

Quantum Shell Effect on Dissociation Energies, Shapes, and Thermal Properties of Metallic Clusters from the Random Matrix Model

V. M. Akulin,* C. Bréchnignac,† and A. Sarfati

Laboratoire Aimé Cotton, CNRS II, Bâtiment 505, 91405 Orsay Cedex, France

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We show that a conceptually simple random matrix model of metallic clusters yields dissociation energies which are in very good agreement with both experimental data and results of *ab initio* calculations. For open shell clusters this model predicts a new phenomenon: a phase transition associated with the loss of spherical symmetry.

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Recent progress of cluster theory mainly relies on the molecular approach, when exact quantum chemical methods [1] or the local density approximation for metallic clusters [2] are employed in *ab initio* calculations. A great deal of attention has been paid to the allowance of possible spontaneous three-axial deformation [3] of clusters, which usually implies cumbersome numerical work. But do we really need to pursue the *ab initio* description for the increasing cluster size?

In this Letter we show that the results of *ab initio* calculations of the alkali metal clusters can be reproduced in the framework of a conceptually simple qualitative theory, which considers the clusters as disordered pieces of solids. This theory also gives very good agreement with the experimental data [4] and can be easily extended to large species.

The purpose of such a theory is not only to get a deeper insight into the physics underlying the behavior of metallic clusters but also to predict new phenomena. In particular, we demonstrate the link between the temperature and the shapes of clusters and show that small metallic clusters experience a high-order phase transition [5] where shape plays the role of the order parameter.

In the first approximation our theory treats metallic clusters as a Fermi gas of electrons moving in an effective spherically symmetric potential well: The one-electron states resulting from the quantization of this motion are populated according to the Fermi distribution at zero temperature. At the next step we assume that other interactions such as thermal perturbation of the cluster density, spontaneous deformation of its shape, as well as the scattering of the electrons at ionic cores of individual atoms, etc., have qualitatively the same effect on the unperturbed one-electron spectrum: All together they just lead to a random coupling [6] of the states. In other words, we assume that all these phenomena contribute additively to the mean square interaction $\langle V^2 \rangle$, which is the only parameter that governs the transformation of the one-electron spectra occupied by cold and noninteracting electrons. We consider this perturbation to all orders with the help of random matrix theory.

Our approach relies on the transformation rule for an arbitrary quantum system perturbed by a random matrix, which has been discussed in details in Ref. [7]. Briefly the essence of the rule is the following: Perturbation of a quantum system by a random matrix results in a transformation of the density of states. The new ensemble averaged density of states reads

$$\tilde{g}(E) = \frac{1}{\pi} \text{Im} \sum_{n,l} \frac{d_{nl}}{\tilde{E}(E) - E_{nl} - i0}, \quad (1)$$

where E_{nl} are the energies and $d_{nl} = 2l + 1$ are the orbital degeneracies of the unperturbed levels. The continuous (from $-\infty$ to ∞) solution $\tilde{E}(E)$ of the transcendental algebraic equation

$$E = \tilde{E} + \sum_{n,l} \frac{\langle V^2 \rangle d_{nl}}{\tilde{E} - E_{nl} - i0} \quad (2)$$

gives a complex-valued renormalization of energies E .

We assume that the random perturbation does not involve spins of the electrons. Therefore the equations

$$N_+ = \int_{-\infty}^{\epsilon_+} \tilde{g}(E) dE, \quad N_- = \int_{-\infty}^{\epsilon_-} \tilde{g}(E) dE \quad (3)$$

hold, respectively, for the numbers N_+ and N_- of valence electrons with the parallel and antiparallel spins and for the corresponding energies ϵ_+ and ϵ_- of the last states occupied by the electrons with given spins. For a cluster with an even number N of valence electrons we have $N_+ = N_- = N/2$, whereas for an odd N we have $N_+ = N_- + 1 = (N + 1)/2$. The net energy of valence electrons reads

$$\mathcal{E}(\langle V^2 \rangle, N) = \int_{-\infty}^{\epsilon_+} E \tilde{g}(E) dE + \int_{-\infty}^{\epsilon_-} E \tilde{g}(E) dE. \quad (4)$$

By solving Eq. (2) numerically for an unperturbed energy spectrum E_{nl} , d_{nl} , and a given size of the perturbation $\langle V^2 \rangle$, we find the nonlinear complex-valued renormalization $\tilde{E}(E)$ of the energy scale and calculate the correspondent density of states Eq. (1). At the next step, for given N we find from Eq. (3) the integration limits ϵ_+ and ϵ_- , and finally from Eq. (4) we determine the energy of the perturbed cluster.

The dimensionless parameter $v^2 = \langle V^2 \rangle g^2$ governs the reconstruction of the state density $\tilde{g}(E)$. Here g is a typical density of one-electron states. By taking $g = 2mr_s^2 N^{2/3} / 3\hbar^2 \approx \pi^2 (E_{2s} - E_{1s})^{-1}$ we arrive at $v^2 = \langle V^2 \rangle 4r_s^4 m^2 N^{4/3} / 9\hbar^4$, where m is electron mass and r_s is Wigner-Seitz radius. Since $\langle V^2 \rangle$ represents the size of random perturbation we can refer to v^2 as a ‘‘disorder parameter.’’ It consists at least of three parts $v^2 = v_{\text{scatt}}^2 + v_{\text{th}}^2 + \eta^2$. The first part allows for the non-separable electron-electron and electron-ion interactions which have not been taken into account in the Fermi-gas model. The second contribution comes from the scattering at phonons, and hence it depends on the temperature $v_{\text{th}}^2 = \lambda_N T$. The third term η^2 is a free parameter proportional to a typical deformation $\langle (\delta R/R)^2 \rangle$.

We estimate $v_{\text{st}}^2 = v_{\text{scatt}}^2 + v_{\text{th}}^2$ by noting that the electronic relaxation time τ in metals originates from the same phenomena as v_{scatt}^2 and v_{th}^2 . Indeed, the relaxation rate $1/2\pi\tau$ equals the mean squared interaction $\langle V^2 \rangle_{\text{st}} \equiv v_{\text{st}}^2 / g^2$ multiplied by the density of states with a fixed spin $g(\epsilon_F) = (9\pi/4)^{1/3} 2Nm r_s^2 / 3\pi\hbar^2$ at the Fermi energy $\epsilon_F = (9\pi/4)^{2/3} \hbar^2 / 2m r_s^2$. Hence we arrive at $v_{\text{st}}^2 = (4N/9\pi)^{1/3} m r_s^2 / 3\hbar^2 \tau$ [8].

The third term has the structure $\eta^2 = C \langle (\delta R/R)^2 \rangle N^{1/3}$. We concentrate here only on the size of η , and therefore we neither specify the numerical factor C nor dictate the mode of the deformation. In our consideration η^2 plays the same role as the order parameter in the second order phase transition theory: It appears if a spontaneous deformation yields a gain of the cluster energy.

The energy Eq. (4) as a function of the cluster size can be separated [9] into two parts. One part is a smooth function on N which reveals macroscopic properties of the metal. The other part is the so-called shell correction \mathcal{E}_{sc} which allows for microscopic quantum properties of the clusters. The smooth part has the general structure $\mathcal{E}_{\text{sm}} = a_v N - a_s N^{2/3} + a_C N^{-1/3} + b_v v^2 N^{2/3} + b_s v^2 N^{1/3}$. Here $a_v N$ is the volume energy of N atoms. The surface contribution $a_s N^{2/3}$ represents the energy of bonds breaking needed for extraction of atoms from the volume at the surface. The term $a_C N^{-1/3}$ gives the Coulomb energy of ionic species [4]. Since $v^2 \sim N^{1/3}$, the terms $b_v v^2 N^{2/3}$ and $b_s v^2 N^{1/3}$ give the linear in v^2 corrections of $a_v N$ and $a_s N^{2/3}$, respectively. As a guess for the parameters a_v and a_s we take the experimental values [4] that have been found at finite temperatures. We determine parameters b_v and b_s by fitting the calculated dissociation energies to the experimental curves. In the same time we specify the parameters a_v and a_s for ions at $T = 0$ and with a better allowance of shell corrections.

In order to find the shell corrections we take the spectrum $E_{nl}^{(339)}$ of the spherically symmetric closed-shell cluster ion M_{339}^+ calculated in the local density

approximation for different alkali metals $M = \text{Li, Na, K}$, and construct the unperturbed spectra of smaller clusters by the scaling $E_{nl}^{(N+1)} = [339/(N+1)]^{2/3} E_{nl}^{(339)}$. We substitute $E_{nl}^{(N+1)}$ into Eq. (2) and obtain the total energy Eq. (4). This model properly takes into account only the shell corrections since they are sensitive to the mutual positions of neighboring levels near ϵ_F that do roughly obey the scaling law. It fails in reproducing the smooth dependence which is not scale invariant. We therefore have to extract only \mathcal{E}_{sc} from the calculated total energy Eq. (4) by subtracting the smooth part.

But how can we identify the smooth part? A remarkable property of the shell corrections allows us to do it: They must vanish for large v^2 . We therefore calculate $\mathcal{E}(v^2, N)$ and identify nine [10] parameters $\alpha_0, \alpha_1, \alpha_2, \beta_0, \beta_1, \beta_2, \gamma_0, \gamma_1$, and γ_2 that for large v^2 make the difference

$$\begin{aligned} \mathcal{E}_{\text{sc}} = & \mathcal{E}(v^2, N) - (\gamma_0 + \gamma_1 v^2 + \gamma_2 v^4) N^{1/3} \\ & - (\beta_0 + \beta_1 v^2 + \beta_2 v^4) N^{2/3} \\ & - (\alpha_0 + \alpha_1 v^2 + \alpha_2 v^4) N \end{aligned} \quad (5)$$

vanishing: $\mathcal{E}_{\text{sc}} \rightarrow 0$. Thus constructed Eq. (5) represents therefore only the shell corrections, and we arrive at

$$\begin{aligned} \mathcal{E} = & a_v N - a_s N^{2/3} + a_C N^{-1/3} \\ & + b_v v^2 N^{2/3} + b_s v^2 N^{1/3} + \mathcal{E}_{\text{sc}}. \end{aligned} \quad (6)$$

In Fig. 1 we show the perturbation-dependent part of Eq. (6) for Li_{N+1}^+ , Na_{N+1}^+ , and K_{N+1}^+ clusters as a function of cluster size for different parameters v^2 . On the top of smooth dependences one sees the transformation of shell corrections for the increasing perturbation: The long-period sawtooth oscillations associated with the spherical degeneracy of electronic orbits at small v^2 turn into even-odd alternations [11] resulting from the residual twofold spin degeneracy. The larger the perturbation the stronger the even-odd alternations, which agrees with the results of Ref. [3]. Near the magic numbers $N = 2, 8, 20, \dots$, an increase of v^2 leads to an increase of energy. For other sizes we see an interplay between dying shell corrections and increasing smooth parts of the clusters energies: The total energy first decreases with an increase of v^2 , then it reaches a minimum value for $v^2 = v_{\text{min}}^2$, and then starts to rise.

We find the disorder parameter v_{min}^2 which minimizes the energy Eq. (6) for each N . If v_{min}^2 exceeds v_{st}^2 , the free parameter may take a positive value $\eta^2 = v_{\text{min}}^2 - v_{\text{st}}^2$; otherwise the minimum energy corresponds to $\eta^2 = 0$. It implies that for a given starting perturbation v_{st}^2 the spherical clusters for which $v_{\text{st}}^2 > v_{\text{min}}^2$ remain spherical. In the opposite case $v_{\text{st}}^2 < v_{\text{min}}^2$ the cluster spontaneously changes its shape and decreases its energy to the minimum value.

For a fixed v_{st}^2 the energies of clusters are given by the bottom envelope $\mathcal{E}_{\text{be}}(v_{\text{st}}^2, N)$ of the family of curves in

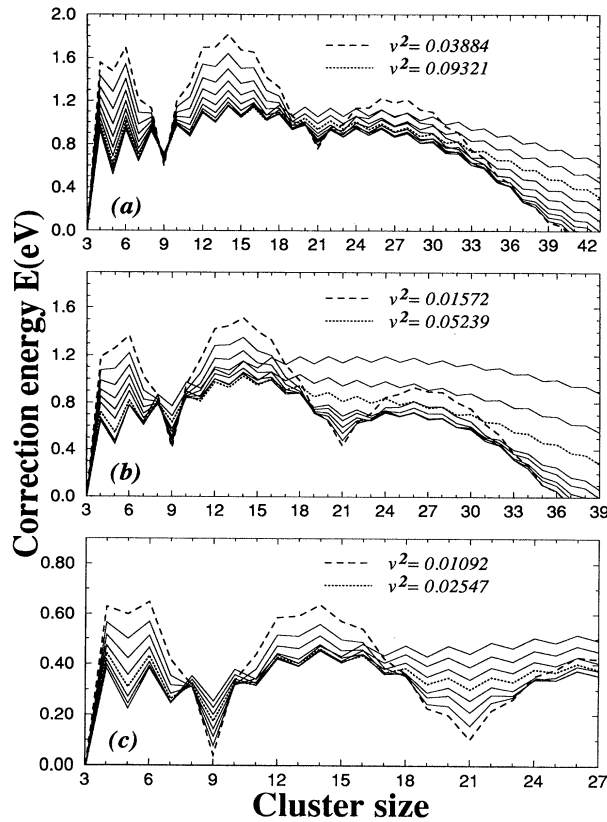


FIG. 1. Shell corrections for (a) Li_{N+1}^+ , (b) Na_{N+1}^+ , and (c) K_{N+1}^+ clusters for different sizes of the disorder parameter v^2 . (In order to magnify the shell corrections a linear dependence has been subtracted.) The bottom envelope $\mathcal{E}_{\text{bc}}(N)$ corresponds to different v^2 and serves for the determination of the dissociation energies.

Fig. 1 with the perturbations $v^2 > v_{\text{st}}^2$. The increments

$$D(v_{\text{st}}^2, N) = \mathcal{E}_{\text{bc}}(v_{\text{st}}^2, N-1) - \mathcal{E}_{\text{bc}}(v_{\text{st}}^2, N) \quad (7)$$

yield the corresponding dissociation energies. In Fig. 2 we depict these dissociation energies for Li_{N+1}^+ , Na_{N+1}^+ and K_{N+1}^+ , along with the experimental data and results of the *ab initio* calculations of three-axial deformed Na_N clusters. One can see that the calculated dependences are in very good agreement with the experiments.

Parameter v_{st}^2 depends on the temperature via the part $v_{\text{th}}^2 = \lambda_N T$. Hence for $v_{\text{st}}^2 > v_{\text{min}}^2$ the energy Eq. (6) also depends on T . In the opposite case of $v_{\text{st}}^2 < v_{\text{min}}^2$ the electronic energy takes the minimum value and does not feel any temperature variations, since the change of η^2 compensates for any small change of $\lambda_N T$. In chemical terms it implies the existence of plural isomeric forms [12] mutually accessible in the configuration space of the clusters. We therefore determine the electronic contribution to the cluster heat capacity as

$$c(N) = \Theta(v_{\text{st}}^2 - v_{\text{min}}^2) \frac{\partial \mathcal{E}(v_{\text{st}}^2, N)}{\partial v_{\text{st}}^2} \lambda_N, \quad (8)$$

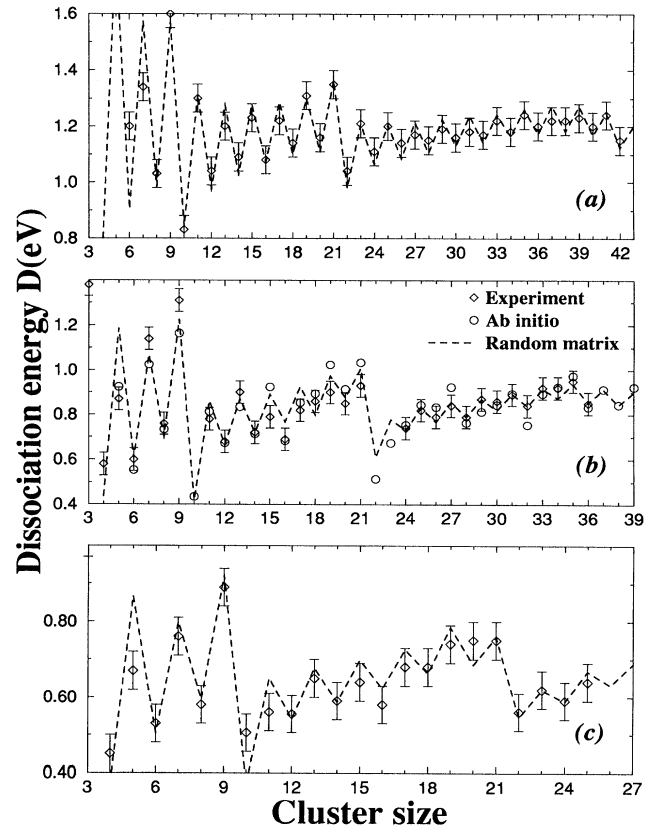


FIG. 2. The dissociation energies of cluster ions as a function of size calculated with the help of Eq. (7): (a) lithium $a_v = 1.27$ eV, $a_s = 0.2$ eV, $b_v = -6.6 \times 10^{-5}$ eV/K, $b_s = 2.6 \times 10^{-5}$ eV/K, $v_{\text{st}}^2 = 0.039 [T \sim (700 \text{ K})(27/N)^{1/3}]$; (b) sodium $a_v = 0.96$ eV, $a_s = 0.4$ eV, $b_v = -2.2 \times 10^{-5}$ eV/T, $b_s = 8.7 \times 10^{-5}$ eV/T, $v_{\text{st}}^2 = 0.016 [T \sim (650 \text{ K})(36/N)^{1/3}]$; and (c) potassium $a_v = 0.87$ eV, $a_s = 0.9$ eV, $b_v = -1.3 \times 10^{-5}$ eV/T, $b_s = 6.5 \times 10^{-5}$ eV/T, $v_{\text{st}}^2 = 0.01 [T \sim (450 \text{ K})(21/N)^{1/3}]$. The experimental data of Ref. [4] and *ab initio* calculations of Ref. [3] (shifted in energy) are given for comparison.

where $\Theta(x)$ is the step function. Note that variation of the Fermi distribution with temperature gives the main contribution to the bulk heat capacities of metals. For small clusters the Fermi liquid remains cold or, in other words, the small clusters remain in their ground electronic terms. The contribution Eq. (8) is just a correction to the dominating vibrational heat capacity, and it never reaches the Dulong-Petit limit $c(N) = 3N$.

In Fig. 3(a) we show the heat capacities $c(N)$ of Na_{N+1}^+ clusters calculated with the help of Eq. (8) for low, high, and moderate temperatures. The heat capacities of Li_{N+1}^+ , and K_{N+1}^+ have similar structures. One can clearly see that at low temperatures only the clusters of the sizes close to the magic numbers have $c(N) \neq 0$. With the increase of the temperatures the intervals of nonzero $c(N)$ become larger. For high temperatures

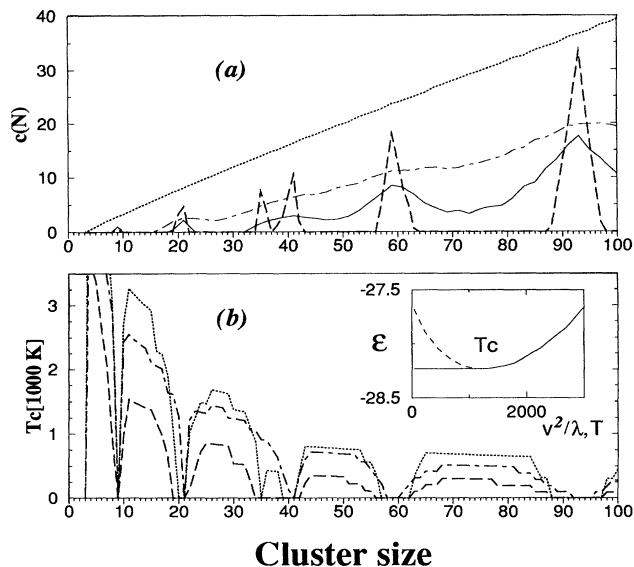


FIG. 3. (a) Electronic contribution to the heat capacity for Na_{N+1}^+ clusters at $T = 0$ (dashed line), at $TN^{1/3} = 4250$ K (solid line), at $TN^{1/3} = 7100$ K (dash-dotted line), and at $T \rightarrow \infty$ (dotted line). The temperature, however, must remain smaller than the gap between the electronic levels. (b) Critical temperatures for Li_{N+1}^+ (dash-dotted line), Na_{N+1}^+ (dotted line), and K_{N+1}^+ (dashed line) cluster ions as a function of the cluster size. The “noise” comes from the crude temperature grid. Dependence of Li_{30}^+ energy on the temperature (solid line) and on the scaled perturbation v^2/λ_{30} (dashed line) is in the inset.

all clusters have nonzero electronic contributions to the heat capacities. The appearance of $c(N)$ at a certain temperature implies a high-order phase transition.

For different sizes the phase transitions occur at different temperatures. In Fig. 3(b) we present the critical temperatures of the phase transitions $T_c = (v_{\min}^2 - v_{\text{scatt}}^2)/\lambda_N$ for Li_{N+1}^+ , Na_{N+1}^+ , and K_{N+1}^+ clusters. The maximum T_c correspond to the clusters with approximately half-occupied electronic orbitals which also have the maximum deformation at lower temperatures. For example, the very last phase transitions occur for $N \sim 10-13$ at $v_{\text{st}}^2 \sim 0.09$ for Li, at $v_{\text{st}}^2 \sim 0.06$ for Na, and at $v_{\text{st}}^2 \sim 0.05$ for K. When we neglect v_{scatt} , it roughly corresponds to the temperatures of 2500, 3200, and 1500 K, respectively. At the experimental temperatures of Ref. [4] the parameter η^2 for these cluster sizes amounts to 0.05, 0.04, and 0.035, respectively.

We conclude by summarizing the starting points and the main results of the paper. We take a spherical cluster and calculate with the help of random matrix theory the effect of a generic perturbation on the total energy of the cluster. We assume that this perturbation originates from the variation of the cluster shape and from the thermal motion of the cluster atoms that destroy the spherical symmetry and make the quantum motion nonseparable. We find the minimum energies and corresponding values

of the perturbation that depend on the cluster size. If for a given temperature and a given cluster size the thermal part of the perturbation cannot ensure the energy minimization, the intended difference comes from the spontaneous distortion of the cluster shape. We compare with the experiment the dissociation energies of the clusters calculated with the allowance of this generic spontaneous deformation and find very good agreement. For each cluster size we also find the critical temperature that corresponds to the minimum energy. Below this temperature the cluster is deformed and its electronic energy is minimum. Above it the cluster acquires the spherical shape and the energy starts to depend on the temperature, which implies a phase transition. The critical temperatures of the phase transition are zero for the closed-shell clusters and maximum for the clusters with nearly half-occupied outer shells.

*Also at Moscow Institute of Physics and Technology, Dolgoprudny, Moscow, Russia.

†To whom all correspondence should be addressed.

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