

# Liquid drop model binding energy of spherical and semi-spherical atomic clusters

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The liquid drop model adapted to atomic clusters is used to calculate the binding energy of spherical and semi-spherical neutral sodium and argon clusters. There are three important terms: volume, surface, and curvature energy. The relative importance of curvature energy is discussed. It is shown that a semi-spherical cluster is less bound compared to a spherical one.

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The density functional theory [1] is successfully employed in the field of atomic cluster physics. Alternatively, with less computational effort, one can use as a first approximation some simple models [2] replacing the many-body effects by an effective single-particle potential, since to a good approximation the delocalized conduction electrons of neutral small metallic clusters form a Fermi liquid like the atomic nucleus [3].

The liquid drop model (LDM) dominated for many decades the theory of nuclear fission, starting with the first explanation, given in 1939 by Meitner and Frisch, of the induced fission process discovered by Hahn and Strassmann. We have used the LDM to develop the analytical superasymmetric fission model [4] allowing to predict in 1980 heavy particle radioactivity [5], prediction mentioned in the New Encyclopaedia Britannica.

In 1990 W. A. Saunders adapted the LDM to the atomic cluster physics, and explained the increase of fissionability with decreasing size of the charged metal cluster which was observed in experiments. The following year J. P. Perdew et al. [6] presented a LDM for a neutral metal cluster with  $z = 1, 2, 3, 4$  valence electrons. They mentioned that the LDM “originally developed for finite systems (nuclei), may actually be more appropriate for infinite ones (metals).” For the ground state properties of neutral clusters or the fission of doubly or multiply charged clusters, the LDM expresses the smooth part of the total energy to which the shell corrections [8] may be added. The interplay between LDM, shape deformations and Strutinsky shell corrections (including the

case of fission) for free clusters was reviewed by Yannouleas *et al.* [7].

Despite large differences between some specific quantities employed in Nuclear Physics and Atomic Cluster Physics, the macroscopic-microscopic method, i.e. the LDM completed with shell corrections could be very useful to solve many problems of the physics of atomic clusters deposited on different types of substrates. It may provide very rapidly a first solution which can be eventually refined within density functional theory.

Within the self-consistent spherical jellium model a metallic cluster is defined by the number of atoms  $N$  and the electronic density parameter  $r_s$  [9]. 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 ionic charge is homogeneously smeared out within the sphere of radius  $R$  to give a rigid positive background. The electrons move self-consistently in the field of this background and under the influence of their mutual Coulomb interactions.

The energy of a metallic crystal is expressed as a sum of volume, surface and curvature terms [6]; this expression can be accurate even for atomic-scale properties.

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

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

The curvature energy is a corection to the surface energy [10]. The Myers-Swiatecki's droplet model is a LDM model plus terms that arise when it is extended to one higher order in the expansion parameters  $A^{-1/3}$  and  $I^2$ ;  $I = (N - Z)/A$ . It removes the assumption of incompressibility and the requirement that the neutron and proton density distributions have a common surface.

The curvature energy is linear in the mean total curvature,  $L$ , of the surface:

$$L = \int dS (\mathcal{R}_1^{-1} + \mathcal{R}_2^{-1}) \quad (2)$$

where  $\mathcal{R}_1, \mathcal{R}_2$  are the principal radii of curvature of the surface-sheet element  $dS$ .  $L$  is shape dependent; if one compares different convex nuclear shapes with the same volume, it has a minimum for the sphere. The Gaussian total curvature is given by

$$K = \int dS (\mathcal{R}_1 \mathcal{R}_2)^{-1} \quad (3)$$

For simple connected closed surfaces,  $K = 4\pi$ , thus it is constant throughout the fission process, and this property may be used for testing the accuracy of numerical calculations involving  $\mathcal{R}_1, \mathcal{R}_2$ .

In the *leptodermous* (thin surface) approach of their droplet model, Myers and Swiatecki expanded the charge independent part of the binding energy per nucleon in terms of the small

quantities  $A^{-1/3}$  and  $I^2$  up to the 2nd order (one order higher than in the LDM). Of the new terms which enter in this model the only one which has a major influence on the saddle-point properties is the curvature correction to the surface energy. The deformation energy with respect to the spherical shape

$$E_{Def} = a_2(1 - b_1 I^2) A^{2/3} (B_{surf} - 1) + a_3 A^{1/3} (B_{curv} - 1) - a_4 A^{1/3} (B_{comp} - 1) + c_1 Z^2 A^{-1/3} (B_{Coul} - 1) - c_2 Z^2 A^{1/3} (B_{red} - 1) \quad (4)$$

where surface, curvature, compression, Coulomb, and redistribution energies are deformation dependent.

The nanostructured coating of surfaces by cluster deposition [11–13] is at present a rapidly growing field. By analyzing some shapes of cluster deposited on a surface obtained by using scanning probe microscopy [14, 15], 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.

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 are using the standard notation of  $(\rho, z)$  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,  $R_s = 2^{1/3} R_0 = 2^{1/3} r_s N^{1/3}$ , in which  $N$  is the number of atoms,  $r_s$  is the Wigner-Seitz radius and  $\rho = \rho(z)$  is the surface equation given by

$$\rho^2 = \begin{cases} (a/c)^2 (c^2 - z^2) & z \geq 0 \\ 0 & z < 0 \end{cases} \quad (5)$$

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  $a^2 c = 1$ .

It is convenient to choose the deformation parameter  $\delta$  defined by

$$a = \left( \frac{2 - \delta}{2 + \delta} \right)^{1/3} ; \quad c = \left( \frac{2 + \delta}{2 - \delta} \right)^{2/3} \quad (6)$$

so that

$$\frac{a}{c} = \frac{2 - \delta}{2 + \delta} = a^3 ; \quad c = \frac{1}{a^2} \quad (7)$$

The eccentricity is defined by the equation

$$e^2 = \begin{cases} 1 - a^2/c^2 & \text{prolate } (a < c) \\ a^2/c^2 - 1 & \text{oblate } (a > c) \end{cases} \quad (8)$$

TABLE I: Wigner-Seitz radius, Volume, Surface, and Curvature energy parameters for sodium, potassium and argon clusters.

Cluster	$r_s$	$\lambda_V$	$\lambda_S$	$\lambda_{curv}$	Refs.
	$\text{\AA}$	eV	eV	eV	
Sodium	2.117	-2.252	0.541	0.154	[16, 17]
Potassium	2.572	-2.198	0.521	0.072	[17]
Argon	1.90	-0.105701	0.189956	-0.082291	[18]

Clusters and nuclei are “leptodermous” systems characterized by a constant density in the volume and a thin surface layer allowing to expand their binding energy in terms of powers of  $N^{1/3}$ . Despite the fact that this expansion is *a priori* valid only for large enough systems (*e.g.* Na<sub>2654</sub>) it “predicts the energy per electron  $E/N$  accurately (within 0.03 eV) even for  $N = 1$ ” [6]. We are interested in sodium monovalent metallic cluster and in argon a noble gas cluster. From the macroscopic LDM point of view they will have different values of the parameters  $r_S$ ,  $\lambda_V$ ,  $\lambda_S$ , and  $\lambda_{curv}$  (see the table I).

For a spherical neutral cluster with  $N$  atoms, the binding energy is given by

$$E_N = \lambda_V N + \lambda_S N^{2/3} + \lambda_{curv} N^{1/3} = E_V^0 + E_S^0 + E_{curv}^0 \quad (9)$$

with energy constants  $\lambda_V$ ,  $\lambda_S$ , and  $\lambda_{curv}$ , given in table I for sodium, potassium and argon clusters. The volume energy,  $E_V^0$  is proportional to the volume (assumed to be conserved), the surface energy  $E_S^0$  is proportional to the surface area and the surface tension  $\sigma$

$$E_S^0 = 4\pi R_0^2 \sigma = 4\pi r_s^2 \sigma N^{2/3} \quad (10)$$

hence  $4\pi r_s^2 \sigma = 0.541$  eV for Na clusters. The curvature energy  $E_{curv}^0 = 0.154 N^{1/3}$  eV is proportional to the integrated curvature and to the curvature tension  $\gamma_c$

$$E_{curv}^0 = 4\pi R_0 \gamma_c = 4\pi r_s \gamma_c N^{1/3} \quad (11)$$

where  $4\pi r_s \gamma_c = 0.154$  eV for Na clusters. When the cluster is ionized, one should add the Coulomb energy term in eq. 9. The numerical coefficients in eq. (9) have been determined [16, 17] by fitting the extended Thomas-Fermi local density approximation total energy [19] for spherical shapes. In the fig. 2 of ref. [16] the smooth line expressed by eq. (9) is compared to the dots from ref. [19]. The two sets of data coincide at magic numbers. Shell effects, explaining the deformation energy of non-spherical atomic clusters, may be added by using Strutinsky’s [8] procedure.

For a spherical Na cluster with  $N$  atoms, the binding energy in eV is

$$E_N = -2.252N + 0.541N^{2/3} + 0.154N^{1/3} \quad (12)$$

where  $E_v^0 = -2.252N$  eV is proportional to the volume. The binding energy per atom ( $-E_b/N$ )

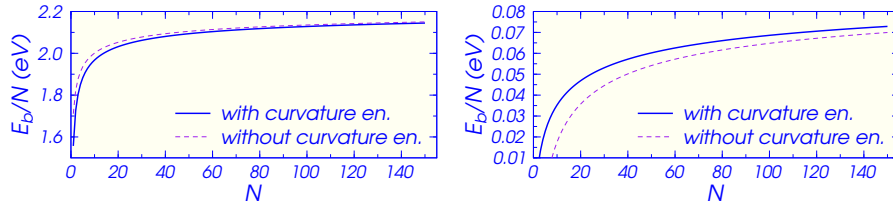


FIG. 1: Binding energy per atom ( $-E_b/N$ ) versus the number of atoms  $N$  for spherical Na (left) and Ar (right) clusters.

versus the number of atoms  $N$  for Na clusters is presented in the left-hand side of figure 1.

For noble gases the Lennard-Jones potential plays an important role

$$U_{LJ}(r_{ij}) = \varepsilon \left[ \frac{1}{2} \left( \frac{r_0}{r_{ij}} \right)^{12} - \left( \frac{r_0}{r_{ij}} \right)^6 \right] \quad (13)$$

where  $r_0$  is the equilibrium pair separation with  $r_0 = 3.8$  Å for Ar-Ar [20] and 3.83 Å for C-Ar.  $\varepsilon$  is the pair well depth with  $\varepsilon = 2.46 \cdot 10^{-2}$  eV for Ar-Ar and  $0.99 \cdot 10^{-2}$  eV for C-Ar. The binding energy per atom for LJ clusters as a function of cluster size was calculated for different types of packing [20].

For a spherical Ar cluster with  $N$  atoms the binding energy [20] in eV is given by

$$E_N = -0.105701N + 0.189956N^{2/3} - 0.082291N^{1/3} \quad (14)$$

In the right-hand side of figure 1 we present the binding energy per atom ( $-E_b/N$ ) versus the number of atoms  $N$  for Ar clusters.

By comparing the two plots in figure 1 one can see, as suggested by the different signs of  $\lambda_{curv}$  for sodium and argon clusters in table I, that in the former case the curvature energy has a negative contribution to the total binding energy, while in the later it increases the total binding.

The deformation energy with respect to spherical shape (surface + curvature) of a semi-spherical cluster is given by

$$E - E^0 = (E_s - E_s^0) + (E_{curv} - E_{curv}^0) = E_s^0 \left( \frac{E_s}{E_s^0} - 1 \right) + E_{curv}^0 \left( \frac{E_{curv}}{E_{curv}^0} - 1 \right) \quad (15)$$

or

$$E - E^0 = E_s^0(B_{surf} - 1) + E_{curv}^0(B_{curv} - 1) \quad (16)$$

where  $B_{surf} = E_s/E_s^0$  and  $B_{curv} = E_{curv}/E_{curv}^0$ . For the relative surface energy of a semi-sphere

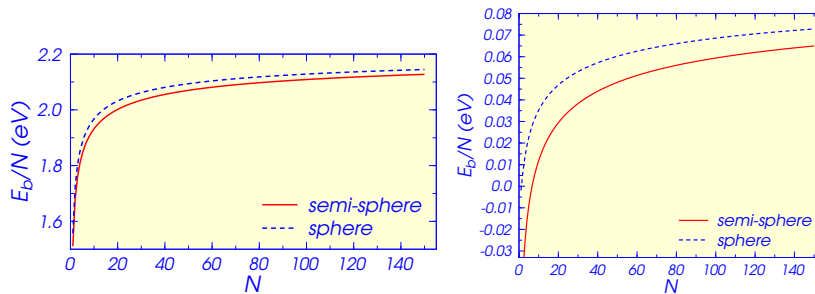


FIG. 2: Binding energy per atom ( $-E_b/N$ ) versus the number of atoms  $N$  for Na (left) and Ar (right) clusters. Comparison between spherical and semi-spherical shapes.

(deformation  $\delta = 0$ ) we obtain

$$B_{surf}(\delta = 0) = (4\pi R_s^2/2 + \pi R_s^2)/(4\pi R_0^2) = (3/4)R_s^2/R_0^2 = 3/4^{2/3} \quad (17)$$

and the corresponding curvature energy

$$B_{curv}(0) = K/4\pi R_0 = (4\pi R_s/2)/(4\pi R_0) = (1/2)(R_s/R_0) = 1/4^{1/3} \quad (18)$$

The mean curvature of a plane is zero, and for a sphere it is  $4\pi$ .

Consequently, the liquid drop part (volume, surface, and curvature terms) of the binding energy of a semi-spherical cluster will be:

$$E_{sN} = \lambda_V N + \frac{3}{4^{2/3}} \lambda_S N^{2/3} + \frac{1}{4^{1/3}} \lambda_{curv} N^{1/3} \quad (19)$$

A cluster with a spherical shape is more tightly bound than a cluster with a semi-spherical shape, as shown in figure 2 for sodium and argon clusters.

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