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Molecular dynamics study of the copper cluster deposition on a Cu(0 1 0) surface

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Abstract

The deposition of copper cluster on the Cu(0 1 0) surface is studied by molecular dynamics simulation. We used a many-body potential based on the tight-binding model to describe the Cu–Cu interaction. Several quantities are calculated to study the influence of the substrate size and substrate temperature on the cluster deposition phenomenon. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Copper; Clusters; Molecular dynamics; Surface diffusion

1. Introduction

An important method of crystal growth is the deposition of single atoms on prepared surfaces. As the number of atoms on a surface increases, so does the probability that two or more atoms combine to form a cluster. These nucleation events are of fundamental importance in the growth of crystalline solids. Investigations with field ion microscope (FIM) has been extremely useful in revealing the properties of clusters and helping to understand the adatom–adatom interactions leading to nucleation. Examination of the aggregation time and dissociation lifetime of clusters have provided direct information on the nature of adatom–adatom and cluster–surface interactions [1–4]. Another recent method to grow thin films is the direct controlled deposition of small clusters on surfaces. In this case the nature of the interactions between the atoms of the cluster and the cluster–surface is essential for characterizing the deposition process. The diffusion of clusters on surfaces involves a sequence of steps that result in displacements of the center of mass and change the configuration of atoms within the cluster and the cluster rearrangement time is important in the study of deposition and growth [4,5]. One important tool to study the microscopic aspects of the surface diffusion is the molecular dynamics (MD) simulation which can give important clues on the dynamics microscopic behavior of atoms on the surface.

In this work we present a MD simulation of the deposition of a copper cluster on the Cu(0 1 0) surface. Some early papers on surface deposition using MD or Monte-Carlo (MC) simulation study the behavior of single particles or clusters [5] however, they do not consider the lattice finite size

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effects in their simulations. The aim in the present work is to study the dynamics and rearrangements of a copper cluster on a flat surface of the same material for temperatures of $T = 0$ K and $T = 800$ K and different system sizes. What is new in this paper is the analyzes of the finite size effects of the substrate in the cluster deposition. This is important because it provides support for the validity of a number of simulations in which the influence of the size of the simulated systems was not taken in to account; rather it was assumed that results are independent of the size of the system.

This work is organized as follow. In Section 2 we describe our simulation scheme. In Section 3 we present our results. In Section 4 we present our conclusions and some final remarks.

2. Simulation method

Our simulation is carried out using MD. We have used a semi-empirical potential [6–8] based on the tight-binding method in the second moment approximation to describe the attractive interatomic interaction and Born–Mayer-type interatomic repulsion was assumed. This potential model has given good results in the MD studies of bulk [7,8] and surfaces [9–13] properties of transition metals.

For a system with only one type of atom the total potential energy is given by

$$E = \sum_{i=1}^{N} \left[\sum_{j=1}^{N} A\mathrm{e}^{-p\left(\frac{r_{i,j}}{r_0}-1\right)} - \sqrt{\left(\sum_{j=1}^{N} \xi^2 \mathrm{e}^{-2q\left(\frac{r_{i,j}}{r_0}-1\right)} \right)} \right]. \tag{1}$$

The indexes i and j stands for particles at position $\vec{r}_i$ and $\vec{r}_j$ respectively, N is the total number of particles and $r_{i,j} = \left|\vec{r}_i - \vec{r}_j\right|$ is the distance between atoms i and j, r_0 is the nearest-neighbor distance (equilibrium distance) in the bulk metal. The parameters A, ξ, p and q are adjusted to reproduce the cohesive energy, equilibrium condition (zero pressure at $T = 0$ K) and the elastic constants of a given metal. For Cu–Cu we use $A = 0.0855$ eV, $\xi = 1.224$ eV, $p = 10.96$, $q = 2.278$ and $R_0 = 2.5562$ according to Ref. [14].

A cutoff is introduced in the potential, which accounts for interactions up to fifth nearest neighbors, in order to accelerate the simulation. Particles in the simulation move according to Newton's law, that generate a set of $3N$ coupled equation of motion which are simultaneously solved by increasing forward in time the physical state of the system in small time steps of size $\delta t = 10^{-14}$ s. We use the Beeman's method of integration [15–18] which is a fourth order predictor–corrector scheme. In order to improve the integration we use a Verlet table [15–18].

The copper substrate is composed distributing N particles, over a frozen layer around their equilibrium position in the fcc (0 1 0) geometry, fulfilling four layers in the y direction which is perpendicular to the substrate as shown in Fig. 1. Periodic boundary conditions are used for the directions parallel to the substrate and open condition for the y direction.

We studied cluster deposition in substrates with four layers in the y direction and dimensions $(L \times L)$ $L \approx 25$ Å $(N = 392$ atoms), $L \approx 50$ Å $(N = 1568$ atoms) and $L \approx 100$ Å $(N = 6272$ atoms). This procedure allows us to analyze the influence of the system size in the deposition dynamics. Once the temperature (T) of the system is fixed we use velocity renormalization to equilibrate the system by letting it evolve in time for $2 \times 10^3\, \delta t$ time steps. We accept that the system is in equilibrium if the deviations in the mean kinetic energy is less than 1%.

The cluster initial geometry is the result of the MD simulation of an agglomerate of 13 copper atoms with periodic boundary conditions in all direction. The number of atoms is chosen in accord

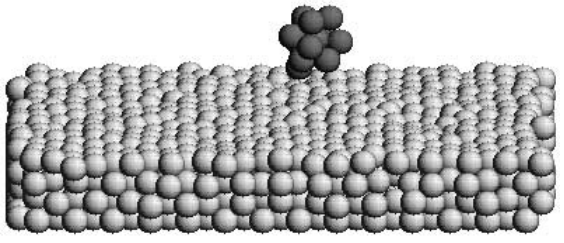

Fig. 1. A typical initial configuration. The substrate dimension is $L \approx 50$ Å ($N = 1568$ atoms) and temperature is $T = 800$ K.

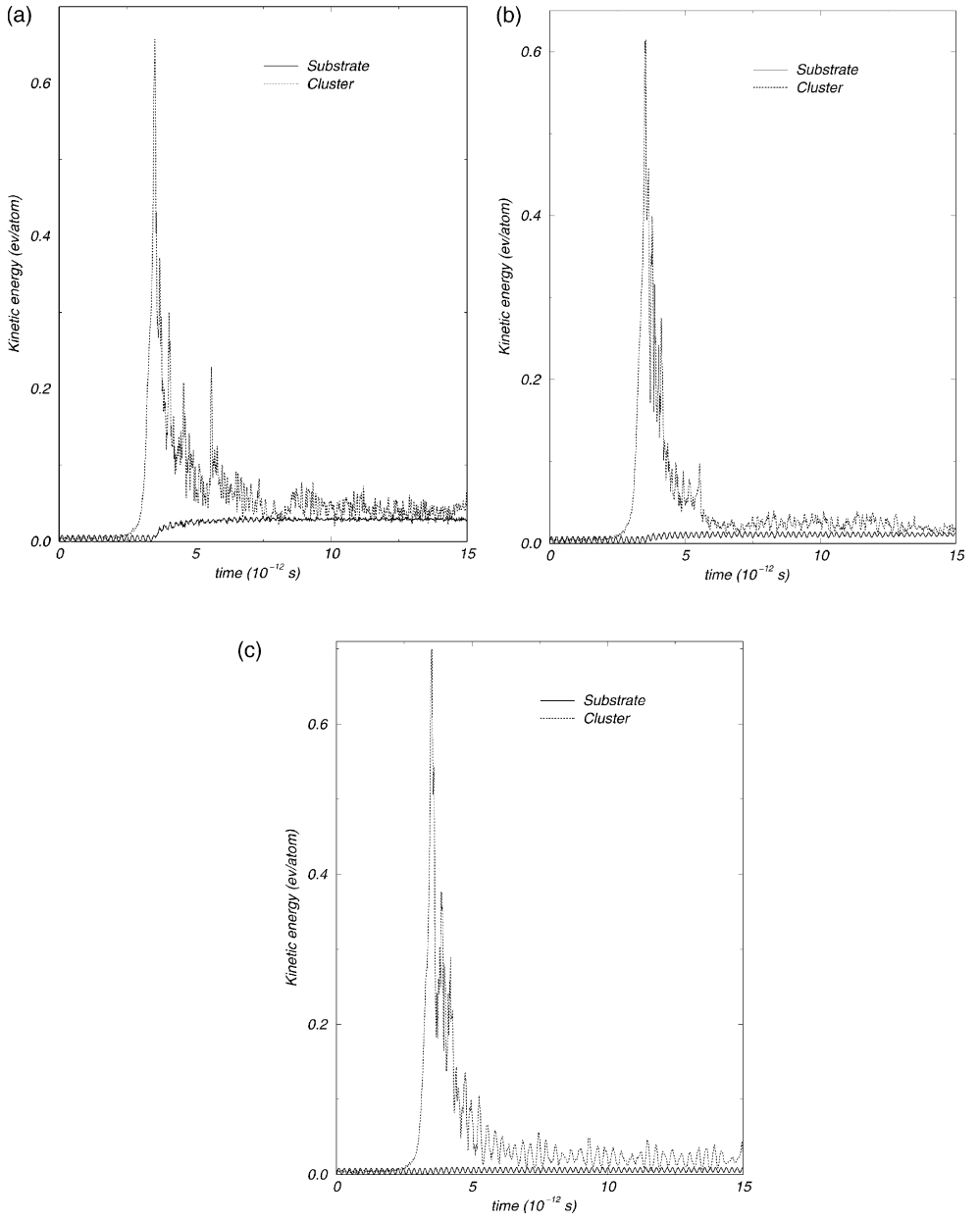

Fig. 2. Cluster and substrate kinetic energy as a function of time. Substrate initially at $T = 0$ K, (a) $L \approx 25$ Å, (b) $L \approx 50$ Å, (c) $L \approx 100$ Å.

to Ref. [19]. The cluster is equilibrated at $T = 0$ K. At the end of the simulation the cluster present a shape similar to an icosahedra [19–22].

After the equilibration of the two subsystems, the cluster is placed closed to Cu(0 1 0) surface, at a distance such that the minimum separation between the cluster and substrate atoms is about 6 Å. The cluster motion is followed for $15 \times 10^3\ \delta t$ time steps which corresponds to 150 ps. Fig. 1 shows a typical initial configuration at $T = 800$ K. We store all velocities and positions for every time step for further analyses.

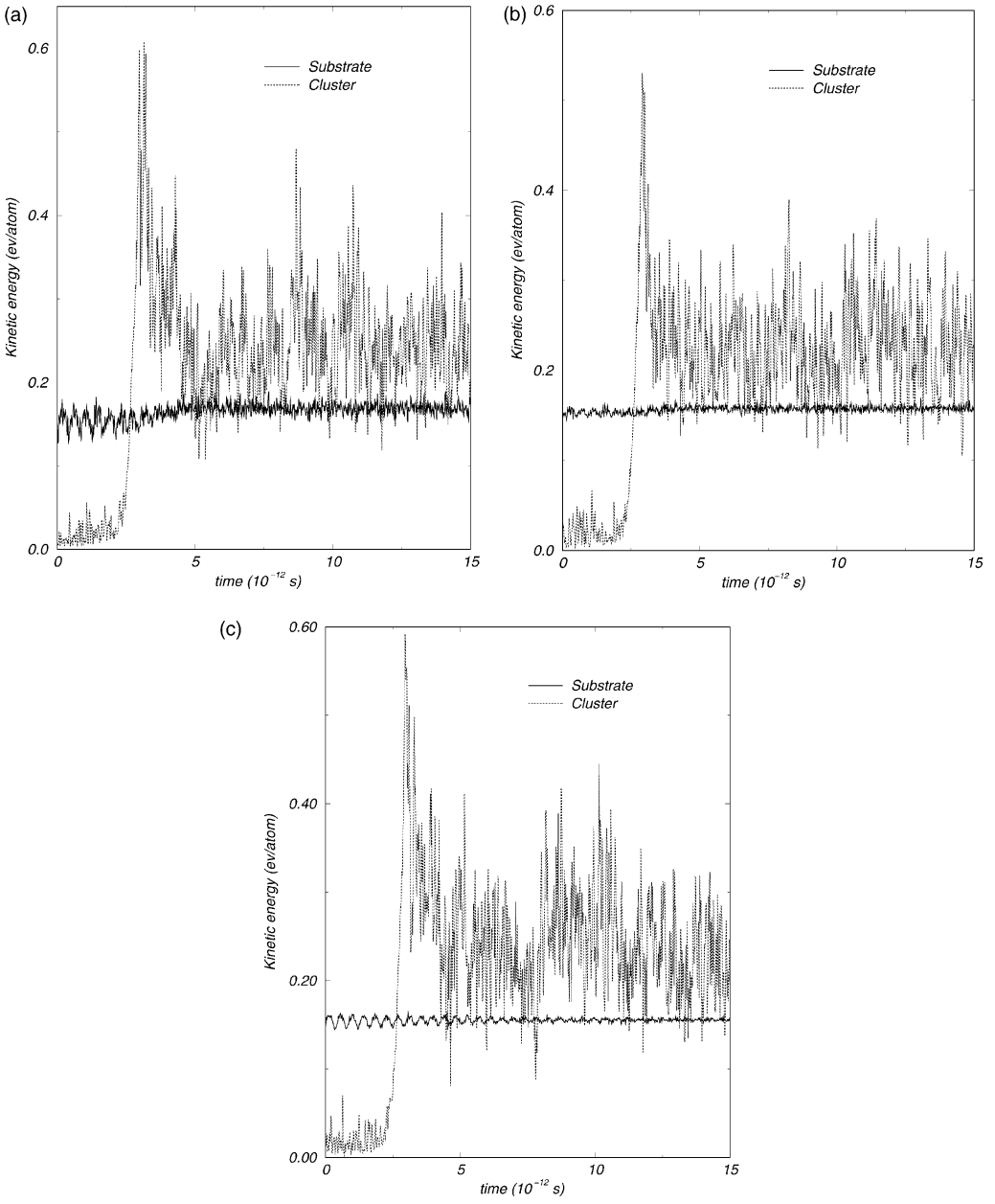

Fig. 3. The same as in Fig. 2 for substrate at $T = 800$ K.

The analyzes of the cluster relaxation on the surface is done by calculating several quantities. First we calculate the kinetic energy of the cluster and substrate. The atomic rearrangements of the cluster and surface from their initial configurations can be evaluated by tree indicators. The structural parameter defined as

$$\lambda = \frac{1}{2N_{\text{clus}}} \sum_{i=1}^{N_{\text{clus}}} \left[\cos\frac{4\pi x_i}{a_0} + \cos\frac{4\pi y_i}{a_0} \right], \tag{2}$$

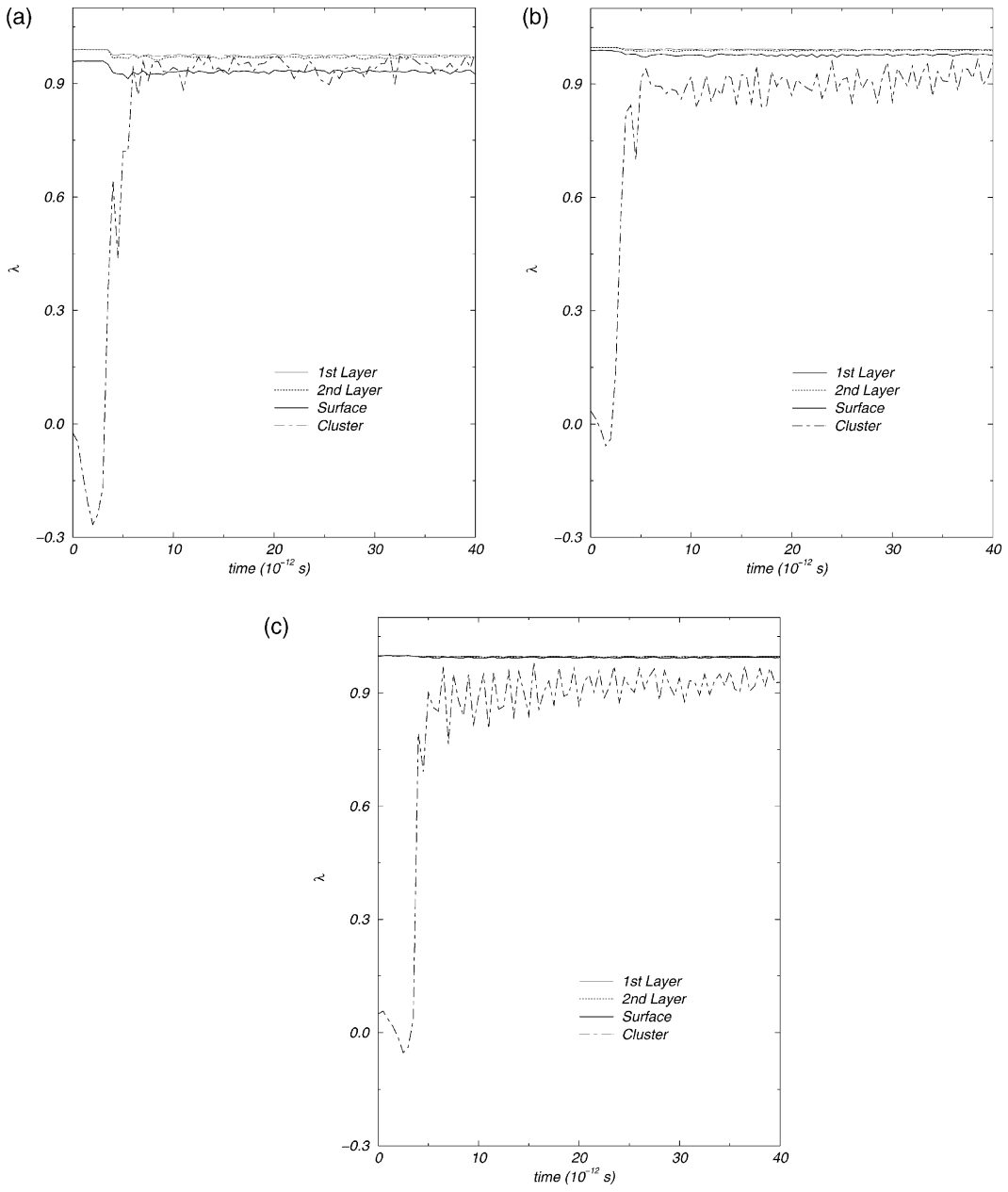

Fig. 4. Time evolution of the structural parameter λ for the layers substrate and for the cluster Cu_{13}. Substrate initially at $T = 0$ K, (a) $L \approx 25$ Å, (b) $L \approx 50$ Å, (c) $L \approx 100$ Å.

where a_0 is the bulk lattice parameter of the substrate and (x_i, y_i) are the coordinates of atom i in the plane parallel to the surface. For a fcc crystal with atoms disposed in exact equilibrium positions, $\lambda = 1$ and smaller than 1 otherwise so, λ gives information about the degree of epitaxy achieved. We also evaluated the mean height of the layers and of the cluster center of mass. These

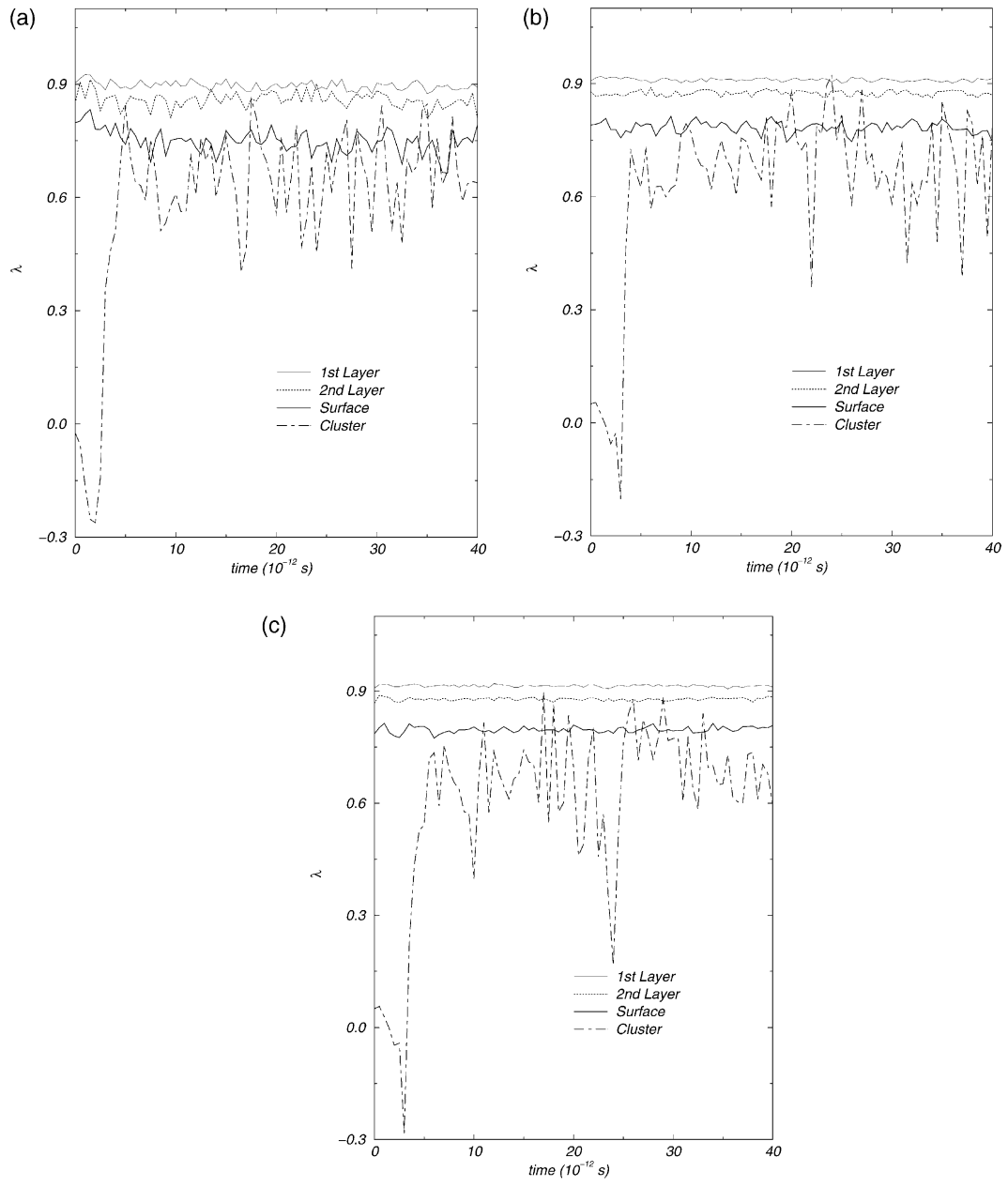

Fig. 5. The same as in Fig. 4 for substrate at $T = 800$ K.

parameters give information about how the cluster arrives and spreads on the surface and about the relaxation of each layer of the substrate.

Another parameter which can give some information about the cluster form are the cluster inertia moments I_{xx}, I_{yy} and I_{zz}. If the cluster has some symmetry and the axis are the principal axes, I_{xx}, I_{yy} and I_{zz} will be the principal moments of inertia. If it has a spherical symmetry $I_{xx} = I_{yy} = I_{zz}$ in a planar symmetry, for example in the xz plane,

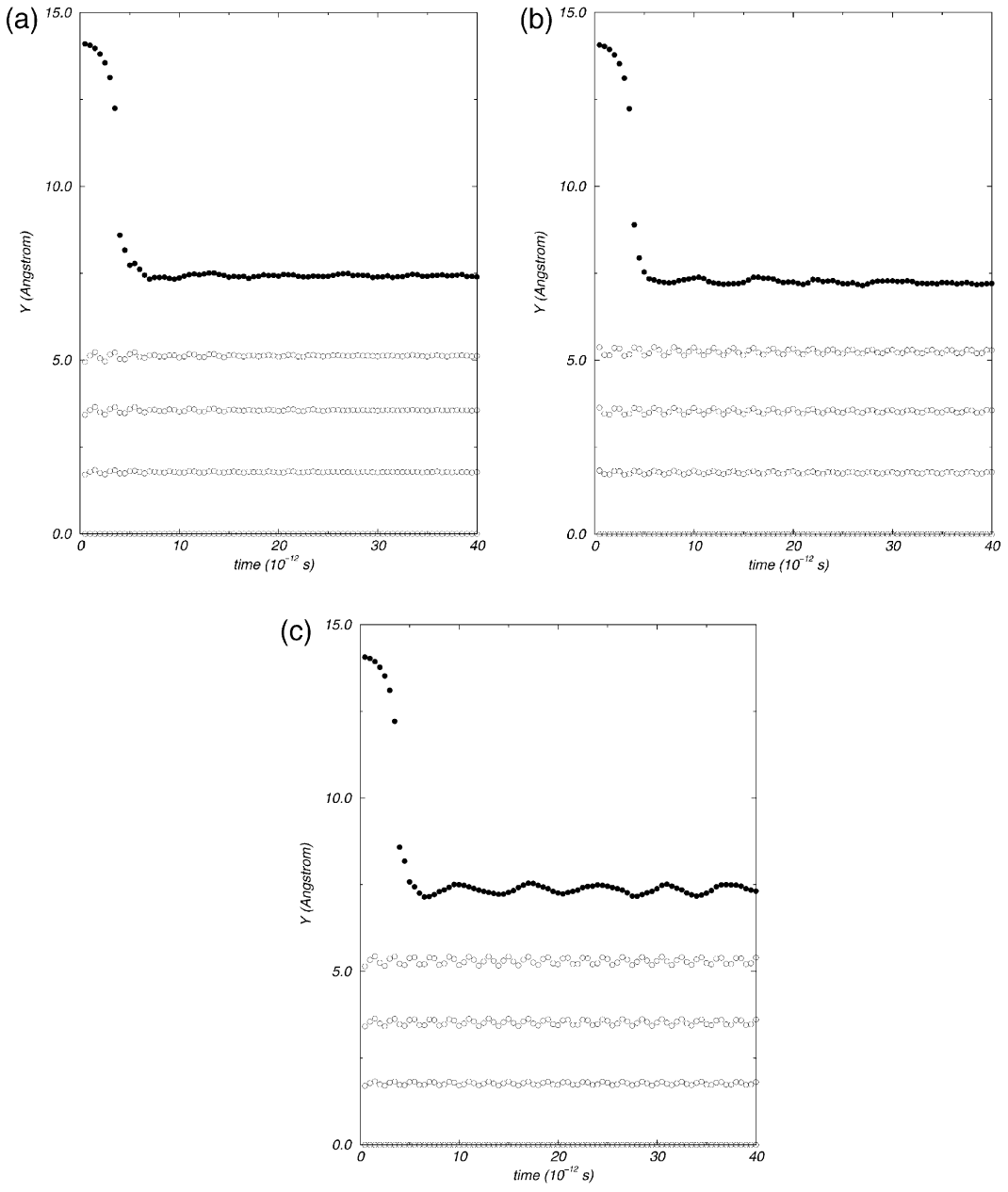

Fig. 6. The mean height of the center of mass of the cluster (●) and of the layers substrate (○) as a function of time. Substrate initially at $T = 0$ K, (a) $L \approx 25$ Å, (b) $L \approx 50$ Å, (c) $L \approx 100$ Å.

$I_{yy} = I_{xx} + I_{zz}$. We evaluate the inertia tensor components of the cluster relative to the center of mass. For the initial cluster configuration $I_{xx} \approx I_{yy} \approx I_{zz}$. After deposition with the atomic rearrangement the cluster tends to lose the spherical symmetry and becomes planar ($I_{yy} \approx I_{xx} + I_{zz}$). This parameter can be used to evaluate the spreading degree of the cluster over the surface.

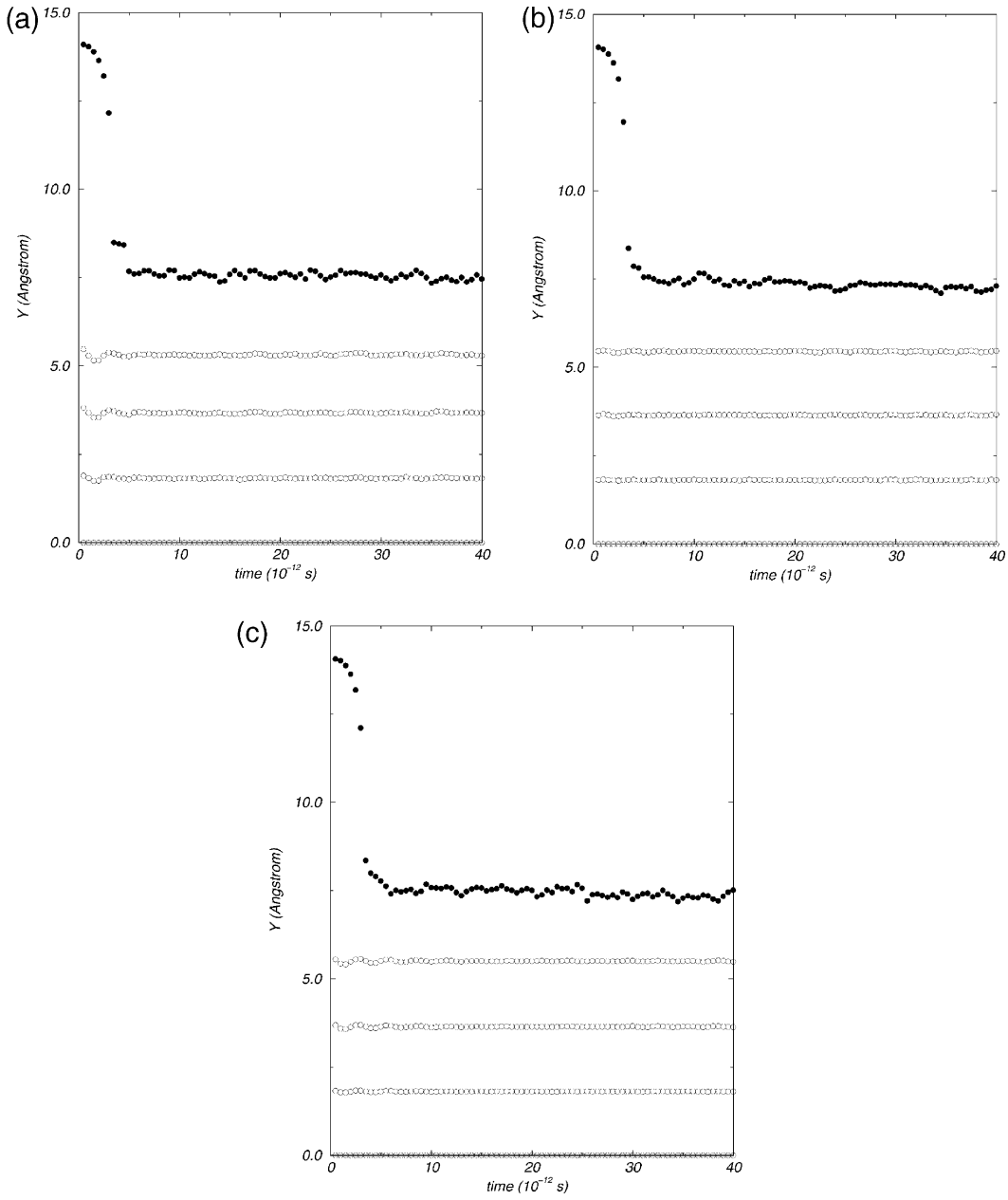

Fig. 7. The same as in Fig. 6 for substrate at $T = 800$ K.

3. Results

When a cluster is deposited on a surface it relaxes changing the surface and its own geometry. Depending on the temperature the cluster can wet more or less the surface and move over it randomly [23]. In our simulation the copper cluster is initially deposited at a distance of 6 Å above the substrate which immediately starts moving to the surface. The time evolution of the kinetic energy of

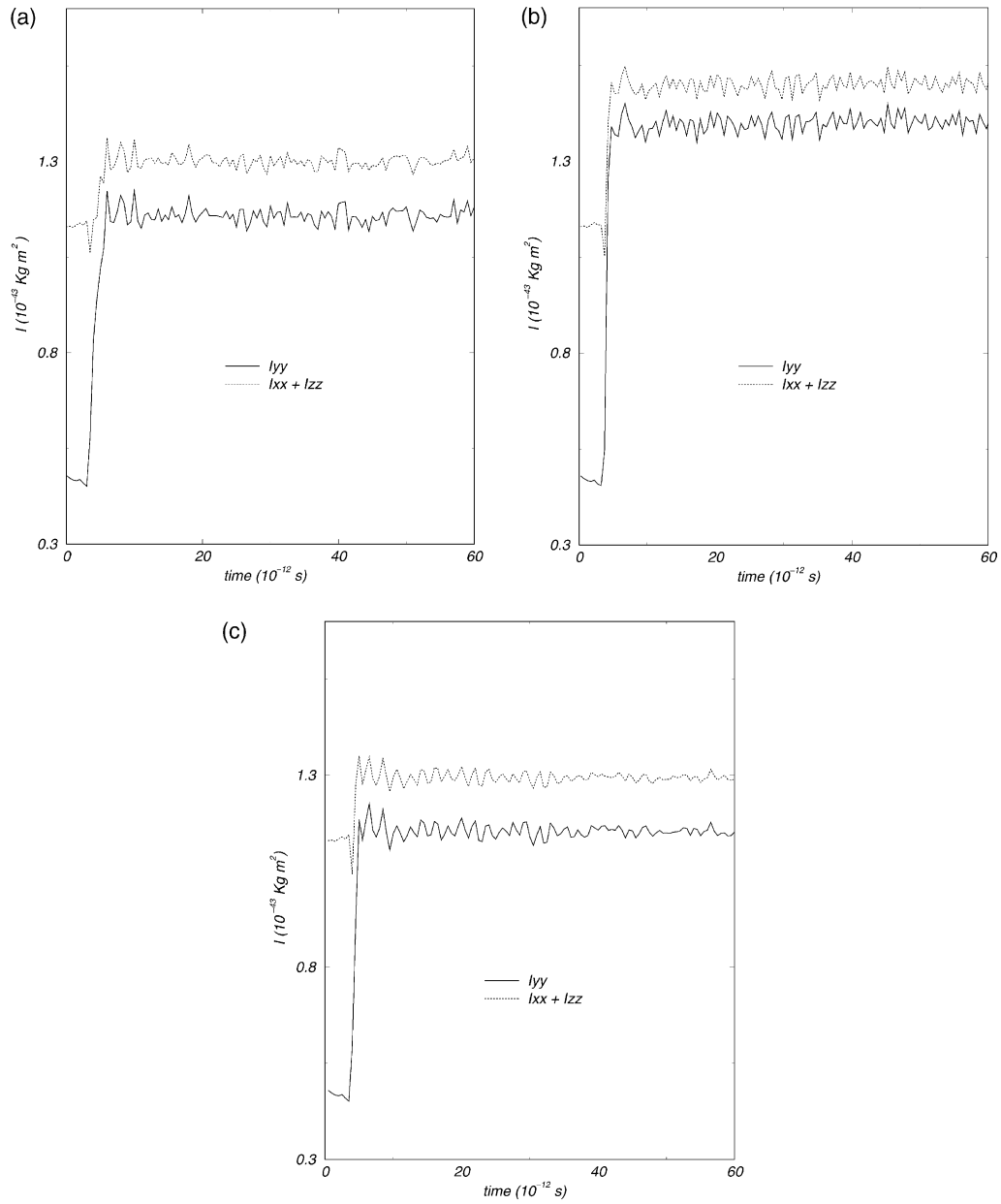

Fig. 8. The time evolution of the inertia moments of the Cu_{13} cluster. Substrate initially at $T = 0$ K, (a) $L \approx 25$ Å, (b) $L \approx 50$ Å, (c) $L \approx 100$ Å.

the cluster and substrate is shown in Figs. 2 and 3 with the substrate at two different temperatures and different sizes as described in the captions. The substrate and the cluster's kinetic energy grow due to the movement towards the substrate and the particles relative movement. Once the cluster reaches the surface it equilibrate and the energy excess is absorbed by the substrate. The transient

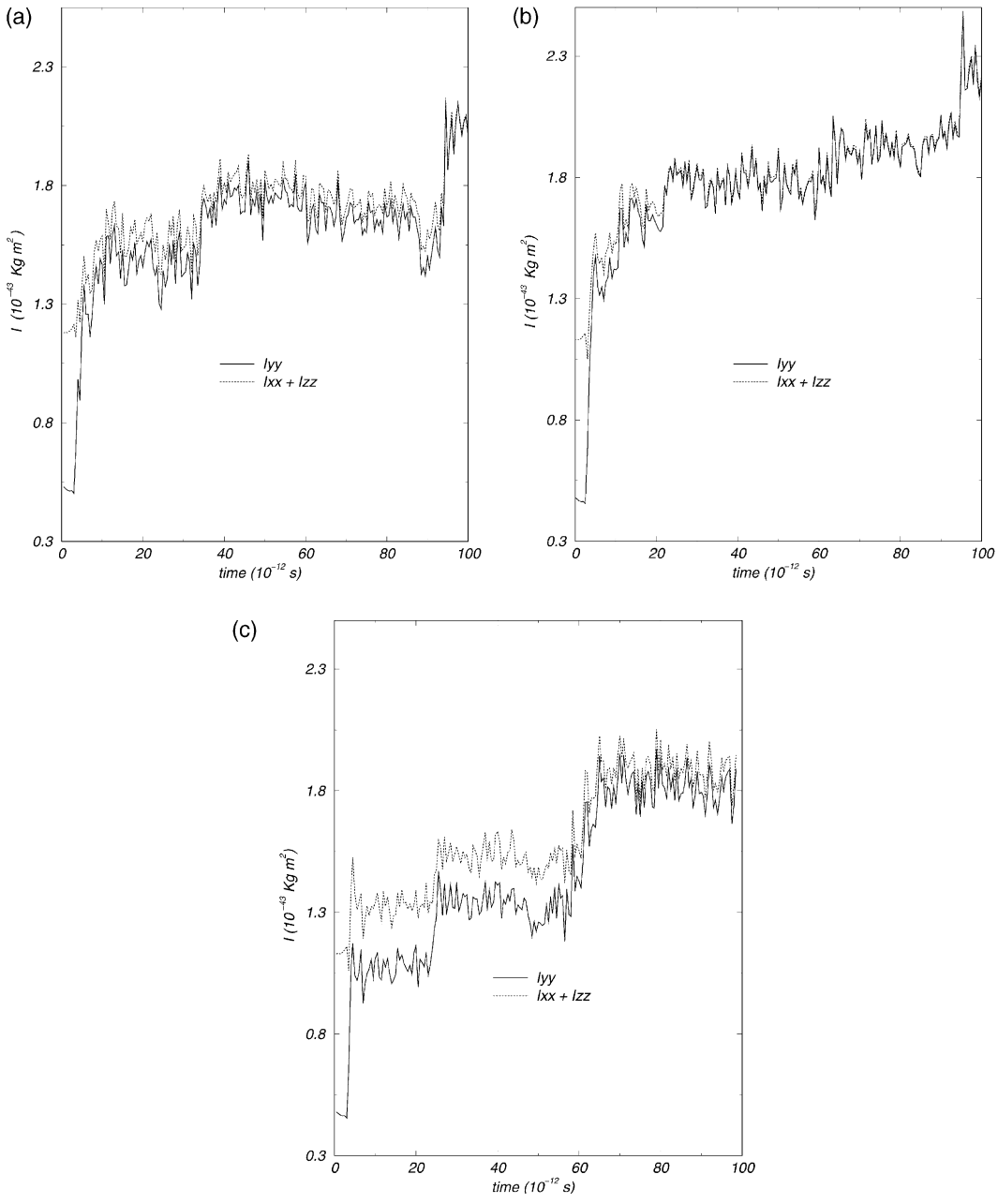

Fig. 9. The same as in Fig. 8 for substrate at $T = 800$ K.

time is very short, being of order of $t_{\text{transient}} \approx 5 \times 10^{-12}$ s. This means that the main rearrangements of the cluster atoms occurs very fast, in fact after the transient time the changes on the cluster geometry are not followed by big changes in energy for any system size. Figs. 4 and 5 shows the parameter λ measured layer by layer as a function of time. As soon as the cluster reaches the substrate it begins to spread over the surface reaching the epitaxial regime, λ_{cluster} assumes the expected

equilibrium value close to $\lambda_{\text{substrate}}$. The value of $\lambda_{\text{substrate}}$ is ≈ 1 for $T = 0$ K decreasing to ≈ 0.9 for $T = 800$ K due to thermal effects. There is no noticeable differences between the three lattice sizes.

In Figs. 6 and 7 we show the time evolution of the mean height of the layers in the substrate and of the center of mass of the cluster for $T = 0$ K and $T = 800$ K and sizes $L \approx 25$ Å, $L \approx 50$ Å, $L \approx 100$ Å. We observe that the layers mean height and the cluster position present an oscillation which is more pronounced for $T = 0$ K (Fig. 6). The substrate oscillate at a frequency which is three times larger than that of the cluster. Once the cluster is deposited on the surface the oscillations are damped and eventually suppressed for small system sizes. For $T = 800$ K (Fig. 7) the oscillations are overdamped and less well defined due to thermal motion. Once we go deeper into the bulk the oscillations lose amplitude having however the same period as those from outer layers. We also did some simulations in a system with six layers and $L \approx 25$ Å, and $L \approx 50$ Å, our results showed that the frequencies do not depend on the system size.

Figs. 8 and 9 show the inertia momenta. For low temperature the cluster relaxes to a spherical configuration while for higher temperature it relaxes to a planar configuration.

When the simulation begins the cluster has a sphere like shape such that $I_{yy} \approx I_{xx} \approx I_{zz}$. As soon as it reaches the surface it rearranges in different configurations depending on T. For $T = 0$ K $I_{yy} < I_{xx} + I_{zz}$ showing that the cluster has an almost semi-spherical configuration. The cluster center of mass diffusion coefficient is very low and can not be measured inside our simulation time. For $T = 800$ K the cluster relaxes to a planar configuration forming a two-dimensional island on the surface such that $I_{yy} \approx I_{xx} + I_{zz}$. The cluster migrates across the surface without dissociation as shown by the snapshots presented in Fig. 11. We have calculated the cluster center of mass diffusion coefficient D for the substrate of size $L \approx 25$ Å by using the displacement correlation function [24]

$$\mathscr{C}(0,t) = \frac{1}{n_{\text{t}} \times N_{\text{conf}}} \sum_{\text{conf}} \sum_{i=1}^{n_{\text{t}}} \langle [r(0) - r(t)]^2 \rangle, \qquad (3)$$

$$D = \lim_{t \to \infty} \mathscr{C}(0,t)/2\,\mathrm{d}t. \qquad (4)$$

Here N_{conf} is the number of configurations in the simulation, n_{t} is the number of beams in the time average, d is the dimensionality of the space and $\langle (\vec{r}(0) - \vec{r}(t))^2 \rangle$ is the mean square displacement. In our simulation we have used $N_{\text{conf}} = 6$ and $n_{\text{t}} = 5$.

In the movement of single particles and small clusters on solid surfaces the behavior of the displacement correlation function for short and long time is well known [24–26]. For very short time (smaller than a few picoseconds) the particle moves ballistically. For long time the particle presents random trajectories that define their Brownian movement. In Fig. 10 we show $\ln(\mathscr{C}(0, t))$ as a function of $\ln(t)$ for the cluster center of mass. Its long time behavior shows that $\mathscr{C}(0,t) \sim t$ with the diffusion coefficient $D = 9 \times 10^{-7}$ cm^2/s which is smaller than that of a single particle on Cu(0 0 1) surface $D \sim 10^{-5}$ cm^2/s [27]. It means that in simulations and growth experiments the

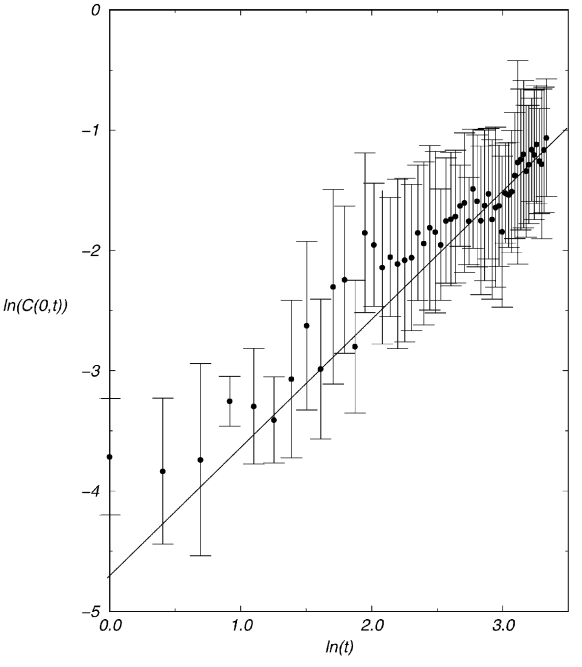

Fig. 10. Displacement correlation function (in units of Å^2) as a function of $\ln(t)$ (time in units of 10^{-12} s). Straight line is the linear fitting of the long time region and shows the Brownian regime. Substrate of size $L \approx 25$ Å and initially at $T = 800$ K.

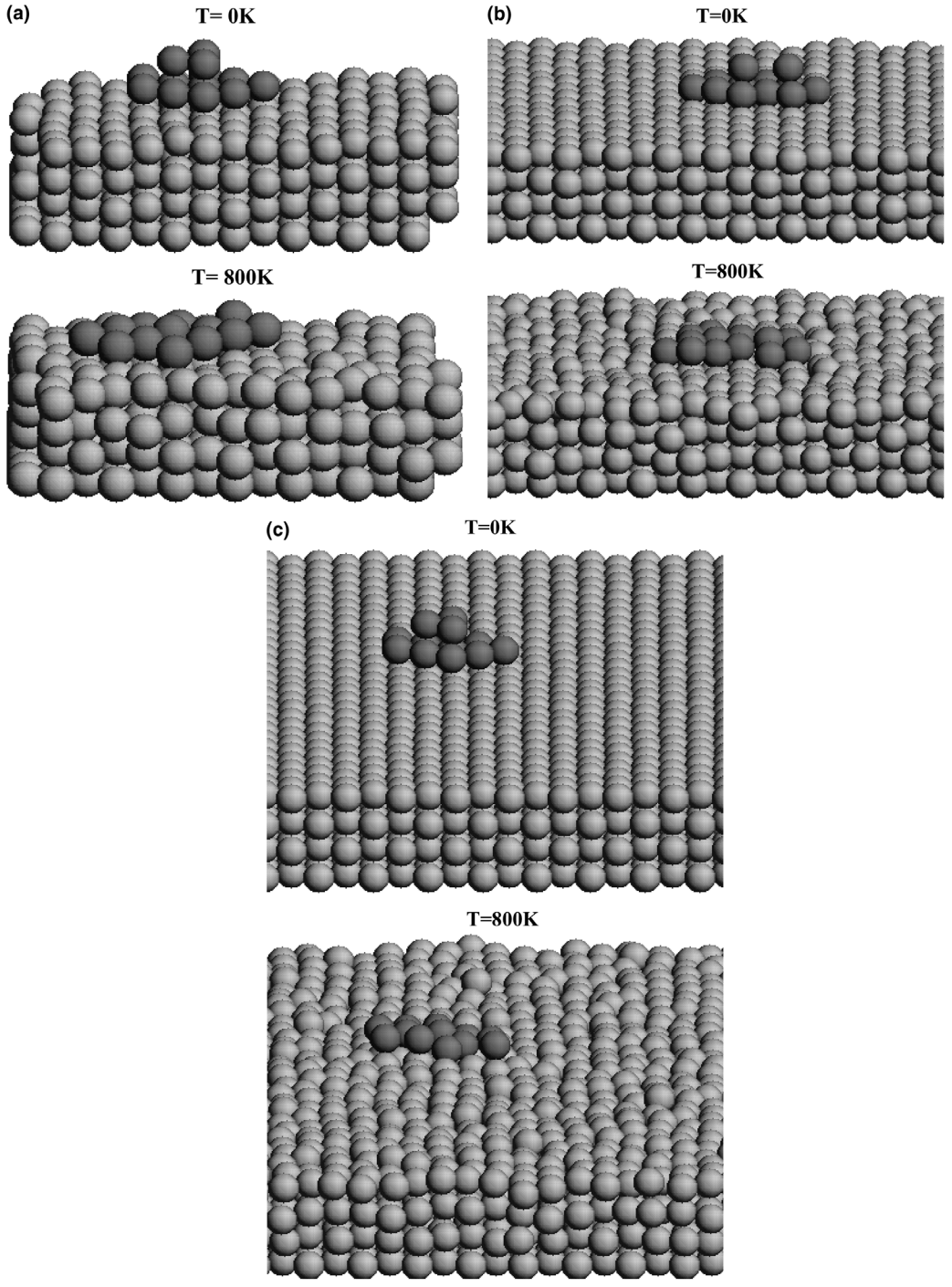

Fig. 11. Snapshots of the structure of Cu_{13} 150×10^{-12} s after deposition at temperatures of $T = 0$ K (top) and $T = 800$ K (bottom), (a) $L \approx 25$ Å, (b) $L \approx 50$ Å, (c) $L \approx 100$ Å.

individual particle diffusion is the most important relaxation mechanism.

In Fig. 11 we show snapshots of the cluster deposition over the surfaces for different temperatures and sizes after 150 ps. Following the movement of the cluster we observed that it maintains its integrity not losing particles while diffuses. Diffusion occurs due to the movement of individual atoms at the boundary of the cluster. The mechanism observed for diffusion was the simple hopping of the peripheral atoms, activated already at $T = 800$ K.

4. Conclusion and comments

In this paper we have studied the deposition of a Cu_{13} cluster on a Cu(0 1 0) surface. For this purpose we have used classical MD simulation for two different temperatures and three system sizes. The temperature region we studied is far below the melting temperature such that, we do not have to worry about effects due to large correlation lengths which appears even for first order phase transitions. We calculated the kinetic energy of the cluster and substrate, the degree of arrangement of the atoms on the system, the cluster inertia tensor, the mean height of the layers in the substrate and of the cluster center of mass. We found that the influence due to system size is quite small for the quantities we have calculated indicating that even a simulation using small systems can give reliable results and a qualitative description of the deposition phenomena. We also calculated the cluster center of mass diffusion coefficient on the surface at $T = 800$ K. Our results indicate that it is one decade smaller than the diffusion coefficient for individual particles. The diffusion mechanism observed was the simple hopping of the boundary atoms.

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