Cluster diffusion by evaporation-condensation

José M. Soler

Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain
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Cluster diffusion on surfaces by two-dimensional evaporation-condensation is studied taking into account both temporal and spatial correlations between evaporations and condensations. It is shown that the effect of these correlations increases with time and with the diffusivity of the evaporated adatoms. The time dependence of cluster diffusion is nonlinear and the diffusion constant scales with cluster radius as R^{-1} for very short times, and as R^{-2} for the (longer) times experimentally relevant. The effect of the perimeter energy is also shown to be nonnegligible, further changing the size dependence of cluster diffusivity.

Cluster diffusion on surfaces has always received much attention because of its relevance to crystal growth. More recently, the use of scanning tunneling microscopy (STM) to monitor cluster movement in a most visual way[1–3] has produced a new burst of interest. Much of this interest is due to the relationship between the motion of steps and clusters, and to the possibility of deducing their mechanisms from the size dependence of cluster diffusivity. Among the proposed mechanisms, theoretical considerations and simulations have usually favored perimeter diffusion of individual adatoms around the cluster, at low and moderate temperatures. At high temperatures, two-dimensional evaporation-condensation (EC) of adatoms to/from the surface terraces could dominate.[5] However, recent experiments of adatom clusters on Ag(100) (Ref. 2) and vacancy clusters on Ag(111) (Ref. 3) have proposed the prevalence of EC at room temperature, on the basis of the cluster-size dependence of the diffusion rate. Also, new diffusion mechanisms, such as cluster sliding and dislocation propagation,[4] have been proposed for clusters on compact surfaces. The present work concentrates exclusively on the EC mechanism.

A simple dimensional argument has been traditionally invoked[5] to assign a $D\propto R^{-1}$ dependence of the EC-diffusion constant D with cluster radius R. The argument assumes a rate of EC events proportional to the cluster perimeter, each making a $(R/N)^2$ contribution to the squared center-of-mass displacement of the cluster (with $N\propto R^2$ the number of atoms in the cluster). However, Van Siclen[6] has recently proposed that correlations between condensations and evaporations will reduce the average displacement, because an evaporated adatom is more likely to recondense close to the evaporation point than further away. Using a stationary-state analysis, he shows that this effect will change the diffusion size dependence to $D\propto R^{-2}$. Unfortunately, his analysis fails to provide a clear answer to whether such correlations are indeed relevant under the experimental conditions, and he also derives the $D\propto R^{-1}$ result in the absence of correlations. Using a different approach, Khare *et al.*[7] also conclude that there are two different regimes, with $D\propto R^{-1}$ and $D\propto R^{-2}$, depending on the diffusion rate of the evaporated adatoms. A similar conclusion is reached also by Sholl and Skodje[8] for the case of EC towards *inside* a cluster of vacancies, a case for which EC correlations had been traditionally included,[3,5] thus giving already $D\propto R^{-2}$.[9] In this work, I study the temporal, as

well as the spatial, correlations between evaporations and condensations, in order to clarify the conditions under which these correlations are important. It is shown that the crossover between correlated and uncorrelated regimes does indeed depend on the diffusion constant of the evaporated adatoms, although the sign of this dependence is the *opposite* of that previously proposed.[7,8] A related and somewhat surprising conclusion is that the effect of the correlations *increases* with time. It is also shown that, in practice, the correct dependence is always $D\propto R^{-2}$ for STM experiments. Finally, the effect of the perimeter energy on the evaporation rate is also considered, finding that it further increases the size dependence of D for adatom clusters.

Consider a circular cluster of radius R, with $N=\pi R^2/\Omega$ atoms, where Ω is the cluster area per atom. Assume that we make repeated measurements of its center-of-mass position $\mathbf{x}_{\mathrm{cm}}$ at fixed time intervals Δt. I will then define a time-dependent cluster diffusion constant as

$$D(R,\Delta t)=\frac{1}{4\Delta t}\langle\Delta x_{\mathrm{cm}}^2\rangle, \qquad (1)$$

where Δx_{cm} is the displacement between two consecutive measurements, and $\langle\rangle$ denotes the average over many of them. We expect that $D(R,\Delta t)$ will reach a constant value $D(R)$ for $\Delta t\to\infty$. If we assume that the cluster can only move by EC, there are three types of events that contribute to its displacement in the time interval Δt:

(i) Evaporation of an adatom after $t=0$, followed by its condensation at a different position of the cluster perimeter before $t=\Delta t$. The contribution of these events is

$$\langle\Delta x_{\mathrm{cm}}^2\rangle=N^{-2}\int_0^{2\pi}d\phi\int_0^{\Delta t}dt j_e\int_0^{2\pi}d\phi'$$

$$\times\int_t^{\Delta t}dt'\,2R^2[1-\cos(\phi'-\phi)]p(\phi'-\phi,t'-t),$$

$$(2)$$

where j_e is the evaporation rate per unit perimeter length, $p(\phi'-\phi,t'-t)$ is the probability that an adatom evaporated at perimeter position ϕ and time t recondenses at (ϕ',t'), and $2R^2[1-\cos(\phi'-\phi)]$ is the squared distance between evaporation and condensation points.

(ii) Evaporation of an adatom that does not condensate again before Δt, with contribution

$$\langle \Delta x_{cm}^2 \rangle = N^{-2} \int_0^{2\pi} d\phi \int_0^{\Delta t} dt j_e R^2$$

$$\times \left(1 - \int_0^{2\pi} d\phi' \int_t^{\Delta t} dt' p(\phi' - \phi, t' - t) \right). \quad (3)$$

(iii) Condensation of an adatom that had evaporated before $t = 0$, or that comes from another cluster or step. If the adatom gas is in equilibrium with the cluster, the rate of these events, and their contribution to $\langle \Delta x_{cm}^2 \rangle$ must be the same as those of type-(ii) events.

All these events are assumed to be uncorrelated. The most obvious correlation effect[6] has been taken into account by considering as single events the evaporations followed by recondensations. Other possible correlations might involve a condensation followed by the evaporation of the same adatom, at a rate different from that of other perimeter adatoms. However, in order to evaluate the probability of such an event, it would be necessary to model the energetics of different perimeter adatoms, going beyond the circular cluster model, which is outside the scope of the present work. Adding all three contributions and using definition (1), I obtain

$$\frac{D(R, \Delta t)}{D(R, 0)} = 1 - \frac{1}{\Delta t} \int_0^{\Delta t} dt \int_0^t dt' \int_0^{2\pi} d\phi \cos\phi p(\phi, t'), \quad (4)$$

where the $D(R, 0)$ is the *uncorrelated* EC diffusion constant

$$D(R, 0) = \frac{\Omega^2 j_e}{\pi R}, \quad (5)$$

valid for times shorter than that required for the evaporated adatoms to make a single jump and return to the cluster.

In order to obtain $p(\phi, t)$, I follow Ref. 6 in using the continuous diffusion equation

$$\frac{\partial n(r, \phi, t)}{\partial t} = D_1 \nabla^2 n(r, \phi, t), \quad (6)$$

to calculate the probability $n(r, \phi, t)$ of finding the evaporated adatom at position (r, ϕ) (cylindrical coordinates used) and time t. D_1 is the diffusion constant of a free adatom. Boundary conditions are reflecting at infinity and absorbing at the cluster perimeter. The initial probability is

$$n(r, \phi, 0) = \frac{1}{r_0} \delta(r - r_0) \delta(\phi), \quad (7)$$

where $r_0 = R + a$, with a the surface lattice constant. This initial position represents that of the evaporated adatom after an initial evaporation jump of length a, from $r = R$, $\phi = 0$, at $t = 0$. The diffusion equation is solved by expanding $n(r, \phi, t)$ in Bessel functions:

$$n(r, \phi, t) = \sum_{m=-\infty}^{+\infty} \int_0^\infty k \, dk \, n_m(k) F_m(kr) e^{im\phi} e^{-D_1 tk^2}, \quad (8)$$

$$F_m(kr) = \cos\theta J_m(kr) - \sin\theta Y_m(kr), \quad (9)$$

$$\tan\theta = \frac{J_m(kR)}{Y_m(kR)}. \quad (10)$$

The calculated recondensation rate is then

$$p(\phi, t) = D_1 \frac{\partial n(r, \phi, t)}{\partial r}$$

$$= \frac{D_1 R}{2\pi} \sum_{m=-\infty}^{+\infty} \int_0^\infty k^2 dk F_m(kr_0) F_m'(kR) e^{im\phi} e^{-D_1 tk^2}, \quad (11)$$
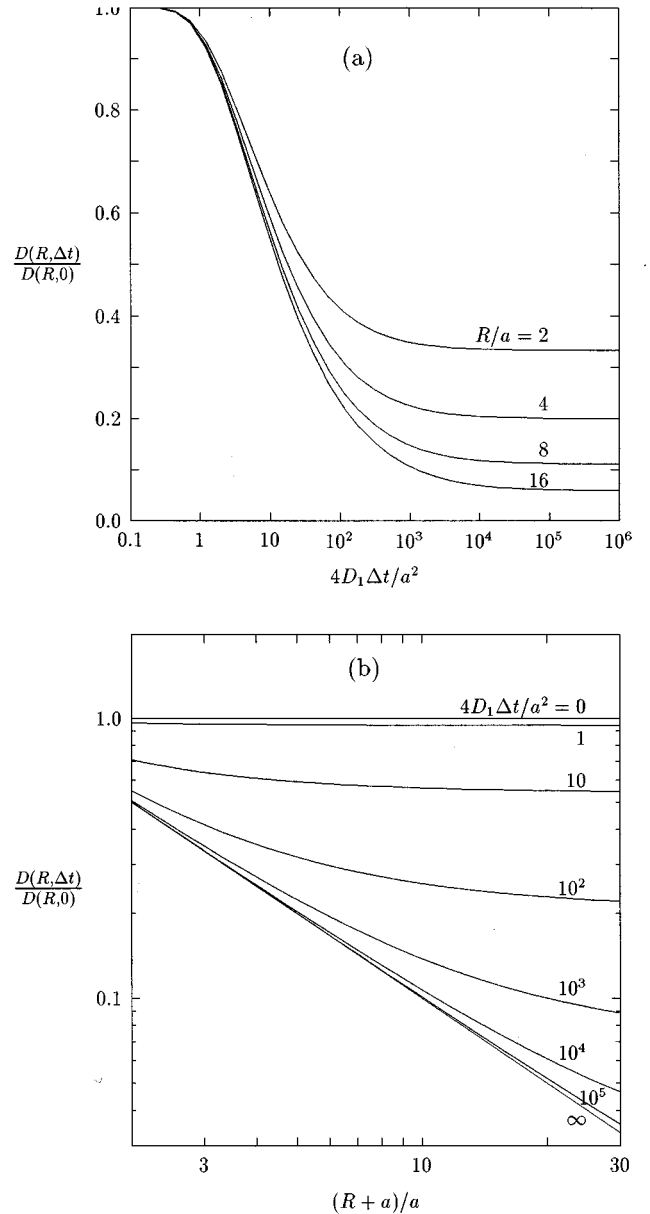

FIG. 1. (a) Diffusion constant $D(R, \Delta t)$, defined by Eq. (1), for clusters of different radius R, as a function of time Δt, in units of the interval between free adatom jumps. D_1 is the adatom diffusion constant on a terrace. a is the surface lattice constant. (b) The same, as a function of cluster size, for different times.

where $F'_m(x) \equiv [dF_m(x)/dx]_\theta$. The diffusion constant is

$$\frac{D(R,\Delta t)}{D(R,0)} = 1 - R \int_0^\infty dk F_1(kr_0) F'_1(kR) \left(1 - \frac{1 - e^{-D_1 \Delta t k^2}}{D_1 \Delta t k^2} \right),$$

$$(12)$$

which can be integrated numerically.

Figure 1 shows the diffusion constant as a function of time and cluster size. It can be seen that the uncorrelated result is valid only for $\Delta t < t_1$, where $t_1 = a^2/(4D_1)$ is the average time between free adatom jumps. For $\Delta t > 10^5 t_1$, the asymptotic value for *correlated* EC diffusion[6] is achieved:

$$D(R) \equiv D(R,\infty) = D(R,0) \frac{a}{R+a} = \frac{a\Omega^2 j_e}{\pi R(R+a)}, \quad (13)$$

which behaves as R^{-2} for large R.

In order to find the relevant regime for STM measurements, we must estimate the time required for cluster motion. In the standard (uncorrelated) EC model, each evaporation or condensation displaces the cluster by $\langle \Delta x_{cm}^2 \rangle \simeq (R/N)^2$, and therefore the number of EC events required for the cluster to move a distance comparable to its radius is $\sim N^2$, or $\sim 10^5$ for a 300-atom cluster. In reality, we have seen that EC correlations strongly decrease the cluster displacement per evaporation, and therefore even more evaporations are required. And since the time between evaporations is typically much longer than t_1, we must conclude that STM experiments indeed measure the asymptotic $D(R,\infty) \propto R^{-2}$, and not $D(R,0) \propto R^{-1}$.

I now turn to the effect of the perimeter energy on the cluster evaporation and diffusion rates. In the standard model, the cluster evaporation and condensation rates (per unit perimeter length) are assumed to be the same for all clusters. However, smaller clusters have a relatively larger perimeter energy, and therefore they evaporate more. It will now be shown that this induces an extra dependence in $D(R)$ (in the following I will assume $\Delta t = \infty$). To study this effect, I will again use a "liquid droplet" or circular-cluster model, because of its simplicity. In this model the perimeter free energy is simply

$$\Delta F = 2\pi R \gamma, \quad (14)$$

with γ the average step free energy, per unit length. The increment in the chemical potential of the two-dimensional adatom gas, in equilibrium with the cluster, is then given by

$$\Delta \mu = \frac{\partial \Delta F}{\partial N} = \frac{\Omega \gamma}{R}. \quad (15)$$

The cluster evaporation, condensation, and diffusion rates increase by a factor $e^{\Delta \mu/kT}$. The extra cluster size dependence can be written as

$$D(R) \propto R^{-b} = R^{-b_0} e^{\Delta \mu/kT} \quad (16)$$

where $b_0 = 2$ is the exponent obtained for $R \to \infty$, i.e., without the perimeter-energy effect. Notice that the dependence of $\ln(D)$ with $\ln(R)$ is *nonlinear*. However, if we insist on a linear regression fit, we can define an effective exponent,

$$b = -\frac{d\ln[D(R)]}{d\ln(R)} = b_0 - \frac{R}{kT}\frac{d\Delta\mu}{dR} = 2 + \frac{\Omega\gamma}{kTR}. \quad (17)$$

When an evaporation occurs towards inside a cluster of vacancies, the cluster perimeter *increases*. This means that the chemical potential, the gas density, the evaporation, condensation and diffusion rates, and the exponent b, all decrease in this case. We must then change the sign of the last term in Eq. (17).

Table I compares the simple prediction of Eq. (17) to the results of one Monte Carlo simulation[10] and two experimental measurements.[2,3] Step energies for Ag surfaces have been obtained from embedded atom calculations.[11] The cluster radius used in Eq. (17) is the geometric mean of those utilized in the log-log fits to obtain the experimental b's. Taking into account the simplicity of the circular-cluster model used, the agreement is very reasonable with the simulation of both adatom and vacancy clusters,[10] as well as with the vacancy-cluster experiments on Ag(111).[3] On the other hand, the agreement is clearly unsatisfactory with adatom-cluster experiments on Ag(100).[2] Part of this discrepancy may be due to the circular-cluster model used, which is less adequate for a square lattice. Also, it must be taken into account that the experimental value of b was strongly based on the diffusion of only three large clusters. Furthermore, the clusters were monitored during 4 h, and their position-autocorrelation was observed to persist for 2 h. This means that there are only two or three independent position measurements for each cluster, and that their diffusion rates have a statistical error of $\sim 50\%$, yielding a rather large uncertainty in the fit of $\ln(D)$ vs $\ln(R)$. Therefore, the conclusion of Wen *et al.*,[2] that their clusters move by EC, must be taken with some caution, since it is based on that fit and a larger b would also be compatible with perimeter diffusion.

In conclusion, I have shown that (a) the cluster diffusion constant D, as defined by Eq. (1), depends on time as well as

TABLE I. Comparison of the predicted and experimental exponent b of the cluster diffusion constant with cluster radius: $D \propto R^{-b}$. The prediction is that of Eq. (17). The Kawasaki system refers to a model simulation of a triangular lattice gas with nearest-neigbor interaction energy $-\epsilon$. N is the average number of atoms per cluster. γ is the step energy, and a is the surface lattice constant.

System	Ref.	N	γa	kT	b_{pred}	b_{expt}
Vac./Kawasaki	10	55	ϵ	0.275ϵ	1.26	1.09 ± 0.08
Adat./Kawasaki	10	55	ϵ	0.3ϵ	2.81	3.14 ± 0.33
Vac./Ag(111)	3	900	190 meV	26 meV	1.60	1.97 ± 0.39
Adat./Ag(100)	2	270	105 meV	26 meV	2.44	~ 1.0

on cluster size; (b) the effect of EC correlations *increases* with time, as well as with the diffusivity of the evaporated adatoms; (c) the commonly accepted cluster size dependence $D(R) \propto R^{-1}$, which assumes uncorrelated EC, is valid only for times shorter than the interval between free adatom jumps; and (d) for the much longer times that are relevant for STM measurements, the correct dependence is $D(R)$ $\propto R^{-(2+\Delta b)}$, where Δb is a nonnegligible perimeter-energy correction, positive for adatom clusters and negative for vacancy clusters.

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