Stable Deformations in Large Metallic Clusters

Aurel Bulgac* and Caio Lewenkopf†
National Superconducting Cyclotron Laboratory and Department of Physics and Astronomy, Michigan State University, East Lansing, Michigan 48824
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Only a relatively small number of metallic clusters exhibit a stable spherical shape. We show that the majority of such clusters tend to acquire a deformed shape, in order to minimize the fluctuating part of the total energy, due to the bunching of the single particle electronic levels in a confined geometry. We have found also that there is a large number of low lying shape isomers. Often the deformation energy surface develops rather wide shallow pockets and such clusters are particularly easy to deform. As a function of the electron number the cluster ground state deformations and isomer energies show some remarkable regularities.

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Even though the initial experimental results on metallic clusters concerning abundances, ionization potentials, photoexcitation came to some extent as a surprise, the natural interpretation was found immediately in terms of electronic quantized orbits [1]. Many of the properties of metallic clusters can be understood by considering only the valence electrons [1, 2] as an essentially degenerate electron gas in a cavity. For nonmagic clusters the energetically most favorable configuration is likely to be nonspherical. The need to consider deformed cluster shapes has been recognized relatively early. In principle one can infer information about the deformation of a cluster either by analyzing the shape of the Mie resonance [1] and likely also by a more detailed analysis of the mass abundance or photoionization spectra. The theoretical analysis of the role of deformation in metallic clusters has been so far limited to relatively small clusters, with at most a few hundred atoms [3–5], with one exception [6].

Here our goal is to give an overall picture of possible deformations for large metallic clusters, with particle number up to 3000. We consider axially symmetric spheroidal deformations with the ratio of the major to the minor axes up to 4:1. Because of the large range of particle number and deformations we cover, the model of the metallic cluster we have chosen is somewhat simplified. We describe the cluster in a jellium approximation and the mean field experienced by the electrons is modeled by an infinite square well potential. In spite of its simplicity, this model gives an unexpected accurate picture of the shell fluctuations. The spherical magic numbers we find are equal to the numbers determined in a self-consistent jellium local density approximation (LDA) approach [7] and very similar to the ones obtained in Ref. [8]. Very similar magic numbers were found in Ref. [9] for icosahedral shaped clusters.

We shall limit our analysis to zero temperature, mainly because of uncertainties in the finite temperature treatment of clusters. Except for the amplitude, which diminishes significantly [7], the electronic shell fluctuations do not change in character with temperature and were still observed in large clusters [10]. The relatively large particle number fluctuations seem to require a canonical treatment [11]. Moreover, a finite temperature LDA should rely on a different parametrization of the exchange-correlation energy. Furthermore, the contribution of the ionic degrees of freedom to the entropy is dominant [12] and thus a jellium approach, which ignores it, is physically incorrect. One might assume that the ionic contribution to the free energy does not exhibit significant fluctuations and therefore could be ignored. If that would be true, it would be difficult to understand why electronic shells are replaced with geometrical shells in large clusters [13].

There is compelling experimental evidence pointing to rather different structures of large cold (solidlike) and warm (liquidlike) sodium clusters [13]. In lithium clusters only electronic shell effects have been observed so far [14]. At finite temperatures sodium clusters are rather easy to deform [12, 15] and for that reason electronic degrees of freedom are likely to play a major role in determining the shape of a given cluster. For cold clusters, with a few thousand atoms, the shape is seemingly determined by geometrical effects instead [13, 16].

We have chosen to explore the quadrupole deformation since it is the most likely one to occur, being characterized by the longest wavelength. In certain instances, the specific structure of the Fermi surface might conspire in such a way as to favor the onset of higher multipole deformations (in particular octupole), even before any quadrupole deformation sets in [4]. The single particle levels have been determined by solving the Schrödinger equation for an infinite square well with an axial spheroidal shape. The shell corrections were obtained by subtracting the smooth part of the total energy using either the Strutinsky procedure [17] or the Weyl analytical expression [18]. Within such an approach one cannot correctly describe the odd-even effects (such as ionization potentials, separation energies, etc.), because spin polarization is not accounted for.

In Fig. 1 we show the fluctuating part of the cluster

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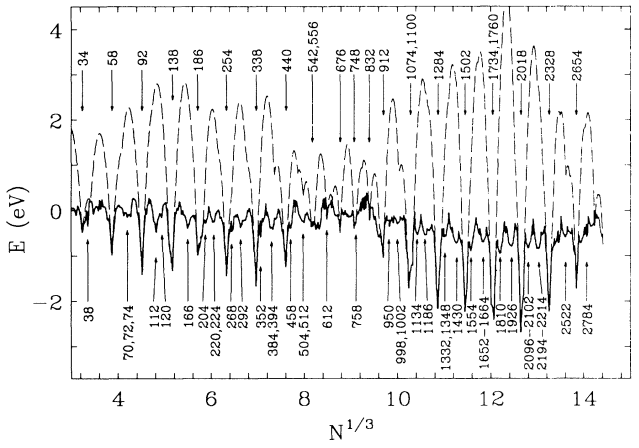

FIG. 1. The shell correction part of the total energy, determined for the most favorable configuration of a given cluster, solid line. The dashed line shows the same quantity computed for spherical geometry only. The numbers in the upper part of the plot designate the spherical magic numbers. The numbers in the lower part correspond to some of the most prominent minima of deformed clusters only.

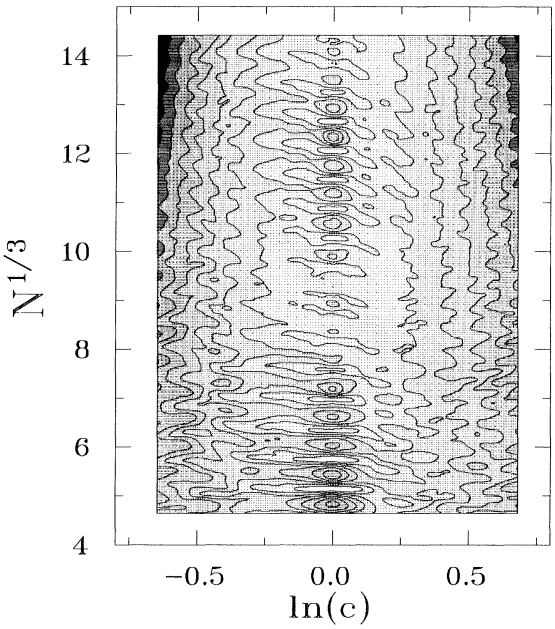

FIG. 2. The contour plot of the deformation energy (scaled with a factor $N^{-1/3}$) as a function of $N^{1/3}$ and the natural logarithm of the ratio of the axes of the spheroid ($c = R_{\|}/R_{\perp}$). The oblate shapes correspond to the negative values of the logarithm of the deformation.

total energy, computed for both spherical clusters and deformed clusters, evaluated at the minimum of the total energy for each particle number. By allowing a cluster to deform the amplitude of the shell correction is significantly reduced and much more structure emerges. The notable beating minimum [19], linked with the so-called supershells [8], is however, rather well defined as are the deep minima, corresponding to the spherical magic numbers. Besides the almost periodic oscillatory character of the shell corrections in the variable $N^{1/3}$ (N—number of valence electrons), one can also see a remnant of the supershell beating minimum for deformed clusters as well. In the region around $N = 1000$ there is an easy to spot area, see Fig. 2, both on prolate and oblate sides, where the amplitude of the shell corrections is rather small.

The interplay between the liquid drop deformation energy and the shell corrections lead to a quite complicated energy surface as a function of deformation and particle number, see Fig. 2. In Fig. 3 we display the ground state deformation for each cluster as a function of $N^{1/3}$ and in Fig. 4 the energy difference between the energy of the first shape isomer and the ground state energy for each cluster.

In the vicinity of each known spherical magic number there is a well defined valley in the deformation-particle number plane. Below the first supershell minimum ($N < 1000$) these valleys are rather stiff in the $N^{1/3}$ direction. Therefore these clusters are easier to deform and moreover the probability to find shape isomers is rather high. One can draw the same conclusion from Fig. 4, which shows that there are somewhat more low lying isomers for $N < 1000$ than for $N > 1000$. Unfortunately we could not find a simple way to characterize the average stiffness and width of the deformation energy. Quite often in the region $N < 1000$ the deformation energy is rather shallow as a function of deformation. On the other hand for $N > 1000$ the character of the deformation energy changes. The valleys are somewhat slanted and for that reason the number of relatively low lying shape isomers is reduced. Only for particle numbers roughly half-way (on the $N^{1/3}$ scale) in between two consecutive spherical magic numbers there is a clus-

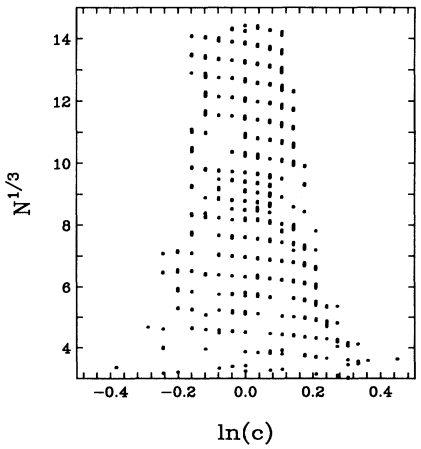

FIG. 3. The ground state cluster deformations ($c = R_{\|}/R_{\perp}$).

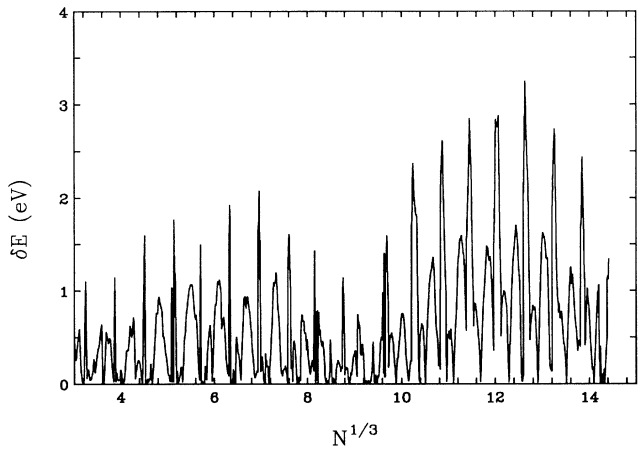

FIG. 4. The excitation energy of the first shape isomer of each cluster. The highest and sharpest peaks correspond to the spherical magic clusters.

ter for which prolate and oblate shapes have essentially the same energy. For the clusters in the region $N < 1000$ the deformation of the lowest lying isomer can be either similar or not with the deformation of the ground state, unlike the larger clusters. This difference between the lighter and heavier clusters can be understood by comparing the magnitude of the shell corrections, which are roughly of the same order of magnitude for all clusters (more accurately they slowly increase as $N^{1/6}$ [20]) with the smooth part (liquid drop) of the deformation energy, which is proportional to $N^{2/3}$.

The enhanced stability of spherical clusters can also be characterized by the energy of the first shape isomer. In this respect spherical and deformed clusters are again very similar. The highest and sharpest peaks in Fig. 4 correspond to spherical magic numbers. Roughly at half distance between two consecutive spherical magic numbers there is another peak, about half as high and wider, corresponding to particularly stable deformed clusters. The position of these peaks correlates almost perfectly with the additional minima in the fluctuating part of the energy, see Fig. 1.

A certain regularity in Fig. 3 is rather obvious. Starting from a spherical magic cluster, with increasing N a cluster acquires at first an oblate deformation (which increases with N) and at some point the cluster suddenly becomes prolate, with a large deformation (which then decreases with N). At the transition point the excitation energy of the shape isomer vanishes, which favors the occurrence of shape coexistence. It will be interesting to establish whether this sharp transition might become more gradual or even change completely if more complicated shapes would be considered. The $N^{1/3}$ scale in Fig. 3 gives the impression that there are approximately equal numbers of oblate and prolate clusters and relatively few spherical ones. An actual counting shows that there are roughly twice as many prolate clusters as compared to oblate ones and twice as many oblate as spherical clusters. However, small changes of the background (in particular the discrete nature of the ion cores, a smoother boundary, thermal fluctuations, etc.) can lead to rather noticeable changes of the potential energy surface of a cluster.

The translation of our results in terms of available experimental data seems to be still an ambiguous procedure. One might be tempted to conclude that the deep minima on the deformation energy surface should be correlated with the additional structures observed in abundance spectra. We have performed such a comparison, between our results, Fig. 1, and the experimental data of Refs. [10, 14]. Even for the spherical magic numbers there are notable differences between what the present or other theoretical studies predict and the observed ones. However, many of the additional minima in Fig. 1 correlate rather well with the positions of the other structures seen in experiments. We see several reasons here for not performing such a detailed comparison at this time. As remarked above, the deformation energy surface exhibits a rather complicated structure, there are many local minima rather close in energy to the ground state. In many cases the deformation energy surface is rather shallow as well and the absolute minima are not well separated from other possible configurations. One might then reasonably expect that in some instances a relatively deep minimum will not manifest itself very prominently in the experimental spectra, simply because of its relatively low statistical weight. The current interpretation of the experimental abundances is done in terms of single atom separation energies, which as we have mentioned earlier, cannot be described accurately in the framework of our model. Moreover, shape dynamics might play a role during a single atom evaporation process. In spite of these rather pessimistic conclusions we think that here we have been able to point to a rather rich shape dynamics of the metallic clusters (even though we have considered only static properties). One can expect that the kinetics of both cluster aggregation, cluster evaporation and fragmentation will be markedly influenced by the rather complicated structure of the deformation potential energy surface. One might speculate that during the aggregation or evaporation process a cluster will follow these valleys of the potential energy surface. Namely, a prolate cluster will become less and less deformed through the addition of atoms and eventually will swing to the other side by becoming more and more oblate. There is an intriguing possibility that the clusters with particle number corresponding to these sudden jumps in shape (located at roughly mid-distance between two consecutive magic numbers on the $N^{1/3}$ scale) might serve as accumulation points during either aggregation of a cluster or atom evaporation, and for that reason be somewhat prominent in the abundance spectra. A comprehensive

study of the role of higher multipoles is very much warranted and also of the role of a net charge, which leads to a dramatic reduction of the effective surface tension.

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Note added.—Recently S. Frauendorf and J. Dudek have brought to our attention Ref. [21], where shell corrections have been considered in ellipsoidal cavities for systems with $N \leq 950$ and D. Tománek has made available to us the preprint [22], where the results for $N \leq 850$ quoted in Ref. [6] are presented.

* Present address: Department of Physics, FM-15, University of Washington, Seattle, WA 98195. Electronic address: bulgac@alpher.npl.washington.edu

† Present address: Department of Physics, FM-15, University of Washington, Seattle, WA 98195. Electronic address: lewenkopf@alpher.npl.washington.edu

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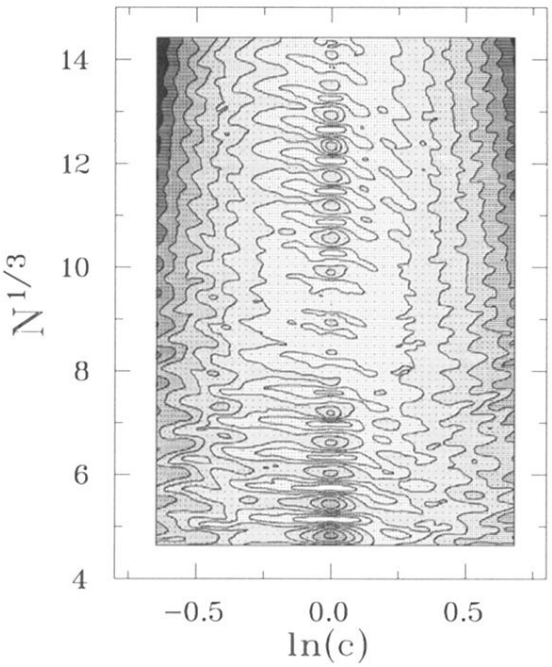

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