VOLUME 67, NUMBER 23 PHYSICAL REVIEW LETTERS 2 DECEMBER 1991

Temperature Dependence of Supershells in Large Sodium Clusters

O. Genzken and M. Brack
Institute for Theoretical Physics, University of Regensburg, D-8400 Regensburg, Germany
(Received 30 July 1991)

We present self-consistent calculations of the electronic shell and supershell structure of sodium clusters with up to $N \sim 1600$ atoms at finite temperatures and $N \sim 2800$ at zero temperature, employing the spherical jellium model in the local-density approximation and numerically solving the Kohn-Sham equations. The finite temperature of the valence electrons is included by treating them as a canonical subsystem embedded in the heat bath of the ions. We present sensitive quantities for the effects of temperature and self-consistency upon the supershell structure and compare our results with recent experiments and former calculations based on phenomenological mean-field potentials.

PACS numbers: 71.45.Nt, 31.20.Sy, 36.40.+d, 65.50.+m

Metal clusters provide a unique example for the study of shell effects in finite fermion systems containing up to several thousand particles. The well-known enhancements in the experimental abundance spectra [1] of small alkali-metal clusters at the "magic" atomic numbers $N=8,20,40,58,92,\ldots$ can be explained in a self-consistent microscopic theory for interacting valence electrons in the field of a uniformly charged sphere representing the ions, i.e., in the so-called self-consistent jellium model [2]. Nishioka, Hansen, and Mottelson [3] recently developed a phenomenological Woods-Saxon potential for the valence electrons, fitted to the microscopic potentials of Ref. [2], and calculated level densities and binding energies of sodium clusters with N up to 4000 (although only calculations for $N \leq 200$ were available in Ref. [2]). They drew attention to the "*supershell structure*" in the level density and the oscillating part of the total binding energy: a pronounced beating pattern in which the shell structure is enveloped by a slowly varying amplitude. In fact, Balian and Bloch have shown in their fundamental work [4] that supershell structure is a very general feature of discrete eigenmodes in a cavity or in any potential confining many particles to a limited domain of space. They explained the beating pattern of the level density by the superposition of amplitudes associated to closed classical trajectories and succeeded in some model cases to reproduce the shape of the exact level density by summing up only the oscillating terms related to triangular and squared classical orbits. Strutinsky *et al.* [5], investigating the contributions from planar and three-dimensional orbits, were able to explain the gross shell structure of atomic nuclei using realistic deformed shell-model potentials. The same kind of analysis was taken up by Nishioka, Hansen, and Mottelson [3], using both their phenomenological Woods-Saxon potential and a self-consistent potential gained from semiclassical density variational calculations [6], to investigate their predicted supershells of metal clusters in the mass range $N \sim 1000$–4000.

The experimental observation of the supershell structure is inhibited by the fact that clusters produced in expansion sources have a finite temperature which tends to reduce the shell effects. For very large clusters with several thousand atoms, the spacing of the main shells near the Fermi energy decreases to ~ 0.05 eV ≈ 600 K, as compared to ~ 0.5 eV ≈ 6000 K for small clusters with $N \sim 100$. An estimated temperature of $T \sim 500$–600 K seems to be realistic under experimental conditions [7]. It can therefore be expected that the finite temperature increasingly suppresses the shell oscillations with increasing mass number and thereby obliterates the supershell structure. A sensitive relevant quantity is the second difference $\Delta_2 F(N) = F(N+1) + F(N-1) - 2F(N)$ of the free energy $F(N) = E(N) - TS(N)$ of a cluster with N atoms, where E is the total internal energy, S is the entropy, and T is the temperature. The quantity $\Delta_2 E(N)$ has often been taken as a measure for the stability of the cluster (see, e.g., Ref. [1]). It has furthermore been argued that if *evaporation* is responsible for producing stable clusters, $\Delta_2 F(N)$ should be proportional to $-\Delta_1 \ln I_N$, where I_N is the fluctuating part of the experimental mass yield [7]. In recent jellium-model Kohn-Sham calculations at finite temperature [8,9], $\Delta_2 F(N)$ has, in fact, been shown to decrease very fast for $N \sim 100$–400 and to be practically zero for $N \geq 500$ already at $T \gtrsim 400$ K.

Nevertheless, in the newest sodium vapor expansion experiments of the Copenhagen-Orsay-Stuttgart collaboration [10,11], a supershell structure in the mass abundance spectrum of sodium clusters has been put into evidence. In order to compensate for the temperature suppression effects, Pedersen *et al.* [10] scaled the experimental quantity $\Delta_1 \ln I_N$ with a factor $N^{1/2}\exp(cN^{1/3})$, acting like a magnifying glass for the shell effects. (The factor $N^{1/2}$ compensates the asymptotic decrease of the average amplitude of shell oscillations at $T=0$, and the parameter c in the exponent involves an estimated effective temperature of ~ 400–500 K; see Ref. [10] for details.) In the resulting plot, magic shell closures with N up to ~ 2720 and an interference minimum of the shell oscillations around $N \sim 800$–1000 can be seen (see Fig. 5 of Ref. [10]).

As shown by Nishioka, Hansen, and Mottelson [3], the details of the supershell structure, i.e., its wavelength and the location of the minima, depends rather sensitively on the kind of potential and parameters used in the calculation. The question therefore arises of how this supershell structure looks in a fully self-consistent model without adjustable parameters.

The self-consistent microscopic treatment of fermion systems at finite temperatures is possible, both for grand canonical and for canonical ensembles, by corresponding extensions of the Kohn-Sham (KS) equations. (We refer to an extensive review article [12] for theory and applications of the KS method at $T > 0$.) The study of large metal clusters with several thousand valence electrons poses serious problems of computation time and numerical accuracy. However, due to the numerical procedures recently developed in Ref. [9], we have become able to present here the first *self-consistent* microscopical results for a fermionic system with particle number up to $N \sim 2800$ exhibiting supershell structure. We employ the spherical jellium model using the local-density functional for exchange and correlations by Gunnarsson and Lundqvist [13]. The Wigner-Seitz radius of bulk sodium, $r_s = 3.96$ a.u., is used, otherwise our calculations are completely parameter free. We treat the valence electrons as a *canonical* ensemble in the heat bath of the ions, minimizing the Helmholtz free energy $F(N)$ at a given temperature. (See Ref. [9] for details and, in particular, for a fast algorithm for the exact calculation of the canonical partition function.) For reasons of computational times, we have restricted the calculations at finite temperature to $N < 1650$.

A canonical treatment with exactly conserved particle number N is important here since we investigate quantities like $\Delta_2 F(N)$ related to the change of N by one or two units. $\Delta_2 F(N)$ is very sensitive to temperature effects through the entropy part $-TS$ in the free energy: The large degeneracies of the spherical magic shells lead to large entropies even at small temperatures.

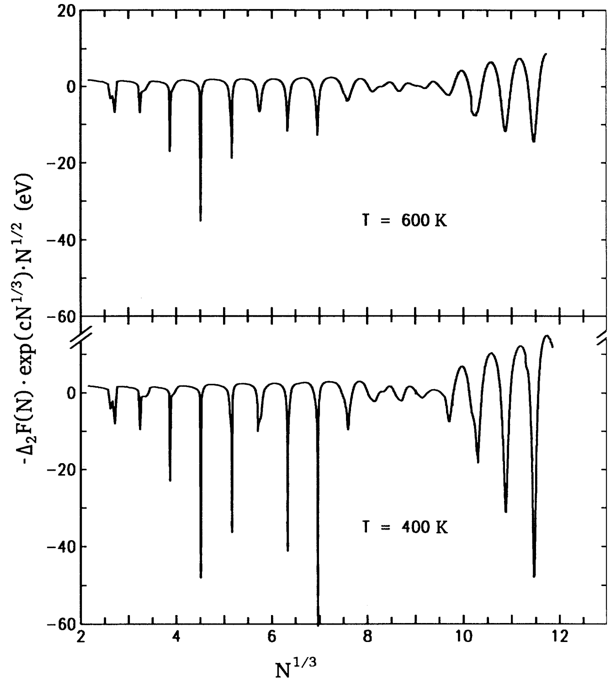

FIG. 1. The negative second difference of the Helmholtz free energy $-\Delta_2 F(N)$ of sodium clusters, calculated in the self-consistent jellium model at the two temperatures $T = 400$ and 600 K. [See text for the scaling factor $N^{1/2} \exp(0.56 N^{1/3})$.]

The results of our calculations of $-\Delta_2 F(N)$ are shown in Fig. 1 for two different temperatures. In order to be able to compare to the experiment, we include the same enhancement factor $N^{1/2} \exp(cN^{1/3})$ as Pedersen *et al.* [10], choosing $c = 0.56$. The shell effects and the supershell structure are clearly visible even at 600 K, with equidistant minima at the shell closures (magic numbers) discussed later in this text. The amplitude is decreasing with temperature and in the transition region between the two supershells, nearly all shell structure is smeared out at 600 K. Note the striking qualitative similarity of this figure with Fig. 5 of the experimental paper [10]. This is quite astonishing since by treating the clusters in the jellium approach, all the structure of the ions is ignored. Nevertheless, we find that our results give a good semiquantitative description of the experimental ones. As discussed in Refs. [7-9], we cannot expect more quantitative agreement, since the evaporation processes which take place between formation and mass separation of the sodium clusters would require a dynamical nonequilibrium treatment in order to explain the details of the final mass yields and to understand the precise value of the parameter c used. What our results are able to demonstrate is that the electronic shell structure dominates the oscillating part of the mass yield even up to the range $N \sim 3000$, and that the finite temperature of the valence electrons plays a crucial role in its quantitative evaluation.

A standard quantity for studying shell effects is the shell-correction energy $\delta F(N) = F(N) - \bar{F}(N)$, where $\bar{F}(N)$ is the *average* free energy of a cluster with N atoms. Here we use a liquid-drop-model (LDM) expansion $\bar{F}(N) = e_b N + a_s N^{2/3} + a_c N^{1/3}$ (cf. Ref. [6]), determining the surface energy a_s and the curvature energy a_c by a simple eye fit such that $\delta F(N)$ is oscillating around zero; this is done separately at each temperature. The bulk energy is fixed at its theoretical value $e_b = -2.2567$ eV, obtained for $r_s = 3.96$ a.u., independently of temperature. (A temperature dependence of r_s and thus of the jellium density could in principle be introduced in the model in order to simulate the thermal expansion of the bulk. This would, however, not change the present results significantly.)

The results for $\delta F(N)$ are plotted in Fig. 2 versus $N^{1/3}$ at the three temperatures $T = 0$, 400, and 600 K. As in

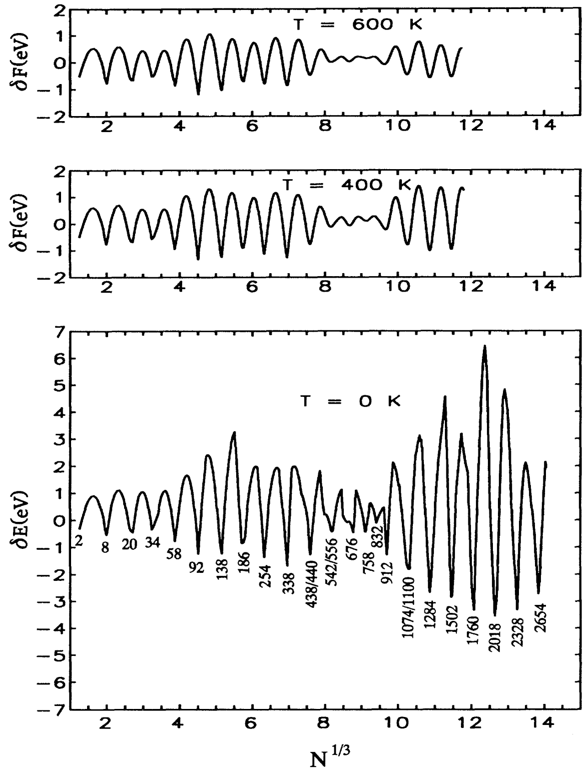

FIG. 2. The shell-correction free energy $\delta F(N)$ (see text for the definition) plotted vs $N^{1/3}$ for three different temperatures. Values of the LDM parameters used at $T=0$ K, $a_s=0.6259$ and $a_c=0.2041$; at $T=400$ K, $a_s=0.5918$ and $a_c=0.3796$; and at $T=600$ K, $a_s=0.5755$ and $a_c=0.4204$ (all in eV). The numbers near the minima of the lowest curve are the magic numbers corresponding to filled major spherical electronic shells.

Fig. 1, constant spacing between the radii $R=r_sN^{1/3}$ of successive magic clusters is observable. The values of the magic numbers are given for the curve for $T=0$ K at the corresponding minima. Sometimes it is not quite clear which of the two adjacent filled shells is more magic; we have then given both numbers in the figure. As in Fig. 1, the amplitude of the beating pattern is reduced with increasing temperature. Two minor shells in the transition region at $N=506$ and $N=638$, still visible at $T=0$ K, are wiped out at $T>0$. All other minima become less sharp than at $T=0$. At 600 K nearly all shell structure in the transition region between the two supershells is smeared out.

It should be mentioned that as a result of the sphericity of all clusters imposed in our calculation, we overestimate the amplitude of the shell effects $\delta F(N)$ [and of the quantity $-\Delta_2F(N)$ discussed above]. In the regions around the maxima we know that the clusters would be deformed, and inclusion of deformation would reduce the amplitude of the shell effects. However, the principle structure of our results and, in particular, the regions around the minima near the spherical magic clusters would not be affected.

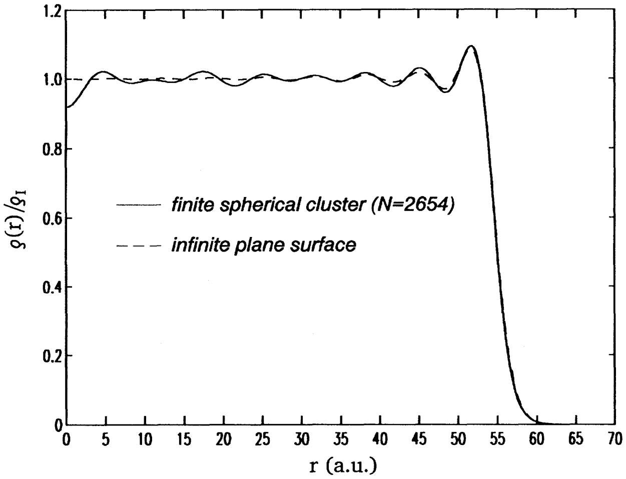

FIG. 3. The density of the valence electrons of a spherical sodium cluster with $N=2654$ atoms (solid line), compared to the density profile of an infinite plane sodium surface (dashed line) taken from Ref. [14]. (Both densities in units of the bulk jellium density.)

In the present calculation the first supershell minimum occurs around $N\sim830$, in contrast to Ref. [3] where the authors found $N\sim1000$ in the transition region. If one compares the Woods-Saxon potential V_{WS} of Ref. [3] with the self-consistent total potential (V_{KS}) of our present Kohn-Sham results for large clusters, one finds at least two main reasons responsible for this difference. The phenomenological potential V_{WS} has a constant surface thickness of 1.41 a.u. for all cluster sizes. This is different for the self-consistent V_{KS}, where we find this value to be approximately correct for $N\leq500$; with increasing particle number we find an increasing slope of the potential around the Fermi energy. Another difference between the two potentials is the missing "Friedel dip" in V_{WS} near the surface, which is contained in V_{KS} as in all self-consistent microscopic calculations dealing with a sufficiently steep surface and which comes from the well-known Friedel oscillations in the density [14]. These two main differences lead to deeper bound single-particle levels, especially for states with high angular momenta. (For example, V_{WS} leads to the magic number $N=40$, whereas with V_{KS} one finds $N=34$ to be a stronger magic shell. The reason is the deeper bound $1f$ state compared to the $2p$ state in V_{KS}.) Thus, by our self-consistent treatment we obtain slightly different shell closures and, as a consequence, a different wavelength for the beating pattern in the supershells than that found with the phenomenological potential of Ref. [3].

To illustrate the Friedel oscillations just discussed, we show in Fig. 3 the density of the valence electrons of the largest magic cluster presented here ($N=2654$) (in units of the jellium bulk density) as a function of the radial variable. We superpose the density profile of an infinite plane metal surface (shown by the dashed line), adjusted such that the surfaces of the two densities coincide. The latter result is taken from the Kohn-Sham calculations by Lang and Kohn [14], with $r_s = 4.0$ a.u. (For this comparison, we used also $r_s = 4.0$ a.u. and the same exchange-correlation energy functional as in Ref. [14].) From this figure, we can clearly distinguish two kinds of quantum oscillations in the spherical cluster. Close to the surface, the oscillations agree almost exactly with the Friedel oscillations of the plane surface density profile shifted to the same position. They are a well-known coherence effect of *all* wave functions near the steep surface and decay inside the bulk region with increasing distance from the surface. The finite cluster, however, also has density oscillations near its center, coming from the *uppermost* filled spherical shells. The phase of these oscillations depends on the angular momentum of the last filled shell and therefore on the particle number, whereas the Friedel oscillations near the surface will remain the same upon adding particles, in the limit $N \longrightarrow \infty$ approaching exactly the dashed line.

We are very grateful to S. Bjørnholm for his continuing support and interest. We also want to thank K. Hansen and H. Nishioka for many stimulating discussions. The hospitality of the Niels Bohr Institute during several visits is warmly acknowledged.

[1] W. D. Knight, W. A. de Heer, and K. Clemenger, Solid State Commun. **53**, 445 (1985); W. A. de Heer, W. D. Knight, M. Y. Chou, and M. L. Cohen, in *Solid State Physics,* edited by H. Ehrenreich and D. Turnbull (Academic, New York, 1987), Vol. 40, p. 93.

[2] W. Ekardt, Phys. Rev. B **29**, 1558 (1984).

[3] H. Nishioka, K. Hansen, and B. R. Mottelson, Phys. Rev. B **42**, 9377 (1990).

[4] R. Balian and C. Bloch, Ann. Phys. (N.Y.) **69**, 76 (1971).

[5] V. M. Strutinsky, A. G. Magner, S. R. Ofengenden, and T. Døssing, Z. Phys. A **283**, 269 (1977).

[6] M. Brack, Phys. Rev. B **39**, 3533 (1989).

[7] S. Bjørnholm, J. Borggreen, O. Echt, K. Hansen, J. Pedersen, and H. D. Rasmussen, Z. Phys. D **19**, 47 (1991).

[8] M. Brack, O. Genzken, and K. Hansen, Z. Phys. D **19**, 51 (1991).

[9] M. Brack, O. Genzken, and K. Hansen, Z. Phys. D **21**, 65 (1991).

[10] J. Pedersen, S. Bjørnholm, J. Borggreen, K. Hansen, T. P. Martin, and H. D. Rasmussen, Nature (London) (to be published).

[11] T. P. Martin, S. Bjørnholm, J. Borggreen, C. Bréchignac, P. Cahuzac, K. Hansen, and J. Pedersen, Chem. Phys. Lett. (to be published).

[12] U. Gupta and A. K. Rajagopal, Phys. Rep. **87**, 259 (1982).

[13] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[14] N. D. Lang and W. Kohn, Phys. Rev. B **1**, 4555 (1970).