Deformation energy of spheroidal, semi-spheroidal and intermediate shape atomic clusters. Analytical relationships within liquid drop model.

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I. INTRODUCTION

The delocalized conduction electrons of neutral small metallic clusters form a Fermi liquid like the atomic nucleus [1]. Consequently the liquid drop model (LDM) developed by lord Rayleigh in 1978 was successfully adapted to nuclear clusters [2]. The LDM [3] expresses the smooth part of the total energy to which the shell corrections may be added. Assuming spherical symmetry, the cluster radius for monovalent metals is $R = r_s N^{1/3}$. The *Wigner-Seitz radius*, r_s, is the radius of a sphere of the same volume as the volume per particle. The energy of a metallic crystal is expressed as a sum of volume, surface and curvature terms

$$E = \alpha V + \sigma A + (1/2)\gamma \int dA \mathcal{R}^{-1} \tag{1}$$

where α, σ, γ are intrinsic volume, surface, and curvature energies and $\mathcal{R}^{-1}$ is the local curvature of surface-area element dA.

The nanostructured coating of surfaces by cluster deposition is a rapidly growing field. By analyzing some shapes of cluster deposited on a surface obtained by using scanning probe microscopy [4, 5], one can see that a semi-spheroid with the z axis of cylindrical symmetry oriented perpendicularly on the surface plane may be a good approximation. In all LDM studies published until now, both in nuclear and atomic cluster physics, the most stable shape (minimum deformation energy) was a sphere. For the first time, we found the surprising result [6, 7] that the superdeformed prolate semi-spheroid is in this case the equilibrium shape.

We investigate the stability of semi-spheroidal shapes by assuming, as a first approximation of one possibility which can be met in practice, 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.

We shall also considewr some other types of shapes obtained from a spheroid by removing more or less than its half; the interaction with surface will be taken into account as well. Our choice is motivated by the fact that the corresponding shell model [8] allows to obtain analytical formulae for the single-particle energies.

II. SHAPES WITH AXIAL SYMMETRY

We are using the standard notation of (ρ, z) for the axially symmetric dimensionless cylindrical coordinates. When the shape is a semi-spheroid the length scale is given by the radius of a sphere with the same volume, $R_s = 2^{1/3}R_0 = 2^{1/3}r_sN^{1/3}$, in which N is the number of atoms, r_s is the Wigner-Seitz radius (2.117 Å for Na [9, 10]) and $\rho = \rho(z)$ is the surface equation of a hemispheroid with semiaxes a and c. Volume conservation leads to $a^2c = 1$.

It is convenient to choose the deformation parameter δ defined by

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

The eccentricity is defined by the equation

$$e^2 = \begin{cases} 1 - a^2/c^2 \;\; prolate \;\; (a < c) \\ a^2/c^2 - 1 \;\; oblate \;\; (a > c) \end{cases} \tag{3}$$

The deformation energy with respect to semi-spherical shape of a neutral cluster is expressed as

$$E - E^{s0} = E_s^{s0}\left(\frac{E_s}{E_s^{s0}} - 1\right) + E_c^{s0}\left(\frac{E_c}{E_c^{s0}} - 1\right) = E_s^{s0}\left(B_{surf}^s - 1\right) + E_c^{s0}\left(B_{curv}^s - 1\right) \tag{4}$$

where for a semi-sphere one has $E_s^{s0} = 3\pi R_s^2\sigma = 3\pi 4^{1/3}R_0^2\sigma = \frac{3}{4^{2/3}}E_s^0$, $E_c^{s0} = 2\pi R_s\gamma_c = 2\pi 2^{1/3}R_0\gamma_c = \frac{E_{curv}^0}{4^{1/3}}$ with E_s^0 and E_{curv}^0 the surface and curvature energy of a sphere with the same volume.

For a spherical Na cluster [9] the binding energy, in eV, is given by $E_N = -2.252N + 0.541N^{2/3} + 0.154N^{1/3}$. The numerical coefficients of the binding energy have been determined [9] by fitting the extended Thomas-Fermi local density approximation total energy [12] for spherical shapes. The liquid drop part of the binding energy of Na semi-spherical clusters will be in eV: $E_{sN} = -2.252N + \frac{3}{4^{2/3}}0.541N^{2/3} + \frac{1}{4^{1/3}}0.154N^{1/3}$.

The area of a surface of revolution about z axis

$$S = \int dS = 2\pi R_0^2 \int_{-c}^{+c} \rho(z)\sqrt{1 + \left(\frac{d\rho}{dz}\right)^2}\,dz \tag{5}$$

The deformation-dependent surface energy for cylindrical symmetry $B_{surf} = S/S_0 = S/4\pi R_0^2$ is given by

$$B_{surf} = \frac{1}{2}\int_{-c}^{+c} dz\rho\sqrt{1+\rho'^2} = \frac{1}{2}\int_{-c}^{+c} dz\sqrt{\rho^2+(\rho\rho')^2} \quad (6)$$

The local curvature $\kappa = 0.5(\mathcal{R}_1^{-1} + \mathcal{R}_2^{-1})$ of a sphere is $1/R_0$ and the integrated curvature $K = \int dS\kappa$ is $4\pi R_0$. $\mathcal{R}_1$ and $\mathcal{R}_2$ are the two principal radii of curvature at a local point on the surface. The shape-dependent part of the curvature energy for cylindrical symmetry is given by

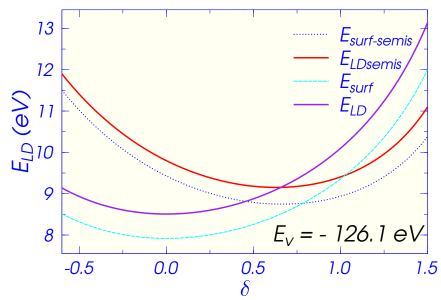

FIG. 1: Absolute values of the deformation-dependent liquid drop surface and total (surface plus curvature) energy versus the deformation parameter δ for Na_{56} clusters. Comparison between spheroidal and semi-spheroidal shapes. The volume energy $E_v = -126.1$ eV was not included in E_{LD} and $E_{LDsemis}$.

$$B_{curv} = \frac{1}{4\pi R_0}\int dS\kappa = \frac{2\pi R_0^2}{4\pi R_0}\int_{-c}^{+c} dz\kappa\rho\sqrt{1+\rho'^2} = \frac{1}{4}\int_{-c}^{+c} dz\frac{1+\rho'^2-\rho\rho''}{1+\rho'^2} \quad (7)$$

The principal radii of curvature of a shape with axial symmetry [11] are expressed as

$$\mathcal{R}_1 = R_0\rho\sqrt{1+\rho'^2} \qquad \mathcal{R}_2 = -R_0\frac{(1+\rho'^2)^{3/2}}{\rho''} \quad (8)$$

III. SURFACE AND CURVATURE ENERGIES OF A HEMISPHEROIDAL SHAPE

We give ρ, z, a, c in units of $R_s = 2^{1/3}R_0$, hence according to the volume conservation, $a^2cR_s^3/2 = R_0^3$ so that $a^2c = 1$

$$B_{surf}^s = \frac{S}{3\pi R_s^2} = \frac{a^2}{3} + \frac{2}{3}\int_0^c dz\sqrt{\rho^2+(\rho\rho')^2} = \frac{a^2}{3} + \frac{2a}{3c^2}\int_0^c dz\sqrt{c^4+z^2(a^2-c^2)} \quad (9)$$

because for a semi-spheroid there is a plane circular surface with the area $\pi R_s^2 a^2$. Deformation dependent curvature energy of a semi-spheroid, $B_{curv}^s = K/(2\pi R_s)$

$$B_{curv}^s = \frac{1}{2\pi R_s}\int dS\kappa = \frac{R_s^2}{R_s}\int_0^c dz\kappa\sqrt{\rho^2+(\rho\rho')^2} = \frac{1}{2}\int_0^c dz\left(1-\frac{\rho\rho''}{1+\rho'^2}\right) = \frac{c}{2} + \frac{a^2c^2}{2}\int_0^c \frac{dz}{c^4+z^2(a^2-c^2)} \quad (10)$$

When $a > c$ (oblate semi-spheroid) and $e^2 = a^2/c^2 - 1$, $a^2 - c^2 = e^2c^2$

$$B^s_{surf} = \frac{a^2}{3} + \frac{2a}{3c^2}\int_0^c dz\sqrt{c^4 + z^2c^2e^2} = \frac{a}{3}\left[2a + \frac{c}{e}\ln\left(e + \frac{a}{c}\right)\right] \quad (11)$$

$$B^s_{curv} = \frac{c}{2} + \frac{a^2c^2}{2}\int_0^c \frac{dz}{c^4 + z^2c^2e^2} = \frac{c}{2} + \frac{1}{2ce^2}\left(\frac{e}{c}\arctan e\right) = \frac{c}{2} + \frac{a^2}{2ce}\arctan e \quad (12)$$

When $c > a$ (prolate semi-spheroid), from the definition of the eccentricity we have $c^2 - a^2 = e^2c^2$, hence

$$B^s_{surf} = \frac{a^2}{3} + \frac{2a}{3c^2}\int_0^c dz\sqrt{c^4 - e^2c^2z^2} = \frac{2a^2}{3} + \frac{ac}{3e}\arcsin e = \frac{a}{3}\left(2a + \frac{c}{e}\arcsin e\right) \quad (13)$$

$$B^s_{curv} = \frac{c}{2} + \frac{a^2c^2}{2}\int_0^c \frac{dz}{c^4 - e^2c^2z^2} = \frac{c}{2} + \frac{a^2}{4ce}\ln\left|\frac{1+e}{1-e}\right| \quad (14)$$

A comparison between the two LDM deformation energies in figure 1 illustrates the difference between the spheroidal and semi-spheroidal shapes of a Na cluster with 56 atoms; in the former case the most stable configuration is a sphere, but in the latter it is a superdeformed prolate semi-spheroid with $\delta = 0.65$ ($c/a = 1.96$). This property is conserved independent of the number of atoms in the cluster.

IV. SIMULATING THE INTERACTION WITH THE SUBSTRATE

Surface tension of the base is changed from σ to $i\sigma$, $\mathbf{i} \in (-\mathbf{1.98}, \mathbf{2})$. i is the *interaction factor*. For $i = 1$ one has the previously studied case.

$$E = E_{base} + E_{ext} = i\sigma S_{base} + \sigma S_{ext} \quad (15)$$

The curvature of a planar surface is zero, hence E_{curv} remains unchanged. For $\delta = 0$ (hemisphere):

$$E^{si0}_s = i\sigma(\pi R_s^2) + \sigma(2\pi R_s^2) = 4^{-2/3}(2+i)E^0_s \quad (16)$$

$$E^{si0}_c = 2\pi R_s \gamma_c = 4^{-1/3}E^0_{curv} \quad (17)$$

where γ_c is the curvature tension. With respect to hemispherical shape

$$E^{si} - E^{si0} = E^{si0}_s\left(B^{si}_{surf} - 1\right) + E^{si0}_c\left(B^{si}_{curv} - 1\right) \quad (18)$$

For an oblate hemispheroid ($a > c$, $e^2 = a^2/c^2 - 1$)

$$B^{si}_{surf} = \frac{i}{2+i}a^2 + \frac{1}{2+i}\left[a^2 + \frac{ac}{e}\ln\left(e + \frac{a}{c}\right)\right] \quad (19)$$

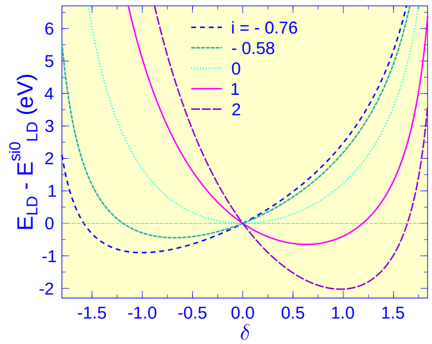

FIG. 2: Minima of deformation energy for different interaction factors i

$$B^{si}_{curv} = B^{s}_{curv} = \frac{c}{2} + \frac{a^2}{2ce} \arctan e \tag{20}$$

For a prolate hemispheroid ($c > a$, $e^2c^2 = c^2 - a^2$)

$$B^{si}_{surf} = \frac{i}{2+i}a^2 + \frac{1}{2+i}\left[a^2 + \frac{ac}{e}\arcsin e\right] \tag{21}$$

$$B^{si}_{curv} = B^{s}_{curv} = \frac{c}{2} + \frac{a^2}{4ce} \ln\left|\frac{1+e}{1-e}\right| \tag{22}$$

From fig. 2 it can be seen that the equilibrium shapes are: oblate hyperdeformed hemispheroid ($\delta = -1, a/c = 3$) when $i = -0.76$, oblate superdeformed hemispheroid ($\delta = -0.68, a/c = 2$) when $i = -0.58$, hemisphere ($\delta = 0, c/a = 1$) when $i = 0$, prolate superdeformed hemispheroid ($\delta = 0.63, c/a = 1.9$) when $i = 1$, prolate hyperdeformed hemispheroid ($\delta = 0.97, c/a = 2.9$) when $i = 2$.

V. SHORT ($h < c$) AND LONG ($h > c$) SPHEROIDAL CAP

Shape independent variables: δ , d_0.

$$\rho^2 = \begin{cases} (a/c)^2(c^2 - z^2) & z \geq d \\ 0 & z < d \end{cases} \tag{23}$$

lengths in units of $R_s = 4^{1/3} r_s N^{1/3}[h_0^2(3-h_0)]^{-1/3}$. Given $d_0 = d(\delta = 0)$. $h_0 = 1 - d_0$. $r_0 = \sqrt{1-d_0^2}$. $r^2 = (a/c)^2(c^2 - d^2)$. Volume conservation leads to

$$h^3 - 3ch^2 + c^3h_0^2(3-h_0) = 0 \tag{24}$$

with a real solution $h = ch_0$. This solution is also good for a long spheroidal cap.

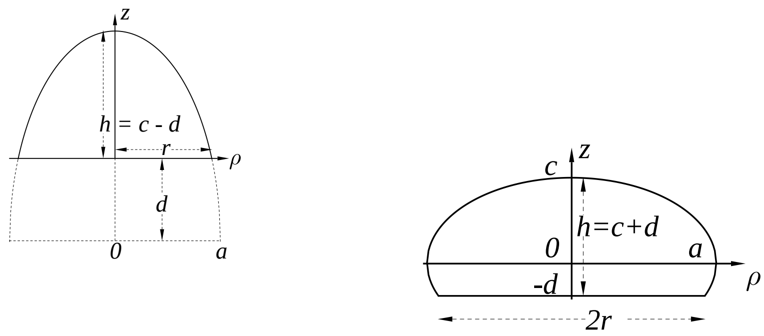

FIG. 3: Short (left-hand side) and long (right-hand side) spheroidal cap

For a spherical cap

$$E_s^{sc0} = \frac{2h_0 + ir_0^2}{4}\left(\frac{R_s}{R_0}\right)^2 E_s^0 = \frac{2h_0 + ir_0^2}{4}\left(\frac{R_s}{R_0}\right)^2 4\pi R_0^2\sigma \tag{25}$$

$$E_c^{sc0} = \frac{h_0 R_s}{2R_0} E_{curv}^0 = \frac{h_0 R_s}{2R_0} 4\pi R_0 \gamma_c \tag{26}$$

Deformation energy relative to the spherical cap

$$E^{sc} - E^{sc0} = E_s^{sc0}\left(B_{surf}^{sc} - 1\right) + E_c^{sc0}\left(B_{curv}^{sc} - 1\right) \tag{27}$$

Oblate shape ($a > c$, $e^2 = a^2/c^2 - 1$) of a short cap

$$B_{surf}^{sc} = \frac{1}{ir_0^2 + 2h_0}\left[ir^2 + a\left(a - \frac{d}{c}\sqrt{c^2 + d^2e^2} + \frac{c}{e}\ln\frac{a + ec}{ed + \sqrt{c^2 + d^2e^2}}\right)\right] \tag{28}$$

$$B_{curv}^{sc} = \frac{h}{2h_0} + \frac{a^2}{2ec}(\arctan e - \arctan\frac{de}{c}) \tag{29}$$

Prolate shape ($c > a$, $e^2c^2 = c^2 - a^2$) of a short cap

$$B_{surf}^{sc} = \frac{1}{ir_0^2 + 2h_0}\left\{ir^2 + a\left[a - \frac{d}{c}\sqrt{c^2 - d^2e^2} + \frac{c}{e}\left(\arcsin e - \arcsin\frac{de}{c}\right)\right]\right\} \tag{30}$$

$$B_{curv}^{sc} = \frac{h}{2h_0} + \frac{a^2}{4ec}\left(\ln\left|\frac{1+e}{1-e}\right| + \ln\left|\frac{ed - c}{ed + c}\right|\right) \tag{31}$$

For a *long cap*. Oblate shape ($a > c$, $e^2 = a^2/c^2 - 1$)

$$B_{surf}^{sc} = \frac{1}{ir_0^2 + 2h_0}\left[ir^2 + a\left(a + \frac{d}{c}\sqrt{c^2 + d^2e^2} + \frac{c}{e}\ln\frac{a + ec}{\sqrt{c^2 + d^2e^2} - ed}\right)\right] \tag{32}$$

$$B_{curv}^{sc} = \frac{h}{2h_0} + \frac{a^2}{2ec}(\arctan e + \arctan\frac{de}{c}) \tag{33}$$

Prolate shape ($c > a$, $e^2c^2 = c^2 - a^2$)

$$B^{sc}_{surf} = \frac{1}{ir_0^2 + 2h_0}\left\{ir^2 + a\left[a + \frac{d}{c}\sqrt{c^2 - d^2e^2} + \frac{c}{e}\left(\arcsin e + \arcsin\frac{de}{c}\right)\right]\right\} \tag{34}$$

$$B^{sc}_{curv} = \frac{h}{2h_0} + \frac{a^2}{4ec}\left(\ln\left|\frac{1+e}{1-e}\right| + \ln\left|\frac{ed+c}{ed-c}\right|\right) \tag{35}$$

Equilibrium shapes of short oblate spheroidal caps ($i < 0$) are less deformed than of long oblate spheroidal caps with the same h_0. On the contrary for prolate shapes ($i \geq 0$).

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PUBLICATIONS, CONFERENCES and SEMINAR in 2008

- **Poenaru, D. N., Gherghescu, R. A., Plonski, R. A., Solov'yov, A. V., Greiner, W.**
  Macroscopic-microscopic theory of semi-spheroidal atomic cluster.
  The European Physical Journal D **47** (2008) 379–393. doi: 10.1140/epjd/e2008-00066-6, HIGHLIGHT PAPER. http://www.springerlink.com/content/015283242219jm76.

- **Poenaru, D. N., Gherghescu, R. A., Solov'yov, A. V., Greiner, W.**
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  Physics Letters A **372** (2008) 5448-5451.

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- **Poenaru, D. N., Gherghescu, R. A., Plonski, I. H., Solov'yov, A. V., Greiner, W.**
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- **Poenaru, D. N., Gherghescu, R. A., Solov'yov, A. V., Greiner, W.**
  Interaction energy at the end cup of a deposited atomic cluster.
  Invited talk, *3rd International Symposium on Atomic Cluster Collisions: structure and dynamics from the nuclear to the MesoBioNano scales (ISACC2008)*, St. Petersburg, Russia, June 3-7, 2008.

- **Gherghescu, R. A., Poenaru, D. N., Solov'yov, A. V., Greiner, W.**
  Ground state and shape isomer deformations of alkali metal atomic clusters.
  Invited talk, *3rd International Symposium on Atomic Cluster Collisions: structure and dynamics from the nuclear to the MesoBioNano scales (ISACC2008)*, St. Petersburg, Russia, June 3-7, 2008.

- **Poenaru, D. N.**
  Atomic clusters on surfaces.
  Invited seminar, Institut für Theoretische Physik der Justus Liebig Universität, Giessen, Germany, 23 May 2008.