PHYSICAL REVIEW A **76**, 043201 (2007)

Shape dynamics during deposit of simple metal clusters on rare-gas matrices

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(Received 12 January 2007; published 2 October 2007)

Using a combined quantum-mechanical–classical method, we study the collisions of small Na clusters with large Ar clusters as a model for cluster deposition. We work out basic mechanisms by systematic variation of the collision energy, system sizes, and orientations. The soft Ar material is found to serve as an extremely efficient shock absorber. The collisional energy is quickly transferred at first impact, and the Na clusters are always captured by the Ar surface. The distribution of the collision energy into the Ar system proceeds very fast at the velocity of sound. The relaxation of shapes goes at a slower pace using times of several picoseconds. It produces a substantial rearrangement of the Ar system, while the Na cluster remains rather robust.

DOI: 10.1103/PhysRevA.76.043201 PACS number(s): 36.40.Gk, 36.40.Jn, 36.40.Qv, 36.40.Sx

I. INTRODUCTION

Clusters on surfaces have been much investigated during the past decade as can be seen, e.g., from the sequence of recent International Symposium on Small Particles and Inorganic Clusters (ISSPIC) proceedings [1–4]. The topic remains of great interest, especially in relation to the synthesis of nanostructured surfaces. A possible method here is the direct deposition of size-selected clusters on a substrate [5,6]. When deposited on a surface, a cluster undergoes a significant modification of its electronic structure and ionic geometry, because of the interface energy, the electronic band structure of the substrate, and the surface corrugation. These questions have been widely investigated from the structural point of view from both the experimental [7–9] and theoretical [10–17] sides. The theoretical description of deposition dynamics is nevertheless a very demanding task. A fully microscopic approach treating all atoms and electrons in detail is extremely involved and applicable only to very small samples if at all. Most theoretical descriptions thus employ simple molecular dynamics approaches with effective atom-atom forces. There are, however, situations where a detailed description of electronic degrees of freedom is desirable, for example when metal clusters are involved, where electronic shell effects are known to play a role in forming the structure.

A step forward is to combine a fully microscopical treatment of the cluster with a much simplified description of the surface. This is a valid and efficient compromise for inert substrates such as, e.g., for the deposition of a metal cluster on an insulator surface. Such an approach was explored, e.g., in the case of Na clusters on NaCl in [17,18], where density functional theory was used for the Na electrons coupled to the surface via an effective interface potential, itself tuned to *ab initio* calculations [13]. This approach, however, ignores any excitation and/or rearrangement of the surface itself, which supposes extremely inert materials. The next step is obviously to restore a minimum of surface degrees of freedom, still having an electronically inert substrate in mind. Such a model was recently developed for the case of Na clusters embedded in rare gases [19,21,25], where the cluster is again treated in full detail and the rare-gas atoms through classical dynamics of position and dipole polarization. Such a "hierarchical" approach is justified for electronically inert substrates. It has much in common with the coupled quantum-mechanical and molecular-mechanical method often used in biochemistry [22–24]. The now explicit, although simple, handling of substrate atoms still restricts calculations to finite systems. The model developed in [20,21,25], nevertheless, allows one to explore a sufficiently large range of sizes to see the appearance of generic behaviors on the way toward the bulk.

The goal of this paper is to study the dynamics of deposition of a small Na cluster on a finite model of an Ar surface. To that end, we consider Na_6, Na_7, or Na_8 clusters as projectiles on Ar_N clusters of various sizes (N between 7 and 87) as target. We analyze the kinetics of deposition in terms of the energy transfer between cluster and substrate, a point for which the explicit dynamical surface degrees of freedom are crucial. We shall also analyze the way in which the metal cluster adapts to the substrate and how the substrate gives way. This is done by tracking the evolution of the shapes of both partners during the deposition process and by varying the Ar cluster size as well as the initial kinetic energy. For this purpose we shall compare several small Na clusters with different shapes in the initial state. It should finally be noted that the considered setup (Na cluster on Ar_N) has two aspects. First, it is an example of cluster-cluster collisions involving partners of very different size and nature, and as such a topic with its own interest. Second, we have in mind an exploratory study of deposition on an Ar surface for which we consider large but finite systems, a method that has been used also in experimental studies (see, e.g., [26]). The widely used alternative is to simulate the infinite surface in terms of a small, but periodically copied, simulation box (see, e.g., [27]). This better allows us to include long-range effects but limits the structural rearrangement of the surface. Thus, modeling the surface by finite clusters is probably more appropriate for our intention of analyzing the shape dynamics.

The paper is organized as follows. Section II provides a short presentation of the model and of the systems considered in the test cases. In Sec. III, we analyze the deposition dynamics in terms of trends and energies. In Sec. IV, we discuss the shape dynamics in more detail.

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II. MODEL

As stated above, we use a hierarchical approach in which the metal cluster is treated in full microscopic detail while the surface is described at a classical level granting each atom mobility as a whole and a dynamical dipole response. This is justified by the clear hierarchy of electronic binding in metals vs rare gases. The many different ingredients make a complete description of the model rather bulky. We give here a short account of the approach and refer to [19,21] for a detailed layout.

The Na cluster is treated using quantum-mechanical single-particle wave functions $\{\varphi_n(\mathbf{r},t), n=1,\ldots,N_{\text{el}}\}$ for the valence electrons, coupled nonadiabatically to classical molecular dynamics (MD) for the positions of the Na ions $\{\mathbf{R}_I, I=1,\ldots,N_{\text{Na}}\}$. The electronic wave functions are propagated by the time-dependent local-density approximation (TDLDA). The electron-ion interaction in the cluster is described by soft, local pseudo-potentials. This TDLDA-MD method has been validated for linear and nonlinear dynamics of free metal clusters [28,29].

Two classical degrees of freedom are associated with each Ar atom: the center of mass $\{\mathbf{R}_a, a=1,\ldots,N_{\text{Ar}}\}$, and the electrical dipole moment $\{\mathbf{d}_a, a=1,\ldots,N_{\text{Ar}}\}$. With the atomic dipoles, we explicitly treat the dynamical polarizability of the atoms through polarization potentials [30]. Smooth, Gaussian charge distributions are used for Ar ionic cores and electron clouds in order to regularize the singular dipole interaction. The Na^+ ions of the metal cluster interact with the Ar dipoles predominantly by their charge. The small dipole polarizability of the Na^+ core is neglected. The cluster electrons do also couple naturally to the Coulomb field generated by the atoms.

The polarization potentials describe the long-range Coulomb part of the interactions. It remains to account for the short-range repulsion. The repulsive Na^+-Ar potential is taken from [31]. The pseudopotential for the electron–Ar-core repulsion has been modeled in the form of [32], slightly readjusted by a final fine-tuning to the NaAr molecule (bond length, binding energy, and optical excitation). For the atom-atom interactions, we use a standard Lennard-Jones potential. A van der Waals interaction is added, computed via the variance of dipole operators [19,21,32]. It provides a contribution to the long-range interaction which is crucial to produce the faint binding of the ground states for small Na-Ar systems. Its dynamical effects stay merely at a quantitative level.

We use standard methods [29] for the numerical solutions. We solve the (time-dependent) Kohn-Sham equations for the cluster electrons on a grid in coordinate space, using time splitting for the time propagation and accelerated gradient iterations for the stationary solution. In the present calculations, we furthermore use the cylindrically averaged pseudo-potential scheme as an approximation for the electronic wave functions [33,34]. Both the Na ions as well as the Ar cores and valence clouds are treated by classical molecular dynamics in full three dimensions (3D). We have checked that a full 3D treatment of the electronic wave functions leads to similar results for the chosen systems, which all stay close to axial symmetry.

TABLE I. Bond energies of dimers entering the calculations discussed in the text.

System	Na-Na dimer	Bulk Ar-Ar	Na-Ar dimer
Bond energy	800 meV	50 meV	5 meV

Table I shows the binding energies for the three possible dimer combinations. There is a clear hierarchy of binding, where the Na cluster is most strongly bound, the Ar cluster one order of magnitude less strongly bound, and the Na-Ar binding another order of magnitude smaller. This leads us to expect a fragile attachment of the two clusters to each other, while the clusters as such remain intact with some readjustment of shape, particularly at the Ar site.

Three Ar clusters of different sizes are used as "substrate," Ar_7, Ar_{43}, and Ar_{87}. The structures of these clusters are optimized for the given model by simulated annealing. The collision partners are various Na clusters taken in their ground-state structures, again obtained by simulated annealing but this time coupled to static Kohn-Sham iterations for the electrons. Most of the results presented below have been obtained for the strongly oblate Na_6 cluster, composed of a ring of five ions and an outer ion, as can be seen from Fig. 1. The top configuration refers to the case where the pentagon hits the Ar cluster first. The reverse configuration corresponds to a Na_6 cluster upside down. We also consider a few other clusters of comparable size but different shapes, especially Na_7 and Na_8. In Na_7, the central pentagon is complemented by one top and, symmetrically, one bottom ion, which altogether delivers a much less oblate shape than Na_6. The Na_8 cluster, in turn, is built as two layers of four ions. Note that it is electronically close to sphericity because it contains the magic number of eight electrons. And indeed, the shape of free Na_8 is, as far as it can be for a small finite cluster, close to spherical. In all cases, we take care of orienting the Ar_N relative to Na_6 in such a way that it presents to the Na cluster the largest possible planar surface. This can be seen in Fig. 1 where the initial configurations for the collisions between Na_6 and Ar_7, Ar_{43}, and Ar_{87} are displayed: The metal cluster initially faces respectively one, five, and

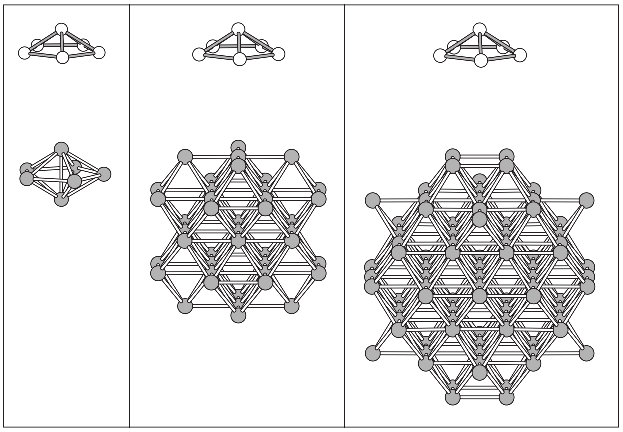

FIG. 1. Initial configurations for the deposition of Na_6 (white balls) on Ar_7 (left), Ar_{43} (middle), and Ar_{87} (right).

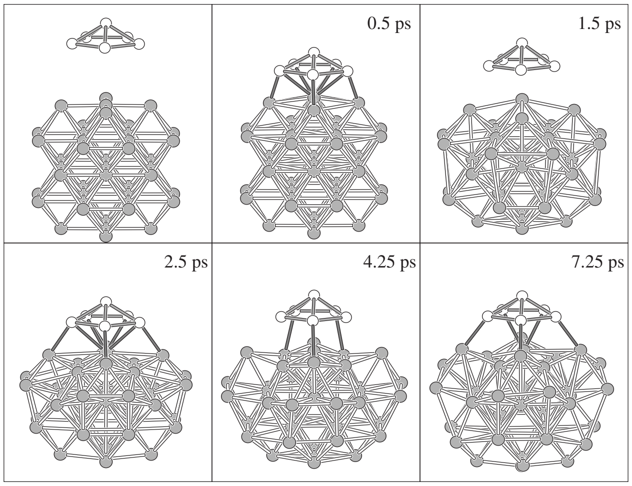

FIG. 2. Snapshots of the deposition of Na_6 on a planar site of Ar_{43}, with an initial kinetic energy of 13.6 meV/ion. Time slots are indicated on each panel.

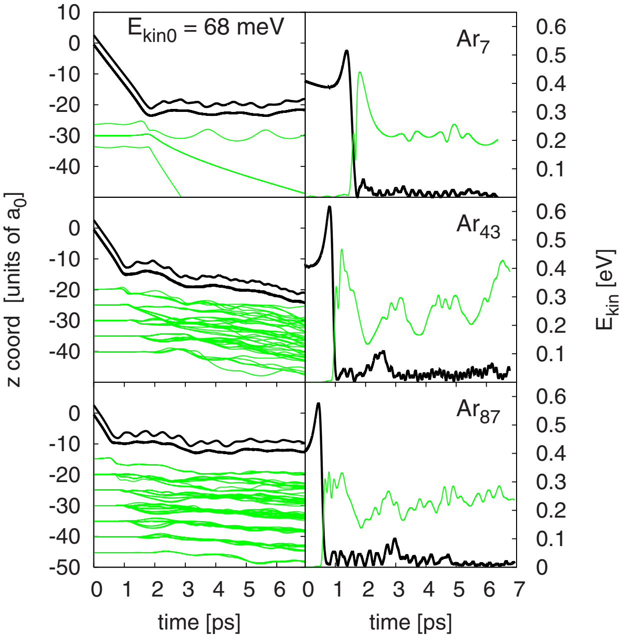

FIG. 3. (Color online) Collision of Na_6 (thick lines) with an initial kinetic energy of 68 meV/ion, on Ar_N (thin curves) for $N=7$ (top), 43 (middle), and 87 (bottom). Left panels, z coordinates; right panels, total kinetic energies, as a function of time.

four Ar atoms. Note that, in the largest system, the top Na ion starts above an interstitial position, whereas it is initially placed above an Ar atom in the two other cases.

The dynamics is started by giving the system a relative boost, with a substrate at 0 K temperature. We have studied the effect of substrate temperature up to 50 K. No significant differences are observed where the deposition mechanisms and associated energy transfers are concerned, although the highest temperature represents a thermal energy of the same order of magnitude (about a factor 2–3 smaller) as the kinetic energy in Na. This shows that relevant effects are primarily of potential nature, especially the balance between short-range (Ar core) repulsion and long-range (Ar polarizability) attraction, both aspects well taken into account in our model. Note also that, experimentally, deposition of metal clusters on rare-gas substrates are performed at very low temperature (typically below 25 K) [35,36]. Using just 0 K temperature is thus fully sufficient for the present aim of a qualitative study.

III. ANALYSIS OF DEPOSITION MECHANISM

A. A visual example

We first consider in Fig. 2 a typical deposition scenario for the example of Na_6 on Ar_{43} with initial kinetic energy $E_{\text{kin0}}=13.6$ meV per Na atom. The Na_6 cluster is accelerated when it comes closer to the Ar cluster, a long-range polarization effect that is counterbalanced by the core repulsion only at very short distance. The pinning process proceeds stepwise with several bounces before the metal cluster is finally attached to the rare-gas cluster. The overall shape of the Na cluster remains basically unchanged while the Ar cluster is somewhat rearranged, as was expected from the relative binding energies in Table I. It should be noted that the initial kinetic energy per atom of the impinging cluster is smaller than the bonding energies of both Na_2 and Ar_2 dimers, but about 2.5 times larger than the binding energy of the NaAr dimer. Not surprisingly, neither pure Na nor pure Ar bonds are broken, but in spite of the faintness of the NaAr bond one observes asymptotic stitching. This implies that an efficient kinetic energy transfer has taken place to cool down the Na-Ar interface, the excess kinetic energy being transferred to the internal energy (potential and heat) of the Ar and/or Na clusters. A part of the potential energy is visibly used to reshape the Ar surface, in order to provide a more convenient contact plane for the Na_6 cluster (see late times in the figure). The energy transfer mechanisms may *a priori* depend both on the initial kinetic energy and on the Ar cluster size. This will be analyzed in the coming sections.

B. Systematics on Ar cluster size

We now turn to the question of the influence of the Ar cluster size and its heat capacity on the deposition process. Figure 3 shows results for Na_6 deposited on various Ar clusters all for the same initial kinetic energy of $E_{\text{kin0}}=68$ meV per Na atom. The separation between the centers of mass of the two clusters is initially $30a_0$ for all systems. The left panels show the detailed z coordinates (symmetry axis and direction of collision) for Na ions and Ar atoms. It is obvious that, at this projectile energy, the Ar_7 cluster is broken into pieces after the impact, while both Ar_{43} and Ar_{87} are massive enough to resist the impact. Thereby the smaller Ar_{43} is visibly more perturbed (molten?) while the heaviest sample Ar_{87} even maintains its shell structure. The kinetic energies shown in the right panels explain that trend. Almost the same total kinetic energy of about 0.3 eV is transferred in all three cases, independent of the Ar_N size. Distributing that equally over the Ar atoms associates a typical temperature to the Ar cluster of about 200 K for Ar_7, 30 K for Ar_{43}, and 10 K for Ar_{87}, which fits well with the observation of breakup, melting, and stability. The largest sample thus serves as a reasonable model for deposition on a surface in this exploratory study. However, true bulk is, of course, thermally very inert due to its large calorific capacity and one would expect even smaller values of temperature in the case of bulk deposition under the same kinematic conditions.

A closer look at the kinetic energies in Fig. 3 shows a few interesting differences. The common feature is an initial energy transfer which leaves about half of the initial energy, i.e., around 0.3 eV, as kinetic energy in the Ar and very little kinetic energy for the Na cluster. The other half is invested in potential energy to provide the large spatial rearrangements. Differences are seen in further evolution. For Ar_7 all rearrangement is finished after the initial encounter and the kinetic energies remain unchanged later on. The severe perturbation of the medium-sized Ar_{43} leads to ongoing rearrangements with long-lasting exchange between the potential and kinetic energy of the Ar cluster. As a side effect, there occurs also some re-heating of the Na_6 cluster. Smaller reflow of potential into kinetic energy is seen for the heaviest Ar_{87}.

Figure 3 also spans very different time scales. The energy transfer at the moment of impact is surprisingly fast. The Na kinetic energy is fully given up within less than 0.5 ps and the energy distribution within the Ar cluster proceeds as a sound wave. This can be seen from the z coordinates of the Ar atoms in the left panels below 2 ps. The perturbation propagates as a straight line through the Ar layers with a speed of $(20-30)a_0/\mathrm{ps}$. Long time scales, on the other hand, remain for the final relaxation processes. The successfully captured Na_6 cluster continues to bounce and oscillate with a relaxation rate of the order of 10 ps. The fine-tuning of the Ar cluster shape seems to proceed at a similar slow scale. Note, however, that this shape evolution, initiated by the sound wave, might differ for an infinite substrate where the sound wave would dissolve into deep layers. In the small finite systems here, the wave is dissipated by diffuse scattering from the opposite surfaces of the Ar cluster which turns collective energy into heat. A large part of the Ar kinetic energy seen in Fig. 3 thus becomes thermal energy. The case of the largest Ar cluster, Ar_{87}, is somewhat different. It presents cleaner surfaces as compared to smaller clusters and it shows a faint reverberation of the wave when the latter reaches the edge of the cluster, as is observed in the lower left panel of Fig. 3. The reflected wave bounces back with almost the same velocity to the side which was hit initially. There it returns some momentum to the Na_6, as can be seen in the small revival of its kinetic energy at about 3 ps (lower right panel). This reverbation is, of course, due to the finite size of Ar_{87} and would not appear in the case of an infinite substrate. Nevertheless, from the metal cluster point of view, this reflection seems to change very little its final shape and distance to the Ar surface. In that sense, this system still mimics the gross features of deposition on an infinite surface.

C. Systematics on initial kinetic energy

It is expected that the deposition depends on the velocity of the projectile. We analyze this effect in the case of Na_6 deposition on Ar_{87}, with varying E_{kin0}. Results are plotted in Fig. 4 for E_{kin0} between 6.8 and 136 meV per Na atom. The striking feature is the overall similarity of all the different cases. This concerns in particular the very fast and almost complete energy transfer from the Na kinetic energy to the other degrees of freedom. A common feature is also the quick capture of the Na cluster and its long-standing residual oscillations. Of course, details of the scenarios differ from one case to the next. The perturbation of the Ar cluster increases naturally with increasing initial energy. There is also an interesting effect at initial times. The kinetic energy of the Na cluster first increases before contact. That is due to the medium-range polarization interaction, which is attractive. The additional acceleration depends on the initial velocity. More energy is gained for the slower velocities because the cluster moves for a longer time in the attractive regime. Thus the kinetic energy is almost quadrupled for the lowest $E_{\mathrm{kin0}} = 6.8$ meV, while only 10% effect is left over for the fastest collision here. In addition to these subtle differences in detail, the energy deposit proceeds in all cases in the same way, namely, in an extremely quick fashion, leaving basically no residual kinetic energy at the side of the Na cluster projectile. One thus finds that, in a relatively large range of projectile kinetic energies, the Na projectile is glued to the Ar target. Except again for oscillations in the most energetic case, the overall structure and position (with respect to the Ar target) of the deposited Na_6 seem to depend very little on the initial energy.

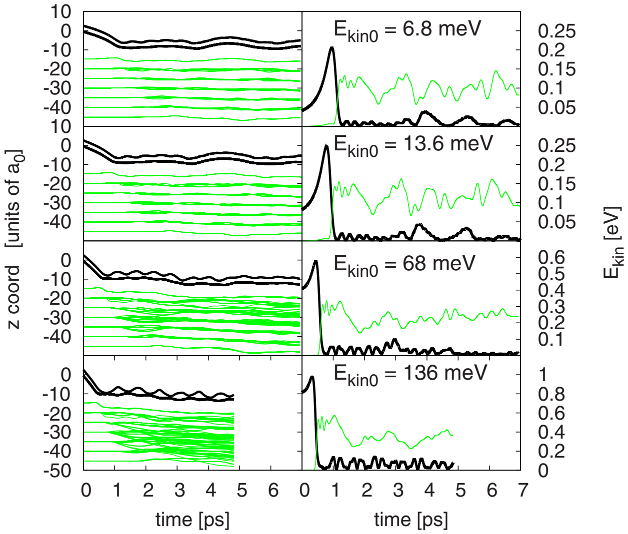

FIG. 4. (Color online) z coordinates (left) and total kinetic energies (right), as a function of time, in the collision of Na_6 (thick curves) with Ar_{87} (thin curves), for four different initial kinetic energies E_{kin0}.

IV. TIME EVOLUTION OF SHAPES

A. Cluster distance

The above calculations show that the relaxation times of the whole deposition process goes beyond times we can reasonably simulate. However, we have seen from Figs. 3 and 4

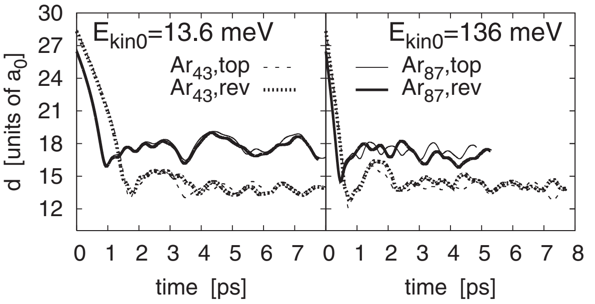

FIG. 5. Deposition coordinate d, defined in Eq. (1), as a function of time, for $Na_6@Ar_{43}$ (dots and dashes) and $Na_6@Ar_{87}$ (full lines), with $E_{kin0}=13.6$ (left panel) and 136 meV/ion (right panel). Results in both systems are presented for the top (dashes and thin curve) and the reverse (dots and thick curve) configuration of the Na_6.

that around 6–7 ps the kinetic energy of the Ar cluster and the cluster distance seem to reach a constant mean value. The closeness of the two clusters can be quantified in terms of a "deposition coordinate" d that we define as

$$d=\left(\frac{1}{N_{\mathrm{Na}}N_{\mathrm{Ar}}}\sum_{I,a}\frac{1}{|\mathbf{R}_I-\mathbf{R}_a|^4}\right)^{-1/4}, \qquad (1)$$

where the index I (a) refers to the Na ion (Ar atom) cores and $\mathbf{R}_I$ ($\mathbf{R}_a$) to its position. The inverse dependence puts weight on the closest partners. The actual power 4 in Eq. (1) is a matter of decision: we calculated with powers $n=1$ up to $n=7$ and found that $n=4$ provides a good compromise between averaging and details.

Figure 5 shows the coordinate d for two different sizes of the Ar clusters and for two different E_{kin0}, i.e., initial Na kinetic energies per ion. The patterns are surprisingly similar for both energies and also similar for both sizes. The Na cluster is caught at first impact. There remain some oscillations at a distance of about $(2-3)a_0$, which relax very slowly (on the order of 10 ps). There is a global difference to the extent that the distance is closer for $Na_6@Ar_{43}$. This is due to the larger rearrangements in that case which, in turn, provide a better contact area for the Na_6.

We have also varied the orientation of the Na cluster. The standard configuration for Na_6 was such that the ring of five Na ions stood closer to the surface while the top ion was pointing away (the situation denoted as "top" in the figure). Within axial symmetry, there is also the reverse situation where the top ion is facing toward the surface (denoted "rev" in the figure). The results for reverse initial configurations are also shown in Fig. 5. They are almost indistinguishable from those for the top configuration. This indicates that the Na_6 remains basically unchanged in all cases. This will be corroborated in the next section studying shape dynamics.

B. Global moments

The results discussed up to now indicate that there may be substantial rearrangements of the Ar substrate. Less is yet known about the shape of the Na cluster: do we have a soft landing, some plastic deformation, or a wetting behavior? In order to quantify these questions we have performed a shape analysis in terms of the first three multipole moments for both Na_6 and Ar_N. These moments are given by

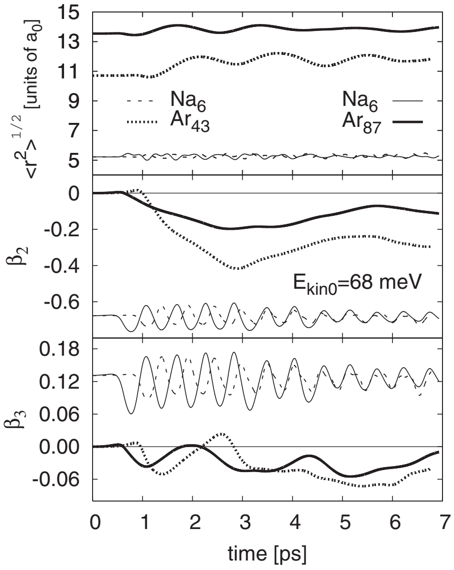

FIG. 6. Three first multipole moments $\sqrt{\langle r^2\rangle}$, β_2, and β_3, as functions of time, for Na_6 (thin dashes and lines) deposited on Ar_{43} (thick dots) and Ar_{87} (thick full lines) for $E_{\mathrm{kin0}}=68$ meV/ion.

$$\sqrt{\langle r^2\rangle}=\sqrt{\langle x^2+y^2+z^2\rangle}=\left(\frac{1}{p}\sum_{i=1}^{p}(x_i{}^2+y_i{}^2+z_i{}^2)\right)^{1/2},$$

$$\beta_2=\sqrt{\frac{\pi}{5}}\frac{1}{\langle r^2\rangle}\langle 2z^2-x^2-y^2\rangle,$$

$$\beta_3=\left(\frac{2}{5\langle r^2\rangle}\right)^{3/2}\left\langle z\left(z^2-\frac{3}{2}(x^2+y^2)\right)\right\rangle,$$

where p is either the number of Na atoms N_{Na} or the number of Ar atoms N_{Ar}, and x, y, and z are the coordinates of the Na (Ar) atom with respect to the center of mass of the Na (Ar) cluster. The rms radius r stands for the overall extension (monopole moment) and the deformations are parametrized as dimensionless quantities which have immediate geometrical meaning independent of system size. For example, a value of $|\beta_2|\approx 0.8$ is a large quadrupole deformation with axis ratio of about 2:1.

Figure 6 shows the three moments for the Na and Ar subsystem in the cases $Na_6@Ar_{43}$ and $Na_6@Ar_{87}$ for the moderate initial kinetic energy $E_{\mathrm{kin0}}=68$ meV per Na ion. The shape of Na_6 is rather rigid in any case. There are some deformation oscillations shortly after impact which relax within about 3 ps. These oscillations are predominantly caused by the outer ion. The ring is tightly bound and stays more robust. Note that the relaxation is much faster than for the overall bouncing oscillations of the cluster (see Fig. 5). That is related to the binding properties shown in Table I, that is, the NaAr binding is softer. The Ar clusters, after the impact with Na_6, increase slightly in size due to heating by energy absorption. The growth is larger for the smaller Ar_{43}

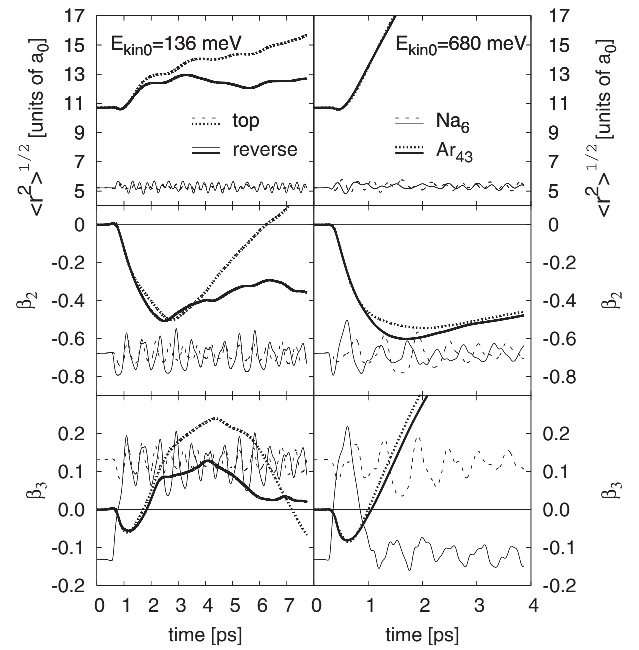

FIG. 7. Three first multipole moments, as a function of time, for Na_6 (thin curves) deposited on Ar_{43} (thick curves), with $E_{kin0}=136$ (left) and 680 meV/ion (right). On each panel are compared the moments obtained from the top (dots and dashes) and reverse (full lines) configurations.

which acquires a higher temperature as discussed above. The Ar clusters do also undergo a strong persistent change in deformation toward a sizably oblate and somewhat pearlike shape. They obviously accommodate their configuration as to establish a most compact combined system.

For the case of Na_6@Ar_{43}, the effects of initial kinetic energy and orientation (Na cluster in "top" or "rev" configuration; see Sec. IV A) are shown in Fig. 7. For the large $E_{kin0}=680$ meV/ion (right panels), the Ar_{43} rapidly emits several atoms, thus yielding a rapidly increasing radius and octupole moment, while a more moderate evolution emerges for the less violent $E_{kin0}=136$ meV/ion. The collision with the Na_6 top configuration is more violent because the whole ring bounces first and at once. This gives rise to an even higher Ar deformation for both initial energies. However, for Na_6, the mean value and amplitude of the shape oscillations are similar in all cases, for both configurations and for both E_{kin0}. Note the change of sign of β_3 for the reverse configuration. This indicates that the outer ion oscillates through the pentagon, within the given time once for $E_{kin0}=136$ meV and twice at 680 meV. But the other two moments stay very robust in spite of the violent collision with the Ar_{43} subsystem.

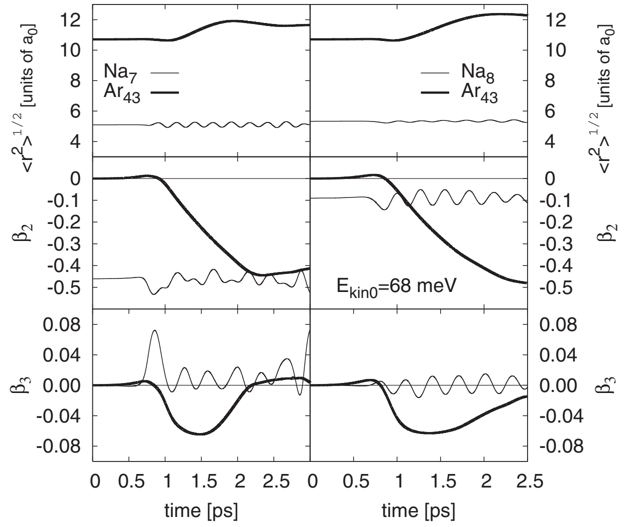

FIG. 8. Three multipole moments, as a function of time, for Na_7 (thin curves, left panels) and Na_8 (thin curves, right panel) deposited on Ar_{43} (thick curves), with $E_{kin0}=68$ meV/ion.

C. Wetting behavior: Comparison with Na_7 and Na_8

We thus find that Na_6 is very robust under any conditions when deposited on the rather soft Ar material. It maintains its oblate shape and overall radius. The top ion is more loosely bound and may undergo larger oscillations, which become apparent in the octupole momentum. The results for Na_6 thus suggest that wetting of the surface is rather unlikely in that combination of materials. However, Na_6 is not a very conclusive test case as it has already a close to planar structure. One ion still sticking out of the surface plane is not very dramatic. In order to countercheck, we considered two neighboring clusters, namely, Na_7 (less oblate than Na_6) and the almost spherical Na_8. The results for the multipole moments are shown in Fig. 8. They are very similar to what we have seen already for collisions with Na_6. The Na_7 or Na_8 clusters basically maintain their shapes while the Ar basis undergoes a substantial rearrangement to create space for landing. There is not the slightest hint of a wetting. There are, of course, small shape oscillations in the Na clusters due to the internal excitation at the time of impact. It is interesting to note that these oscillations differ in detail between the two clusters. Na_8 with its magic electron number eight seems to be more rigid and shows generally a smaller oscillation amplitude.

V. CONCLUSIONS

In this paper we have investigated slow collisions of a small Na cluster with a large Ar cluster as a test case for deposition on an Ar surface. To that end, we have employed a hierarchical model treating the Na cluster in full detail by time-dependent density-functional theory and the Ar atoms at a thoroughly classical level with position and polarization as dynamical variables. We have studied in detail the influence of various parameters on the deposition scenario, namely, initial collision energy, Ar cluster size, and relative orientation of the Na cluster.

We have found that, except for the case of the smallest Ar system, the basic scenario is robust in the sense that it depends very little on the collision parameters. The Na clusters are well bound, while Ar binding is much softer and the Na-Ar binding even less. As a consequence, the Ar substrate constitutes a very efficient shock absorber. The impinging Na cluster is stopped immediately at first impact and attached to the Ar system, while the latter takes over practically all the initial Na energy. It seems impossible to tune conditions under which the Na cluster is reflected. Enhancing the initial energy rather leads to destruction of the Ar system. The initial large energy transfer from the Na cluster to the Ar system is very quick, taking less than 0.5 ps. The transferred energy is distributed also very quickly over all Ar atoms, propagating like a shock wave with the speed of sound through the medium. About half of the energy goes into potential energy and part of it is used up for a large spatial rearrangement of the Ar cluster, which aims to provide the most compact combined system. These rearrangements proceed on a slower time scale of 4–10 ps. We have observed that in all cases the shape of the Na cluster is little affected by the dynamical processes during deposition. It always safely attaches to the surface but is only loosely bound and keeps nearly its free shape. The interface interaction is too weak to induce a wetting mechanism for this material combination.

Calculations with larger clusters and planar surfaces for the same combination confirm the above findings. It is now most interesting to check other combinations of materials. Work in that direction is in progress.

ACKNOWLEDGMENTS

This work was supported by the DFG, Project No. RE 322/10-1, the French-German exchange program PROCOPE Grant No. 04670PG, the CNRS Program “Matériaux” (CPR-ISMIR), the Institut Universitaire de France, and the Humbodlt Foundation, and has benefited from the Calmip (CAlcul en MIdi-Pyrénées) computational facilities.

[1] *Proceedings of ISSPIC9, Lausanne, 1998*, edited by U. Landmann [Eur. Phys. J. D 9 (1999)].

[2] *Proceedings of ISSPIC10, Atlanta, 2000*, edited by I. Hertel [Eur. Phys. J. D 16 (2001)].

[3] *Proceedings of ISSPIC11, Strasbourg, 2002*, edited by C. Bréchignac and Ph. Cahuzac [Eur. Phys. J. D 24 (2003)].

[4] *Proceedings of ISSPIC12, Nanjing, 2004*, edited by G. Wang [Eur. Phys. J. D 34 (2005)].

[5] C. Binns, Surf. Sci. Rep. **44**, 1 (2001).

[6] W. Harbich, in *Metal Clusters at Surfaces, Structures*, edited by K. H. Meiwes-Broer (Springer, Berlin, 2000).

[7] Y. Z. Li, R. Reifenberger, and R. P. Andres, Surf. Sci. **250**, 1 (1991).

[8] D. M. Schaefer, A. Patil, R. P. Andres, and R. Reifenberger, Phys. Rev. B **51**, 5322 (1995).

[9] Ch. Kuhrt and M. Harsdorff, Surf. Sci. **245**, 252 (1995).

[10] G. Rajagopal, R. N. Barnett, and U. Landman, Phys. Rev. Lett. **67**, 727 (1991).

[11] H. P. Cheng and U. Landmann, Science **260**, 1304 (1991).

[12] H. Häkkinen, R. N. Barnett, and U. Landmann, Europhys. Lett. **28**, 263 (1994).

[13] H. Häkkinen and M. Manninen, Europhys. Lett. **34**, 177 (1996).

[14] C. Kohl and P.-G. Reinhard, Z. Phys. D: At., Mol. Clusters **38**, 81 (1996).

[15] C. Kohl and P.-G. Reinhard, Z. Phys. D: At., Mol. Clusters **39**, 225 (1997).

[16] C. Kohl, E. Suraud, and P.-G. Reinhard, Eur. Phys. J. D **11**, 115 (2000).

[17] A. Ipatov, E. Suraud, and P.-G. Reinhard, Int. J. Mol. Sci. **4**, 301 (2003).

[18] A. Ipatov, P.-G. Reinhard, and E. Suraud, Eur. Phys. J. D **30**, 65 (2004).

[19] B. Gervais, E. Giglio, E. Jacquet, A. Ipatov, P.-G. Reinhard, and E. Suraud, J. Chem. Phys. **121**, 8466 (2004).

[20] F. Fehrer, P.-G. Reinhard, E. Suraud, E. Giglio, B. Gervais, and A. Ipatov, Appl. Phys. A: Mater. Sci. Process. **82**, 151 (2005).

[21] F. Fehrer, M. Mundt, P.-G. Reinhard, and E. Suraud, Ann. Phys. **14**, 411 (2005).

[22] M. J. Field, P. A. Bash, and M. Karplus, J. Comput. Chem. **11**, 700 (1990).

[23] J. Gao, Acc. Chem. Res. **29**, 298 (1996).

[24] N. Gresh and D. R. Garmer, J. Comput. Chem. **17**, 1481 (1996).

[25] F. Fehrer, P.-G. Reinhard, and E. Suraud, Appl. Phys. A: Mater. Sci. Process. **82**, 145 (2005).

[26] U. Buck and R. Krohne, Phys. Rev. Lett. **73**, 947 (1994).

[27] C. Xirouchaki and R. E. Palmer, Vacuum **66**, 167 (2002).

[28] P.-G. Reinhard and E. Suraud, *Introduction to Cluster Dynamics* (Wiley, New York, 2003).

[29] F. Calvayrac, P.-G. Reinhard, E. Suraud, and C. A. Ullrich, Phys. Rep. **337**, 493 (2000).

[30] B. G. Dick and A. W. Overhauser, Phys. Rev. **112**, 90 (1958).

[31] G. Reza Ahmadi, J. Almlöf, and J. Roegen, Chem. Phys. **199**, 33 (1995).

[32] F. Duplàe and F. Spiegelmann, J. Chem. Phys. **105**, 1492 (1996).

[33] B. Montag and P.-G. Reinhard, Phys. Lett. A **193**, 380 (1994).

[34] B. Montag and P.-G. Reinhard, Z. Phys. D: At., Mol. Clusters **33**, 265 (1995).

[35] J. T. Lau, W. Wurth, H.-U. Ehrke, and A. Achleitner, Low Temp. Phys. **29**, 223 (2003).

[36] F. Conus, J. T. Lau, V. Rodrigues, and C. Félix, Rev. Sci. Instrum. **77**, 113103 (2006).