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FRAGMENTATION OF HIGHLY CHARGED METALLIC CLUSTERS

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ABSTRACT

Multiply charged metal clusters undergo fission at a certain size. This critical size can be predicted by the liquid drop model when some modifications are taken into consideration. In this work we revise the asymmetric liquid drop model (ALD) and modify it for the alkali metals. This modification addresses those fragmentation channels in which a parent cluster with charge Ze fissions into two fragments. One of the fragments is small and singly charged whereas the second fragment is large and carries the rest of the charge. A different energetic balance equation is presented in which the ionization energy of a single atom and the energy of formation of a small cluster are included. Results and comparison to experiments is provided for Na and Cs clusters. Prediction of the critical size of Na and Cs clusters with Ze>7 is part of the discussion.

The complexity of problems connected with formation, stability, structure, and phase transformations of charged metallic clusters have gained significant theoretical interest in the last few years. An example is the dramatic structural transformations taking place in small atomic clusters due to the excess off positive charge in a confined space.[1] Clusters of a given size can only support a maximum amount of charge before fission occurs.[2-4]

Experimental data collected during the last years[5-14] give quantitative results on the Coulomb induced fission phenomenon.[4] Although theoretical work[2-4] indicates that competition between evaporation and Coulomb processes might contribute to the fission process, there exists considerable controversy concerning the symmetric versus asymmetric fragmentation arising from fission. The liquid drop model[15] (LDM) has mainly been ruled as inadequate to describe the fission reaction.[16,17] Instead, for Na clusters an amazingly simple relation, $N_c=(Z+1)^3$, seems to relate Z,charge on a cluster, with the "critical size" N_c (smallest observed cluster supporting a charge Z).[13] Approximately the same rule is followed by Cs clusters[14] with charges up to 7. In both experiments Martin et al. could not elucidate if fragmentation followed a symmetric or asymmetric channel and attempted to estimate the value of the energy barrier needed for a cluster to evaporate neutral atoms.[2] Fission and evaporation are then two competing processes. The picture that emerges from these studies is the following. If the Coulomb repulsion is larger than the evaporation barrier, then the cluster undergoes fission at the critical size. If the opposite is true, then the cluster will evaporate atoms until the balance between evaporation barrier and Coulomb repulsion is reversed.

On the other hand, the fission experiments of Saunders[8,9] on Au clusters caused by collisions with Kr atoms do not follow a simple rule. The critical size for doubly charged Au clusters was found to be 9 and 26 for triply ionized clusters. In this work Saunders indicates that fission is dominated by the asymmetric channel in which one of the fragments is a singly ionized trimer. Simulations on small doubly charged Na clusters also indicate asymmetric fragmentation with a singly charged trimer being a favored product. [18]

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Liquid drop model:

The liquid drop model assumes that the cluster binding energy is counterbalanced by a repulsive Coulomb energy. The cluster is a classical charged continuum with finite surface. Namely, the energy of a cluster of radius R, N atoms, and charge Ze is

$$E_{LD} = E_b N + 4\pi\sigma R^2 + (Ze)^2/2R \tag{1}$$

where E_b is the bulk binding energy/atom, σ is the surface tension and $R = r_{sw}N^{1/3}$, with r_{sw} being the Wigner-Seitz radius. In LD for symmetric fragmentation (SLD), the fissility parameter $f = E_{Coulomb} / 2\ E_{Surf}$ should satisfy the condition $f < 0.351$ for the parent cluster to be stable. The maximum allowable value of f defines then the minimum size at which a cluster fissions.

Asymmetric Liquid Drop Model

The LD might be modified by assuming that a cluster fissions into two spherical clusters of different sizes N_1 and N_2 with charges Z_1e and Z_2e when the balance of energies after and before fission

$$E_{final}\text{-}E_{initial} = 4\pi\sigma\ (R_1{}^2 + R_1{}^2 - R^2) + 0.5\ e^2\ (Z_1{}^2/R_1 + Z_2{}^2/R_2 - Z^2/R) \tag{2}$$

changes sign from positive to negative. Here R, R_1 and R_2 are the radii of the parent cluster and of the two cluster fragments. The radius of the parent cluster is $R = r_{sw}N^{1/3}$ and the corresponding radii of fragments 1 and 2 are $R_i = r_{sw}N_i{}^{1/3}$ Thus,

$$\Delta E = E_{final} - E_{initial} = \Gamma\ [N_1{}^{2/3} + (N_2{}^{2/3} - N^{2/3})] +$$

$$+\ [Z_1{}^2/N_1{}^{1/3} + Z_2{}^2/N_2{}^{1/3} - Z^2/N^{1/3})] \tag{3}$$

where $\Gamma = 8\pi\sigma\ (r_{sw})^3/e^2$ and energies are given in units of $e^2/2r_{sw}$.

Energetic balance occurs at a certain cluster size and fixed Z, defining a critical size N_c for asymmetric fission when ΔE is minimum and positive. Then, if

$$\begin{array}{ll} \Delta E > 0 & \text{no fission occurs} \\ \Delta E < 0 & \text{fission occurs.} \end{array} \tag{4}$$

The critical size N_c corresponding to a channel N_1, N_2, Z_1, Z_2 is then obtained by minimizing the positive difference ΔE with respect to N_1 for every pair Z, Z_1. The minimization process is carried out numerically.

This model will be referred as asymmetric LD (ALD). The fissility parameter is f=-1. In Table 1 we give the ALD calculated values of N_c and N_1 when $\sigma = 200$ erg/cm^2 for Na (74 erg/cm^2 for Cs) and r_{sw}=2.08 A for Na (2.98 A for Cs). In this model the best fission channels favor a small singly charged fragment and a large cluster with charge Z-1.

Table 1. Critical sizes and most probable channels of fission for Na clusters and Cs clusters under the ALD model. Experimental results are after Ref. 13 and 14.

	Na			Cs		
Z	exp [13,14]	N_c (ALD)	(N_1, Z_1)	exp [14]	N_c (ALD)	(N_1, Z_1)
2	27	31	6,1	19	28	5,1
3	63	116	4,1	49	107	3,1
4	123	299	3,1	94	276	3,1
5	206	616	3,1	155	567	3,1
6	310	1101	3,1	230	1012	3,1
7	445	1790	3,1	325	1644	3,1

Modified Asymmetric Liquid Drop Model

Neither SLD or ALD fully describe the Coulomb induced fission because evaporation processes that modify the initial and/or final states are absent from either description. There is however another effect that we consider more important. In the process of asymmetric fission, the parent cluster needs to supply an 'energy of formation' of the two fragments. As in ALD, we assume that the fission channel results into two clusters one of which is singly charged. The energy of formation of the fragments contains two parts, the ionization energy and the energy necessary to reconstruct the system.

When a cluster is just about to undergo fission the system is far from thermodynamic equilibrium. Besides, experimental factors such as warming upon ionization indicate that the cluster temperature might be high at the moment of fission. Under this situation entropic effects should be important. In this paper we assume that a high temperature deformation mode sets in as a function of the the number of atoms in the parent cluster. In this mode there is a contraction of the cluster density in a large region of the parent cluster compensated by a density expansion in a smaller region. Under these circumstances, the energetic balance favoring fission is such that

$$\Delta E = \Delta E_C + \Delta E_S + \varepsilon(N)_{N_1} = 0 \qquad (5)$$

where the Coulomb energy balance is

$$\Delta E_C = (Z_2^2/N_2^{1/3} - Z^2/N^{1/3}) + IP \qquad (6)$$

and the surface energy balance is

$$\Delta E_S = \Gamma\,(N_2^{2/3} - N^{2/3}) \qquad (7)$$

Here IP is the atomic ionization potential of the material under consideration. The reconstruction energy $\varepsilon(N)_{N_1}$ is a function that depends parametrically on N_1. We assume a simple linear dependence of this function with N:

$$\varepsilon(N)_{N_1} = \rho\,(N_1)\,N \qquad (8)$$

This new model is referred as *modified asymmetric liquid drop* MALD. The zero order MALD model is recovered when the reconstruction energy $\varepsilon(N)_{N_1}$ is zero. A similar balance as Eq.. (6)

for sodium clusters has been considered[17] in the past where instead of the IP energy the bulk work function was included as a constant energy.

Critical sizes for Na and Cs clusters obtained in the zero order MALD are reported in Table 2, where $IP_{Na}=5.14$ eV and $IP_{Cs}=3.89$ eV. As is evident, these results are in better agreement with experiment for $Z<5$ than the ALD results . However, for $Z > 4$ the critical sizes obtained within the zero order MALD become worst with increasing Z. Our next step is to allow for a non-vanishing reconstruction energy $\varepsilon(N)_{N_1}$ and to fit the value of the parameter ρ to the experimental results.[13,14] The parametric dependence of $\varepsilon(N)_{N_1}$ with N_1 can also be determined from the fit. We found that the best fitted value $\rho(7) = 0.028$ eV is the same for both Na and Cs and the small singly charged cluster has $N_1 = 7$. Results for N_c are reported in Table 2. The agreement with experiment is excellent. Prediction of N_c for $Z > 7$ is also reported in the table.

Table 2. Critical sizes and most probable channels of fission for Na and Cs clusters under the MALD model.

	Na			Cs		
Z	N_c(zero order)	N_c (MALD)	(N_1, Z_1)	N_c(zero order)	N_c (MALD)	(N_1, Z_1)
2	22	22	7,1	14	14	7,1
3	62	57	7,1	47	43	7,1
4	154	125	7,1	115	94	7,1
5	310	218	7,1	228	161	7,1
6	591	328	7,1	399	241	7,1
7	875	448	7,1	615	329	7,1
8	1319	575	7,1	924	422	7,1
9	1890	704	7,1	1373	517	7,1
10	2606	835	7,1	1890	613	7,1

In Fig. 1 we give a three dimensional representation of the balance equation, Eqs. (5-8), for Cs when Z=6 and N_1=7. The cut defines a line of critical sizes. In Figs. 2 it is shown the

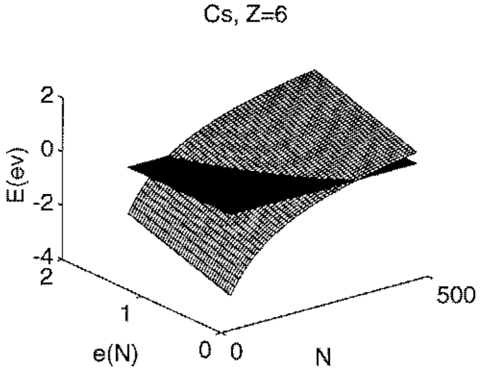
Cs, Z=6

Fig. 1 Three dimensional representation of the balance equation Eqs. (5-8) for cesium clusters with charge 6. The cut defines a line of critical sizes.

behavior of ΔE with N. In these figures the values where the curves cut the abscissa correspond to the N_c obtained in the zero order MALD. The straight line represents $\varepsilon(N)$ for $N_1=7$. Values of N where $\varepsilon(N)$ cuts ΔE give our best estimation for the critical sizes N_c.

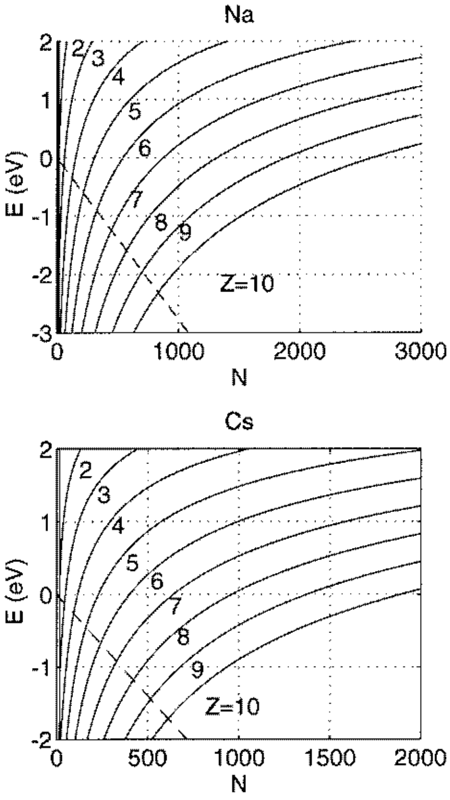

Fig. 2 Energy difference $\Delta E_c + \Delta E_s$ as a function of N (the size of the parent cluster) for Z=2 through 10 (continuous lines) and reconstruction energy $\varepsilon(N)$ for $N_1 = 7$ (dashed line). (top) Na clusters; (bottom) Cs clusters.

We have presented a simple model that modifies the LD by including both the ionization energy of the material under study and the energy of reconstruction when the parent cluster fissions. At the moment of fission, this reconstruction energy is carried away by the fragments as kinetic energy. This phenomenon has been mentioned[12] in the experimental work. Finally, our prediction of asymmetric fragmentation where one of the fragments is a singly small cluster is in agreement with the dynamical simulations[18] of small Na clusters.

Exploratory Molecular Dynamics simulations of Lennard Jones clusters with 50 to 60 atoms show that when the charge is localized, the dynamically preferred fragmentation channel generates either a small singly charged cluster and a large one with the rest of the charge, or a bare charged atom and a large cluster with some evaporated atoms.[19]

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