Molecular dynamics study of neutral and multiply charged sodium clusters

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Received 20 January 1997; in final form 17 February 1997

Abstract

The fission mechanism of multiply charged sodium clusters was investigated with molecular dynamics and a new potential featuring a local density approximation second-moment approach. We show that the critical size at which 2+, 3+ and 4+ charged clusters undergo fission due to Coulomb forces depends strongly on the cluster temperature. The smallest critical sizes occur for cold clusters. Master curves predicting upper bounds to the cluster temperature at the fissioning critical size are provided. A scaling of the cluster ion critical size with a power law of the total charge is used to predict the energy barrier that sodium clusters need to surmount to undergo fission. © 1997 Elsevier Science B.V.

1. Introduction

A considerable experimental [1–10] and theoretical [11–14] effort has taken place in the study of the fission of multiply charged alkali metal clusters. The minimum size at which the fission of multiply charged cluster occurs is known as the critical size for fission due to Coulomb forces. Critical sizes have been reported for alkali metal clusters charged as high as 7+ by multi-step photoionization supplemented with laser warming [2]. Cluster fragmentation and fission patterns of ionized clusters present strong analogies to corresponding phenomena exhibited by heavy atomic nuclei. Experimental fission patterns (symmetric versus asymmetric fission) and fission barriers have been interpreted [2–4,6–9,11,15] within the framework of the liquid-droplet model of nuclear theory [16]. Predictions exist of fission channels of 2+ cluster ions using the local density approximation (LDA) and the deformed-jellium model [13,14]. The most common assumption in describing the fission process of charged metal clusters is that small singly charged fragments evaporate from the cluster until a singly ionized cluster is left behind. Then, it is possible to model the process as a chemical reaction by considering a static energy balance between reactants and products overcoming an activation barrier [7,9,14]. Temperature effects are missing in these approaches and recently, it has been demonstrated using ion bombardment that temperature effects are important [10] in the fission mechanism. Chandezon et al. [10] observed different critical sizes for clusters undergoing fission from different ion beam measurements and correlated these differences with temperature effects.

The fragmentation process of small sodium 2+ cluster ions containing up to 12 sodium atoms [17] has been studied based on LDA for the electronic structure in conjunction with molecular dynamics (MD) to account for entropic contributions. This approach is computationally demanding for tackling the fission...
mechanism which involves larger cluster ions sustaining charges larger than two. On the other hand, atomistic simulations are playing an increasingly important role in the design of modern materials. Because the predicted properties are only as accurate as the interatomic potentials used in these simulations, the development of improved model potentials is crucial. The tight-binding (TB) approach [18,19] is a useful method used in conjunction with molecular dynamics. The electronic structure of many metals is accurately described in the TB approximation [20].

In this work, we present a new many-body potential for sodium developed from a complete density functional band structure calculation and based on a second-moment expansion of the local density of states. We use this new potential to study the fission mechanism of sodium 2+, 3+ and 4+ cluster ions containing 13 to 150 atoms. The temperature dependence of the cluster ion critical size for fission is calculated. We predict that the critical size increases as a function of temperature and give quantitative estimates over a wide range of temperatures for clusters charged up to 4+. Our calculated critical sizes at high temperatures are in agreement with experimental values for hot clusters [2-4,10]. An interesting scaling of the critical sizes with a power law for the total charge allows the prediction of the energy barrier that needs to be surmounted for a multiply charged cluster to undergo fission.

2. Many-body potential for sodium

First principles calculations within LDA of the total energy and electronic bands for fcc and bcc sodium crystals were performed using an augmented-plane-wave (APW) method [21]. The band states were calculated self-consistently in the semirelativistic approximation with spin-orbit coupling neglected. We performed the APW band calculations with 55 points in the Brillouin zone for the bcc structure and with 89 points for the fcc lattice [21]. A convergence in the energy levels of 0.5 mRy assured a convergence in total electronic energy of less than 0.05 mRy.

A new analytical potential was constructed using a TB second-moment approximation (SMA) [18]. The SMA is similar to the embedded atom formalism and the TB approximation has been successfully proposed for several metals [20]. In this approach the total cohesive energy of the crystal can be decomposed into one-atom effective binding energies in the following way:

$$U_{coh} = \sum_i \left\{ e_0 \sum_{j \neq i} \exp \left(-p \left(\frac{r_{ij}}{r_0} - 1\right)\right) \right\}$$

$$- \left[ \sum_{j \neq i} \zeta_0^2 \exp \left(-2q \left(\frac{r_{ij}}{r_0} - 1\right)\right) \right]^{1/2},$$

where the first term is repulsive and the second term is the attractive interaction treated in the SMA of the local density of states. Sums are over neighbors within four coordination shells in a crystal and over all atoms in clusters. In this work $r_0$ is a free parameter as suggested in Ref. [19], so we have a total of five parameters: $e_0 = 1.1727$ mRy, $p = 10.13094$, $r_0 = 6.9921$ au, $\zeta_0 = 21.398$ mRy, $q = 1.30218$. These parameters were determined using Eq. (1) and fitting to the APW total energy as a function of lattice constant. Since LDA, although accurate for the solid, has a substantial error for the free atom, we have shifted the atomic energy so that Eq. (1) evaluated at the LDA equilibrium volume gives the experimental value of the cohesive energy 1.13 eV [22].

The bulk modulus calculated with both our new potential and APW is 87.1 kbar and the Gruneisen constant is 1.61 whereas the experimental values are 73.5 kbar [23] and 1.4 ~ 1.7 [24], respectively. The lattice constant, 7.68 Å, is within 5% of experimental values. The melting temperature for the bcc crystal, calculated from Lindemann’s criterion [25], is 332.9 K, comparable to the experimental value of 370.9 K.

3. Energetics of neutral sodium clusters

The new model potential is expected to work best when calculating the energetics of large sodium clusters where most of the atoms have a full coordination shell. However, it gives satisfactory binding energies ($E_b = U_{coh}$) even for the smallest clusters. Fig. 1 shows a comparison of $E_b$ calculated in this work from Eq. (1) with experiment [7] and with several first principles calculations [26-28]. The geometries of the clusters were obtained dynamically performing an MD annealing process and further minimizing the last
resulting configuration. As shown in Fig. 1, the calculated binding energies are in excellent agreement with the experimental results. In addition, an estimate of the surface energy was obtained by fitting the calculated $E_b$ (in eV) to the expression $E_b = 1.13 - \epsilon_s N^{-1/3}$. This fit is shown in Fig. 1 (solid line) yielding $\epsilon_s = 1.076$ eV. Under this potential, in the size range $55 \leq N \leq 10,000$, we observe that icosahedral clusters have the lowest binding energy when compared to relaxed spherical clusters of equal size carved from both the bcc lattice and the fcc lattice.

We also calculated the cluster Helmholtz free energy, $F = E - TS$, in the harmonic approximation at three low temperatures $T$ for sizes $13 \leq N \leq 309$. These results are shown in Fig. 2. It is apparent that as clusters grow larger they become more stable and their free energy tends slowly towards the bulk value. Furthermore, the melting temperature $T_m$ of a cluster was calculated as a function of the cluster size within Lindemann’s approximation [25] assuming that the ratio between the root-mean-square atomic displacement in the clusters and $r_0$ is 0.15. Knowing both, $F$ and $T_m$, permits the tracing of a phase portrait in the plane $F$ vs $N$. This portrait is given in Fig. 3 where each point indicates the free energy per particle at $T_m$ for every given size. Below the line the clusters are liquid-like and above the line the clusters are solid-like. This phase portrait shows clearly that the solid-like phase increases its stability as the cluster grows larger.

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**Fig. 1.** Binding energy vs. cluster size $N^{-1/3}$. This work (dot), Ref. [7] (cross), Ref. [26] (solid dot), Ref. [27] (triangle), Ref. [28] (square). The solid line is the fit to our calculation.

**Fig. 2.** Free energy per atom vs. cluster size $N$ at three different temperatures: 105 K (dot), 55 K (cross), 5 K (triangle).

**Fig. 3.** Phase portrait in the plane of free energy per atom vs. cluster size. Each point is the free energy at the melting temperature for each cluster size. The solid line guides the eye.
4. Multiply charged sodium clusters

Furthermore, we use the new potential to model the fission mechanism of multiply charged clusters in the size range $13 \leq N \leq 150$. These cluster ions support a positive charge $Q$ acquired from multiple ionization. We assume that the charge is distributed uniformly over the cluster by assigning a point fractional effective charge $q = Qe/N$ to each atom. This assumption is reasonable in the size range studied here because the clusters have at most four atomic layers from their center. No macroscopic volume is dominant over a surface with a thickness of four atomic layers. The Hamiltonian for representing a multiply charged cluster with total charge $Q$ is:

$$H = \frac{1}{2} \sum_i m_i v^2_i + U_{coh} + \frac{1}{2} C \sum_{i \neq j} \left[ q_i q_j \frac{q^2 \alpha}{r_{ij}^4} - \frac{q^2 \alpha}{r_{ij}^6} \right],$$

where the $v_i$, $m_i$ are the ion velocities and masses, $U_{coh}$ is given in Eq. (1), $q_i$ are the effective charges of the ions and $\alpha = 0.31 \, \text{Å}^3$ is the polarizability of the sodium ions. The constant $C$ is zero for neutral clusters and one when the cluster is charged.

MD at constant energy was used throughout by solving the equations of motion with Verlet’s algorithm [29] and a time step of $6.792 \times 10^{-14} \, \text{s}$. Simulations were performed using Eq. (2). To simulate the fission process we define two additional parameters: (i) a maximum atomic distance from the cluster center of mass $R_{\text{max}}$; (ii) a maximum bond length $R_b$ defined as $r_0$ incremented by the maximum averaged amplitude of atomic vibrations at a given temperature. Near the melting temperature $R_b$ is about $1.4 r_0$ and $R_{\text{max}}$ is approximately $2.6 R_b$ for clusters with $N \approx 55$. These two parameters are size and temperature dependent. Therefore, each simulation has its own set of values for these parameters. A cluster is defined as that aggregate of $N$ atoms held together by the interaction energy (Eq. (2)) when all interatomic distances are smaller than $R_b$. Neutral clusters ($C = 0$) at sufficiently low temperatures are composed of bonded atoms exclusively. For charged clusters ($C = 1$), fission occurs when the size is too small to sustain the charge. A cluster loses one particular atom when the distance from that atom to all other atoms is larger than $R_b$ and its distance from the cluster center of mass is larger than $R_{\text{max}}$. If a single atom is stripped, the event is discarded and another simulation is started. If the cluster loses simultaneously more than two atoms, then we check whether the stripped atoms belong to another cluster or not by using the same criterion for bonding. If the stripped atoms have indeed formed a second cluster, the event is considered as fission and retained for this study. This dynamical study of the fission mechanism is important because the entropic effects are automatically included.

Various annealing computer experiments were carried out. First, an initial configuration of the neutral cluster ($C = 0$ in Eq. (2)) is chosen and the cluster is equilibrated at a low temperature. Second, the neutral cluster is slowly heated to about $200 \, \text{K}$ and equilibrated at that temperature. Third, the cluster is charged instantaneously by switching $C = 1$ and the simulation is continued for $25,000$ time steps. Fourth, the charged cluster is heated slowly until it fissions. This four-stage process is repeated for every cluster size $N$ and for every total charge $Q$. Relevant quantities such as the temperature at which fission occurs, are kept on file. A total of 36 final simulations were obtained for $Q = 2$ and a total of 45 simulations were accumulated for $Q = 3$. For $Q = 4$ the computing time for the experiment becomes quite long and in this Letter we report only 15 successful fission events. In addition, we saw that when the temperature was increased too rapidly (picosecond range or less), then the cluster exploded into many fragments without a consistent fission pattern.

Fig. 4 illustrates our results for $Q = 2$, $3$ and $4$. Each point shows the highest temperature reachable by a cluster of a given size and charge that undergoes fission. Thus, the horizontal axis depicts the cluster critical size. For each cluster size, we performed many calculations by choosing different initial times to charge the equilibrated cluster. About two thirds of those simulations were unsuccessful events, meaning that at least a single atom was stripped before fission. The unsuccessful events are not plotted in Fig. 4. The successful events presented lifetimes of the order of several nanoseconds before fission. As is evident from Fig. 4, there is a maximum critical size for every value of $Q$ beyond which we were unable to detect fission before evaporation. This maximum critical size for $Q = 2$ is $27$, for $Q = 3$ is $63$ and for $Q = 4$ is $110$. The first two results are in perfect agreement with the
Fig. 4. Cluster temperature vs. critical size for multiply charged sodium clusters: $Q = 2$ (cross), $Q = 3$ (circle), $Q = 4$ (rhombus).

Fig. 5. Fission barrier per atom vs. the scaled critical size $N_c/Q^\gamma$ with $\gamma = 1.64, 1.8, 1.83$ for $Q = 2$ (cross), $Q = 3$ (circle), $Q = 4$ (rhombus), respectively. The solid triangles are the Bohr–Wheeler fission barrier.

Experimental observations of $27 \pm 1$ and $63 \pm 1$ [2]. In the case of $Q = 4$ our maximum critical size is 110 whereas several experimental values have been reported, namely $123 \pm 2$ [3,4], $122 \pm 2$, $118 \pm 2$ and $115 \pm 5$ [10] depending upon the ion bombardment energy 5, 19 and 40 keV, respectively. Our result is in better agreement with the highest bombardment energy experiment in which the reaction time of the cluster is the shortest (about $10^{-15}$ s).

We conclude from Fig. 4 that in the nanosecond time range, smaller clusters are able to sustain larger charges at low temperatures. In fact, we predict that when a charged cluster of a given size is heated it becomes unstable and fissions. This is a novel result that warrants future experimental studies. The cluster temperature can be equated to the energy barrier/atom $V_0 \propto kT$ that the cluster must surmount to undergo fission. A scaling is shown in Fig. 5 where a collapse of the data in Fig. 4 is obtained when the cluster critical sizes are scaled by a power law of $Q$: $N_c/Q^\gamma$. We find $\gamma = 1.63, 1.80, 1.83$ for $Q = 2, 3, 4$, respectively. This scaling clearly separates a $V_0$ region where clusters fission from another region where no fission is observed. Note, however, that if the simulation is continued for times longer than a few nanoseconds, the temperature needed to undergo fission might be lower than that reported in Figs. 4 and 5. For this reason we cannot directly compare our temperature at which fission occurs with the experimental estimates of 500 K in the 40 keV bombardment experiments [10]. For $N_c = 27$ and $Q = 2$ the fission barrier is 1.6 eV in agreement with Ref. [14]. The solid triangles in Fig. 5 correspond to the scaled formula of the Bohr–Wheeler fission barrier[16]: $V_0 = 98.6N^* -1/3 (1 - n_c^* / N^*)^3 / 135$ with $N^* = 6N$ and $n_c^* = 16.33$. Actual results from the simulation for the Bohr–Wheeler $n_c$ parameter are 9.4, 19, 30 for $Q = 2, 3, 4$, respectively.

5. Conclusion

Summarizing, Figs. 4 and 5 are master plots from where experimentalists could extract upper bounds to the cluster ion temperatures (or energy barrier) when the fissioning critical size has been measured. We show the quantitative effect of temperature in the fission process of multiply charged sodium clusters. In addition, we emphasize that temperature and entropy of large multiply charged cluster ions strongly modulate the Coulomb fission mechanism. Finally, for the purpose of this study we have constructed a new analytical potential for sodium from first principles.

Acknowledgements

EBB acknowledges support from the Provost’s Office of GMU for the research assistantship allocated to YL.
References


