Dynamics of Na clusters in/on insulating substrates

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Abstract. We apply a hierarchical model for Na clusters in/on insulating substrate (Ar or MgO) to explore three different regimes of cluster dynamics. The effect of the interface is scrutinized for optical response of Na₈ embedded in Ar matrix and deposited on MgO(001) surface. The different mechanical properties of Ar and MgO surface are explored in studying the collision with a Na₆ cluster at different initial energies. The stabilization of highly charged Na clusters through a substrate is discussed for strong laser ionization of Na₈ in Ar matrix and on MgO surface.

1. Introduction
The impressive progress of laser physics has motivated research on the dynamics of clusters exposed to strong perturbations, see e.g. [1]. Practically, a great deal of cluster research is done for clusters in contact with a substrate, deposited or embedded, see e.g. [2–4]. Most of these studies are concerned with the details of structure and chemical bonding. Highly excited dynamics of embedded or deposited clusters is still at the edge of present days possibilities, in particular from the theoretical side. The challenge is to describe large substrate systems together with the quantum dynamical details of an electronically active, but small, subsystem. For such situations, hierarchical approaches have been developed called quantum-mechanical molecular-mechanical modeling (QM/MM) [5–8]. These have been recently implemented for metal clusters in contact with electronically inert substrates [9–11]. We will report here a few selected applications of the QM/MM modeling for Na cluster with Ar or MgO substrate to cluster dynamics: the effect of the interface on optical response, the dynamics of cluster deposition, and (hindered) Coulomb explosion of a cluster which is highly charged by a strong laser pulse.

2. Formal framework
The hierarchical QM/MM model has been described in detail elsewhere, for MgO substrate in [11, 12] and for Ar substrate in [9, 13, 14], for a recent review see [15]. Here we give a brief summary.

The constituents of the Na cluster and their degrees of freedom are: \( \varphi_n(\vec{r}, t) \), \( n = 1...N_{el} \) for the valence electrons of the Na cluster, and the positions of the Na⁺ ions. The Na cluster is treated in by time-dependent local-density approximation with molecular dynamics (TDLDA-MD), the valence electrons quantum-mechanically and the ions classically [16, 17]. The MgO
substrate is composed of two species, Mg$^{2+}$ cations and O$^{2-}$ anions with the degrees of freedom: $\vec{R}_{i(c)}$, $i(c) = 1...M$ for the positions of the O cores, $\vec{R}_{i(v)}$, $i(v) = 1...M$ for the centers of the O valence clouds, $\vec{R}_{i(k)}$, $i(k) = 1...M$ for the positions of the Mg$^{2+}$ ions. The cations are electrically inert and are modeled as charged point particles. The anions are easily polarizable which is accounted for by associating to it two constituents: A valence electron distribution and the complementing core. All parts of the MgO substrate are described as classical degrees of freedom. The difference $\vec{R}_{i(c)} - \vec{R}_{i(v)}$ describes the electrical dipole moment of an O$^{2-}$ anion. The Mg and O ions are arranged in crystalline order corresponding to bulk MgO. The dynamical degrees of freedom for Mg and O are taken into account in an active cell of the MgO(001) surface region underneath the Na cluster. The active cell is embedded in an “outer region” of MgO material where only ions are kept fixed, while oxygen dipoles remain fully dynamical. Beyond that region, only the Madelung potential is considered. The effect of the outer region on the active part is given by a time-independent shell-model potential taken over from [18]. The Ar substrate is composed of only once species, neutral Ar atoms, each of which being characterized by its position and dipole moment (exactly as O$^{2-}$ anions).

The atomic dipoles allow to explicitly treat the dynamical polarizability of the atoms through polarization potentials [19], which are the dominant agents at long range. The dipole parameters are adjusted to reproduce the dynamical polarizability of the material at low frequencies. The short-range repulsion between the constituents is obtained by adding especially constructed local core potentials. In case of Ar, the Van-der-Waals interaction is also accounted for in an approximate way [13].

The modeling for the case of Ar substrate was developed and tested first in [20] and its TDLDA extension in [9]. The QM/MM model for MgO substrate was developed first for noble metal ad-atoms and clusters [21–24] and has been extended to alkaline clusters in [11].

3. Results and discussion
3.1. A word on cluster structure
The ionic structures of free Na$_6$ and Na$_8$ are illustrated in figure 1. Na$_6$ has fivefold symmetry, consisting out of a ring of 5 ions plus one ion at the symmetry axis on top of the ring. Na$_8$ is a highly symmetric configuration consisting out of two rings of 4 ions each twisted relative to each other by 45° to minimize Coulomb energy.

Various substrates are considered. The MgO(001) substrate consists of six layers each containing 784 Mg$^{2+}$ ions and 784 O$^{2-}$ ions. The ions in the lowest layer are fixed to prevent it from relaxing and forming an artificial second surface. The active cell consists of three layers, each containing square arrangements of 242 Mg$^{2+}$ cations and 242 O$^{2-}$ anions [11, 12]. The Ar(001) substrate is built from layers of 8×8 Ar atoms. These plaquettes are copied periodically in lateral direction to simulate a planar surface. Six layers are used if not explicitly quoted differently. Embedding in Ar matrix is simulated by using a large Ar cluster at whose center a cavity is carved by removing 13 Ar atoms [13]. We will consider here Ar$_{164}$ and Ar$_{434}$ surroundings.
3.2. Optical response
Figure 2 shows the dipole strengths for Na\textsubscript{8} in various configurations. The right panel

demonstrates the effect of embedding in an Ar matrix for the mode along \(z\)-direction (symmetry axis). All spectra exhibit a clean Mie plasmon peak with only little strength left at other places. The surprising fact is that the average resonance position changes only very little by the embedding (compare blue with black line). We have also computed the average peak frequency by switching off the polarization potentials, thus leaving only the effect of short range repulsion (red thin line) which causes a strong blue shift. This large shift is almost perfectly counterweighted by the attractive effect of dynamical polarization of the medium. The balance can change a little bit when considering substrates of heavier rare-gases with their larger polarizabilities [25].

The left panel of figure 2 shows the effect of deposition on MgO. The modes horizontal to the surface (upper left panel) show only moderate changes. There is a slight red shift of the average resonance peak and a spectral fragmentation because one 1\textit{ph} state is coming close to the resonance. The net red shift emerges from the fact that there is only a small core repulsion in horizontal direction (coming from surface corrugation). The vertical mode is heavily perturbed by fragmentation over several 1\textit{ph} states. This is caused by symmetry breaking which enables coupling of the negative-parity dipole mode to the swamp of 1\textit{ph} modes with even parity [26].

3.3. Dynamics of cluster deposition
Figure 3 illustrates the deposition dynamics of a Na\textsubscript{6} cluster at moderate collisional energies for Ar(100) and MgO(100) surface. A broader range of energies and configurations for Ar substrates is discussed in [15, 27]. The Na\textsubscript{6} center-of-mass starts from 15 \(a_0\) above the surface facing the ring side towards the surface. The initial boost gives it a kinetic energy \(E_{\text{kin}}^0\) of 0.1 Ry (left) or 0.01 Ry (right) per Na ion. The low energy case (middle and right panels) show fast stopping and quick capture of the Na cluster. The other aspects of the process develop very differently for
Figure 3. Dynamics of deposition of a Na$_6$ cluster on MgO(001) substrate (upper panels) or Ar(001) (lower panels). Left: time-evolution of $z$-coordinates for an impinging kinetic energy of 0.6 Ry. Middle: time-evolution of $z$-coordinates for a much smaller impinging kinetic energy of 0.06 Ry. Right: time evolution of kinetic energies of cluster ions and substrate atoms for a kinetic energy of 0.06 Ry.

the two different substrates. For Ar(100), stopping is achieved by the substrate which is highly excited and leaves little energy to the cluster just sufficient to allow gentle oscillations of the top ion through the ring forth and back. The Mg(100) surface, however, is hardly excited at all and the sticking of Na$_6$ is achieved by conversion of the initial center-of-mass energy into huge internal cluster excitation. The complementing information on kinetic energies (right panels) confirms this: the soft substrate Ar(100) absorbs nearly all impact energy while the rather hard MgO(100) substrate remains almost unaffected. Both cases agree in that the main energy transfer proceeds at a very short time scale, within a few ten fs. Further thermal equilibration takes much longer at a scale of ns, far beyond simulation time [28]. The high energy cases (left panels) show both a reflection of the cluster, but different in detail: MgO(001) leads to hard reflection with little energy loss while the Ar(001) surface absorbs a great deal of incoming energy and is substantially stirred up.

The dissipative effect of the Ar substrate depends much on the number of active layers. There are experiments which consider only a few layers of Ar deposited on a metal carrier [29] which delivers a mechanically inert support. On the other hand, the Ar layers behave as a soft mechanical stopper in a deposition process while being chemically inert [30]. Figure 4 shows the effect of varying the number of layers (2, 4 and 8). The pattern of the $z$-coordinates (left panels) indicate already a significant change from almost “hard” reflection to dissipative attachment. The kinetic energies (middle panels) corroborate this, showing increasing energy transfer to the substrate with increasing number of layers. The right panel contains a global analysis of absorbed energy. There is a strong increase of absorption for the first few layers which then levels off to an asymptotic value at around 6 layers.
Figure 4. Dynamics of deposition of a Na₈ cluster on different layers of Ar on "metal support".
Left: time-evolution of z-coordinates for an impinging kinetic energy of 0.4 Ry for 2 layers (lower), 4 layers (middle) and 8 layers (upper). Middle: time evolution of kinetic energies of cluster ions and substrate atoms for the cases as shown in the left panels. Right: Relative loss of cluster kinetic energy ($E_{\text{kin, out}}/E_{\text{kin, in}}$) as a function of the number of layers.

3.4. Dynamics after strong laser ionization
Laser irradiation leads to strong ionization of the cluster which can exceed the limits of Coulomb-stability of the cluster. This has been much studied in the past under the notion “appearance size”, for a review see [31]. For Na clusters, the smallest Na cluster with charge state $Q = 2^+$ has been observed for Na$_{10}^{2+}$ in experiments with laser pulses [32]. Free Na$_8$ becomes unstable for ionization $Q \geq 2^+$. The interesting question is how a substrate modifies the charge stability.

Figure 5 shows results of laser excitation of Na$_8$ embedded in Ar$_{434}$. The short and intense laser pulse produces very quickly a net ionization stage of $Q = 2^+$ (lower), $3^+$ (middle), or $4^+$ and so deposits a large amount of energy in the Na$_8$ cluster. This fast initial electron emission proceeds much similar as for the free cluster. The finite Ar environment does not impose any hindrance for the escaping electrons. The Coulomb pressure generated by the almost instantaneous ionization starts to drive the cluster ions apart. The dominant effect is radial expansion, visualization in the figure in terms of radial coordinates $r = \sqrt{x^2 + y^2 + z^2}$. The cavity inside Ar is spacious. Thus we see for the initial 200 fs a fast expansion/explosion of the cluster almost as in the free case. The expansion is stopped abruptly if the cluster encounters the repulsive Ar core. The stopping radius increases with the charge state $Q$. After stopping, the cluster turns over into oscillations for a while. The Ar atoms take up the momentum from the stopped ions which then propagates like a sound wave through the Ar medium. The perturbation $Q = 4^+$ is strong enough to produce finally an emission of Ar atoms from the outmost shell. The sound wave distributes the energy very quickly over all shells exciting them to more or less hefty fluctuations. The Ar amplitudes increase with increasing charge state $Q$ which is related to the initial amount of Coulomb energy $\propto Q^2$. In spite of the strong energy inflow, the Ar matrix stays basically intact and represents an efficient cage for the highly charged Na cluster. Charge states $2^+$ and $3^+$ are finally stabilized. Only transient stabilization is achieved for $Q = 4^+$. At
Figure 5. Dynamics of a Na$_8$ cluster embedded in an Ar$_{434}$ and excited by a short laser pulse to initial charges states $Q = 2^+$ (lower), $Q = 3^+$ (middle), and $Q = 4^+$ (upper). The laser pulse had frequency $\omega = 0.14$ Ry, pulse length $T_{\text{pulse}} = 50$ fs, polarization along the $z$ axis (symmetry axis of Na$_8$) and intensity tuned to obtain the wanted ionization stages $Q$. Left: time-evolution of radial-coordinates of cluster ions (red thick curve) and substrate atoms (green thin dashes). Right: time evolution of kinetic energies of cluster ions (red thick curve) and substrate atoms (green thin dashes). About 4 ps, the cluster expansion revives and starts a Coulomb driven diffusion through the medium (visible when looking for longer time spans [33]).

The kinetic energies shown on the right panels allow to read off a few time scales. The initial Coulomb explosion lasts only for about 200 fs. The distribution of energy over the Ar shells is done within 0.5-0.7 ps for $Q = 3^+$ and even faster for $Q = 4^+$. It propagates at about the speed of the sound wave which is about $30$ a$_0$/ps, close to the velocity of sound in pure Ar. The more gentle stopping for $Q = 2^+$ does not transfer so much energy at the first encounter. The motion turns to stable oscillations of embedded Na$_8^{2+}$ where energy transport between the various sub-systems proceeds on much longer time scales [28].

The stabilization by a cage for embedded clusters is plausible. One wonders what the effect of the substrate may be for deposited clusters. This is illustrated in figure 6 for the case of Na$_8$@MgO(001) laser-ionized to charge state $Q = 3^+$. The upper panel shows for comparison free Na$_8$ under the same conditions. The $z$-coordinates (upper left panel) signal a clear Coulomb explosion. The trajectories (upper right panel) indicate a strictly radial expansion of all the 8 ions. The case of the deposited cluster (lower panels) behaves much differently. The cluster does not breakup nor release single ions. The system sticks together in spite of the huge charge state, of the dramatic perturbation and of much open space above the surface. Here, the glue
Figure 6. Dynamics of a free $\text{Na}_8$ cluster (upper) and a $\text{Na}_8$ cluster (lower) deposited on MgO(001) surface and excited by a short laser pulse to initial charges state $Q = 3^+$. The laser pulse had frequency $\omega = 0.14$ Ry, pulse length $T_{\text{pulse}} = 60$ fs, and intensity tuned to obtain ionization $Q = 3^+$. Left: time-evolution of $z$-coordinates of cluster ions (red) and substrate atoms (Mg green, O blue). Right: trajectories of Na ions and substrate atoms in the $x$-$z$-plane. The $z$-direction is vertical to the surface and $x$ horizontal.

is delivered by the strong and attractive polarization interaction with the substrate. The final state is not a compact cluster. It rather looks like an almost unperturbed lower ring of 4 ions still tied to the surface while the outer 4 ions remain only loosely connected and undergo large spatial fluctuations.

4. Conclusions and outlook

We have applied a recently developed hierarchical modeling for Na clusters in contact with Ar or MgO substrate to three different examples from cluster dynamics with the aim to explore the effect of the interface.

The optical response of metal clusters produces a dominant peak, the Mie plasmon resonance. Its average position is almost unaffected by the interface. This is result of a subtle balance between core repulsion and attractive dynamical polarizability of the material. However, the detailed fragmentation of the spectrum over $1p\ell$ states near the resonance is volatile and can change with change of surroundings. In particular, the reflection symmetry breaking through a substrate surface dissolves the mode vertical to the surface into a very broad distribution.

The collision of a cluster with Ar(001) or MgO(001) surface shows at first glance similar trends, reflection at high initial energies and cluster attachment for low energies. However, the mechanisms work out differently in detail. The soft Ar substrate acts as an efficient energy absorber producing a soft landing in case of attachment and a strongly dissipative “reflection” which, in fact, almost destroys the impact spot of the surface. The hard material MgO(001), on the other hand, takes up very little energy from the colliding cluster. This produces almost clean reflection but leaves a large amount of internal cluster excitation in case of attachment.
Laser excitation was tuned to produce quickly highly charged clusters and so to allow a study of Coulomb driven cluster expansion (or explosion). We find that embedding in Ar matrix as well as deposition on MgO surface both stabilize high charge states of the cluster which would Coulomb-expplode immediately for a free cluster. The mechanisms, however, are different. Embedding in a rare-gas matrix confines the cluster by inertia of the surrounding atoms. Deposition on a polarizable, insulating substrate stabilizes the high charges by a strong and attractive polarization interaction.

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