COMPRESSION OF METALLIC CLUSTERS IN THE STABILIZED JELLIUM MODEL

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ABSTRACT

The stabilized jellium model is used to study the compression of the interior ionic density of small metallic clusters (with respect to the bulk density) due to surface tension. Results from the Kohn-Sham equations using the Local Density Approximation are compared with the liquid drop model.

1. Introduction

Surface tension compresses a finite system. The change in the interior density can be significant for a system composed of few particles.

We study here the self-compression of simple metal clusters within the stabilized jellium model, the simplest picture which may describe this effect over the whole range of bulk densities. We use the Kohn-Sham equations and the liquid drop model, considering three different metals (Al, Na and Cs) which cover the range of physical densities. This work is an extension of Ref. 1: we now report quantal results not only for Na but also for Al and Cs. In contrast with that work, we use now the Local Density Approximation (LDA), with the Perdew-Wang parametrization[2] for the correlation energy, instead of the Local Spin Density Approximation (LSD), with the Vosko-Wilk-Nusair correlation energy (LDA and LSD yield similar results, with LSD slightly more realistic and closer to the liquid drop model). The numerics has also been improved.

2. Kohn-Sham calculations

In the stabilized jellium model,[3] the energy of a spherical cluster is a function of the number of valence electrons N, the density parameter r_s (the ionic charge density is $\overline{n} = 3/4\pi r_s^3$), the valence z and the "pseudopotential core radius" r_c, which is adjusted to achieve bulk stability at the observed electron density: $E = E(N, r_s, z, r_c)$. This energy can be evaluated solving the self-consistent Kohn-Sham equations of density functional theory.[4] We then look for the minimum of the energy per valence electron

$$\frac{\partial}{\partial r_s}(E(N, r_s, z, r_c)/N)_{|r_s=r_s^*} = 0 \quad ,$$

with the derivative taken at fixed N, z and r_c. The result is the density parameter of the compressed system, r_s^*.

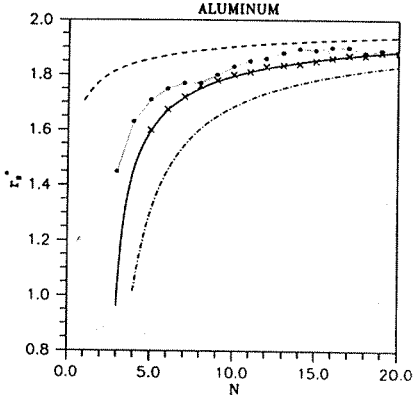

Fig.1 - Equilibrium density parameter r_s^* for an N-electron neutral cluster of stabilized jellium representing Al ($r_s^B = 2.07$ bohr, $z = 3$). Heavy dots: Kohn-Sham results. Crosses: Exact (numerical) solution, within the liquid drop model. Solid curve: Solution in the cubic approximation. Dash-dotted curve: Solution in the quadratic approximation. Dashed curve: Asymptotic solution.

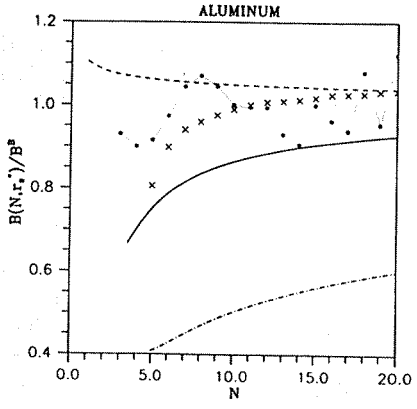

Fig.2 - Ratio of the elastic stiffness to its bulk value, for an N-electron neutral cluster of stabilized jellium representing Al. See caption of Fig.1.

Figs. 1, 3 and 5 show the results for Al, Na and Cs, respectively. We note that no r_s^* has been obtained in the case of Al for less than 3 valence electrons ($N = 3, 6, 9$, etc. are the physically meaningful cases). The self-compression effect is very strong for Al and less pronounced for Na and Cs. Shell effects are visible: for instance, there is a local minimum in the curve r_s^* versus N for $N = 8$. The result for Na is similar to that presented in Fig. 2 of Ref. 1.

We have also evaluated the elastic stiffness of the finite system:

$$B = B(N, r_s^*, z, r_c) \simeq \frac{1}{12\pi r_s^* N} \frac{\partial^2}{\partial r_s^2} (E(N, r_s, z, r_c))_{|r_s = r_s^*} \quad .$$

This second derivative, taken at the equilibrium density, goes over to the bulk modulus B^B when $N \to \infty$. It is calculated numerically by making a least square fit of a fourth order polynomial to the curve $E(N, r_s, z, r_c)$, around the minimum.

Figs. 2, 4 and 6 show the results for the three considered metals. The stiffness of small clusters of Al has roughly the same value as in the bulk (clusters with

$N = 7, 8, 9, 18$ and 20 have even a larger stiffness than the bulk solid). The stiffness of small clusters of Na and Cs is always lower than its bulk value. Note the discrepancy with the result for Na presented in Fig. 4 of Ref. 1, where the systematically too- high Kohn-Sham values of the elastic stiffness were due to a numerical error in evaluating the second derivative of the energy. The occurrence of shell closures is reflected in the higher values of the stiffness for systems with $N = 2, 8$ and 20.

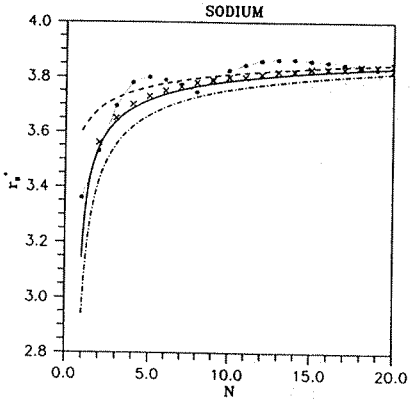

Fig.3 - Same as Fig.1, for Na ($r_s^B = 3.99$ bohr, $z = 1$).

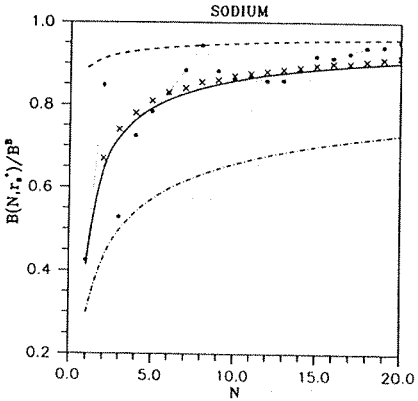

Fig.4 - Same as Fig.2, for Na.

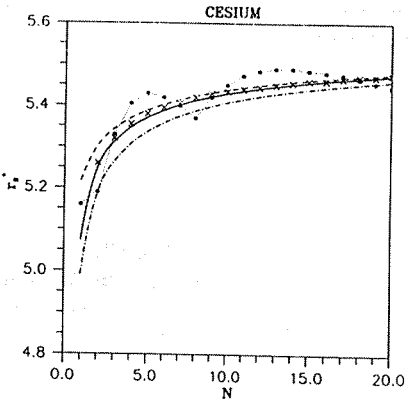

Fig.5 - Same as Fig.1, for Cs ($r_s^B = 5.63$ bohr, $z = 1$).

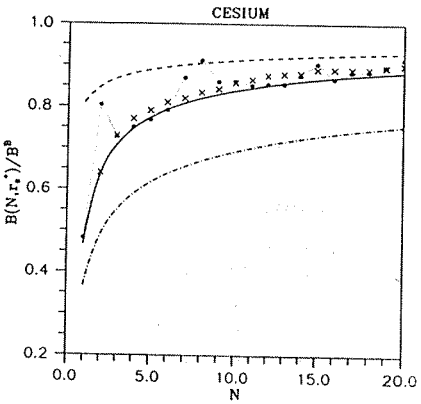

Fig.6 - Same as Fig.2, for Cs.

3. Liquid drop model

In the continuum or liquid drop model, shell fluctuations are absent. The energy can be written as a simple power series of the electron number N:

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

where a_v is the average energy per electron for a bulk system of uniform density, a_s is a surface energy coefficent and a_c is curvature energy coefficient. The surface and curvature coefficients can be determined from the semi-infinite density profile with the aid of the so-called "leptodermous expansion".[5]

Now, the equilibrium density parameter r_s^* for a cluster with N valence electrons can be evaluated numerically, looking for the minimum of the liquid drop energy. Alternatively, we can find analytical expressions for r_s^*, approximating the liquid drop energy by its Taylor expansion to third order in $(r_s - r_s^B)$, with r_s^B the bulk density parameter: $E(N, r_s, z, r_c) \simeq E(N, r_s^B, z, r_c) + (r_s - r_s^B)E' + \frac{1}{2}(r_s - r_s^B)^2 E'' + \frac{1}{6}(r_s - r_s^B)^3 E'''$. Here $E' = E'(N, r_s^B, z, r_c) = a_v' N + a_s' N^{2/3} + a_c' N^{1/3} = \frac{\partial}{\partial r_s} E(N, r_s, z, r_c)_{|r_s = r_s^B}$, etc. From the condition of bulk stability, $a_v' = 0$. The other needed derivatives of the liquid drop model coefficients have been evaluated numerically. For Na, Cs and Al their values can be found in Ref. 1. One obtains: $r_s^* \simeq r_s^B + (\sqrt{(E'')^2 - 2E'E'''} - E'')/E'''$. Dropping the term $(r_s - r_s^B)^3$ (quadratic approximation), the solution is: $r_s^* \simeq r_s^B - E'/E''$, which, taken in the asymptotic limit $N \to \infty$, gives: $r_s^* \simeq r_s^B - a_s' N^{-1/3}/a_v''$.

Figs. 1, 3 and 5 display the equilibrium density parameter r_s^* as a function of the number of electrons N, in the cubic, quadratic and asymptotic approximations, together with the exact numerically-determined liquid drop value. We see that the exact numerical result is close to the result of the cubic approximation. The asymptotic expression overestimates this correct result, while the quadratic approximation underestimates it. The liquid drop provides a nice average of the Kohn-Sham result.

Figs. 2, 4 and 6 show the elastic stiffness as a function of N, in the different degrees of approximation to the liquid drop model. Again, the exact liquid drop result provides an average over the quantal results. The cubic approximation is not good enough for Al, but works well for Na and Cs. In any case, the quadratic approximation is not reliable.

4. Conclusions

We have found, as expected, that the equilibrium parameter $r_s^* < r_s^B$, *i.e.*, the ionic density is higher in the cluster than in bulk. This effect is stronger in Al than in Na and Cs. A quantum-mechanical calculation of the interior density as a function of the electron number displays small shell-structure oscillations around the average behavior predicted by the liquid drop model.

References

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3. J. P. Perdew, H. Q. Tran and E. D. Smith, *Phys. Rev.* **B42** (1990) 11627.
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