Single Jump Mechanisms for Large Cluster Diffusion on Metal Surfaces

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The random motion of large, two-dimensional adatom clusters and vacancy clusters over a metal surface is described by a diffusion coefficient $D \propto d^{-n}$, where d is the diameter of the cluster and the integer n identifies the diffusion mechanism. For *circular* clusters, $n = 3$ when center-of-mass motion occurs by adatom diffusion along the periphery of the cluster, while $n = 2$ or 1 when cluster diffusion occurs by *correlated* or *uncorrelated* adatom evaporation and condensation, respectively. A *faceted* adatom cluster diffuses by evaporation and condensation of facet ledges, giving $n = 0$ when cluster diffusion is determined by the rate at which erosion of a ledge is initiated.

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The dynamics of atom clusters adsorbed on surfaces influence such technologically and scientifically important processes as crystal and thin film growth by atom deposition, surface roughening, catalysis, and mass transport diffusion. Current research primarily addresses cluster nucleation and growth [1] and small cluster ($N < 20$ atoms) diffusion [2], which may occur by single atom jumps, concerted jumps (on close-packed surfaces), and gliding (when the cluster is not in registry with the surface lattice). The larger, two-dimensional clusters into which these grow are generally regarded simply as immobile precursors to three-dimensional island growth. However, Hamilton, Daw, and Foiles [3] have recently proposed a dislocation mechanism for diffusion of moderate-sized monolayer clusters ($N < 50$) on fcc (111) surfaces that may additionally facilitate rapid diffusion of larger, heteroepitaxial islands with misfit dislocations in their lowest energy configurations. A somewhat similar diffusion mechanism, in which friction at the cluster-substrate interface limits the cluster mobility, is presented by Kukushkin and Osipov [4]. Advances in direct imaging techniques [scanning tunneling microscopy (STM), scanning transmission electron microscopy, and field ion microscopy] have also increased interest in cluster dynamics.

Wen *et al.* [5] have recently reported STM observations of large ($100 \leq N \leq 800$), two-dimensional silver clusters diffusing over a Ag(100) surface. By monitoring the trajectories of various clusters, they showed that the cluster motion was indeed Brownian (random) with diffusion coefficient that varied little with cluster size. Of importance to the present investigation are their observations that the clusters had "an approximately square shape, although irregularities such as rounded corners and crooked edges are common," and that these large clusters showed little change in size over a period of several hours while smaller clusters disappeared. Wen *et al.* point to the latter phenomenon as evidence for Ostwald ripening, whereby larger clusters grow at the expense of smaller ones, so that the monitored clusters must be in "dynamic quasiequilibrium" with the population of Ag adatoms on the surface.

In a similar STM experiment, Morgenstern *et al.* [6] observed the random diffusion of large ($100 \leq N \leq 5000$), monatomic-deep vacancy clusters over a Ag(111) surface. These clusters appear faceted as well, while their motion is unambiguously described by the diffusion coefficient $D \propto d^{-2}$, where d is the diameter of the cluster.

In both cases, the researchers ascribe the cluster motion to adatom evaporation and condensation at the periphery of the cluster (atoms are exchanged between the cluster and the surrounding "gas" of adatoms on the surface). This and other possible large cluster diffusion mechanisms based on single atom jumps (rather than collective motion) are considered in this Letter.

The most straightforward mechanism to evaluate is that of cluster diffusion by adatom diffusion along the cluster periphery. The diffusion coefficient for the cluster is

$$D_c = \tfrac{1}{4}\lambda_c^2 \Gamma_c , \tag{1}$$

while that for an adatom bound to the cluster periphery is similarly

$$D_p = \tfrac{1}{2}\lambda_p^2 \Gamma_p , \tag{2}$$

where λ and Γ are the jump distance and jump frequency, respectively, of the cluster or adatom. Movement of the cluster center of mass a distance λ_c requires that all N cluster atoms be transported the same distance; this latter action is equivalent to transporting a single cluster atom a distance

$$\lambda_p = N\lambda_c = \frac{\pi R^2}{\Omega}\lambda_c , \tag{3}$$

where R is the radius of the cluster and Ω is the surface area occupied by an atom in the cluster. The cluster jump frequency Γ_c is equal to the rate at which a cluster atom makes a jump along the periphery, so that

$$\Gamma_c = \Gamma_p c_p^{\mathrm{eq}} 2\pi R , \tag{4}$$

where c_p^{eq} is the equilibrium concentration of adatoms at the periphery, per unit length of cluster periphery.

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Combining Eqs. (1)–(4) produces the cluster diffusion coefficient

$$D_c = \frac{\Omega^2}{\pi} \frac{D_p c_p^{\mathrm{eq}}}{R^3}, \tag{5}$$

where D_p and c_p^{eq} can be estimated from molecular dynamics simulations or total energy calculations if not from experiment.

Cluster diffusion by adatom evaporation and condensation requires that the cluster and adatom populations be in equilibrium. The diffusion coefficient will have a different cluster size dependence according to whether or not a spatial correlation exists between the evaporation and condensation events. In either case, the flux of adatoms attaching to the cluster (assuming no appreciable barrier to attachment) is

$$j_a = \frac{D_a}{a_0} c_a^{\mathrm{eq}}, \tag{6}$$

where D_a is the surface diffusion coefficient for adatoms, c_a^{eq} is the equilibrium concentration of adatoms on the terrace, and a_0 is the surface lattice parameter (nearest neighbor distance). The cluster jump frequency is then

$$\Gamma_c = j_a 2\pi R = \frac{2\pi R}{a_0} D_a c_a^{\mathrm{eq}}. \tag{7}$$

For the case of no correlation, a cluster diffuses by evaporation of a cluster atom and simultaneous attachment of an adatom elsewhere at the cluster periphery (since the cluster exists in equilibrium with the adatom population). By an argument equivalent to that preceding Eq. (3), the linear distance λ_a between such evaporation and condensation events is related to λ_c by

$$\lambda_a \approx \frac{\pi R^2}{\Omega} \lambda_c \tag{8}$$

and has a value given by the average distance between any two points on the cluster periphery (this is made more precise later). However, this approach ignores the fact that an emitted atom is likely to be quickly "recaptured" near its initial position at the cluster periphery. Indeed, in a closed system at equilibrium, *all* emitted atoms will eventually be readsorbed by the cluster. Thus a spatial correlation exists between atom evaporation and condensation that must be reflected in the value of λ_a.

To account for this correlation, consider a source of (fictional) adatoms at the point $(r, \theta) = (R_a, 0)$ just adjacent to the circular cluster, where the origin of the cylindrical coordinate system is at the cluster center, and $R_a = R + a_0$ (see Fig. 1). This source can be written as a two-dimensional delta function of "strength" unity [7],

$$\sigma = \delta(\boldsymbol{r} - R_a \hat{z}) = \frac{1}{2\pi r} \delta(r - R_a) \sum_{m=-\infty}^{\infty} e^{im\theta}. \tag{9}$$

Then the equilibrium population $c(r, \theta)$ of adatoms on the surface originating from this source is simply the solution to the Laplace equation in cylindrical coordinates, with appropriate boundary conditions.

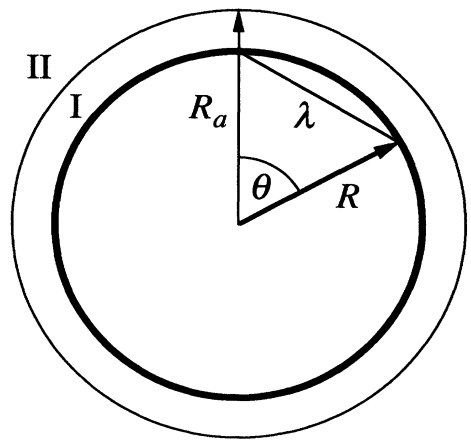

FIG. 1. Circular cluster of radius R, with source of "fictional" adatoms just outside the cluster at the point $(r, \theta) = (R_a, 0)$. The circle of radius R_a separates regions I and II. An adatom emitted at the source point $(R_a, 0)$ and subsequently readsorbed at (R, θ) has traveled a linear distance λ.

The surface external to the cluster is divided into regions I ($r < R_a$) and II ($r > R_a$), as indicated in Fig. 1. The boundary conditions are that all adatoms incident on the cluster are absorbed there ($c_{\mathrm{I}} = 0$ at $r = R$); all adatoms at infinity are reflected ($\nabla c \cdot \boldsymbol{n} = 0$ at $r = \infty$, where $\boldsymbol{n}$ is the unit vector in the radial direction); the adatom concentration is continuous across the boundary $r = R_a$ ($c_{\mathrm{I}} = c_{\mathrm{II}}$); and the adatom flux is discontinuous across the boundary $r = R_a$, due to the presence of the "line source" $\int \sigma\, dr$ there [$D_a \nabla(c_{\mathrm{I}} - c_{\mathrm{II}}) \cdot \boldsymbol{n} = \int \sigma\, dr$ at $r = R_a$]. Laplace's equation is solved by expanding c_{I} and c_{II} in cylindrical harmonics and imposing the boundary conditions to obtain the expansion coefficients. The solution near to the cluster is found to be

$$c_{\mathrm{I}}(r, \theta) = \frac{1}{2\pi D_a} \ln\left(\frac{r}{R}\right) + \frac{1}{2\pi D_a} \sum_{m=1}^{\infty} \frac{r^{2m} - R^{2m}}{m r^m R_a^m} \cos m\theta. \tag{10}$$

The flux of (fictional) adatoms precipitating at the circular cluster is

$$j(\theta) = D_a \left. \frac{\partial c_{\mathrm{I}}(r, \theta)}{\partial r} \right|_{r=R}. \tag{11}$$

But $j(\theta)$ is also the probability that an adatom initially at the source point $(R_a, 0)$ will diffuse over the surface (external to the cluster) to the point (R, θ) at the cluster periphery. From Fig. 1, the distance λ between those two points obeys the relation

$$\lambda^2 = 2R^2(1 - \cos\theta). \tag{12}$$

Then the average value

$$\overline{\lambda_a^2} = \int_r \int_{\theta=0}^{2\pi} \lambda^2 j(\theta) \delta(r - R) r\, d\theta\, dr = 2R^2\left(1 - \frac{R}{R_a}\right) \approx 2a_0 R. \tag{13}$$

Combining Eq. (8), with λ_a replaced by $\sqrt{\overline{\lambda_a^2}}$, and Eqs. (1) and (7) produces the diffusion coefficient

$$D_c = \frac{\Omega^2}{\pi}\frac{D_a c_a^{\mathrm{eq}}}{R^2}, \tag{14}$$

describing the random diffusion of a circular cluster by correlated adatom evaporation and condensation.

For the (less likely) case of cluster diffusion by uncorrelated adatom evaporation and condensation, the (fictional) adatom flux $j(\theta) = 1/(2\pi R)$, so that the result of Eq. (13) is $\overline{\lambda_a^2} = 2R^2$. Combining Eqs. (1), (7), and (8) then produces the cluster diffusion coefficient

$$D_c = \frac{\Omega^2}{\pi a_0}\frac{D_a c_a^{\mathrm{eq}}}{R}. \tag{15}$$

By contrast, faceted clusters diffuse as facet ledges are completed or eroded. (A completed ledge is the row of atoms making up one facet, or edge, of the cluster; a partial ledge is terminated by one or two kinks.) To maintain the cluster size, the cluster and adatom populations must again be in equilibrium and, additionally, the rate of ledge nucleation on a facet and the rate of facet erosion must be substantially equal. However, the rate of ledge nucleation equals the cluster perimeter length multiplied by the nucleation rate per facet length, and so is proportional to the cluster size d, while the rate of facet erosion, which is limited by the rate at which cluster "corner" atoms (where two facets meet) erode, is largely independent of cluster size. Thus faceted clusters are stable only above a minimum size, and their motion is described by a diffusion coefficient that is essentially independent of cluster size.

An expression for D_c can be obtained by assuming that a facet ledge inevitably erodes whenever a corner atom leaves the cluster. The cluster jump frequency is then

$$\Gamma_c = n_f \nu_m \exp\left(-\frac{E_m}{k_B T}\right), \tag{16}$$

where n_f is the number of facets and ν_m and E_m are the vibrational frequency and migration energy of the cluster corner atom, respectively. The cluster jump distance $\lambda_c \approx a_0$, so that the diffusion coefficient

$$D_c = \frac{n_f a_0^2}{4}\nu_m \exp\left(-\frac{E_m}{k_B T}\right) \tag{17}$$

for a faceted cluster.

This last equation is easily evaluated for the large, faceted Ag clusters adsorbed on a Ag(100) surface observed by Wen *et al.* [5]. Substituting $n_f = 4$, $a_0 = 4.09/\sqrt{2}$ Å, $\nu_m \approx 10^{12}$ s^{-1}, $E_m = 0.82$ eV [8], and $T = 300$ K produces the diffusion coefficient $D_c = 1.4 \times 10^{-17}$ cm^2 s^{-1}, which falls well within the narrow range $(0.53-2.7) \times 10^{-17}$ cm^2 s^{-1} found experimentally.

Diffusion of the large vacancy clusters over a Ag(111) surface observed by Morgenstern *et al.* [6] evidently occurs by correlated adatom or vacancy evaporation and condensation [9], since the size dependence of the measured diffusion coefficient agrees with that in Eq. (14). [Equation (14) is unchanged when the source σ is placed inside the cluster and the distribution of "fictional" adatoms within the vacancy cluster is calculated.] To estimate D_c due to adatom diffusion within the vacancy cluster, the equilibrium adatom concentration c_a^{eq} is replaced by $(1/\Omega)\exp(-G_a/k_B T)$, where $G_a = 0.709$ eV is the Gibbs free energy for adatom formation on Ag(111) [10]. With the additional substitutions $\Omega = 7.243$ Å^2, $D_a = (4.1 \times 10^{-4}$ cm^2 s$^{-1})\exp[(-0.044$ eV$)/k_B T]$ [11] and $T = 300$ K, the diffusion coefficient $D_c = (2.1 \times 10^{-32}$ cm^4 s$^{-1})/R^2$, with the cluster radius R specified in cm. Similarly, to estimate D_c due to vacancy diffusion through the surface atomic layer surrounding the cluster, the equilibrium vacancy concentration c_v^{eq} is replaced by $(1/\Omega)\exp(-G_v/k_B T)$, where $G_v = 0.549$ eV is the Gibbs free energy for vacancy formation at the Ag(111) surface [10]. The surface vacancy diffusion coefficient $D_v = (1.3 \times 10^{-3}$ cm^2 s$^{-1})\exp[(-0.314$ eV$)/k_B T]$ [12], so that Eq. (14), with $D_a c_a^{\mathrm{eq}}$ replaced by $D_v c_v^{\mathrm{eq}}$, produces $D_c = (9.5 \times 10^{-34}$ cm^4 s$^{-1})/R^2$.

These cluster diffusion coefficients are much smaller than the experimental value $D_c = (1.3 \times 10^{-28}$ cm^4 s$^{-1})/R^2$ [6]. To reconcile this latter value with the cluster diffusion mechanism of adatom evaporation and condensation requires that a supersaturation of adatoms be contained within the cluster, or that the adatom formation energy be approximately 0.5 eV (note that this value is the difference in binding energies of an adatom on the terrace and an adatom at the base of a step). The sum of the formation and migration energies can be found experimentally by measuring the vacancy cluster diffusivity at several temperatures.

In summary, diffusion coefficients have been derived for large, two-dimensional adatom clusters and vacancy clusters that reflect the mechanism by which diffusion occurs. These expressions are applied, with some success, to recent experimental results for adatom cluster diffusion on Ag(100) and vacancy cluster diffusion on Ag(111) surfaces. It should be noted, finally, that diffusion by facet growth and erosion may be prevented by impurity adsorption at the cluster; for example, Van Siclen [13] recently showed, by embedded-atom-method-type calculations, that In adatoms segregate to corner sites in Cu clusters on Cu surfaces.

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