $\langle R^2(t) \rangle$ is the mean square displacement of the atom in time t , and d is the dimensionality of the motion ($d = 1$ for motion in a channel and 2 for motion on a surface). Since the diffusion coefficient must be time independent, eq. (1) makes sense for times long enough so that the mean square displacement is proportional to time. There is evidence that this is not true for all systems.

Measurements of the specific heat [2] of chemisorbed layers of helium on a graphite surface can be interpreted only by assuming that the adsorbed atoms move freely on the surface. Such motion is characterized by an average uniform velocity rather than a dif-

fusion coefficient, and the mean square displacement is proportional to the square of the time of observation. Of course this comes about only for times shorter than the scattering time, which is extremely long in such systems. These experimental results are supported by quantum mechanical calculations [3] which show that the helium atoms are delocalized when adsorbed on graphite or noble gas surfaces and they can move with practically no activation energy.

These experiments indicate that two extremes of motion are possible and should be considered when analyzing the displacement of an adsorbed atom on a solid surface. We give precise definitions later, but we note here the main characteristics of these extremes. The purely diffusional motion has a mean square displacement proportional to the time of observation, while the purely coherent has a mean square displacement proportional to the square of that time.

In this note, we present a simple realistic stochastic model in order to analyze the microscopic origin of the two types of motion and to understand the intermediate situation in which the motion is neither purely diffusive nor purely coherent. We use a dynamic model in which the hamiltonian is split into a deter-

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ministic part, H_0 , which describes the behavior of the atom on a rigid lattice and a stochastic part, $V(t)$, which simulates the effect of the thermal motion of the lattice on the state and motion of the atom. The model allows us to compute the mean square displacement of the atom as a function of time. This analysis leads to the following conclusions. If $V(t)$ is zero, the mean square displacement is proportional to t^2 and the purely coherent extreme emerges. If the terms in H_0 which give rise to the atom motion are zero and $V(t)$ is not zero, then the mean square displacement is proportional to t and the purely diffusional extreme results. If both H_0 and $V(t)$ are non-zero the motion of the atom is coherent at short times and becomes diffusional after a time longer than an intrinsic time depending on the intensity of the thermal fluctuations of the atom-lattice coupling. The diffusion coefficient in this case contains a part from the purely diffusional extreme, but also contains a contribution from the coherent extreme.

We emphasize that the analysis is dynamic and no activated complex type of assumptions are necessary to describe the motion.

2. The model hamiltonian

Consider the hamiltonian, H_0 , of the atom in the two dimensional, periodic potential of the static lattice. The solutions of the Schrödinger equation for this situation are the usual band states, characterized by a two dimensional wave vector, k , and an index specifying the band (which we drop in the interest of simplicity). This set, $|k\rangle$, is a complete and orthonormal basis as is the Fourier transformed set $|n\rangle \equiv N^{-1/2} \sum_k \exp(-ik \cdot R_n) |k\rangle$. Hence

$$H_0 = \sum_n E_n |n\rangle\langle n| + \sum_{n \neq m} J_{nm} |n\rangle\langle m|. \quad (2)$$

Here N is the number of sites available to the chemisorbed atom and R_n is their position. The index n counts the sites of minimum energy for the adsorbed atom. The energy of the atom at site n is E_n and J_{nm} is the off diagonal matrix element of H_0 in the site representation. We shall call this quantity the transfer matrix element and note that it determines the probability that an atom transfers from n to m .

Since the lattice is not rigid, and the adsorbed atom

vibrates in a direction perpendicular to the surface, we must include these effects in the hamiltonian. These motions are perceived by the atom as fluctuating changes in the height and width of the barrier between sites (leading to faster or slower motion of the atom). We introduce fluctuating transfer matrix elements $F_{nm}(t)$ in order to mimic this effect. Besides changing the barrier, the thermal motion also causes fluctuations of the energy of the atom (which also influences the transfer probability), which we simulate by adding fluctuating site energies, $F_n(t)$, in the hamiltonian, which then becomes

$$H = H_0 + V(t) \\ \equiv H_0 + \sum_n F_n(t) |n\rangle\langle n| + \sum_{n \neq m} F_{nm}(t) |n\rangle\langle m|. \quad (3)$$

To complete the model, we assume that $F_n(t)$ and $F_{nm}(t)$ are gaussian processes with short time correlation and that $F_n(t)$ and $F_{nm}(t)$ are not correlated, that is,

$$\langle\langle F_n(t) \rangle\rangle = \langle\langle F_{nm}(t) \rangle\rangle = \langle\langle F_n(t) F_{nm}(t') \rangle\rangle = 0, \quad (4)$$

$$\langle\langle F_n(t) F_n(t') \rangle\rangle = 2\gamma_0 \delta_{nn'} \delta(t-t'), \quad (5)$$

$$\langle\langle F_{nm}(t) F_{n'm'}(t') \rangle\rangle = \{2\gamma_1 (n-m) \delta_{nm'} \delta_{mn'} (1-\delta_{nm}) \\ + 2\gamma_2 (n-m) \delta_{nm'} \delta_{mm'} (1-\delta_{nm})\} \delta(t-t'). \quad (6)$$

The choice of the gaussian processes may be justified since the fluctuations are due to the disturbances of many degrees of freedom. The gaussian processes will be used in truncating the equation of motion for the density matrix. We take the time correlations to be delta functions since the time scale of the migration of the adsorbed atom is assumed to be separated from the time scales of these fluctuations. In eq. (5), we further assumed that the fluctuations of the energy at different sites are not correlated. In eq. (6), we assumed that random transfer takes place only between neighboring sites and that the random transfers at different places are not correlated. We distinguish two kinds of processes, (i) $n = m'$, $m = n'$ and (ii) $n = n'$, $m = m'$, by γ_1 and γ_2 .

It is also possible to compute the quantities F_n and F_{nm} from a microscopic model and obtain them as functions of the lattice and vibrational coordinates [4]. The averages in eqs. (4)–(6) then become the thermal

averages over lattice vibrations. The quantities γ_i are a measure of the intensity of the fluctuation of the energy of the atom and of the transfer matrix. The temperature dependence of these quantities cannot be established within the framework of this model, but that can be done in a theory which includes the motion of the lattice and the coupling to the atom [4]. However, on physical grounds, we expect γ_i to be monotonically increasing functions of temperature. The delta functions in time imply that the autocorrelation functions of the random energy and random transfer matrix elements decay much faster than the time scale of the atomic displacement on the surface.

3. Mean square displacement

Using the model defined in eqs. (3)–(6), we now derive the mean square displacement of the atom on the surface. At $t = 0$ the atom is located on site n_0 ; the density matrix at time t will then be

$$\rho(t) = e^{-iH\delta t}$$

$$\times \exp_T \left[-i \int_0^t d\tau e^{iH\delta\tau} V^x(\tau) e^{-iH\delta\tau} \right] \rho(0). \quad (7)$$

We use the notation $A^x \rho \equiv A\rho - \rho A$, with the rule $A^x B^x \rho = A^x(B\rho - \rho B) = A(B\rho - \rho B) - (B\rho - \rho B)A$. The exponential operator is defined by its power series expansion and \exp_T stands for the time ordered exponential. The probability that the particle, at site n_0 at $t = 0$, will be at site n at time t is given by

$$P_n(t) = \langle n | \langle \langle \rho(t) \rangle \rangle | n \rangle. \quad (8)$$

The mean square displacement is then given by

$$\langle R^2(t) \rangle \equiv \sum_n R_n^2 P_n(t). \quad (9)$$

In order to compute $\langle R^2(t) \rangle$, we must derive a differential equation for $f_{nm}(t) \equiv \langle n | \langle \langle \rho(t) \rangle \rangle | m \rangle$ by taking the time derivative and using eq. (7). If we assume $F_n(t)$ and $F_{nm}(t)$ are gaussian random variables then a cumulant expansion [5] of the average of the exponential operator which appears in eq. (7) breaks off at the second cumulant. The resulting differential equation for $f_{lm}(t)$ is

$$\begin{aligned} \dot{f}_{lm}(t) = & -i \sum_p [J_{lp} f_{pm}(t) - J_{pm} f_{lp}(t)] \\ & - 2\gamma_0(1 - \delta_{lm}) f_{lm}(t) - 2 \left\{ \sum_p \gamma_1(p) \right\} f_{lm}(t) \quad (10) \\ & + 2\delta_{lm} \sum_p \gamma_1(i-p) f_{pp}(t) + 2\gamma_2(l-m) f_{ml}(t). \end{aligned}$$

The derivation of this equation is straightforward but tedious; the details are not given here.

We now solve eq. (10) for the two limiting cases mentioned above. As already stated, we find coherent motion in the limit that $\gamma_i = 0$ and $J_{nm} \neq 0$ (corresponding to $V(t) = 0$). This means that the motion of the adatom parallel to the surface is uncoupled to the thermal motion of the surface atoms or of the adatom perpendicular to the surface. The purely diffusional limit is found for the case in which $J_{nm} = 0$ (all n and m) so that the motion is entirely caused by the fluctuating terms.

(a) *Coherent motion*: we treat this limiting case first. Taking $\gamma_0 = \gamma_1 = \gamma_2 = 0$, eq. (10) becomes

$$\dot{f}_{lm}(t) = -i \sum_p [J_{lp} f_{pm}(t) - J_{pm} f_{lp}(t)]. \quad (11)$$

In the nearest neighbor approximation ($J_{lp} = 0$ unless l and p are nearest neighbors, in which case $J_{lp} = J$) and for one dimensional motion, we find ($n_0 = 0$ for convenience)

$$P_n(t) = J_n^2 (2Jt) \quad (12)$$

and

$$\langle R^2(t) \rangle = \frac{1}{2} (2Jta)^2, \quad (13)$$

where a is the lattice constant, J_n is the n th order Bessel function. For two dimensional nearest neighbor interactions, we find

$$\langle R^2(t) \rangle = \frac{1}{2} \sum_{i=1}^2 (2J_i a_i t)^2.$$

This simple calculation shows that $\langle R^2 \rangle \propto t^2$ in the coherent limit and the motion is characterized by a velocity proportional to Ja . These results are easily generalized to non-nearest neighbor interactions.

(b) *Purely diffusional motion*: we now take $J_{nm} = 0$ and make the nearest neighbor approximation for the

γ_i which requires that $\gamma_i(l-m)$ is zero unless $l = m(\gamma_i \equiv \gamma_0)$ and $l = m \pm 1$ ($\gamma_i \equiv \gamma_1$ or γ_2). Eq. (10) becomes [for the diagonal elements $f_{mm}(t)$] in one dimension

$$\dot{P}_m(t) = -2\gamma_1 [2P_m(t) - P_{m+1}(t) - P_{m-1}(t)]. \quad (14)$$

This equation is that of a random walker with the solution

$$P_n(t) = I_n(4\gamma_1 t) e^{-4\gamma_1 t}, \quad (15)$$

if $P_n(0) = \delta_{n,0}$, where I_n is the n th order modified Bessel function. The mean square displacement is given by

$$\langle R^2(t) \rangle = 4\gamma_1 a^2 t. \quad (16)$$

Note that the continuum limit of eq. (14) is

$$\partial P(x, t) / \partial t = 2\gamma_1 a \partial^2 P(x, t) / \partial x^2,$$

which is the diffusion equation with diffusion coefficient $a^2\gamma_1$, which agrees with the result of eq. (16) for the mean square displacement. Note that the expression, eq. (15), for the conditional probability $P_n(t)$ is that of a symmetrized Poisson process [6] which is known to be a diffusional stochastic process. Also, the diffusion coefficient is proportional to γ_1 , i.e., the intensity of the fluctuations in the transfer matrix elements. Finally, note that γ_0 is absent from the expression for the diffusion coefficient indicating that, in this limit, the fluctuations in the site energy do not influence the movement of the atom unless some coherent motion is present.

(c) *The intermediate case:* the intermediate case, in which neither $J_{nm} = 0$ nor $\gamma_i = 0$, is the case of most interest experimentally. For the case of He on a graphite surface, computations show that He J_{nm} are very large, and at low temperatures we expect γ_i to be small; therefore, this is very close to the purely coherent regime. In the case of W atoms on a W surface, studied by field ion microscopy, the binding at a site is strong and J_{nm} is probably very small. At high temperatures, the γ_i are expected to be large and thus the motion should be close to be purely diffusional in character. For other cases, J and γ_i may be comparable in magnitude and the intermediate case will obtain. The effects of the coexistence of both types of motion can be seen by solving eq. (10) in the nearest neighbor one dimensional case, and computing the mean square

displacement. We find

$$\langle R^2(t) \rangle = a^2 \{ 4\gamma_1 t + (2J/\alpha)^2 (e^{-\alpha t} - 1 + \alpha t) \}, \quad (17)$$

with

$$\alpha = 2\gamma_0 + 4\gamma_1 + 2\gamma_2. \quad (18)$$

We see that, except at long t , the mean square displacement is not proportional to t^2 or t . If, however, the time of observation is longer than the intrinsic time, τ_D ,

$$\tau_D \equiv \alpha^{-1} = (2\gamma_0 + 4\gamma_1 + 2\gamma_2)^{-1}, \quad (19)$$

then the diffusion limit obtains, for then

$$\langle R^2(t) \rangle = a^2 (4\gamma_1 + 4J^2\tau_D) t \quad (20)$$

for $t \gg \tau_D$. Using eqs. (1) and (20) we can define a diffusion coefficient

$$D = a^2 (2\gamma_1 + 2J^2\tau_D). \quad (21)$$

Various features of this case should be noted: (i) the intrinsic time, τ_D , depends solely on the intensity of the fluctuations of the energy and transfer matrix elements. More intense fluctuations lead to a quicker onset of diffusional motion. The two intensities γ_0 and γ_1 enter in a symmetrical manner in τ_D and either one can cause the onset of the diffusional motion. (ii) The ways in which γ_0 and γ_1 influence the migration of the atom are distinct. The energy fluctuations, γ_0 , influence the motion of the atom only through the coherent motion. If $J = 0$, γ_0 disappears from eqs. (17), (20), and (21). (iii) The diffusional motion which is perceived at long observation times has a contribution from the coherent motion and so is different from the purely diffusional case ($J = 0$). In fact we may write

$$D = D_{p.d.} + v^2\tau_D, \quad (22)$$

where $D_{p.d.}$ is the diffusion coefficient of the purely diffusional motion ($a^2\gamma_1$) and v^2 is the mean square velocity in the coherent motion ($2J^2a^2$). (iv) For all systems, the motion ultimately becomes diffusional. The purely coherent motion is the extreme case in which the time of observation needed to see diffusion is infinite.

4. Conclusions

We have shown in this note that certain aspects of the motion of an adatom on a solid surface can be analyzed in terms of a simple, but realistic stochastic model. The hamiltonian is divided into two parts, one representing the motion of the adatom on the rigid surface, the other representing the thermal fluctuations which modify the site energy and transfer matrix elements. If these fluctuations are assumed to be a gaussian random process and a nearest neighbor interaction is assumed, the mean square displacement of the adatom can be computed exactly. The results are given in terms of three parameters, J , γ_0 and γ_1 . The first characterizes the motion of the atom in the potential of a fixed lattice. The second characterizes the intensity of the site energy fluctuations, while the third characterizes the fluctuations of the transfer matrix elements. To discuss the results we defined the purely coherent motion ($J \neq 0$, $\gamma_0 = \gamma_1 = 0$) and the purely diffusional ($J = 0$, $\gamma_0, \gamma_1 \neq 0$). The mean square displacement is proportional to t^2 in the first case and to t in the second. The coherent motion is characterized by a root mean square velocity, $v^2 = \frac{1}{2}(2Ja)^2$, while purely diffusional motion is described by a diffusion coefficient, $D = a^2\gamma_1$. In the case in which all three parameters differ from zero, both types of motion coexist, and a proper diffusion coefficient exists only for times of observation longer than $\tau_D \equiv (2\gamma_0 + 4\gamma_1 + 2\gamma_2)^{-1}$. The observed diffusion coefficient is the sum of the purely diffusional case and a coherent contribution, $v^2\tau_D$. The same discussion has been applied to other transport processes, for example exciton transport in organic crystals [7] and electron transport †.

The arguments presented here are limited to perfect lattices, in which all sites are equivalent. The presence of defects may seriously modify our conclusions.

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† After the completion of this work we have found that Dr. A. Madhukar has independently used the same model to discuss the electric conductivity of one dimensional crystals. The analysis is different but his qualitative results agree with ours. We are grateful to Dr. Bell for bringing Madhukar's unpublished work to our attention and to Dr. Madhukar for useful conversations.