Potential energy surfaces of semi-spheroidal atomic clusters

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Abstract. The nuclear shell correction method is adapted to atomic clusters deposited on a surface. Analytical relationships for the deformation-dependent liquid drop model (LDM) energies of oblate and prolate semi-spheroidal atomic clusters have been obtained. A superdeformed prolate semi-spheroid is the most stable semi-spheroidal shape within LDM. It is also the shape with maximum degeneracy of quantum states of the semi-spheroidal harmonic oscillator used to compute the shell and pairing corrections. The deformation energy surface versus deformation and number of atoms illustrates these remarkable properties.

1. Introduction
The nanostructured coating of surfaces by cluster deposition \cite{1} is at present a rapidly growing field. By analyzing some shapes of cluster deposited on a surface obtained by using scanning probe microscopy \cite{2, 3}, we expect that a semi-spheroid with the z axis of cylindrical symmetry oriented perpendicularly on the surface plane may be a good starting point to study some of the possible shapes encountered in practice if the interaction energy between the deposited cluster and the substrate may be neglected.

The electronic shell structure in monovalent free-electron metal clusters \cite{4} has shown a strong analogy with the single-particle states of atomic nuclei, despite gross differences in the physical forces binding the two systems. Moreover, the delocalized electrons of a metallic cluster may be considered to form a Fermi liquid like the atomic nucleus. Consequently several theories and computation techniques from nuclear physics could be adapted to atomic clusters \cite{5, 6}. They have been extensively used particularly to investigate the fission process of ionized clusters \cite{7–10} as well as the shell, supershell \cite{11, 12} structures, and the shapes of metal clusters \cite{13–15}. We should mention in particular the macroscopic-microscopic method \cite{16–19} which is used in the present work.

For the semi-spheroidal shapes considered below, both the macroscopic deformation energy \cite{20} and the microscopic single-particle energy \cite{21} levels we need to calculate the shell corrections are expressed by analytical relationships. The oblate and prolate semi-spheroid is in the same time an equipotential surface of this model and the basic shape of the corresponding liquid drop model (LDM). We investigate the stability of semi-spheroidal shapes by assuming, as a
first approximation, a vanishing interaction energy with the surface on which the cluster is deposited, so that the neutral atomic cluster may be considered to be free.

In all studies using an harmonic oscillator published since 1955, including the Clemenger-nilsson model [22], the maximum degeneracy of the quantum states was reached for a spherical shape, explaining the high stability of the doubly magic nuclei or of the metal clusters with spherical closed shells. To our surprise the maximum stability of the semi-spheroidal quantum harmonic oscillator occurs at a superdeformed prolate shape (semiaxes ratio $a/c = 1/2$).

In a similar way, in all LDM studies published until now, both in nuclear and atomic cluster physics, the most stable shape (minimum deformation energy) was a sphere. One would expect that for a semi-spheroid the most stable shape would be a semi-sphere or an oblate shape. We found the surprising result that the superdeformed prolate semi-spheroid is in this case the equilibrium shape. In this way both LDM and the shell structure suggest the enhanced stability of such a distorted shape.

2. Liquid drop model

The cylindrical symmetry of the shapes we consider allows to use the the dimensionless coordinates $(\rho, z)$, the length scale being the radius of a semi-sphere with the same volume, $R_s = 2^{1/3} R_0 = 2^{1/3} r_s N^{1/3}$, in which $r_s$ is the Wigner-Seitz radius (2.117 Å for Na [23–25]) and $\rho = \rho(z)$ is the surface equation given by

$$\rho^2 = \begin{cases} (a/c)^2 (c^2 - z^2) & z \geq 0 \\ 0 & z < 0 \end{cases}$$  \hspace{1cm} (1)$$

where $a$ is the minor (major) semiaxis for prolate (oblate) semi-spheroid and $c$ is the major (minor) semiaxis for prolate (oblate) semi-spheroid. Volume conservation leads to $a^2 c = 1$.

The (quadropolar) deformation parameter, $\delta$, is defined [22] by

$$a = \left( \frac{2 - \delta}{2 + \delta} \right)^{1/3} \hspace{1cm} c = \left( \frac{2 + \delta}{2 - \delta} \right)^{2/3}$$  \hspace{1cm} (2)$$

and the eccentricity is expressed as

$$e^2 = \begin{cases} 1 - a^2/c^2 & \text{prolate} \hspace{0.5cm} (a < c) \\ a^2/c^2 - 1 & \text{oblate} \hspace{0.5cm} (a > c) \end{cases}$$  \hspace{1cm} (3)$$

The deformation energy with respect to semi-spherical shape of a neutral cluster is given by

$$E - E^{s0} = (E_s - E_s^{s0}) + (E_c - E_c^{s0}) = E_s^{s0} \left( \frac{E_s}{E_s^{s0}} - 1 \right) + E_c^{s0} \left( \frac{E_c}{E_c^{s0}} - 1 \right)$$  \hspace{1cm} (4)$$

$$E - E^{s0} = E_s^{s0} \left( B_{surf}^s - 1 \right) + E_c^{s0} \left( B_{curv}^s - 1 \right)$$  \hspace{1cm} (5)$$

where for a semi-sphere one has

$$E_s^{s0} = 3\pi R_s^2 \sigma = 3\pi 4^{1/3} R_0^2 \sigma = \frac{3}{4^{2/3}} E_0^{\sigma}$$ ; \hspace{0.5cm} E_c^{s0} = 2\pi R_s \gamma_c = 2\pi 2^{1/3} R_0 \gamma_c = \frac{E_{\sigma}}{4^{1/3}}$$  \hspace{1cm} (6)$$

with $E_0^{\sigma}$ and $E_{\sigma}^{\text{curv}}$ the surface and curvature energy of a sphere with the same volume.

The liquid drop part (volume, surface, and curvature terms) of the binding energy of Na semi-spherical clusters are given, in eV, by:

$$E_{sN} = -2.252 N + \frac{3}{4^{2/3}} 0.541 N^{2/3} + \frac{1}{4^{1/3}} 0.154 N^{1/3}$$  \hspace{1cm} (7)$$
When $a > c$ (oblate semi-spheroid), $e^2 = a^2/c^2 - 1$, we obtain for the shape dependent terms:

$$B_{surf}^s = \frac{a}{3} \left[ 2a + \frac{c}{e} \ln \left( e + \frac{a}{c} \right) \right]$$

(8)

$$B_{curv}^s = \frac{c}{2} + \frac{1}{2ce^2} \left( \frac{e}{c} \arcsin e \right) = \frac{c}{2} + \frac{a^2}{2ce} \arctan e$$

(9)

When $c > a$ (prolate semi-spheroid), $e^2 - a^2 = e^2c^2$, we get

$$B_{surf}^s = \frac{a}{3} \left( 2a + \frac{c}{e} \arcsin e \right)$$

(10)

$$B_{curv}^s = \frac{c}{2} + \frac{a^2}{4ce} \ln \left| \frac{1+e}{1-e} \right|$$

(11)

For a semi-spherical shape $B_{surf}^s = B_{curv}^s = 1$. A typical variation of the deformation energy, $E_{LD}$, with the shape coordinate $\delta$ is shown in the upper part of the figure 1, for a semi-spheroidal sodium cluster having 148 atoms. The minimum corresponds to $\delta = 2/3$, that is a superdeformed ($a/c = 1/2$) prolate shape.

3. Single-particle shell model

The three-dimensional semi-spheroidal harmonic oscillator was developed [21] by using just the half of the parabolic potential along the axis of symmetry $V_z(z)$ without taking into account an additional term proportional to $(1^Z - 1^Z)_n$ which was considered [22] in order to explain the experimental magic numbers larger than 40. In this way we obtain analytical solutions for the electronic levels. The potential along the symmetry axis, $V_z(z)$, has a wall of an infinitely large height at $z = 0$, and concerns only positive values of $z$, implying opacity of the surface. As a consequence, only negative parity states along the $z$ axis (with integer quantum number $n_z = 1, 3, 5, ... n$) are allowed. In units of $\hbar\omega_0$ the variation of eigenvalues with deformation, $\epsilon(\delta) = E(\delta)/(\hbar\omega_0)$, is given by

$$\epsilon = \frac{2}{(2 - \delta)^{1/6}(2 + \delta)^{2/3}} \left[ n + \frac{3}{2} + \delta \left( n_\perp - \frac{n}{2} + \frac{1}{4} \right) \right]$$

(12)
Each level may be labeled by two quantum numbers, nonnegative integers, \( n, n_\perp \). The eq. (12) is the same as for the spheroidal harmonic oscillator, but for semi-spheroidal shapes one should only allow the values of \( n \) and \( n_\perp \) for which \( n_z = n - n_\perp \geq 1 \) are odd numbers.

For the semi-spherical shape (\( \delta = 0 \)) the magic numbers are 2, 6, 14, 26, 44, 68, 100, 140, ... For \( \delta = -0.4 \) (\( a/c = 3/2 \)) the magic numbers are: 2, 6, 12, 22, 36, 78, 108, 144, ... They are: 2, 8, 18, 20, 34, 38, 50, 58, 64, 80, 92, 100, ... for \( \delta = 0.4 \) (\( a/c = 2/3 \)) and 2, 8, 10, 14, 22, 26, 46, 54, 66, 84, 96, 114, 138, 156, ... for the hyperdeformed prolate shape \( \delta = 1 \) (\( a/c = 1/3 \)). The largest degeneracy is obtained for a superdeformed prolate shape with \( \delta = 2/3 \) (\( a/c = 1/2 \)) with the magic numbers 2, 8, 20, 40, 70, 112, 168, ... identical to those of the spherical harmonic oscillator. The single-particle shell gap of the semi-spheroidal harmonic oscillator in eV is given by

\[
\hbar \omega_0(N) = \frac{13.72}{r_s R_0}
\]

where \( r_s \) and \( R_0 \) are expressed in Å.

4. Shell and pairing corrections

For atomic nuclei, Strutinsky [16] gave a microscopic definition of shell corrections. We adapt the method for atomic clusters. The deformation energy in the framework of the macroscopic-microscopic method is given by macroscopic (LDM) + (shell + pairing) corrections

\[
E_{\text{def}} = E_{\text{LDM}} + \delta E = E_{\text{LDM}} + \delta U + \delta P
\]

In order to use Strutinsky’s prescription we know the doubly degenerate energy levels \( \epsilon_i = \)

![Figure 2](https://example.com/figure2.png)

Figure 2. Contour plot of shell corrections versus the deformation, \( \delta \), and the number of atoms in the cluster, \( N \), for semi-spheroidal Na clusters.

\( E_i / \hbar \omega_0 \) of the semi-spheroidal quantum oscillator in units of \( \hbar \omega_0 \). The shell, \( \delta U \), and pairing, \( \delta P \), corrections are obtained as a difference between a sum over the single-particle energies, or a weighted sum over the quasi-particle energies and a corresponding quantity obtained by a smoothing procedure [26]. In units of \( \hbar \omega_0 \) the shell corrections, \( \delta u = \delta U / \hbar \omega_0 \) is given by

\[
\delta u(n, \varepsilon) = \sum_{i=1}^{n} 2\epsilon_i(\varepsilon) - \bar{u}(n, \varepsilon)
\]
where the summation is performed over \( n = N/2 \) particles (\( N \) is the number of atoms in the cluster), and \( \tilde{u} \) is a smoothed quantity [26].

In a similar way the pairing corrections, \( \delta p = \delta P/\hbar \omega_0 = p - \bar{p} \), are obtained as a difference between the pairing correlation energies for the discrete level distribution

\[
p = \sum_{k=k_i}^{k_f} 2v_k^2\epsilon_k - 2 \sum_{k=k_i}^{Z/2} \epsilon_k - \frac{\Delta^2}{G}
\]

and for the continuous level distribution with density \( \tilde{g} \),

\[
\bar{p} = -\left(\tilde{g}\Delta^2\right)/2 = -\left(\tilde{g}_s\Delta^2\right)/4
\]

where the pairing gap \( \Delta \) and the Fermi energy \( \lambda \) from the expression of the occupation probability by a quasiparticle

\[
v_k^2 = \frac{1}{2} \left[ 1 - \frac{\epsilon_k - \lambda}{\sqrt{(\epsilon_k - \lambda)^2 + \Delta^2}} \right]
\]

are obtained by solving the nonlinear BCS system of two equations. \( G \) is the pairing strength. In figure 2 we give a contour plot of the shell corrections versus the deformation, \( \delta \), and the number of atoms in the semi-spheroidal sodium cluster, \( N \). One can see that the most pronounced minima (colored in blue) appear at the superdeformed prolate deformation \( \delta = 2/3 \). There is also very clearly seen the parabolic evolution of minima (due to the bunching of levels) from lower to higher deformation parameters: e.g. from \( N = 6 \) at \( \delta = -0.4 \) to \( N = 6 \) at \( \delta = 0 \) and to \( N = 8 \) at \( \delta = 2/3 \); from \( N = 14 \) at \( \delta = 0 \) to \( N = 20 \) at \( \delta = 2/3 \); from \( N = 26 \) at \( \delta = 0 \) to \( N = 40 \) at \( \delta = 2/3 \), and from \( N = 34 \) at \( \delta = -0.4 \) to \( N = 44 \) at \( \delta = 0 \).

![Figure 3](image-url)  
**Figure 3.** Potential energy surface \( E_{def} = E_{LD} - E_{LD}^{0s} + \delta E \) versus the deformation \( \delta \) and the number of atoms \( N \) for semi-spheroidal atomic clusters of sodium. \( E_{LD}^{0s} \) is the liquid drop energy of a semi-spherical shape.

The smoothing effect of the pairing corrections, \( \delta P \), which is out of phase and smaller in amplitude compared to the shell corrections, \( \delta U \), can be seen from the example given at the bottom of figure 1. By adding the shell and pairing corrections to the liquid drop energy we obtain a ground state deformation (minimum of \( E \)) at about \( \delta = 0.5 \) for \( N = 148 \).

![Figure 4](image-url)  
**Figure 4.** The contour plot corresponding to figure 3.
5. Total deformation energy

In figure 3 one can see a potential energy surface (PES) representing the deformation energy

\[ E_{\text{def}} = E_{LD}^0 - E_{LD}^s + \delta E \]

versus the deformation \( \delta \) and the number of atoms \( N \) for semi-spherical atomic clusters of sodium. \( E_{LD}^0 \) is the liquid drop energy of a semi-spherical shape. By confining the number of atoms in the interval 4 – 46 we expect to get a realistic result, as a threedimensional harmonic oscillator without a term proportional to \( (l^2 - \langle l^2 \rangle_n) \) is able to reproduce the experimental spherical magic numbers 2, 8, 20, and 40.

In figures 3 and 4 it is clear that the deepest minimum corresponds to the super-deformed prolate semi-spheroid with \( \delta = 2/3 \) and \( N = 40 \). Also, from the figure 4 one can see that the majority of semi-spheroidal clusters of Na with \( N \leq 46 \) will have the ground-state deformation around \( \delta = 2/3 \).

In conclusion, if some super-deformed semi-spheroidal shapes will be observed in an experiment of cluster deposition on a planar surface, the fact may be interpreted as an evidence for a negligible interaction energy between the deposited cluster and the surface material.

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