Fast Diffusion of a Lennard-Jones Cluster on a Crystalline Surface

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We present a molecular dynamics study of large Lennard-Jones clusters evolving on a crystalline surface. The static and the dynamic properties of the cluster are described. We find that large clusters can diffuse rapidly, as experimentally observed. The role of the mismatch between the lattice parameters of the cluster and the substrate is emphasized to explain the diffusion of the cluster. This diffusion can be described as a Brownian motion induced by the internal vibrations of the cluster and/or the vibrations of the substrate, a mechanism that has not been previously considered for cluster diffusion.   [S0031-9007(97)03355-3]

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Understanding the interaction of particles of nanometer size with surfaces is important, both from a fundamental point of view and for controlled growth of thin films and nanostructures. Recently, the diffusion of large clusters containing hundreds of atoms was investigated both experimentally [1] and theoretically [2]. These studies have focused on clusters epitaxially oriented on the surface, and have found relatively low diffusion coefficients, of order 10^{-17} cm^2 s^{-1}. In contrast, Bardotti *et al.* [3] have shown experimentally that large (one hundred to a few thousand atoms) gold or antimony clusters, nonepitaxially oriented, have a surprisingly high diffusion coefficient (of the order 10^{-8} cm^2 s^{-1} at room temperature) on a graphite substrate. This observation is reminiscent of early work by Kern *et al.* [4], in which a noticeable diffusion phase preceding epitaxial locking was observed for small gold crystallites on a NaCl surface. The essential conclusion that can be drawn is that "large" (a few nanometers) objects can have large surface diffusion coefficients at room temperature, a result that might seem rather counterintuitive to many surface scientists. Indeed, most diffusion mechanisms that have been considered for surface diffusion of composite objects such as clusters involve a combination of single-atom diffusion events (e.g., evaporation condensation [2]), and yield diffusion constants much smaller than the above-mentioned result. Although these mechanisms have been shown to describe correctly the diffusion of clusters of adatoms in epitaxy on the substrate, they do not seem to be relevant to explain the fast diffusion that is observed in Refs. [3,4].

In this Letter, we present the results of a molecular dynamics (MD) study of the cluster diffusion problem, with particular emphasis on the consequences of epitaxial or nonepitaxial cluster-substrate configurations. The nonepitaxial case is important for growth of nonepitaxial thin films or for films prepared by *preformed* cluster deposition [5]. A simple model, aimed at clarifying the generic aspects of the question rather than modeling a particular case, was used. Both the cluster and the substrate are made up of Lennard-Jones atoms, interacting through potentials of the

form $V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. Empirical potentials of this type, originally developed for the description of inert gases, are now commonly used to model generic properties of condensed systems. The substrate is modeled by a single layer of atoms on a triangular lattice, attached to their equilibrium sites by weak harmonic springs that preserve surface cohesion. The Lennard-Jones parameters for cluster atoms, substrate atoms, and for the interaction between the substrate and the cluster atoms are, respectively, $(\epsilon_{cc}, \sigma_{cc})$, $(\epsilon_{ss}, \sigma_{ss})$, and $(\epsilon_{sc}, \sigma_{sc})$. ϵ_{cc} and σ_{cc} are used as units of energy and length. ϵ_{sc}, σ_{ss}, and T, the temperature of the substrate, are the control parameters of the simulation. The last two parameters are then constructed by following the standard combination rules: $\epsilon_{ss} = \sigma_{ss}^6$ and $\sigma_{sc} = \frac{1}{2}(\sigma_{cc} + \sigma_{ss})$. Finally, the unit of time is defined as $\tau = (M\sigma_{cc}^2/\epsilon_{cc})^{1/2}$, where M is the mass of the atoms which is identical for cluster and substrate atoms.

Our simulation uses a standard molecular dynamics technique with thermostatting of the *surface* temperature [6]. The equations of motion are then integrated using the leap-frog algorithm [6], which is a simple, time reversible, and very stable integration scheme [7]. The run is started from a configuration in which the cluster atoms occupy sites of a cubic lattice near the substrate. The system is then equilibrated for 500τ, after which the trajectories are recorded. Diffusion constants D are obtained from the mean-squared displacement of the cluster center of mass. Typically, the length of the runs used to compute D was 2500τ, with some longer runs of $12\,500\tau$. This means that diffusion constants smaller than $5 \times 10^{-4}\sigma_{cc}^2\tau^{-1}$, for which the cluster does not visit an area of more than $25\sigma_{cc}^2$ over the length of the simulation, are not accessible.

We first briefly describe the static properties of our supported clusters. At the temperature at which most runs were carried out, $T = 0.3\epsilon_{cc}$, the clusters are in a crystalline fcc or hcp configuration. They take the spherical cap shape of a solid droplet [Fig. 1(a)] partially wetting the substrate. The contact angle θ that can be defined following Ref. [8] is roughly independent of the cluster particle number N, for $50 < N < 500$. This angle can be
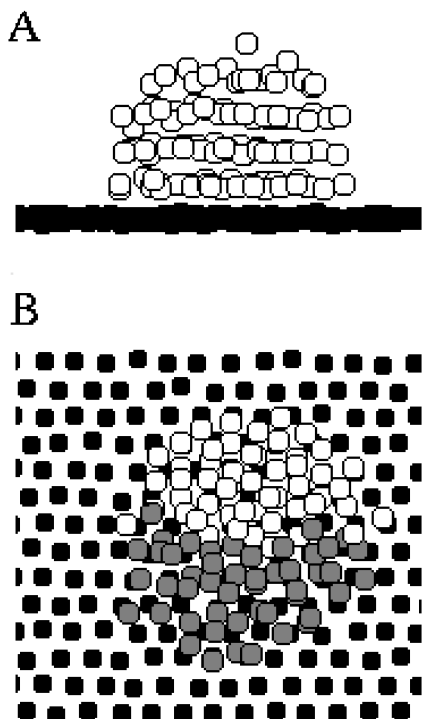
A

B

FIG. 1. Configuration of the cluster on the crystalline surface. (a) Side view: The cluster is partially wetting the surface. (b) Top view: The two halves of the cluster have been colored at the beginning of the run. After the cluster center of mass has moved by roughly three substrate lattice constants from its original position, the two parts of the cluster are still well distinct. The cluster diffusion can then not be explained in terms of single-atom mechanisms ($N = 100$, $\sigma_{ss} = 0.7$, $\epsilon_{sc} = 0.4$, $T = 0.3$).

changed by tuning the cluster-substrate interaction. For large enough ϵ_{sc}, total wetting is observed, and the cluster dissociates. As noted in [8], this shows the relevance of macroscopic concepts such as contact angle and wetting even for nanometer-sized particles.

We now turn to the dynamical behavior of the supported cluster. Most of the runs were carried out at a reduced temperature of 0.3 so that the cluster is clearly solid. In that case, visual observation of atomic trajectories during the run indicate that the diffusion inside the cluster, or on its surface, is completely negligible. Except for the vibrational motion of the atoms, the cluster behaves as a rigid object. This is clearly visible in Fig. 1(b), where the two halves of the cluster, colored white and grey at the beginning of the run, clearly retain their identity after the cluster *center of mass* has moved over 3.5 lattice parameters. Hence the motion of the cluster appears to be controlled by collective motions of the cluster as a whole rather than by single atomic jumps. This collective diffusion mechanism will depend essentially on three parameters: the lattice parameter of the substrate, the temperature, and the cluster size. We consider in turn the influence of each parameter.

We first investigate the effect of the ratio of the cluster lattice parameter to the substrate lattice parameter for $T = 0.3\epsilon_{cc}$ and $N = 100$, by varying the interaction diameter of the substrate atoms in the range of $0.5\sigma_{cc}$ to $1.5\sigma_{cc}$ The lattice constant d of the substrate atoms is also correspondingly scaled in such a way that σ_{ss}/d remains constant, equal to its value for a Lennard-Jones solid at zero pressure. The results for the diffusion coefficient are shown in Fig. 2. When the substrate and cluster are commensurate ($\sigma_{ss} = \sigma_{cc}$), the cluster can lock into a low energy epitaxial configuration. A global translation of the cluster would imply overcoming an energy barrier scaling as $N^{2/3}$, the contact area between the cluster and the substrate. In that case, single-atom mechanisms as described in [2] will dominate, and the diffusion will be very slow. Indeed on the time scale of the MD simulations, diffusion was vanishingly small in that case. The points in Fig. 2 at $\sigma_{ss} \sim \sigma_{cc}$ do not, in fact, represent true diffusion constants, since in these cases the center of mass did not move by more than a few lattice constants over the whole duration of the run. However, for small deviations from this commensurate case, the diffusion becomes measurable on the time scale of the MD runs. This can be understood from the fact that the effective potential in which the center of mass moves is much weaker, as the cluster atoms, constrained to their lattice sites inside the rigid solid cluster, are unable to adjust to the substrate potential. The effect is rather spectacular. A 15% change on the lattice parameter induces a 2 orders of magnitude change on the diffusion coefficient. For the same reason, the diffusion coefficient decreases slightly when σ_{cc} is getting close to $2\sigma_{ss}$. Finally, we note that the effect is not exactly symmetric on both sides of the
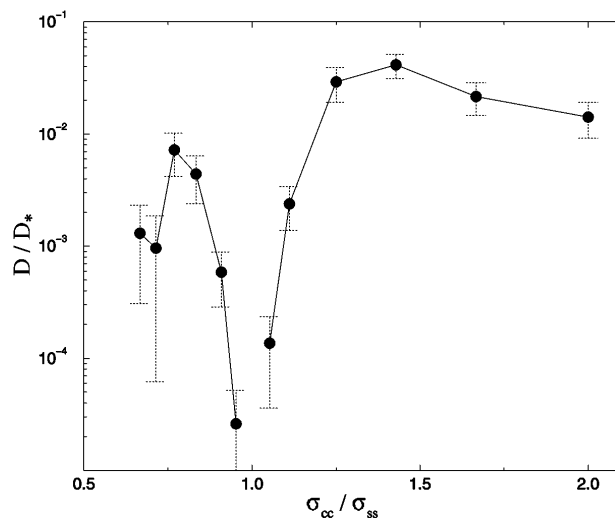

FIG. 2. Dependence of the diffusion coefficient on the mismatch between the lattice parameter of the substrate and the cluster. A small change in the lattice parameter of the cluster lead to a huge change in the diffusivity ($N = 100$, $\epsilon_{sc} = 0.4$, $T = 0.3$, run length $= 12\,500\tau$).

commensurate situation. Clusters with atoms smaller than the substrate atoms tend to diffuse more slowly, since the potential wells for these atoms will be deeper than for big adatoms.

Next, we study the influence of temperature for fixed values of σ_{ss} and ϵ_{sc}, $\sigma_{ss} = 0.9$ and $\epsilon_{sc} = 0.4$. The diffusion constant can be fitted by an Arrhenius law (Fig. 3), with an activation energy E of $0.66\epsilon_{cc}$ and a prefactor D_0 of $0.02D_\star$ where $D_\star$ is equal to $\sigma_{cc}(\epsilon_{cc}/M)^{1/2}$. However, the mechanisms involved here are not simple, single-atom activated processes. Not too much meaning should then be given to the activation energy and prefactor.

In order to establish a connection with experiments, we can identify ϵ_{cc}/k_B to a typical melting temperature (1000 K for Au). Using $\sigma_{ss} \sim 5$ Å and $M \sim 10^{-25}$ kg, we find that our diffusion coefficients would fall in the range of 10^{-5} cm^2 s^{-1} for a 100-atom cluster. This is in reasonable agreement with the values obtained in [3], but differs strikingly from the values obtained with single-atom mechanisms.

Finally, for the same values of ϵ_{sc} and T, the effect of cluster size on the diffusion constant is considered for different lattice parameter values. As the number N of atoms in the cluster is varied between $N = 10$ and $N = 500$, the diffusion constant decreases, roughly following a power law $D \sim N^\alpha$ (Fig. 4). This power law exponent α depends significantly on the mismatch between the cluster and the substrate lattice parameters. For high mismatches ($\sigma_{ss} = 0.7, 0.8$), α is close to -0.66. As the diffusion constant is inversely proportional to the cluster-substrate friction coefficient, this result is in agreement with a simple "surface of contact" argument yielding $D \sim N^{-2/3}$. On the other hand, when the lattice mismatch is equal to 0.9, α one obtains $\alpha \approx -1.4$, although the shape of the cluster, characterized by the contact angle, does not
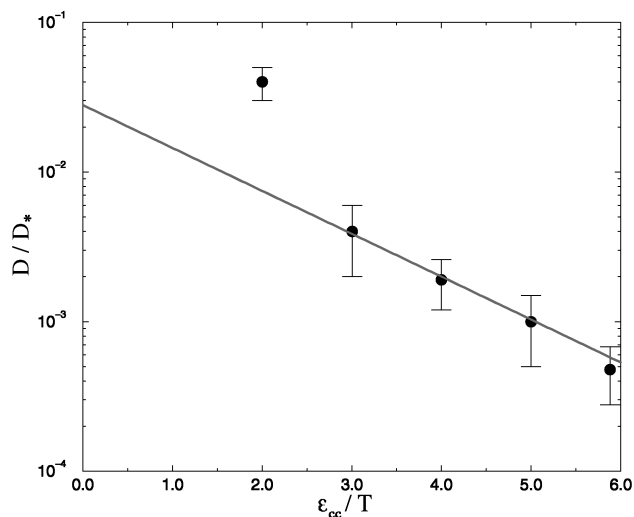
appreciably change. Moreover, the trajectory followed by the cluster center of mass changes qualitatively. In the runs with a large mismatch, this trajectory is Brownian-like, with no apparent influence of the substrate. In contrast, when the mismatch is small, the center of mass of the cluster follows a "hopping-like" trajectory, jumping from site to site on the honeycomb lattice defined by the substrate. When $\sigma_{ss} = \sqrt{3}/2$, there seems to be a transition between the two regimes around $N = 200$.

In an attempt to disentangle the contribution of the cluster internal vibrations to the diffusion process from that of the substrate vibrations in the small mismatch case ($\sigma_{ss} = 0.9$), we now consider idealized cases in which one of the two subsystems is artificially "frozen," so that its contribution vanishes. First, we consider the case of cluster supported by a frozen substrate, with atoms constrained to their equilibrium positions. The external potential experienced by the cluster atoms is thus purely static. The cluster is first equilibrated using constant temperature MD at $T = 0.3\epsilon_{cc}$, and this equilibration period is followed by a constant energy simulation. The results for the diffusion constant are very close to those obtained with a thermalized substrate. This shows that such clusters have enough internal degrees of freedom to play the role of being their own thermostat, and that their internal vibration modes can be an efficient motor for the diffusion.

Next, we consider the other extreme case of a frozen cluster deposited on a thermalized substrate. The cluster
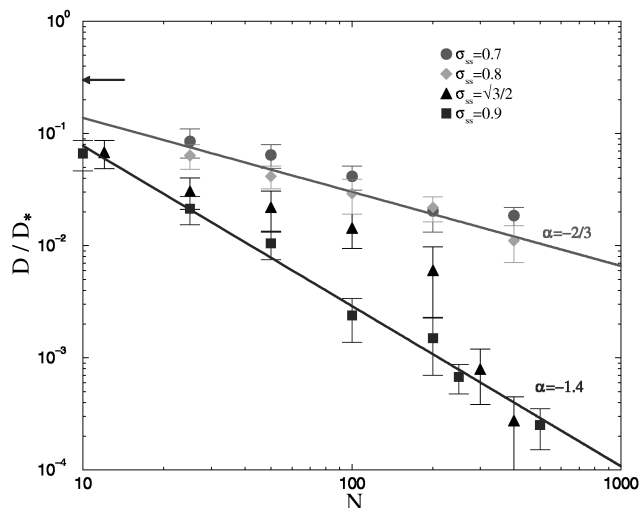

FIG. 4. Dependence of the diffusion coefficient of a cluster as a function of its number of particles. Data correspond to different mismatches between the cluster and the substrate lattice parameters. The diffusion coefficient decreases as a power law with exponent α. The two different slopes correspond to different diffusion regimes: The weaker dependence corresponds to a Brownian trajectory; the stronger correspond to a "hopping-like" diffusion. For comparison, the arrow indicates the diffusion coefficient of a single adatom with $\sigma_{ss} = 0.9$. ($\epsilon_{sc} = 0.4$, $N = 100$, run length = $12\,500\tau$).

FIG. 3. Temperature dependence of the diffusion coefficient. The diffusion follows an Arrhenius law.

is first equilibrated, either on a perfectly flat substrate exerting an average potential equivalent to that of the triangular lattice of Lennard-Jones atoms, or in free space. In the first case, it adopts the usual spherical cap shape, while in the second case a quasispherical, faceted shape is observed. This last shape would be reasonable for a cluster made of a highly cohesive material. After this equilibration phase, the cluster is frozen and deposited on the thermalized substrate as a solid body. The center of mass trajectory is integrated using the quaternion algorithm [6].

Not surprisingly, the diffusion is dependent on the way the system has been equilibrated. For a spherical rigid cluster, the system rotates until a facet comes into contact with the substrate, then diffuses without rotating for the rest of the MD run. Hence despite the more or less spherical shape of the cluster, rotation does not seem to give an important contribution to the diffusion. In that case, the diffusion depends on the shape and size of the facet the cluster rests on, so that the results in this case are not well reproducible. For a cluster equilibrated on a flat surface, the diffusion constant follows the same power law as in the free cluster case. This surprising result suggests that the diffusion mechanism in our case cannot be simply explained in terms of dislocation migration within the cluster as proposed to explain the diffusion of 2D islands in [9]. As the substrate atoms are tethered to their lattice site, strong elastic deformations of the lattice or dislocations are excluded. Hence, the motor for diffusion is here the vibrational motion of the substrate, and its efficiency appears to be comparable to that of the internal cluster modes.

In summary, the surprisingly high diffusivity of large clusters can be understood with two main ingredients. When the cluster is not commensurate with the substrate, the modulation of the potential felt by the center of mass is small. In this case the cluster is not locked by the substrate and can vibrate relatively freely. The vibrations (phonons) of the substrate and the internal vibrations of the cluster both create a "random" force on the cluster center of mass, which executes a Brownian motion in this weak external potential. The two components of this random force appear to have similar intensities, and, at the temperature we consider, are sufficiently strong to overcome the small energy barriers, resulting in a rapid diffusive motion. Our calculation demonstrates the efficiency of this Brownian-like mechanism, which was not considered in earlier studies of cluster diffusion, for explaining the diffusion of rather large objects. Further analysis of the vibrational coupling between the substrate and the cluster will be necessary to fully understand the mass dependence of the diffusion constant.

[1] J. M. Wen *et al.,* Phys. Rev. Lett. **73**, 2591 (1994); K. Morgenstern *et al.,* Phys. Rev. Lett. **74**, 2058 (1995); G. L. Kellogg, Phys. Rev. Lett. **73**, 1833 (1994), and references therein.

[2] A. F. Voter, Phys. Rev. B **34**, 6819 (1986); J. M. Soler, Phys. Rev. B **50**, 5578 (1994); S. V. Khare *et al.,* Phys. Rev. Lett. **75**, 2148 (1995); D. S. Sholl and R. T. Skodje, Phys. Rev. Lett. **75**, 3158 (1995); C. deW. Van Siclen, Phys. Rev. Lett. **75**, 1574 (1995); J. M. Soler, Phys. Rev. B **53**, 10 540 (1996).

[3] L. Bardotti *et al.,* Phys. Rev. Lett. **74**, 4694 (1995); Surf. Sci. **367**, 267 (1996).

[4] R. Kern, G. Le Laye, and J. J. Metois, *Current Topics in Materials Science* (North-Holland, Amsterdam, 1979), Vol. 3, Chap. 3.

[5] P. Melinon *et al.,* Int. J. Mod. Phys. B **9**, 339–397 (1995).

[6] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, New York, 1987).

[7] D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic Press, San Diego, 1996).

[8] J. Hautman *et al.,* Phys. Rev. Lett. **67**, 1763 (1991).

[9] J. C. Hamilton, Phys. Rev. Lett. **77**, 885 (1996).