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# Metal clusters on an inert surface: a simple model

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**Abstract.** The shapes of metal clusters (with 2 to 14 valence electrons) on an inert surface are studied with a simple model based on the ultimate jellium model. It is shown that within certain approximations the surface-cluster interaction can be described with an external potential in the Kohn-Sham method. No restrictions for the cluster geometry are imposed. The results show that depending on the strength of the interaction and on the size of the cluster, the ground state is either planar or three-dimensional, but in many cases both geometries are stable and there is a marked energy barrier between them. The results agree qualitatively with ab initio calculations of Na clusters on a NaCl(100) surface.

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## 1 Introduction

Interaction of clusters with surfaces has become an intensive area of research during the last years [1–7]. On a metallic surface the cluster forms a metallic bond and, for example, alkali metal clusters are likely to wet the surface. If the cluster is of the same metal as the substrate it will form an epitaxial layer [6]. On a nonmetallic surface clusters can keep their identity and have structures closely related to those of free clusters in the vacuum [7]. The strength of the cluster-surface interaction is then expected to determine how much the cluster geometry and electronic properties are changed when the cluster is brought in contact with the surface.

A strong interaction with the surface can lead to wetting in which case a small cluster will collapse in a two-dimensional (2D) cluster. The 2D cluster can still have its own distinct electronic structure without a strong chemical bond with the substrate. In this case alkali metal clusters are expected to exhibit 2D shell structure [7, 8] closely related to that observed in 2D quantum wells [9].

Many properties of alkali metal clusters can be explained with help of the jellium model and its extensions [10, 11]. Especially, sodium and potassium clusters can be understood with simple models. The simplest model which allow unrestricted shape deformation is the so-called ultimate jellium [12], where the positive charge spatially completely follows the electronic distribution.

The purpose of the present work is to examine the effect of the surface on the geometry and electronic structure of metal clusters. Such calculations have already been made with ab initio molecular dynamics. These calculations give accurate description of a specific system like Na clusters on NaCl(100) [6, 7]. Nevertheless, since the jellium provides a simple explanation of most properties of free alkali clusters, it is expected that many properties of clusters on surfaces can also been learned by studying the jellium model. Furthermore, a simple model allows for studies of significantly larger systems than those currently feasible by ab initio molecular dynamics.

We suggest a simple model for adding the effect of an inert surface on the jellium model of clusters. The results show that for $N > 7$ both 2D and 3D geometries can coexist. There is a potential barrier between these two geometries and the strength of the cluster-surface interaction determines which of them is the ground state. The 2D structures show a 2D shell structure with magic numbers 2, 6, 12, etc. The clusters with full shell are circular in shape whereas all other clusters are deformed.

The plan of the paper is as follows. In Sect. 2 we present the model and briefly the computational techniques. In Sect. 3 we discuss the results. Conclusions are given in Sect. 4.

## 2 Theory

In the conventional jellium model the positive ions of the metal are replaced with a homogeneous positive background charge [10]. The background density is determined by the bulk density of the metal in question. In the ultimate jellium model [12] the background density is not fixed but adjusts itself to minimize the total energy. The bulk density of the ultimate model is close to that of sodium and, in fact, the model gives good results for the deformation parameters and for the binding energy variation as a function of cluster size for sodium clusters [12–14].

In the present paper we study the cluster-surface interaction using the ultimate jellium model for the cluster. However, we start from a more general density functional model and assume that the binding energy between a cluster and a surface can be determined from a pairwise interaction $V_s$ between the ions and the surface:

$$E_b = \sum_i V_s(\mathbf{r}_i), \tag{1}$$

where $r_i$ is the position of the ion. In the jellium model the ions are replaced with the positive background charge and, consequently, we first assume that (1) describes the interaction between the background and the surface. Using the density functional method of Kohn and Sham the total energy can be written as an energy functional (in atomic units)

$$\begin{aligned} E[n] &= T_0[n] + E_{xc}[n] + \int d\mathbf{r} n_+(\mathbf{r}) V_s(\mathbf{r}) \\ &+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n_+(\mathbf{r}) n_+(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} - \int d\mathbf{r} \int d\mathbf{r}' \frac{n_+(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &+ \frac{1}{2} \int d\mathbf{r} \int d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}, \end{aligned} \tag{2}$$

where $T_0$ is the kinetic energy, $E_{xc}$ is the exchange-correlation energy, $n_+(\mathbf{r})$ density of the positive background, and $n(\mathbf{r})$ electron density. By minimizing the energy with respect to the positive background density:

$$\frac{\delta E[n]}{\delta n_+(\mathbf{r})} = 0, \tag{3}$$

we get a relation between the surface potential and the positive background density

$$V_s(\mathbf{r}) = -\int d\mathbf{r}' \frac{n_+(\mathbf{r}') - n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|}. \tag{4}$$

The variation with respect to the electron density yields

$$\begin{aligned} \frac{\delta E[n]}{\delta n(\mathbf{r})} &= \frac{\delta T_0[n]}{\delta n(\mathbf{r})} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} - \int d\mathbf{r}' \frac{n_+(\mathbf{r}') - n(\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|} \\ &= \frac{\delta T_0[n]}{\delta n(\mathbf{r})} + V_{\text{eff}}(\mathbf{r}), \end{aligned} \tag{5}$$

where the last step defines the effective potential $V_{\text{eff}}$. Equations (4) and (5) imply that

$$V_{\text{eff}}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} + V_s(\mathbf{r}). \tag{6}$$

The effective potential does not have a Coulomb term even if the cluster interacts with the surface. The electron density and the electronic level structure can thus be calculated without Coulomb integrals. Nevertheless, since $n_+(\mathbf{r}) \neq n(\mathbf{r})$ a Coulomb term appears in the total energy expression. With help of Eq. (4) the total energy can be written as

$$\begin{aligned} E &= T_0[n] + E_{xc}[n] + \int d\mathbf{r} n(\mathbf{r}) V_s(\mathbf{r}) \\ &+ \tfrac{1}{2} \int d\mathbf{r} [n_+(\mathbf{r}) - n(\mathbf{r})] V_s(\mathbf{r}). \end{aligned} \tag{7}$$

The Kohn-Sham method with the local-spin-density approximation for the exchange-correlation energy (for a review see [15]) is used to calculate the electron density and the total energy of the cluster.

Above we assumed that the surface interacts with the ions of the cluster. If we assume instead that the interaction is between the surface and the electrons of the cluster we get the same effective potential, Eq. (5), but the total energy will be

$$E = T_0[n] + E_{xc}[n] + \int d\mathbf{r} n(\mathbf{r}) V_s(\mathbf{r}). \tag{8}$$

In reality none of these models is correct for a metal cluster. The surface will polarize the cluster as a whole which leads to an attractive polarization force. Nevertheless, a local approximation for the polarization leads again to the same equation for the effective potential. For simplicity we use Eq. (8) for calculating the total energy of the cluster in contact with the surface. Notice that this is the same as Eq. (7) with the approximation that $n_+(\mathbf{r}) = n(\mathbf{r})$.

As a test case we try to imitate the potential between a cluster and a NaCl(100) surface. First we use a one-dimensional potential

$$V_s(z) = \min \begin{cases} A[(\frac{\sigma}{z})^6 - (\frac{\sigma}{z})^4] \\ V_0 \end{cases}, \tag{9}$$

where $A$, $\sigma$ and $V_0$ are parameters and $z$ the coordinate perpendicular to the surface. Inside the surface the potential is assumed to be a constant ($V_0$). Far out from the surface the potential is assumed to be caused by polarization forces resulting to the $z^{-4}$-dependence. The exponent of the repulsive part of the potential was chosen so that it describes well the interaction of a monoatom with the NaCl surface, calculated by ab initio methods [16].

We also studied effects of the surface corrugation. For that purpose a sinusoidal corrugation was added to the attractive part of the potential:

$$V_s(\mathbf{r}) = V_s(z) + [\sin(kx) + \sin(ky)] \frac{C}{z^4}, \tag{10}$$

The parameters $k$ and $C$ determine the wave length and amplitude of the corrugation.

A plane wave method was used to calculate the electronic structure of the cluster in contact with the surface potential. The method is described in detail in Ref. [12]. For each cluster several initial shapes for the effective potential was used for obtaining both 2D isomers and 3D isomers.

## 3 Results and discussion

### *3.1 Competition between 3D and 2D geometries*

Free clusters with seven or more electrons are three-dimensional. If the surface potential is strong enough the ground state will have a two-dimensional geometry: The cluster will form an island of monolayer on the surface. With reasonable parameters for the surface potential two shape-isomers were obtained, a 2D geometry and a 3D geometry. The strength of the surface potential determines which of the two isomers is the ground state.

Figure 1 shows the total energy of the 8-electron cluster in contact with the surface as a function of the depth of the surface potential. The well-depth of $V(z_0) = -0.15$ eV corresponds to that obtained from ab initio calculations for

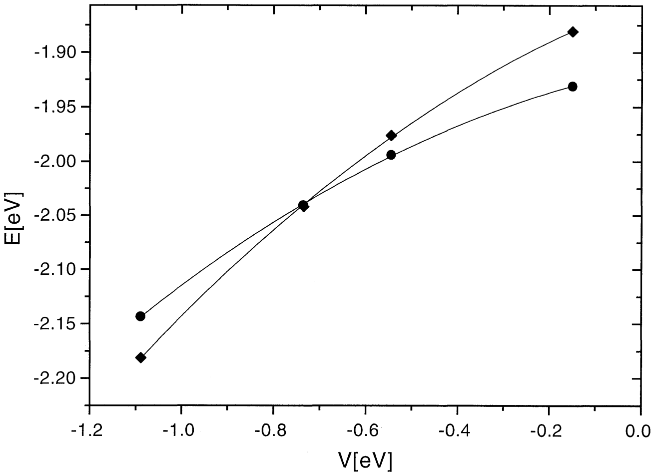

**Fig. 1.** Dependence of the total energy per electron of a 8-electron cluster on the strength of the surface interaction. *Squares* show the result for the 2D isomers and *black dots* for the 3D isomer

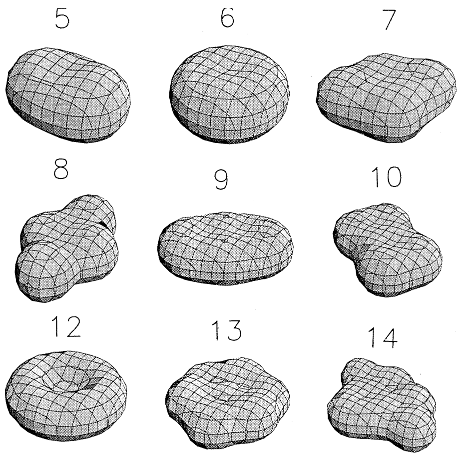

**Fig. 2.** Shapes of the 2D clusters on the surface. The three-dimensional plots are isodensity surfaces with $n$ = $0.00125a_0^{-3}$ (38% of the bulk density). The figures do not have an absolute length scale. The result for the 13-electron cluster is a ‘saddle-point’ geometry. The clusters are viewed from above the surface: The visible flat faces are those on the vacuum side of the cluster

Sodium atom on a NaCl(100) surface. In the jellium model that surface favors a nearly spherical 3D geometry. As expected, when the strength of the surface potential is increased the 2D geometry becomes energetically favored.

It should be emphasized that in all cases both the 2D and the 3D isomers are stable and there is a clear potential barrier between the two geometries. In the ultimate jellium model it is not possible to estimate the height of the barrier since no restrictions are used. However, depending upon the shape of the initial potential the final geometry converges to either of the two geometries. The possibility of getting trapped by a saddle point was excluded by adding random perturbations to the effective potential during the first 50 iterations.

The shapes of the 3D geometries of clusters with 8 to 14 electrons were very similar with those obtained in vacuum, i.e. without the surface potentials [12].

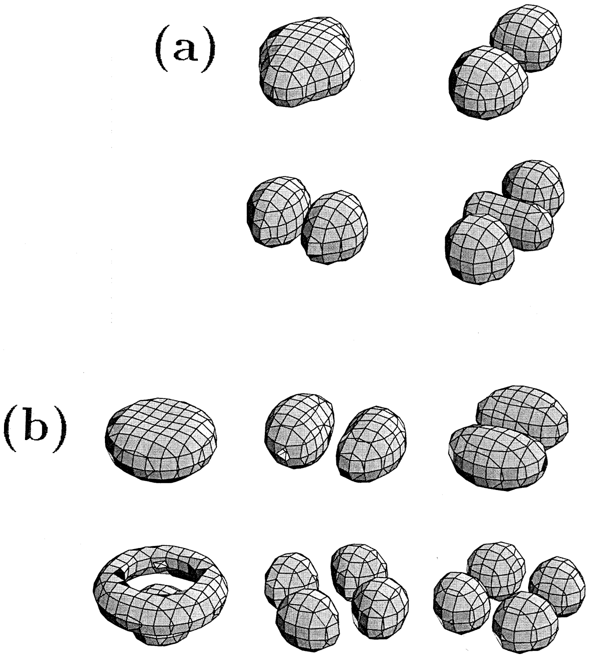

**Fig. 3.** Single-electron densities for the 2D 8-electron (**a**) and 12-electron (**b**) cluster. The plots show constant-density surfaces with density $n$ = $0.0003a_0^{-3}$. The viewing direction is the same as in Fig. 2

### *3.2 Two-dimensional clusters on the surface*

We studied the geometries and energetics of two-dimensional clusters on the surface using the potential parameters obtained from the ab initio calculations ($V(z_0) = -0.15$ eV). The 2D geometries were found by starting the iteration from a flat initial potential with random variations. For the clusters studied in the present work, it was easy to find unique 2D geometries for cluster with N=2–10 and for N=12 and N=14. For N=11 and N=13 no 2D geometry was found: Independent of the initial geometry these clusters always converged to a 3D geometry. However, for a 13-electron cluster we found a 2D ‘saddle-point’ geometry, which however, after further iterations gradually converged to a 3D geometry with a monotonic decrease of the total energy.

Figure 2 shows the ground state geometries of 2D clusters on the surface. Also the saddle-point geometry of the 13 electron cluster is shown. The geometries of the smallest clusters can be understood with help of the individual wave functions in circular geometry: In going from 2 to 6 the filling of the single particle levels goes as $1s^2$, $1s^2p_x$, $1s^2p_x^2$, $1s^2p_x^2p_y$, $1s^2p_x^2p_y^2$. In larger clusters there is a strong mixing of $s$ and $d$ levels. Figure 3 shows the individual single particle wave functions of 8 and 12 electron clusters.

The geometry of 12-electron cluster (Fig. 2) is interesting since it is not perfectly planar but forms a shallow bowl. The reason is the fourth single-particle level, ‘2$s$ state’, as seen in Fig. 3. A more symmetric planar structure would not allow as uniform density inside the cluster.

### *3.3 2D shell structure*

Fermions confined in a 2D potential exhibit a shell structure different from that of 3D clusters. Such 2D systems

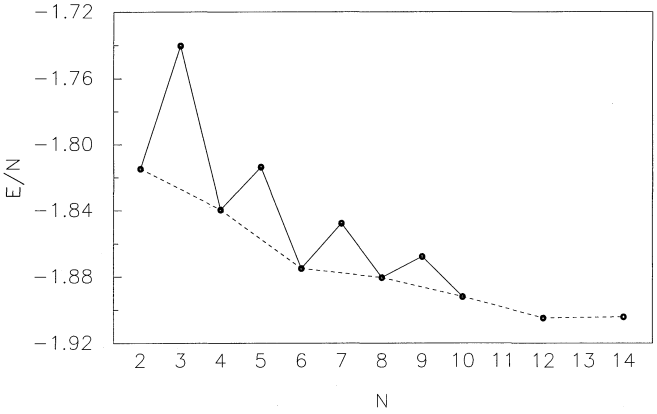

**Fig. 4.** The total energy per electron of 2D clusters on the surface. Even clusters are connected with a *dashed line* to clarify the effect of the magic numbers 6 and 12

are electrons in a quantum dot [9] and 2D metal clusters on inert surfaces [7]. While the geometry of a quantum dot is determined by electric field created with external gates, the geometry of metal clusters on the surface is determined by the electronic structure just as in the case of 3D metal clusters. The magic numbers in a circular 2D potential are 2, 6, 12 etc. The clusters with magic number of electrons are circular whereas all other geometries are deformed.

Figure 4 shows the total energy of the planar clusters on a surface as a function of the number of electrons. The energy shows a strong odd-even staggering as a consequence of the deformation. The staggering is similar to that of 3D clusters [14, 17, 8]. The dashed line connecting the results for even clusters has a cusp at $N$ = 6 and at $N$ = 12, which are the magic numbers.

### *3.4 Effect of surface corrugation on the cluster shape*

The effect of surface corrugation on the cluster shape and the binding energy was studied by using surface potential of Eq. (10). The strength of the potential in $z$-direction was kept at $V_s(z_0) = -0.15$ eV as before. The parameter $C$ in Eq. (10) was chosen so that the amplitude of the corrugation at $z_0$ was 0.2 eV. The wave-length of the corrugation was varied around a value that corresponds to the lattice parameter of bulk NaCl.

As a test case we chose the 8-electron cluster which has a rather low symmetry. The corrugation of the surface potential had a very small effect on the cluster shape. Moreover, the binding energy was nearly independent on the position or direction with respect of the corrugation. We can conclude that on a nearly flat surface like NaCl(100) the corrugation of the surface potential has only a marginal effect on the cluster shape and binding energy. This is in agreement with the findings of ab initio calculations [7] which show that the planar sodium clusters ($N < 7$) have nearly the same geometries on NaCl(100) as in the vacuum.

## 4 Conclusions

We have presented a simple model to study properties of simple metal clusters on inert surfaces. On the surface clusters can have 2D geometries even if they do not exist in vacuum. Both 2D and 3D geometries can be stable at the surface and in many cases there seems to be a clear potential barrier between them.

The 2D structures show a shell structure with magic numbers 2, 6, 12 etc and an odd-even staggering which is related to the shape deformation of non-magic clusters.

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