

ATOMIC MIGRATION ON DISORDERED SURFACES

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A model of atomic migration along disordered surfaces is presented. The disorder is assumed to give rise to a distribution of activation energies. The migration is assumed to be incoherent and governed by a continuous time random walk. We calculate mean square displacements and trapping rates at irreversible sinks and show that anomalous behavior for long times is found if the distribution of activation energies falls off exponentially at large energy.

1. Introduction

In recent years, there has been considerable interest in the migration of atoms on solid surfaces, as evidenced by the large number of review articles in this topic [1–4]. Much of the theoretical work has been based on an activated complex type theory [5], although some recent work has attempted a more microscopic approach [6,7]. The basis for the latter is the interaction between the motion of the adsorbed atom parallel to the surface and the motion of the surface atoms perpendicular to the surface. This brings about a “dynamic disorder” which affects the motion of the adsorbed atom. The work of Kitahara et al. [6] used the stochastic model of Haken et al. [8] to discuss the transition from low temperature coherent migration to high temperature diffusion, under the assumption that the potential surface felt by the adsorbed atom was periodic at the equilibrium distances, and had fluctuations about this. The work of Efrima and Metiu [9] included the possibility of activation over the barrier by thermal fluctuations, but also assumed a periodic potential.

However, it is unlikely that the surface of any solid is perfectly regular [5,10], and this will introduce static disorder into the problem. The purpose of the present note is to consider the effects of static disorder on adsorbate migration. We will be concerned solely with the high temperature region so that *no* coherent motion is possible. The experimental situation for most cases which have been studied corresponds to this regime, since almost no migration occurs at low temperatures and there is some hint of deep trapping [10].

In addition, the usual theoretical approach assumes a constant diffusion coeffi-

cient [6,7,9]: however, this concept has recently been questioned (in other cases) at both short [11] and long times [12–14].

In this work, we start from the assumption that the migrating atom is undergoing a random walk on the surface. Since the rate of hopping from one site to another depends on the local environment, the atom sees a distribution of hopping rates as it migrates. Another way of saying this is that the atom experiences a distribution of waiting times on a site. The natural way to describe this is the continuous time random walk (CTRW) model, discussed in detail by Montroll–Weiss [15] and others [12,13].

In this paper, we use this model to discuss atomic migration on disordered surfaces. In section 2, a brief description of the CTRW equations is given. In section 3 a model for treating the disorder in terms of a distribution of activation energies is given, and in section 4, a model for irreversible trapping of the migrating atom is given and solved in the CTRW model. Section 5 is a summary of our results.

2. The CTRW equations

We briefly review the theory of the CTRW as given by Scher and Montroll [12] and the asymptotic form of $\langle R^2(t) \rangle$, the mean square displacement of the atom derived therein is described.

The CTRW on a lattice describes a walker which hops randomly on a periodic lattice with random hopping times distributed according to a function $\psi(t)$. This distribution function, in our model, will be the image of the distribution function for the hopping rates $\rho(\omega)$. The asymptotic time behavior of the walker (\equiv adsorbed atom) is found by investigating the asymptotic behavior of $\psi(t)$. The interesting result is that, due to the functional form of $\psi(t)$, containing the information about disorder, the familiar Gaussian diffusion is *not* always recovered.

The equations for the $\langle R^2(t) \rangle$ in this model are derived in the work of Scher and Montroll and others [12,13] and will not be repeated. In the framework of the Scher–Montroll theory [12], the Laplace transform of $\langle R^2(t) \rangle$ is:

$$\langle \tilde{R}^2(u) \rangle = \int e^{-ut} \langle R^2(t) \rangle dt = \sum_s s^2 p(s) \frac{\tilde{\psi}(u)}{[1 - \tilde{\psi}(u)]u}, \quad (3)$$

where the time dependence is contained in the term

$$\tilde{\psi}(u)/u [1 - \tilde{\psi}(u)], \quad (4)$$

the simplest situation is that of $\tilde{\psi}(u)$ having at least a first moment:

$$\tilde{\psi}(u) \sim 1 - u\bar{t}, \quad u \rightarrow 0, \quad (5)$$

where

$$\bar{t} = \int t \psi(t) dt \quad (6)$$

is the average hopping time. Then,

$$\langle R^2(t) \rangle \sim t/\bar{t}, \tag{7}$$

which is the conventional long time diffusional limit. The situation is different when $\tilde{\psi}(t)$ does not have the first moment.

To connect $\rho(\omega)$ and $\psi(t)$, or $\tilde{\psi}(u)$, we assume that [16]

$$\psi(t) = \int_0^\infty \omega e^{-\omega t} \rho(\omega), \tag{8}$$

$$\tilde{\psi}(u) = \int \frac{\rho(\omega)}{\omega + u}. \tag{9}$$

We shall now apply these equations to model system which mimics the effects of disorder on the migration.

3. A model for disorder on atomic migration

We now introduce a model system for which we calculate the mean square displacement $\langle R^2(t) \rangle$ as a function of the ratio between temperature and the disorder parameter.

The model assumes:

(a) that the site-to-site atom migration is activated with an Arrhenius law dependence:

$$\omega = \omega_0 \exp(-\Delta/kT), \tag{10}$$

where Δ represents a potential barrier.

(b) the surface disorder results in a distribution of activation energies according to $g(\Delta)$ representing random potential barriers.

Then,

$$\rho(\omega) = \left[g(\Delta) \left| \frac{d\omega}{d\Delta} \right| \right]_{\Delta = -kT \ln(\omega/\omega_0)}. \tag{11}$$

The dynamics of the adsorbed atom is given in terms of eqs. (1), (2) and (11): a random walk with a distribution of hopping rates. We can now apply the CTRW to calculate the long time dependence of $\langle R^2(t) \rangle$.

In order to do this, we must have a form for the disorder induced distribution of activation energies. It will turn out that the long time behavior of $\psi(t)$ (and hence $\langle R^2(t) \rangle$) is dominated by the small ω limit of $\rho(\omega)$. This will be, from eq. (10), the large Δ limit of $g(\Delta)$.

We will take a $g(\Delta)$ which has an exponential fall-off for large Δ [17,18]. Since the small Δ part of $g(\Delta)$ will be unimportant for the long time behavior, the exact

form will not matter. We therefore take the form used successfully by Bernasconi et al. [17] and Higashi et al. [17] to interpret experimental data in disordered systems:

$$g(\Delta) = \begin{cases} g_0 \exp(-\Delta/kT_0), & \Delta_0 \leq \Delta \leq \Delta_1, \\ 0, & \text{otherwise,} \end{cases} \quad (12)$$

T_0 represents the "width" of the static disorder. This gives from eq. (11):

$$\rho(\omega) = \begin{cases} \gamma(T)\omega^{-\alpha}, & \omega_0 \exp(-\Delta_1/kT) \leq \omega \leq \omega_0 \exp(-\Delta_0/kT), \\ 0, & \omega_0 \exp(-\Delta_0/kT) \leq \omega, \end{cases} \quad (13)$$

where

$$\alpha = 1 - T/T_0, \quad g_0 = (kT_0)^{-1} \exp(-\Delta_0/kT_0),$$

and $\gamma(T)$ is the temperature dependent normalization factor. For the purpose of our discussion here, we assume that $\exp(-\Delta_1/kT) \approx 0^*$. It is now clear that as α changes sign from positive ($T < T_0$) to negative ($T > T_0$), the analytic properties of $\rho(\omega)$ in the vicinity of $\omega = 0$ change drastically. For $\alpha < 0$, corresponding to the high temperature regime $T > T_0$, $\rho(\omega)$ is regular at $\omega = 0$, and therefore $\tilde{\psi}(u)$ in eq. (9) has at least a first moment. On the other hand $\alpha > 0$ corresponds to a singular $\rho(\omega)$ at $\omega = 0$.

In the high temperature regime we find a long time *diffusive* migration which defines a *constant diffusion* coefficient according to eq. (7), having the Arrhenius temperature dependence $\exp(-\Delta_0/kT)$. In the low temperature regime, one should follow the steps in the previous section in order to find $\tilde{\psi}(u)$ and then $\langle R^2(t) \rangle$. It turns out [16] that

$$\tilde{\psi}(u) \sim 1 - Au^{(1-\alpha)}, \quad u \rightarrow 0, \quad (14)$$

A being independent of u .

Substituting $\tilde{\psi}(u)$ in eq. (14) for $\langle R^2(t) \rangle$ we arrive at the interesting result

$$\langle R^2(t) \rangle_{t \rightarrow \infty} \sim t^{1-\alpha}, \quad (15)$$

which "defines" a time dependent diffusion coefficient

$$D(t) \sim t^{-\alpha} = t^{-[1-T/T_0]}. \quad (16)$$

Thus, $D(t)$ becomes very small for long times (tending to zero) at $T < T_0$, which describes a *quasi-trapped* atom due to surface disorder. Adopting the concept of constant diffusion coefficient for this regime will result in an overestimate of atom migration rate over the whole temperature regime.

It should be emphasized that the distinction between high and low temperatures regime is much sharper if one measures the charge transport of a carrier on a

* For a more detailed discussion on the role of the cutoff $\exp(-\Delta_1/kT)$ see ref. [16].

disordered surface. In this case there should be a noticeable transition from *no dc conductivity* (corresponding to $D(t) \rightarrow 0$ at $t \rightarrow \infty$) to a finite value (corresponding to regular diffusion).

The model we presented here describes a possible mechanism for the onset of hopping obeying the Arrhenius law for migration of an adsorbed atom on a surface. The results are sensitive to the choice of $g(\Delta)$.

The use of an exponential form for $g(\Delta)$ is motivated by two considerations. First, it has been used before for problems in disordered systems [17]. Secondly, it exhibits the possibility of a transition from diffusive to nondiffusive behavior as T is lowered. For forms of $g(\Delta)$ which fall off substantially faster than exponential (i.e. $g(\Delta) \sim \exp[-(\Delta/kT_0)^\delta]$, $\delta > 1$) the motion will always be diffusive, while for $g(\Delta)$ which fall off more slowly than exponential (i.e. $\delta < 1$ in the above) the motion is always nondiffusive. This can be seen easily by computing $\langle 1/\omega \rangle$ or \bar{t} from $g(\Delta)$ using eqs. (11) and (9). Unfortunately, the correct form for $g(\Delta)$ is not known, even for model systems [18]; however, the qualitative results for general forms of $g(\Delta)$ have now been given.

4. Adsorbed atom trapping

It has been experimentally shown [10] that at temperatures low enough to prevent detrapping, migrating atoms may be trapped at certain trapping sites, where they stay localized (if the temperatures are not high enough to induce migration). No information about trapping rates or sites is available except for this experimental observation.

In this section we briefly comment on the possible trapping rates of an atom on a disordered surface. We still remain in the framework of the previous model system. The basic assumptions are:

- (a) the traps are deep, and no detrapping is possible even when transition from "localization" to migration occurs.
- (b) the trapping is controlled by the atom migration over the surface sites ("diffusion" controlled).

The trapping rate $K(t)$ is then given by the Laplace transform of [19]:

$$\tilde{K}(u) = \frac{1}{[1 - \tilde{\psi}(u)] R(0, \tilde{\psi}(u))} - 1, \tag{17}$$

where $R(0, \tilde{\psi}(u))$ is the one-dimensional or two-dimensional generating function [15] (or the lattice Green function with argument $\tilde{\psi}(u)$).

For one dimension (1D)

$$R(0, z) = (1 - z^2)^{-1/2}, \quad z \rightarrow 1. \tag{18}$$

For two dimensions (2D)

$$R(0, z) = -\frac{1}{\pi} \log(1 - z), \quad z \rightarrow 1, \tag{19}$$

therefore, for the diffusive case – high temperature regime $T > T_0$ – where $\tilde{\psi}(u) \sim 1 - u\bar{t}$, we obtain the expected rates [19]:

$$1D: \quad K(t) \sim t^{-1/2}, \quad (20)$$

$$2D: \quad K(t) \sim 1/\log(At) \quad (21)$$

However, for $T < T_0$, $\alpha > 0$ one can easily show that [using eq. (14)]

$$1D: \quad K(t) \sim t^{(-1-\alpha)/2} = t^{(-1+T/2T_0)}, \quad (22)$$

$$2D: \quad K(t) \sim t^{-\alpha}/\log(Bt)^{1-\alpha} = \frac{t^{-(1-T/T_0)}}{\log(Bt^{T/T_0})}.$$

These results seem reasonable, since for $T < T_0$ the atom is quasi-localized and thus the probability of reaching a trap decreases quickly with time at long times.

The above derivations have been done in the framework of Smoluchowski's approach assuming a constant number of sinks during the trapping process. If, however, this number decreases after each trapping event, a modification of this approach has to be made [20]. Both results will of course be compared to experiment when available in order to learn more about the nature of the trapping centers on surfaces.

5. Conclusions

In this article we have pointed out the fact that the migration of an atom adsorbed on a disordered solid surface cannot be always described in the framework of the usual diffusion equation. The disorder is modeled by a distribution of activation energies, making the migration correspond to the CTRW rather than the usual random walk. We have shown that the time dependence of $\langle R^2(t) \rangle$, which is a measurable quantity, may be unexpected and interesting, reflecting the possible quasi-localized nature of the atom. Under other circumstances $\langle R^2(t) \rangle$ has the usual time dependence characteristic of a diffusion constant.

The model provides a coherent picture for the freezing of motion at low temperatures and for the changes in $\langle R^2(t) \rangle$ at long time with increasing temperatures (relative to T_0)

We have also calculated the trapping rates at temperatures low enough to prevent detrapping in the same framework. These model calculations suggest a possible way to study the nature of surface traps. $K(t)$ is found to be strongly dependent on $\rho(\omega)$ and on the dimensionality of the motion of the atom.

Throughout this work we have assumed the existence of disorder and its specific distribution function $g(\Delta)$. These assumptions although still having no experimental backing, have enabled us to calculate all the characteristics of the model.

In spite of the conjectural nature of our model, we believe that the approach and

the model calculations presented here may provide a deeper insight to the problem of migrating adsorbed single atoms, and generalize the concepts of diffusion, mean square displacement and atom trapping.

In the light of the complexity of the problem we hope that the generalization of the above concepts due to disorder, which is *believed* to exist on surfaces, will increase the interest in the role of imperfections and in the details of the evolution of the trapping and migration processes.

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