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SELF-COMPRESSION OF METALLIC CLUSTERS UNDER SURFACE TENSION

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The stabilized jellium model is used to explore the physics of self-compression for spherical clusters of simple-metal atoms. Within the continuum or liquid drop model, strong compression of the interior ionic density of a small cluster (with respect to the bulk density) results from cooperation between surface tension and surface suppression of the elastic stiffness. The latter effect is due to the large negative value of σ'', the second derivative of surface tension with respect to uniform strain. Self-compression also renormalizes the effective curvature-energy coefficient, and contributes to the asymptotic (large-radius) size effect on the ionization energy. A quantum-mechanical calculation of interior density as a function of electron number displays small shell-structure oscillations around the average behavior predicted by the liquid drop model. Numerical results are presented for clusters of Al, Na, and Cs. For compact 6-atom clusters of these metals, predicted bond lengths are smaller than their bulk values by 10%, 6%, and 4%, respectively.

1. INTRODUCTION

SURFACE TENSION can compress a finite system such as a classical liquid drop, a metallic cluster [1], or an atomic nucleus [2]. If the interior density is initially at its bulk value, the radius will contract and the interior density will grow until any further decrease of the surface contribution to the energy is balanced by an increase of the volume contribution. The percentage change in the interior density, although negligible for a macroscopic cluster, can be significant for one composed of just a few atoms.

In this work, we explore the physics of self-compression for spherical clusters of simple metals. To get a lucid picture, we use the continuum or liquid drop model [2, 3] (Section 2). We find that it is not just the volume, surface, and curvature energy coefficients which are needed, but also their derivatives with respect to uniform strain. More interestingly, we find that the strong self-compression of small clusters results from cooperation between surface tension and surface suppression of the elastic stiffness. With the help of quantal calculations (Section 3), we also study how shell-structure effects (neglected in the liquid drop model) influence self-compression.

Unlike the atoms in a classical liquid or the nucleons in a nucleus, the valence electrons in a metallic cluster are not self-bound; they are held together by the external potential of the positive ions. In the simple jellium model, the ions are replaced by a uniform positive background of density

$$\bar{n} = 3/4\pi r_s^3, \tag{1}$$

truncated sharply at a radius

$$R = r_s N^{1/3}, \tag{2}$$

where N is the number of valence electrons present in the neutral cluster. Due to the long-range electrostatic force between the positive background and the electrons, the electron density in the interior of the cluster tends to agree with the background density. At the surface, the electron density spills out and gradually decays to zero.

But bulk ($N \to \infty$) jellium is stable only at $r_s = 4.19$ bohr. (We use atomic units in which $e^2 = \hbar = m = 1$.) For the study of self-compression, the jellium model is inadequate even for Na

($r_s^B = 3.99$), where it underestimates the bulk modulus by a factor of 3. It is useless for metals of much higher (e.g., Al, $r_s^B = 2.07$) or lower (e.g., Cs, $r_s^B = 5.63$) bulk valence electron density, where it fails by predicting negative surface energies or negative bulk moduli, respectively. For our study, we invoke the recently-proposed "stabilized jellium" model [4]: Start with the energy functional of jellium, then subtract the spurious electrostatic self-interaction of the positive background in each "ion" of radius $z^{1/3}r_s$ (where z = valence), and add a constant potential which acts on the valence electrons only inside the radius R. This constant potential (which equals zero at $r_s^B = 4.19$) represents the average difference between the external potential of an array of local electron-ion pseudopotentials and that of the jellium background, and can be expressed in terms of a "pseudopotential core radius" r_c adjusted to achieve bulk stability at the observed valence electron density:

$$\lim_{N\to\infty} \frac{\partial}{\partial r_s}\left(\frac{E(N,r_s,z,r_c)}{N}\right)\Bigg|_{r_s=r_s^B} = 0. \tag{3}$$

Here E is the total energy of the stabilized jellium cluster. The derivative is taken at fixed z, r_c, and N. This "stablized jellium" model yields realistic estimates of the surface energy for all simple metals, and of the bulk modulus or inverse compressibility for the alkali metals, while overestimating the bulk modulus of Al by a factor of two. (The "ideal metal" [5], which has the same surface properties as stabilized jellium, predicts negative bulk moduli.) Our model is completely specified by the bulk density parameter r_s^B and the valence z, which characterize each simple metal and fix r_c.

The equilibrium density parameter r_s^* for a cluster with a finite number N of valence electrons is the solution of

$$\frac{\partial}{\partial r_s}\left(\frac{E(N,r_s,z,r_c)}{N}\right)\Bigg|_{r_s=r_s^*} = 0, \tag{4}$$

where again the derivative is taken at fixed z, r_c, and N. We find, as expected, $r_s^* \le r_s^B$, i.e., the ionic density is higher in the cluster than in bulk. For the simple metals Al, Na, and Cs, which cover the normal range of valence electron densities, we shall find r_s^* and related properties as functions of N. Of particular interest is the elastic stiffness or inverse compressibility of the finite system,

$$B(N,r_s^*,z,r_c) = \frac{1}{12\pi r_s^*}\frac{\partial^2}{\partial r_s^2}\left(\frac{E(N,r_s,z,r_c)}{N}\right)\Bigg|_{r_s=r_s^*}, \tag{5}$$

which tends to the bulk modulus B^B as $N \to \infty$.

In a real metallic cluster, self-compression occurs via a shortening of inter-atomic distances (Section 3). Thus, the physically meaningful cases are $N = 2,3,4,\ldots$ for the monovalent metals Na and Cs, and $N = 6,9,12,\ldots$ for the trivalent metal Al.

2. LIQUID DROP MODEL FOR SELF-COMPRESSION

The energy $E(N,r_s,z,r_c)$ for a spherical cluster of stabilized jellium may be evaluated by a quantal density functional method (Section 3). But, for simplicity, we begin with the continuum description of the energy provided by the liquid drop model, which has found important applications not only to nuclei [2] but also to metals [3]:

$$\begin{aligned} E(N,r_s,z,r_c) &= \alpha(r_s,z,r_c)V \\ &\quad + \sigma(r_s,z,r_c)S + \gamma(r_s,z,r_c)C \\ &= a_v(r_s,z,r_c)N + a_s(r_s,z,r_c)N^{2/3} \\ &\quad + a_c(r_s,z,r_c)N^{1/3}, \end{aligned} \tag{6}$$

where $V = 4\pi R^3/3$ is the volume, $S = 4\pi R^2$ is the surface area, and $C = 2\pi R$ is half the surface integral of the curvature. Here α, σ, and γ are material-dependent volume, surface, and curvature energy parameters (e.g., σ is the surface tension), while $a_v = (4\pi/3)r_s^3\alpha$, $a_s = 4\pi r_s^2\sigma$, and $a_c = 2\pi r_s\gamma$. (The dependence upon r_s, z, and r_c is henceforth implicit.) For stabilized jellium, a_v is the average energy per electron for a bulk system of uniform density. σ and γ are evaluated within the local density approximation for exchange and correlation from Kohn–Sham [7] solutions for the semi-infinite (planar surface) problem [8]. Although equation (6) is an asymptotic expansion, strictly valid for $N \to \infty$, it provides a useful average of the shell-structure oscillations of the quantal result, and is accurate even for $N = 1$ (a monovalent atom of stabilized jellium [9, 10].

By equation (4), we must vary r_s to minimize $E(N,r_s,z,r_c)$ at fixed r_c, z, and N. The physical minimum should be fairly close to r_s^B; we neglect a possible global minimum of equation (6) at $r_s = 0$, which falls outside the domain of validity of the

liquid drop model. The numerically-determined minimum of $E(N, r_s, z, r_c)$ is reasonably close to that of its Taylor expansion to third order in $(r_s - r_s^B)$:

$$E(N,r_s,z,r_c) \approx E(N,r_s^B,z,r_c) + (r_s - r_s^B)E'(N,r_s^B,z,r_c) + \tfrac{1}{2}(r_s - r_s^B)^2 E''(N,r_s^B,z,r_c) + \tfrac{1}{6}(r_s - r_s^B)^3 E'''(N,r_s^B,z,r_c), \quad (7)$$

with

$$E'(N,r_s^B,z,r_c) = \partial E/\partial r_s|_{r_s=r_s^B},$$

etc. The first derivative of the liquid drop model energy is

$$E' = a_v' N + a_s' N^{2/3} + a_c' N^{1/3}, \quad (8)$$

and similar expressions hold for higher derivatives. From the condition (3) of bulk stability, the first term of equation (8) must vanish:

$$a_v' = \partial a_v/\partial r_s|_{r_s=r_s^B} = 0. \quad (9)$$

The other needed derivatives of the liquid drop coefficients have been evaluated numerically by the method of [8] and are reported in Table 1.

For the cubic problem of equation (7), the equilibrium condition of equation (4) is

$$E' + (r_s^* - r_s^B)E'' + \tfrac{1}{2}(r_s^* - r_s^B)^2 E''' = 0, \quad (10)$$

or

$$r_s^* - r_s^B \approx \frac{-E'' + \sqrt{(E'')^2 - 2E'E'''}}{E'''}. \quad (11)$$

When r_s^* is very close to r_s^B, the expansion (7) may be truncated at quadratic order, so that equation (11) simplifies to

$$r_s^* - r_s^B \approx \frac{-E'}{E''} = \frac{-a_s' N^{2/3} - a_c' N^{1/3}}{a_v'' N + a_s'' N^{2/3} + a_c'' N^{1/3}}. \quad (12)$$

In the asymptotic limit $N \to \infty$, equation (12) becomes

$$r_s^* \approx r_s^B[1 - \beta N^{-1/3}], \quad (13)$$

where

$$\beta = \frac{a_s'}{r_s^B a_v''}. \quad (14)$$

In Figs 1–3, we compare the numerically-determined equilibrium density parameters $r_s^*(N)$ with the analytic solutions (11), (12), and (13) of the cubic, quadratic, and asymptotic problems. For $N \geq 2$, the solution of the cubic problem is usually an adequate representation of r_s^*, which is overestimated by the asymptotic solution and underestimated by the solution of the quadratic problem. For Al, however, we found no minimum of equation (6) for $N \leq 4$; this is a failure of the liquid drop model, since stabilized jellium finds a minimum for $N \leq 4$ in the quantal calculation of Section 3.

The elastic stiffness of the cluster, defined by equation (5), may also be evaluated numerically. In the cubic expansion of equation (7), it becomes

$$B(N, r_s^*, z, r_c) \approx \frac{1}{12\pi r_s^* N}[E'' + (r_s^* - r_s^B)E'''], \quad (15)$$

Table 1. Parameters of the liquid drop model of equation (6) *for stabilized jellium, and their derivatives with respect to* r_s *at fixed* z *and* r_c. (*Atomic units*)

	Al ($r_s^B = 2.07, z = 3$)	Na($r_s^B = 3.99, z = 1$)	Cs ($r_s^B = 5.63, z = 1$)
a_v	−0.7019	−0.2301	−0.1705
a_s	0.0321	0.0219	0.0153
a_c	0.0239	0.0088	0.0047
a_s'	0.1540	0.0143	0.0059
a_c'	−0.0165	−0.0058	−0.0029
a_v''	0.4181	0.0369	0.0143
a_s''	−0.5278	−0.0317	−0.0109
a_c''	−0.0189	0.0030	0.0013
a_v'''	−1.3509	−0.0621	−0.0172
a_s'''	1.7514	0.0575	0.0153
a_c'''	0.1515	−0.0000	−0.0005
β	0.1779	0.0971	0.0734
λ	−0.1055	0.1108	0.1913
$\tilde{a}_c$	−0.0045	0.0060	0.0035
Δc	−0.0296	0.0027	0.0019

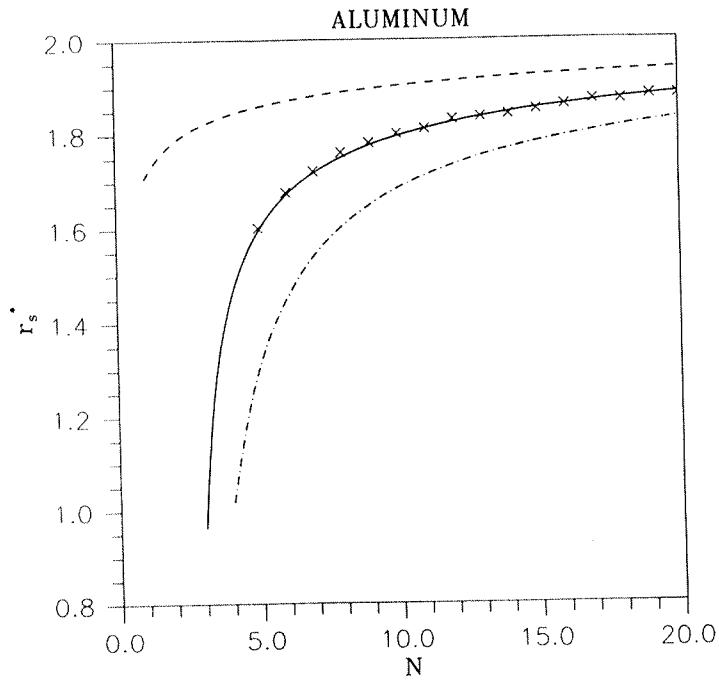

Fig. 1. Equilibrium density parameter r_s^* for an N-electron neutral cluster of stabilized jellium representing Al ($r_s^B = 2.07, z = 3$), within the liquid drop model. Dashed curve: Asymptotic solution (13). Dash–dotted curve: Solution (12) of the quadratic problem, which drops the $(r_s - r_s^B)^3$ term of equation (7). Solid curve: Solution (11) of the cubic problem, which retains the $(r_s - r_s^B)^3$ term of equation (7). Crosses: Exact (numerical) solution within the liquid drop model of equation (6).

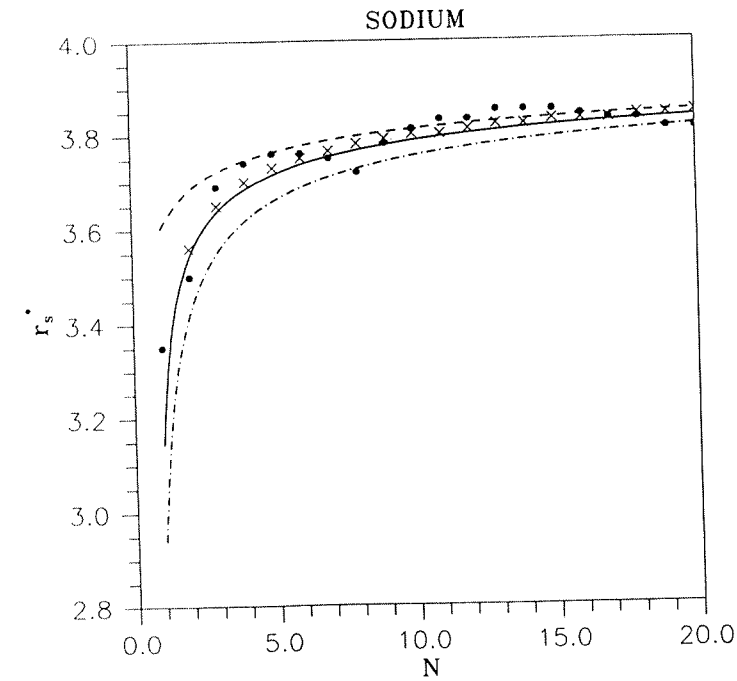

Fig. 2. Same as Fig. 1, for Na ($r_s^B = 3.99, z = 1$). Heavy dots: Quantal results (beyond the liquid drop model).

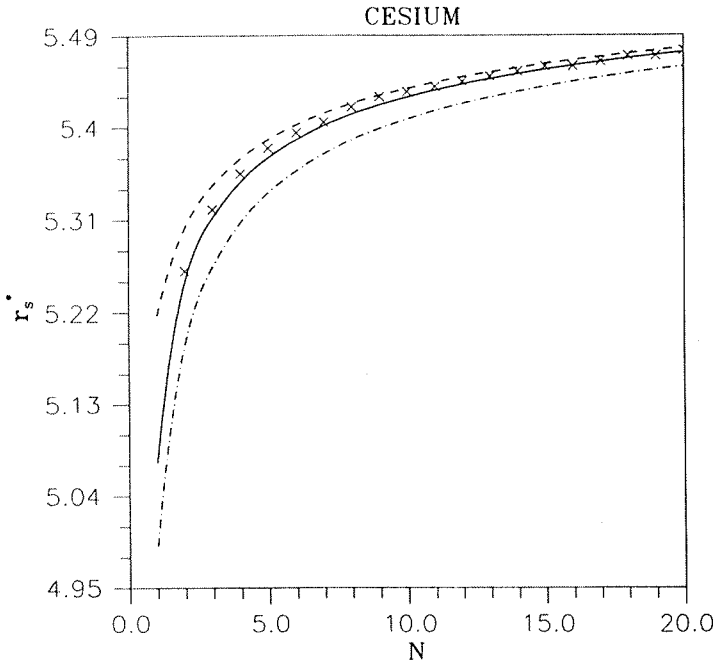

Fig. 3. Same as Fig. 1, for Cs ($r_s^B = 5.63, z = 1$).

In the asymptotic limit $N \to \infty$, we find

$$B(N, r_s^*, z, r_c) \approx B^B[1 - \lambda N^{-1/3}], \tag{16}$$

where

$$B^B = a_v''/(12\pi r_s^B) \tag{17}$$

is the bulk modulus, and

$$\lambda = \frac{-1}{a_v''}\left[a_s'' + \frac{a_s'}{r_s^B}\left(1 - \frac{a_v'' r_s^B}{a_v''}\right)\right]. \tag{18}$$

Figure 4 shows $B(N, r_s^*, z, r_c)/B^B$ for Na, in different approximations. Note that surface effects make

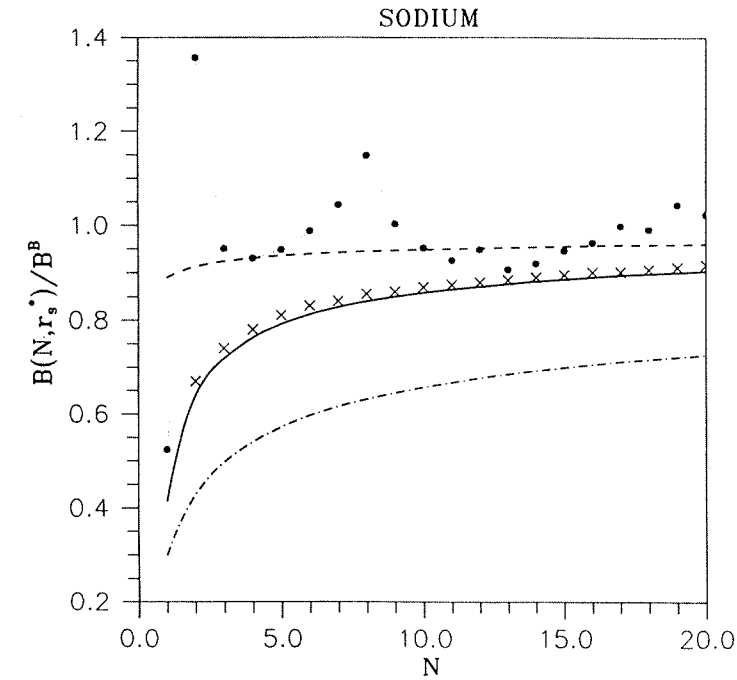

Fig. 4. Ratio of the elastic stiffness to its bulk value, for an N-electron neutral cluster of stabilized jellium representing Na. See captions of Figs 1 and 2.

$B(N, r_s^*, z, r_c)$ less than B^B, i.e., they suppress the elastic stiffness and so cooperate with the surface tension to produce a strong self-compression.

Equation (15) displays two competing effects on the elastic stiffness $B(N, r_s^*, z, r_c)$. Self-compression ($r_s^* < r_s^B$) tends to increase B, but this effect is overwhelmed by the surface contribution ($a_s'' < 0$) to E'', which decreases B. We find $a_s'' < 0$ because $\sigma'' < 0$, as Brack, Guet, and Håkansson [2] found for nuclei. If we had ignored the r_s dependence of σ and γ (i.e., $a_s'' = 8\pi\sigma = 2a_s/(r_s^B)^2$, etc.), we would have found $B(N, r_s^*, r_c) > B^B$, and correspondingly weaker self compressions.

Self-bound systems like nuclei or classical liquid drops have [11] $\sigma' = 0$, where the derivative is taken with respect to the interior particle density parameter r_s. But stabilized jellium has $\sigma' \neq 0$, since this derivative is taken with respect to the interior background density parameter, and the positive background profile at the surface is not allowed to relax. (The stabilized jellium model is valid [4] only for a background density that is *constant* inside a sharp surface, and zero outside.)

Also of interest is the liquid drop expansion for the energy of the relaxed (i.e., self-compressed) cluster. After inserting equation (13) into equation (7) and expanding to order $N^{1/3}$, we find

$$E(N, r_s^*, z, r_c) = a_v N + a_s N^{2/3} + \tilde{a}_c N^{1/3}, \tag{19}$$

where

$$\tilde{a}_c = a_c - \frac{1}{2}\frac{(a_s')^2}{a_v''} \tag{20}$$

is a renormalized curvature coefficient. A similar renormalization of a_c occurs in nuclei [2]. Table 1 compares a_c and $\tilde{a}_c$. We note that these quantities have opposite signs for Al. Of course, the relaxation energy $(\tilde{a}_c - a_c)N^{1/3}$ is negative.

Finally, we consider the effect of self-compression on the asymptotic chemical potential and ionization energy of a cluster. The chemical potential at the equilibrium density is

$$\mu(N, r_s^*, z, r_c) = \mu(N, r_s^B, z, r_c) + (r_s^* - r_s^B)\frac{\partial}{\partial r_s}\mu(N, r_s, z, r_c)|_{r_s = r_s^B} + \cdots. \tag{21}$$

In the limit $N \to \infty$, [12]

$$-\mu(N, r_s^B, z, r_c) \approx W + c/R, \tag{22}$$

where the work function W and size-effect coefficient c depend upon r_s^B, and $c \approx -0.08$ (independent of r_s^B) for jellium [13]. Thus

$$-\mu(N, r_s^*, z, r_c) \approx W + (c + \Delta c)/R, \tag{23}$$

where self-compression contributes

$$\Delta c = \frac{-a_s' r_s^B}{a_v''} W'. \tag{24}$$

The first ionization energy of a large cluster is [12] $-\mu(N, r_s^*, z, r_c) + 1/2R$. Table 1 shows that Δc is negligible for Na and Cs, but noticeable for Al.

3. QUANTAL EFFECTS, AND CONCLUSIONS

Beyond the liquid drop model of Section 2, we have performed Kohn–Sham [7] calculations for spherical clusters of stabilized jellium, within the local spin density approximation, and have found the r_s^* which yields the minimum quantal energy at fixed z and r_c for each N. Details of the calculation may be found in [8]. Figure 2 presents the results of this calculation for Na clusters. We see that the liquid drop model provides an excellent average over the shell-structure oscillations. The closed-shell cluster $N = 8$ shows a greater self-compression than clusters with neighboring values of N.

Figure 4 shows the quantal result for the elastic stiffness of equation (5). It is larger than the liquid drop result, and maximizes at the magic numbers $N = 2$ and 8.

The case $N = z = 1$ represents a monovalent atom of stabilized jellium. Besides the local energy minimum at finite r_s^*, its quantal energy shows a global minimum when $r_s^* \to 0$. Because the self-interaction of the positive background has been eliminated, the background can collapse to a point nucleus, forming a hydrogen atom. Thus, although our model for the bulk metal is stable against homogeneous deformations, it is not stable against inhomogeneous ones which localize the positive charge on a point lattice.

A more realistic description of metallic clusters at the atomistic level can be achieved with electron-ion pseudopotentials. Martins, Car, and Buttet [1, 14] have performed pioneering calculations for small Na clusters, finding the geometry that minimizes the energy for each N. Their results [14] for the average distance between nearest-neighbor atoms seem to display the self-compression we have found in the stabilized jellium model. For $N \leq 5$, their Na clusters are planar, in contrast to our spherical stabilized jellium clusters. However, their $N = 13$ cluster has a compact shape which invites comparison with our model: They find an average nearest-neighbor

distance which is 95% of its bulk value [15], and we find an r_s^* which is 96% of its bulk valence.

In summary, we have studied the self-compression of metallic clusters within the stabilized jellium model [4], the simplest picture which might describe this effect over the whole range of bulk densities. Both liquid drop model [1–3, 16] and quantal calculations have been reported.

We find substantial self-compressions of small clusters. Within the liquid drop model, the size of the effect is enhanced by cooperation between surface tension, which drives the compression, and surface suppression of the elastic stiffness. The latter effect is surprising, since shorter bond lengths imply stiffer bonds; it is a consequence of the strong r_s- or strain-dependence of the surface and curvature energy coefficients σ and γ. From another viewpoint, it is a consequence of the fact that some of the bonds at the surface are missing. Self-compression reduces the effective curvature-energy coefficient, and influences the R^{-1} contribution to the ionization energy for a cluster of large radius R.

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CORRIGENDUM

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In Fig. 4, numerical error in the evaluation of the second derivative produced quantal or Kohn-Sham values for the elastic stiffness of Na clusters that were systematically too high. The corrected values, which now oscillate around the liquid-drop-model trend line, are shown in Fig. 4 of M. Brajczewska, C. Fiolhais, A. Vieira, and J.P. Perdew, in Many-Body Physics, edited by C. Fiolhais, M. Fiolhais, C. Sousa, and J.N. Urbano (World Scientific, Singapore, 1994). (Although the corrected values are based upon the local density approximation, they should be directly comparable to the original values, based upon the local spin density approximation, for N = 2, 8, 18, and 20.) Quantal results for the density and elastic stiffness of Al and Cs clusters have also been reported there.