Decay of Charged Stabilized Jellium Clusters

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ABSTRACT

The stabilized jellium model is a simple modification of the jellium model, which more realistically describes simple metals of high density, such as Al, Ga, Pb, etc. We analyzed the fragmentation processes of charged spherical Al clusters in the framework of the stabilized jellium model. Kohn–Sham calculations of the parents and daughters, using the local density approximation, have been made. We evaluated the dissociation energies of Al_N^+ , Al_N^{2+} , and Al_N^- , with $N = 1–30$ atoms, in all possible decay channels. We discuss the most favorable decay channels, which are ruled by the shell structure (magic numbers of valence electrons in the parents and the daughters) oscillations around an average trend given by a liquid drop model. We compare our calculations with others and with the available experimental data. © 1995 John Wiley & Sons, Inc.

1. Introduction

In previous works, the surface and cohesive properties of bulk-stabilized jellium and the energetics of small stabilized jellium clusters were studied [1–4]. In this work, we studied the decay of charged aluminum clusters containing up to 30 atoms within the stabilized jellium model.

The stabilized jellium model retains the simplicity and universality of the jellium model, widely used in cluster physics. Both are simple in the sense that the ions are replaced by a continuous charge background and universal in the sense that the only input parameters are the density parameter r_s (the ionic charge density is $\bar{n} = 3/4\pi r_s^3$, for dis-

tances smaller than the cluster radius $R = r_s N_c^{1/3}$, with N_c the number of valence electrons of the neutral cluster) and the valence z . The stabilized jellium model cures some deficiencies of the jellium model: unrealistic binding energies at all densities, unrealistic bulk moduli at low densities, and unrealistic surface energies at high densities. All these results follow from the instability of jellium at densities different from $r_s \approx 4.00$ bohr. In the stabilized jellium model, which is clearly more realistic than is jellium for Al (which has $r_s = 2.07$ bohr and $z = 3$), we add to the electrostatic potential inside the cluster a constant potential, different for each metal, and constructed in order to have stability of the bulk metal at the observed density.

In the stabilized jellium model, the energy of a spherical cluster can be evaluated by solving the self-consistent Kohn–Sham equations of density functional theory. We adopted the local density approximation (LDA), with the Perdew–Wang correlation energy [5]. These equations read

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \psi_\alpha(\mathbf{r}) = \epsilon_\alpha \psi_\alpha(\mathbf{r}), \quad (1.1)$$

where α denotes a set of quantum numbers. The effective potential is

$$v_{\text{eff}}(\mathbf{r}) = v_+(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + \mu_{xc}(\mathbf{r}), \quad (1.2)$$

where v_+ is the electrostatic potential for the interaction between the background and the electrons; $n(\mathbf{r})$, the electronic density; and $\mu_{xc}(\mathbf{r})$, the exchange–correlation potential. We have

$$v_+(\mathbf{r}) = \begin{cases} -\frac{N_c}{2R} \left[3 - \left(\frac{r}{R} \right)^2 \right] + \langle \delta v \rangle_{WS} & (r < R) \\ -\frac{N_c}{r} & (r > R), \end{cases} \quad (1.3)$$

with

$$\langle \delta v \rangle_{WS} = -\frac{k_F^2}{5} + \frac{k_F}{4\pi} + \frac{r_s}{3} \frac{d\epsilon_c}{dr_s} \quad (1.4)$$

the constant potential of the stabilized jellium model (ϵ_c is the correlation energy per electron of the uniform electron gas and $k_F = [(9\pi/4)^{1/3}/r_s]$). The second term is the Hartree potential. The exchange–correlation potential $\mu_{xc}(\mathbf{r})$ is given by

$$\mu_{xc}(\mathbf{r}) = \frac{\partial}{\partial n(\mathbf{r})} [n(\mathbf{r})\epsilon_{xc}(\mathbf{r})], \quad (1.5)$$

with $\epsilon_{xc} = -3k_F/4\pi + \epsilon_c$.

The total electronic density is

$$n(\mathbf{r}) = \sum_\alpha |\psi_\alpha(\mathbf{r})|^2, \quad (1.6)$$

with the sum extended to all occupied electronic levels.

Once the self-consistent density of the cluster is known, the total energy is given by the functional

$$E(n(\mathbf{r})) = \sum_\alpha \epsilon_\alpha - \left(U[n] + \int d^3r \mu_{xc}(\mathbf{r})n(\mathbf{r}) \right) + U_B[n_+] + \int d^3r \epsilon_{xc}(\mathbf{r})n(\mathbf{r}), \quad (1.7)$$

where

$$U[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (1.8)$$

is the electronic Coulomb repulsion energy and

$$U_B[n_+] = \frac{3}{5} \frac{N_c(N_c - N_c^{1/3})}{R} \quad (1.9)$$

is the background Coulomb repulsion minus the self-repulsion energy within each Wigner–Seitz cell.

Of course, we can evaluate the energy of neutral Al clusters, with the number of electrons equal to $N_e = 3N$ (N being the number of atoms) as well as the energy of charged clusters, with the number of electrons equal to $N_e + Z$ (Z being the number of excess electrons).

We analyzed the fragmentation process and the relative stability based on energetic considerations. For the sake of simplicity, spherical symmetry is imposed not only on the parents but also on the products.

We consider positive- and negative-charged clusters with up to two electronic charges and consider all possible decay channels. For instance, for double-charged Al, channels such as the fission into charged products,

as well as the evaporation process,

were considered. The dissociation energy (or heat of reaction) is given by

$$\Delta E(N, p) = E_{N-p}^{+} + E_p^{+} - E_N^{2+}, \quad (1.12)$$

in the first case, and

$$\Delta E(N, p) = E_{N-p}^{2+} + E_p - E_N^{2+}, \quad (1.13)$$

in the second case. Similar expressions hold for the decay of single-charged clusters.

A negative ΔE implies that energy is released and fragmentation is spontaneous in that particular channel. A positive ΔE , on the other hand, implies that the parent cluster is stable against that particular decay.

It is clear that a pure energetic criterion is not enough to discuss stability: The dissociation energy may be negative, for instance, for the fission process of double-charged clusters, but the initial system may be metastable, due to the Coulomb barrier between the products. Excitation above the barrier, induced by collisions or radiation, will eventually lead to the decay expected on the basis of the dissociation energy. From the experimental data on the decay of double-charged clusters of simple metals

(Na is the most studied case [6,7]), it is known that fission, producing one light and one heavy charged fragment, is favored for small clusters, whereas evaporation becomes the most important deexcitation channel after some cluster size. It is also known that single-charged clusters are stable against dissociation. But, again, excitation can lead to fragmentation and a competition appears between the emission of a charged light product and that of an atom.

We examine how the stabilized jellium model performs to describe the fragmentation of Al. In the next section, we present the results, and in the final section, the main conclusions are drawn.

2. Results

In Figure 1, we show the results of the spherical Kohn–Sham calculation of the energy per atom of Al clusters (neutral, with charge +1 and with charge +2). The magic numbers appear as local minima in the energy curves. They correspond to enhanced stability, due to the closure of shells or subshells in the self-consistent potential. The magic

numbers of stabilized jellium are the same as those of the jellium model, at least for the relatively small number of electrons considered here. (Nevertheless, the system is bound much more in the stabilized jellium than in the jellium model). They are 2, 8, 18, 20, 34, 40, 58, 92, which correspond to the closure of the following orbitals: $1s^2$, $1p^6$, $1d^{10}$, $2s^2$, $1f^{14}$, etc.

Superimposed on the quantal results, we also show the liquid drop or continuous approximation for the energy, which averages out shell effects. In the liquid drop model, the energy of a neutral cluster is written as a simple power series of the electron number N_e :

$$E_0(N_e, r_s, z) = a_v(r_s, z)N_e + a_s(r_s, z)N_e^{2/3} + a_c(r_s, z)N_e^{1/3}, \quad (2.1)$$

where a_v is the average energy per electron for a bulk system of uniform density; a_s , the surface energy coefficient; and a_c , the 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 [2] (for Al, $a_v = -19.10$ eV, $a_s = 0.87$ eV, and $a_c = 0.65$ eV, in the stabilized jellium model). The energy of

FIGURE 1. Energy per atom as a function of the number of atoms for neutral, single, and double positively charged Al clusters. Heavy dots refer to the Kohn–Sham results and continuous lines refer to the liquid drop model.

FIGURE 2. The dissociation energy $\Delta E(N, p)$, calculated in the Kohn–Sham scheme, as a function of the size of parents (N) and daughters (p and $N - p$), for some decay channels of double- and single-charged Al clusters.

a charged cluster can also be described by a continuous approximation. In [8,9], the following liquid drop formula of a charged cluster with Z excessive electrons has been obtained in the jellium model:

$$E(Z) = E_0 - Z \left(W + \frac{c}{R} \right) + \frac{Z^2}{2R}, \quad (2.2)$$

where W is the work function, and c , a coefficient that, in principle, can be expressed on the basis of the semi-infinite problem. This expression should also be valid for stabilized jellium, given the essential similarity of both energyfunctionals.

The work function of Al in the stabilized jellium model is 4.26 eV [2]. Lacking any first principles

calculation of c , we evaluated it by taking finite single-charged and neutral clusters and considering an extended Thomas–Fermi approximation (TFDW-4) for the kinetic energy functional of the self-consistent density. The ionization energy $I = E(Z = -1) - E(Z = 0)$ was obtained. Then, a careful fitting of the ionization energy by the formula

$$I = W + \left(\frac{1}{2} + c \right) \frac{1}{R} \quad (2.3)$$

gave the value $c = -0.1$ (this value is similar to $c = -0.07$, obtained for jellium clusters with the same density [10]). We stress that the liquid drop model formula (2.2) was derived using the so-called displaced profile model, which is only valid when the charge Z is small in comparison with the total number of electrons $N_c + Z$.

We see from Figure 1 that the liquid drop formula (2.2) gives an average of the quantal results for charged clusters that is as good as in the neutral case. In Figure 2, we represent the “landscape” $\Delta E(N, p)$ of the dissociation energy of charged clusters as a function of the size of parents and daughters. The shell structure is clearly visible as local maxima (magic fathers) and local

minima (magic daughters). The horizontal lines serve to guide the eye to localize the magic fathers and the vertical lines do the same for the magic daughters (only the main shell closures for 2, 8, 20, and 40 electrons are shown). In some case, special stability occurs near magic configurations, since these are impossible to obtain. The stabilized jellium model (as the jellium model) yields stronger fluctuations of the dissociation energies for spherical shapes than it is expected to give for deformed shapes.

Figure 3 shows liquid drop model “landscapes” for two decays of positively charged clusters. We see that strong asymmetrical decays ($p = 1$) are favored in that model, namely, emission of Al^+ and Al . However, we should doubt of the validity of the liquid drop model for describing particles as small as the ionized or the neutral atom.

Figure 4 displays the most favored decay channels for each N , i.e., those with the least dissociation energy. In the range of sizes being considered, Al_N^{2+} are unstable against decay into two charged fragments, except $N = 7, 12, 20$, and 30 (with, respectively, 19, 34, 58, and 88 electrons), which have closed or nearly closed shells. The most unstable clusters are those that lead to double magic final

FIGURE 3. The dissociation energy $\Delta E(N, p)$ of positively charged Al clusters as a function of the size of parents (N) and daughters (p and $N - p$) in the liquid drop model.

FIGURE 4. Dissociation energy $\Delta E(N, p)$ of charged Al clusters in the most favored channel for each parent N . Each favored channel is labeled by the corresponding p , in the Kohn–Sham results. The smooth curve refers to the liquid drop model.

configurations: $p = 1, 3$, and 7 (with, respectively, $2, 8$, and 20 electrons). These are also the most common favored channels. The liquid drop model predicts a transition from unstable to stable Al_N^{2+} clusters at a critical number $N_c \approx 23$. In this liquid drop description, we took the Kohn–Sham result for the energy of the lighter product ($p = 1$ for all channels) since this value is expected to be more realistic.

Single-charged clusters are always stable in the liquid drop framework. But the quantal calculation predicts in some cases fragmentation into magic or near magic pieces as, for instance, $\text{Al}_9^+ \rightarrow \text{Al}_3^+ + \text{Al}_6$. The most frequent channels correspond to having $p = 1$ and 6 as neutral products.

Single-charged negative clusters are stable, with few exceptions, ruled by shell closures in the products. The most frequent channel is $\text{Al}_N^- \rightarrow \text{Al}_{N-3}^- + \text{Al}_3$. We note that Al_2^- was the lightest negative ion that we found to be a solution of the Kohn–Sham equation. Furthermore, we did not find any bound

Al_N^{2-} cluster. In fact, a well-known failure of the LDA is the inability of providing single and multiple negatively charged ions for the smallest clusters [11–13].

Finally, Figure 5 shows the quantal and liquid drop results for ΔE of some typical decays. Again, we replaced the liquid drop energy of the lighter fragment by the more accurate Kohn–Sham result. The liquid drop formula averages very well the quantal results. In the channel $\text{Al}_N^{2+} \rightarrow \text{Al}_{N-1}^+ + \text{Al}^+$, the local minima of the dissociation energy occur for $2, 8, 20, 41$, and 68 valence electrons and a similar behavior occurs for other channels. An interesting experimental point is the competition between the decay of Al_N^+ by evaporation and the emission of an ionized monomer. We see in the present study that the latter process is favored, in the liquid drop picture, for the sizes being studied. The quantal dissociation energy is also lower when the magic Al^+ is emitted, with very few exceptions.

FIGURE 5. Quantal (heavy dots) and liquid drop model (continuous line) results for the dissociation energy of some typical decay channels of charged Al clusters.

3. Conclusions

We have analyzed, based on energetic considerations, the decay processes of single- and double-charged clusters. We used the stabilized jellium model since this retains the simplicity of jellium while providing a much more realistic account of the static properties of clusters. We may conclude that the dissociation energies of the various decay channels are ruled both by the shell structure of parents and daughters and by the liquid drop model, which predicts asymmetric fragmentation. We tested a liquid drop formula for charged clusters and evaluated on its basis the upper critical size for having the so-called Coulomb explosion of charged clusters.

Let us sketch the main theoretical studies available on cluster fragmentation. The role of magic configurations in describing the properties of simple metal clusters is well known [14,15]. Chou and

Cohen were among the first to use the spherical jellium model to predict magic numbers of aluminum clusters [16]. Iñiguez et al. [17] established the importance of magic numbers for the fragmentation of double-ionized jelliumlike metallic clusters. Rao et al. [18] justified the jellium results on the basis of ab initio self-consistent theories (the case of Li was reported). Iñiguez et al. [19] corrected the usual jellium model by adding, in a convenient fashion, the ions and considering non-local exchange-correlation effects. Their spherical averaged pseudopotential approximation is similar in spirit to our stabilized jellium model. The role of the Coulomb barrier in the dissociation of double-charged clusters was emphasized by Garcias et al. [20]. More recently, Barnett et al. [21] used a molecular dynamics method to conclude that the dominant decay of Na_N^{2+} should be the production of $\text{Na}_{N-3}^+ + \text{Na}_3^+$, for $4 \leq N \leq 12$ (we note that for the decay of Al_N^{2+} , for $1 \leq N \leq 4$, the favored channel in our study is $\text{Al}_{N-1}^+ + \text{Al}^+$).

Most of these studies refer to alkali metals. The structure and properties of neutral Al clusters have been studied by some authors, including Upton [22] and Jones [23], but little has been done on the decay of charged Al clusters.

However, some experimental studies are available for the fragmentation of Al_N^+ induced by argon collisions and by radiation (Jarrold et al. [24] and Ray et al. [25]). The first authors found in the mass spectrum peaks corresponding to Al_7^+ , Al_{13}^+ , and Al_{14}^+ , in turn, corresponding, to magic or near magic numbers 20, 38, and 41. In our study, the Al_7^+ shows up very clearly as a stable parent. They also concluded that the main charged product of Al_N^+ is Al^+ , for $N < 14$, and Al_{N-1}^+ , for $N > 14$. We were not able to distinguish this transition. No double positive clusters with mass lower than that of Al_{13}^+ were observed in the mass abundance spectrum and the Al_{15}^{2+} was also absent. In our calculations, Al_{13}^+ is in the threshold of stability and Al_{15}^{2+} is clearly unstable. Somewhat different results were obtained in the photodissociation experiments: The lowest energy channel for Al_7^+ and Al_9^+ is indeed the formation of $Al_{N-1} + Al^+$, but for Al_8^+ and $Al_{10}^+ - Al_{17}^+$, the most favored channel is $Al_{N-1}^+ + Al$, i.e., there is a transition to evaporation at $N \approx 9$. In our calculations, Al_7^+ decays by $Al_6 + Al^+$ and Al_8^+ decays by $Al_7^+ + Al$, but there are discrepancies with the data, such as predicting $Al_9^+ \rightarrow Al_6^+ + Al_3$, etc.

The difference in the dissociation energies corresponding to different channels is small and a simple improvement of our description is possible by considering deformed clusters. This can be made by adding the Strutinsky shell correction to the smooth liquid drop model. Self-compression effects can also be included.

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