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Abstract

We show that the diffusion coefficient of an adsorbed cluster can be decomposed into two factors, one depending upon a weighted length of the 'active' perimeter and the other depending upon a subtle correlation between hops taken by cluster atoms during diffusion. Both of these factors are structure dependent. Monte-Carlo simulations are performed for clusters on a triangular lattice.

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1. Introduction

An important component of many surface phenomena is the diffusion of adsorbed
atoms, either singly or in clusters. Experimental studies of cluster diffusion
include numerous observations of diffusion of small metal clusters on clean metal
surfaces (1-8). There have also been many numerical and theoretical
investigations of cluster diffusion (9-20). In these studies general
mathematical frameworks for the description of cluster diffusion have been
established. In this paper we present an analysis of cluster diffusion which, in
particular, provides insight into the dependence of the diffusion coefficient
upon the size and the structure of the cluster. We also show that cluster
diffusion can be considered as a correlated walk of the cluster center of mass
on a lattice. Monte-Carlo simulations are performed for clusters on a triangular
lattice.

2. Definition of Model and Analysis

Here a cluster is defined as a group of particles any two of which are connected
directly or indirectly, through other particles in the cluster, by nearest-
neighbor bonds. The cluster diffuses as a result of its particles executing
independent hops to vacant nearest-neighbor sites, with the constraint that hops
which cause the cluster to break apart are not allowed. Molecular dynamics
simulations of cluster diffusion have been performed with and without this 'no-
dissociation' constraint (9). Only at sufficiently low temperatures do the two
cases give the same results. Although similar considerations could be
incorporated into Monte-Carlo simulations of cluster diffusion, we restrict
ourselves to the case of 'no-dissociation' so that the effects of the cluster
size and structure can be disentangled from the effects of cluster lifetime.
Although there exist systems where diffusion and dissociation occur at
approximately the same temperatures (21), typically the activation energy for a
dissociative hop is larger than the activation energy for a non-dissociative hop
(13,14). In such cases there is a well-defined range of low temperatures where
our model applies. It should also be noted that for some systems exhibiting
surface reconstructions concerted motion (i.e., simultaneous jumps) of several
atoms are observed (22). Since this probably results from the peculiar energetics
exhibited by a reconstructive system, we do not incorporate such concerted motion
into our model.

The hop rate for particles in the cluster is $hw(\alpha, \delta b)$, where h is the rate at
which hops are attempted, $w(\alpha, \delta b)$ is the probability of success of a hop and is
taken to be $\alpha^{\delta b/2}/(\alpha^{\delta b/2}+\alpha^{-\delta b/2})$, and δb is the change in the number of nearest-
neighbor bonds b in the cluster if the hop were successful. The parameter α can

be considered to be the Boltzmann factor for the lateral interaction between two nearest-neighbor particles (with $\alpha>1$ corresponding to attractive lateral interactions) even though the 'no-dissociation' constraint would be somewhat non-physical with this interpretation of α. For each cluster size there can be many cluster configurations each consisting of different arrangements of the particles and different orientations of the cluster. It is clear that the probability of occurrence of a cluster configuration in the equilibrium distribution is proportional to α^b. When α is equal to one, the probability of occurrence for each cluster configuration is equal. Thus, the clusters are random animals. When α is larger than one (attractive lateral interactions), the clusters correspond to the correlated animals that result from cooperative lattice filling (23). In this case the clusters with the largest number of nearest-neighbor bonds occur most frequently, i.e., compact clusters occur more frequently than ramified ones.

For all values of α, however, the equilibrium ensemble averaged perimeter $<<t>>$ of the clusters, in the limit of infinite number of particles N in the cluster, scales as $<<t>>\sim N$ (24). For compact clusters, which have a larger weight than ramified clusters when α is larger than one, the perimeter scales as $N^{1/2}$. Thus, we would expect a crossover from $<<t>>\sim N^{1/2}$ for small N to $<<t>>\sim N$ for large N. The crossover occurs at progressively larger N when the α is increased. There are several measures of the cluster perimeter. Conventional ones include the number of vacant sites t_v which are nearest-neighbors of particles in the cluster and the number of particles t_f which have at least one vacant nearest-neighbor vacant site. As shown below, it is more appropriate here to consider a weighted 'active' perimeter t_α by $t_\alpha=\Sigma w(\alpha,\delta b)$, where the sum is over all possible hops for that cluster configuration. Note that t_1 is simply half the number of hops that can possibly occur.

We can define the diffusion coefficient using

$$D = \lim_{\tau\to\infty} \tau^{-1} <R_{cm}\cdot R_{cm}>_\tau, \tag{1}$$

where R_{cm} is the position of the center of mass of the cluster, and $< >_\tau$ is the average taken over many walks at time τ. To elucidate the behavior of D, it is instructive to consider the analogous quantity

$$\lim_{n_h\to\infty} n_h^{-1} <R_{cm}\cdot R_{cm}>_{n_h} \equiv C(\alpha,N)/N^2, \tag{2}$$

in which the number of successful hops n_h plays the role of time. The motivation for this definition of the 'correlation factor' $C(\alpha,N)$ is as follows. If the center of mass were undergoing a pure random walk, then $C(\alpha,N)$ would simply equal one, noting that after each particle jumps, the center of mass moves a distance $1/N$ (25). Thus, deviations of $C(\alpha,N)$ from unity measure the correlation in its walk.

The process by which the cluster diffuses on the lattice is ergodic so that, for $\tau\to\infty$, we obtain $<n_h>_\tau\sim h\tau<<t_\alpha>>$. Therefore, in the limit of $\tau\to\infty$, we can write

$$<R_{cm}\cdot R_{cm}>_\tau = C(\alpha,N)\ <n_h>_\tau/N^2$$

$$= hC(\alpha,N)\ \tau<<t_\alpha>>/N^2, \tag{3}$$

from which, using Equation (1), we obtain

$$D = hC(\alpha,N)\ <<t_\alpha>>/N^2. \tag{4}$$

Equation (4) shows that the diffusion coefficient for a cluster can be decomposed into a factor depending upon the weighted 'active' perimeter and a factor depending upon the correlation between hops. We present below the results for $<<t_\alpha>>$ and $C(\alpha,N)$ from simulations of clusters on a triangular lattice.

3. Simulation Results

In Fig. 1, we plot log $<<t_\alpha>>$ as a function of log N. The value of α for each plot is indicated in the figure. When α is equal to one, it is clear that $<<t_\alpha>> \sim N$ even for cluster size N as small as 10. However, as the value of α increases, the asymptotic regime, in which $<<t_\alpha>> \sim N$, is reached at progressively larger values of N. For the case in which $\alpha=5$, the asymptotic regime is not reached even at N=100, and the scaling $<<t_\alpha>> \sim N^{1/2}$, expected for compact clusters, is observed for the cluster size range that we simulated.

In Fig. 2, we plot the mean-square displacement as a function of time for $\alpha=5.0$. The cluster size for each plot is indicated in the figure. It can be seen that the correlation factor $C(\alpha,N)$ is less than one, indicating (negative) correlation between hops. This means that the correlation between hops causes the center of mass of the cluster to diffuse slower than the 'correpsonding' random walker. That is, the cluster center of mass undergoes a correlated walk. The results for $\alpha=1.0$ and $\alpha=2.5$ are similar. For the case in which $\alpha=1$ and $N=3$, i.e., the random animal trimers, the correlation factor is exactly one because there is no correlation between hops (25). (All dimers, regardless of the value of α, have a correlation factor of one.)

In Fig. 3 log $C(\alpha,N)$ is plotted as a function of log N. The confidence limits are approximately ±0.05 for each of the data points. Since the range of cluster

Fig.1

Fig.2

Fig.3
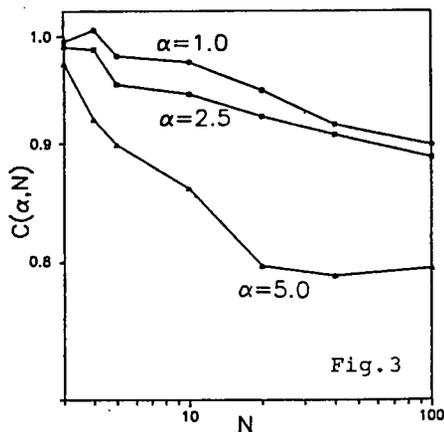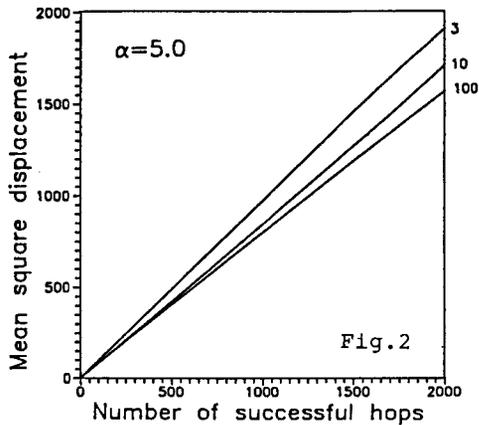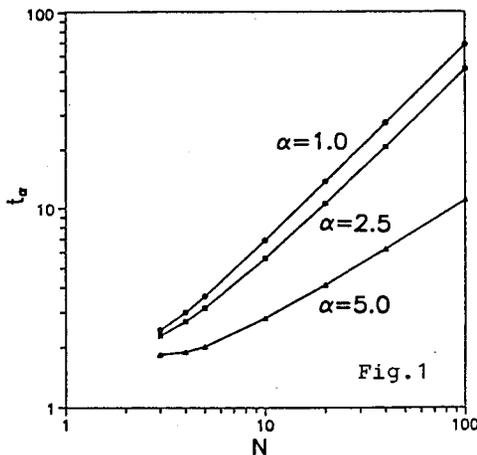
sizes simulated is rather limited, it is not sufficient to clearly establish whether a scaling relation exists between $C(\alpha,N)$ and N. However, assuming that $C(\alpha,N) \sim N^{-\epsilon}$ is valid, we obtain a value of approximately 0.03 for ϵ in the cases in which $\alpha=1.0$ and $\alpha=2.5$. The results for $\alpha=5.0$, in which case a crossover in cluster structure occurs, suggest that a higher effective exponent may be observed for small N and large α.

4. Discussion

Using Equation (4) and the simulation results it is easy to understand how a scaling relation $D \sim N^{-y}$ can arise. For metal clusters on clean metal surfaces, in which case α is relatively high (approximately 20 for Rh on Rh(100) at a temperature of 2000 K), our analysis predicts an exponent of $y=3/2+\epsilon$ for cluster sizes up to, at least, 100. It should be noted that this holds regardless of the geometry of the lattice on which the cluster diffuses, so long as the mechanism of diffusion consists of particles moving along the perimeter of the cluster. In the limit of large N, the exponent obtained would be $y=1+\epsilon$. Real clusters for which this exponent holds probably do not exist as ramified clusters would be quite unstable to dissociate. Therefore, for experimentally observable clusters the diffusion coefficient is more likely to behave as $D \sim N^{-3/2-\epsilon}$ than as $D \sim N^{-1-\epsilon}$. Molecular dynamics simulations of Rh clusters of size up to 75 atoms show an exponent of $y \approx 1.76$ (13,14). In comparing this with our result of $y \approx 1.53$, it should be noted that there are many differences between molecular dynamics simulations and the Monte-Carlo simulations used here, such as the absence of dynamical correlations in the Monte-Carlo simulations.

5. Conclusions

We have shown that the diffusion coefficient of a cluster is a product of $<<t_\alpha>>$ which depends on the weighted length of the 'active' perimeter and $C(\alpha,N)$ which depends on the correlation between hops. The analysis that we have presented provides a basis whereby the dependence of the diffusion coefficient of a cluster upon its structure and size can be readily understood. In particular, if a scaling relation $D \sim N^{-y}$ is valid, it is possible to understand, using Equation (6), how the structure of the cluster and the correlation between its hops determines the value of the exponent y. Clusters for which the diffusion coefficient is experimentally accessible would probably have a value of $3/2+\epsilon$ for the exponent y. The simulations show the interesting result that, in general, there is correlation between the hops taken by a diffusing cluster so that cluster diffusion results in a correlated walk by the cluster center of mass.

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