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Fission of metallic clusters in the liquid drop model

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Abstract

Using the liquid drop model and the jellium model, we calculate fission barrier heights as a function of charge and mass asymmetry for a family of shapes consisting of two spheres connected by a quadratic surface. We find the fissibility for which a mass asymmetric splitting gives place to the symmetric one (Bussinaro–Gallone point) and evaluate the size of charged clusters of alkali metals for which the fission barrier height is equal to the evaporation energy (critical sizes). The results for the critical sizes agree very well with experiment.

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1. Introduction

We know from experiment that metallic atomic clusters with excess charge are unstable due to the magnitude of their Coulomb energy. These clusters undergo two processes: breaking out in charged pieces (fission) or expelling a neutral atom (evaporation). Evaporation is preferred for large clusters, but fission prevails for small clusters. For a critical cluster size, N_c , where fission barriers and evaporation energies are comparable, the two decay processes compete [1].

From the theoretical point of view, the liquid drop model (LDM) combined with the jellium model [2] (where the ions are replaced by a continuous positive background) is a useful tool to explain cluster fission. In a charged cluster two opposite forces exist. The surface tension obliges the system to have a

minimal surface. On the other side, the electrostatic repulsive force due to the extra charge drives to expansion and deformation. Fission occurs when the second force surpasses the first. This can only happen if the energy of the fragments is lower than the energy of the mother cluster, i.e., when the reaction heat (or Q -value) is negative. However, since the process is controlled by a barrier, knowledge of the barrier height is essential to evaluate the decay probability associated to each channel.

Fission of metallic clusters displays remarkable similarities with nuclear fission where the LDM is well known. But metallic clusters show an additional degree of freedom with respect to nuclei, namely that we are, in principle, free to consider any charge in the parent and daughter clusters. Based on the LDM, we will evaluate, for different charged metal clusters fission barriers along different fission channels. We

compute the Coulomb energy exactly, for a given family of shapes [3], assuming that the charge is bound to the surface. Based on the barrier heights, we analyze the asymmetry in mass distribution between the fragments. The critical numbers N_c are also estimated for multiply charged clusters of some alkali metals.

Cluster fission has been studied by several authors. Bréchnignac et al. [1] measured the critical size for doubly charged clusters of sodium and potassium, and were also able to determine the fission barrier for some doubly charged clusters [4]. Näher et al. [5,6] obtained the critical size of alkali metal clusters with up to seven electrons removed.

On the theoretical side, Saunders [7] used the LDM to predict some critical sizes for doubly charged clusters of sodium and gold. He calculated $N_c = 30$ for Na and $N_c = 18$ for Au using the LDM, but considering only symmetric reactions. Näher et al. [6] applied the LDM, with the so-called “funny hills” parametrization for the cluster shapes (including asymmetric configurations), but did not predict the observed critical numbers. Garcias et al. [8] used a semi-empirical model for the Coulomb interaction between the emergent fragments, obtaining a good description of the critical numbers. Similar results were achieved by Fröbrich [9], employing an empirical model for that interaction and using fission decay rates. Recently, Vieira and Fiolhais [10] and Yan-nouleas and Landman [11] have used the two-centre shell model to obtain shell corrections to the LDM fission barriers of small clusters. There are also a few molecular dynamics calculations of fission [12].

The LDM is introduced in Section 2, where we compare reaction heats with fission barriers heights as a function of mass and charge asymmetry and evaluate the Bussinaro–Gallone point, i.e., the fissibility corresponding to the instability of the barrier against mass asymmetry. Section 3 contains the results on critical sizes, and conclusions.

2. Liquid drop model and fission barriers

In the framework of the LDM, the energy of a spherical metallic cluster with N monovalent atoms

and z lacking electrons (the charge is $q = +ez$), is given by

$$E_{\text{LDM}}(N, z) = a_v V + \sigma S + \gamma C + z \left(W + \frac{c}{R_0} \right) + \frac{(ez)^2}{2(R_0 + d_s)}, \quad (1)$$

where $V = \frac{4}{3}\pi R_0^3$ is the volume, $S = 4\pi R_0^2$ is the surface area, $C = 2\pi R_0$ is half the mean curvature, and $R_0 = r_s N^{1/3}$ is the radius of the cluster, r_s being the density parameter. The parameters a_v , σ , γ are the liquid drop coefficients for a neutral cluster. The term with c is a first order quantal correction to the work function W related to the finite size of the cluster. The last term is the classical electrostatic energy, obtained under the assumption that the cluster is a perfect conductor. The parameter d_s accounts for the charge spill-out effect: the excess charge lies on a radial centroid displaced d_s from the jellium surface. The volume term will not be considered since volume is conserved during deformation and fragmentation.

The LDM is known to provide a good average of quantal density functional results for the reaction heats [13]. Let us consider the binary fission of a spherical cluster with N atoms and charge z in two spherical pieces with N_1 and $N_2 = N - N_1$ atoms and charges z_1 and $z_2 = z - z_1$, respectively. For simplicity and convenience, we set, for the time being, $\gamma = c = d_s = 0$. The energy released, divided by the surface energy E_S^0 , may be written as

$$\begin{aligned} Q(x, \alpha, \beta) &= [E_{\text{LDM}}(N_1, z_1) + E_{\text{LDM}}(N_2, z_2) \\ &\quad - E_{\text{LDM}}(N, z)] / E_S^0 \\ &= [\alpha^{2/3} + (1 - \alpha)^{2/3} - 1] \\ &\quad + 2x \left(\frac{\beta^2}{\alpha^{1/3}} \frac{(1 - \beta)^2}{(1 - \alpha)^{1/3}} - 1 \right), \end{aligned} \quad (2)$$

where $x = (ez)^2 / 16\pi\sigma r_s^3 N$ is the quotient between the Coulomb and twice the surface energy, called the fissibility parameter. For $x = 1$, the initial system is unstable relatively to fission, while, for $x = 0$, the

system is neutral and cannot fragment. The parameters $\alpha = N_1/N$ and $\beta = z_1/z$ measure the asymmetry of mass and charge of the fragments. Eq. (2) holds in nuclear physics with $\beta = \alpha$ [14].

Fig. 1a shows $Q(x = 0.5, \alpha, \beta)$. The minimum of Q is located at $(\alpha = 0.07, \beta = 0.32)$. If x increases, this minimum moves up along the bold line, $\beta_{\min} = \Delta(\alpha)$, with

$$\Delta(\alpha) = \frac{\alpha^{1/3} - (1 - \alpha)^{1/3}}{\alpha^{1/3} + (1 - \alpha)^{1/3}}. \quad (3)$$

Reactions with high β and low α and vice versa are highly unfavorable.

A negative reaction heat is only a necessary condition for a cluster to break. In order to estimate decay probabilities of charged clusters we need to evaluate barriers heights for each channel. In particular, we should look for the channels with the lowest energy barriers.

To know the barrier height we need to extend the LDM formula to deformed shapes, corresponding to intermediate fission configurations. The surface term in Eq. (1) is then replaced by $E_S = \sigma \int dA$, while the electrostatic energy, E_C , is calculated numerically assuming, as before, that all excess charge is distributed on the surface. We solve the Poisson equation following the method described in Ref. [15].

To parametrize the cluster surface we adopt Blocki's shapes, which consists of two spheres joined

by a smooth neck [3,16]. This family of shapes is described by three parameters measuring elongation, neck width, and mass asymmetry, defined respectively by:

$$\rho = m \frac{d}{R_1 + R_2}, \quad \lambda = \frac{l_1 + l_2}{R_1 + R_2}, \quad \Delta = \frac{R_1 - R_2}{R_1 + R_2}, \quad (4)$$

where d is the center to center distance, $R_1 = R_0 \alpha^{1/3}$ and $R_2 = R_0(1 - \alpha)^{1/3}$ are the radii of the two fragments, and l_1 and l_2 are the thickness of the lens-shaped piece of a sphere which lies within the matching quadratic surface. The parameter Δ is the same as in Eq. (3).

If we define $B_S = E_S/E_S^0$ and $B_C = E_C/E_C^0$, the LDM energy for a deformed cluster, $E_{\text{LDM}} = E_{\text{LDM}}(N, q, \rho, \lambda, \Delta)$, after convenient normalization, is given by

$$\frac{E_{\text{LDM}}}{E_S^0} = B_S + 2x B_C. \quad (5)$$

The normalized energy barrier becomes

$$\xi = \frac{E_{\text{LDM}}^{\text{sad}} - E_{\text{LDM}}^{\text{sph}}}{E_S^0} = (B_S^{\text{sad}} - 1) + 2x(B_C^{\text{sad}} - 1), \quad (6)$$

where $E_{\text{LDM}}^{\text{sad}}$ and $E_{\text{LDM}}^{\text{sph}}$ are the energies of the saddle and the spherical shapes, and B_S^{sad} and B_C^{sad}

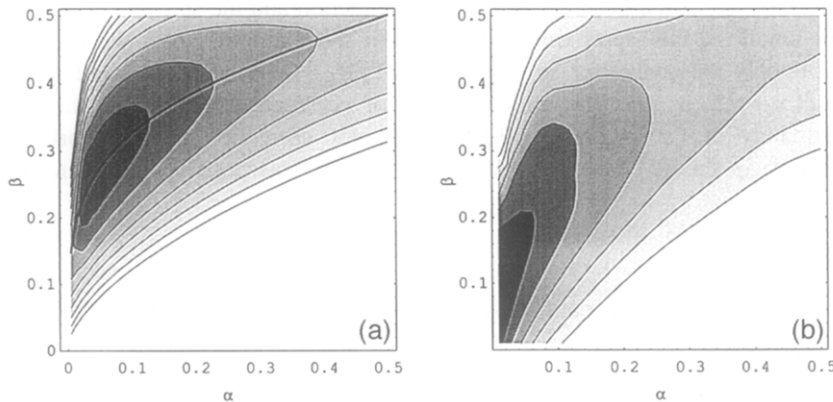


Fig. 1. (a) Q -values $Q(x = 0.5, \alpha, \beta)$ (only negative values are represented) as a function of mass and charge asymmetry (see text for the definition of α and β). The bold line represents $\beta_{\min} = \Delta(\alpha)$ (see Eq. (3)). (b) Barrier height divided by the surface energy of the initial spherical cluster, $\xi(x = 0.5, \alpha, \beta)$, as a function of the same variables.

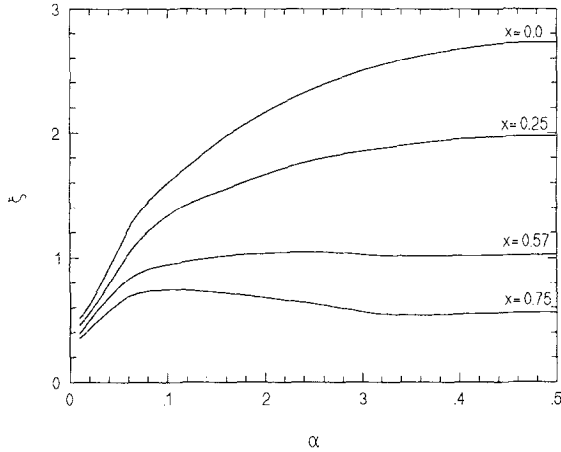


Fig. 2. Dimensionless barrier height, $\xi(x, \alpha, \beta = \alpha)$, for several values of the fissibility x . The Bussinaro–Gallone fissibility, x_{BG} , occurs when the second derivative of ξ with respect to α , at $\alpha = 0.5$, changes sign. We found $x_{BG} = 0.57$.

are B_S and B_C evaluated at the saddle point in the variables ρ, λ (Δ is fixed).

To search for the saddle point, we started by evaluating the minimum of the energy along the fission line defined by the equation $\lambda = 1 - 1/\rho$. We then proceeded backwards following the line of fast variation of the neck [10,16], $\lambda = 1 - \sqrt{\rho - k}$, with k a constant, up to $\lambda = 1$. From there, we have followed the path $\lambda = 1 - \Delta^2/\rho$. For small x , the saddle point is located close to the fission line. As x approaches 1, the saddle point moves to configurations closer to a sphere. Since we have assumed a path, our evaluation of the saddle point is only approximative. For small x , this approximation is very good, while it is only reasonable for large x .

Fig. 1b shows $\xi(x=0.5, \alpha, \beta)$. The minimum is located approximately at $(\alpha = 0.01, \beta = 0.10)$. The similarity with Fig. 1a should be pointed out.

In Fig. 2 we present $\xi(x, \alpha, \beta = \alpha)$. As in nuclear fission, the asymmetric reaction is preferred for small x and the symmetric reaction is preferred for large x . However, the transition from asymmetric to symmetric fission, the so-called Bussinaro–Gallone point, occurs at $x_{BG} = 0.57$, where for nuclei $x_{BG} \approx 0.40$, the precise value depending on the particular shape parametrization [17–19]. This disagreement should be due to the difference in the charge distribution.

3. Critical numbers

A very important number is the cluster size $N = N_c$ for which the barrier height equals the evaporation energy. For each charge z , we have searched for a solution of the equation

$$E_{LDM}^{sad}(N, z, \alpha, \beta) - E_{LDM}^{sph}(N, z) = E_{eva}(N, z), \quad (7)$$

where $E_{eva}(N, z) = E_{LDM}(N-1, z) + E_{LDM}(1, 0) - E_{LDM}(N, z)$ is the evaporation energy. We assume, as in Ref. [8], that the preferred fission channel is $[N]^{z+} \rightarrow [N-3]^{z-1+} + [3]^+$, i.e., $\alpha = 3/N$ and $\beta = 1/z$. This channel is the most common in the experimental data.

Since we have assumed an asymmetric channel, we consider now, for the sake of precision, the curvature energy, the size correction of the work function and the spill-out effect in the LDM formula. In the curvature term we use is $C = \frac{1}{4} \int (1/R_{min} + 1/R_{max}) dA$, with R_{min} and R_{max} the principal radii of curvature at a point of the surface. For the first order correction to the work function we use a simple interpolation between the initial spherical

Table 1

LDM coefficients for Na, K and Cs. The values of $a_s = 4\pi\sigma r_s^2$ and $a_c = 2\pi\gamma r_s$, were taken from Ref. [20], c from Ref. [21], and d_s from Ref. [22]

Metal	r_s (bohr)	a_s (eV)	a_c (eV)	c (eV)	d_s (bohr)
Na	3.93	0.57	0.25	-2.26	1.32
K	4.96	0.54	0.17	-2.26	1.17
Cs	5.62	0.50	0.09	-2.26	1.02

Table 2

LDM critical sizes, N_c , of charged clusters of Na, K and Cs, in comparison with experimental data and other theoretical results

		z					
		2	3	4	5	6	7
Na	our work	26	68	129	209	311	404
	Ref. [8]	26	63	117	185	268	366
	Ref. [9]	22	62	123	208	316	451
	exp. (Ref. [6])	27 ± 1	$63 \pm$	123 ± 2	206 ± 4	310 ± 10	445 ± 10
K	our work	23	58	110	176	242	344
	Ref. [8]	24	59	110	173	249	337
	exp. (Ref. [6])	20 ± 1	55 ± 1	110 ± 5			
Cs	our work	22	57	105	168	233	330
	Ref. [8]	23	57	105	165	236	319
	exp. (Ref. [6])	19 ± 1	49 ± 1	94 ± 1	155 ± 2	230 ± 5	325 ± 10

cluster and final spherical fragments. The spill-out effect is taken into account by placing the charge on a surface which is separated by d_s from the cluster surface. Table 1 shows the values of the LDM coefficients used in our calculations.

Table 2 displays the critical numbers N_c obtained for several clusters of simple metals and compares them with experimental results. A very good agreement between our LDM theory and experiment is observed (for potassium we are not aware of data for $z > 4$). We should remark that the LDM does not predict necessarily the channel $[3]^+$.

Included in Table 2 are the results of Garcias et al. [16] and Fröbrich [9]. The first authors have used

a different surface energy and have not included R and $1/R$ effects. They have fitted the Coulomb energy to Thomas–Fermi results in a somewhat ad hoc fashion. On the other hand, the comparison of the fission and evaporation decay rates as done by Fröbrich [9] is, in principle, a better method for estimating N_c than the rule given by Eq. (7). (In that method the Q -values are also taken into account.) But we stress that the Coulomb energy is computed exactly in our work, while in Ref. [9] it is fitted to reproduce experimental results. Moreover this author considers the fragmentation channel $[N]^{z^+} \rightarrow [N-1]^{z-1^+} + [1]^+$ which is unlikely to occur in practice since it has a higher Q than the channel we take.

If we plot the critical sizes in a logarithmic scale, the points lie approximately on a straight line, $\ln(N_c) = s \ln(z) + \text{const}$ (Fig. 3). We find $s = 2.20$ for Na, $s = 2.15$ for K and $s = 2.16$ for Cs. These slopes are lower than the average experimental value 2.3 obtained in Ref. [6]. They are higher than the value 2 proposed by Rayleigh on the simple assumption that a charged drop breaks when the electrostatic energy equals the surface energy.

In the present work, we have shown how the mass distribution and the fission threshold are evaluated in the LDM. In a pure LDM analysis shell effects are absent. The role of shell fluctuations in the barrier height should be investigated systematically. However, we expect the LDM to have a reasonable predictive power for critical numbers of large enough clusters, for which shell corrections are less important.

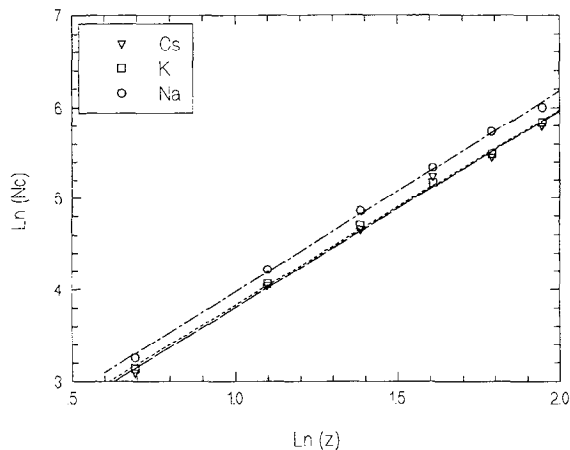


Fig. 3. Logarithm of the critical size, $\ln N_c$, as a function of the logarithm of the number of missing electrons, $\ln z$, for clusters of Na, K and Cs, determined in the framework of the LDM theory. A straight line fits the results very well.

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