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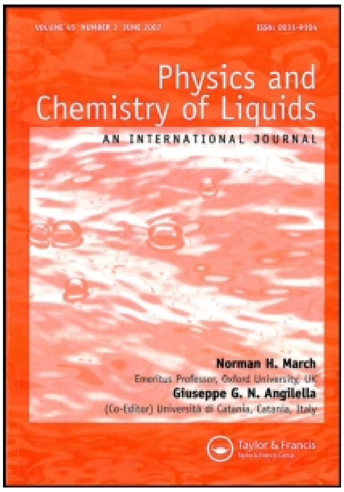

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SCREENING OF AN ION IN A FINITE ELECTRON GAS AND ITS RELATION TO CLUSTER STRUCTURE

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The interpretation of experiments for very large Na clusters (sizes of a few thousand atoms) suggest that these have icosahedral structures, and that the transition to the bcc structure of the bulk has not yet taken place. We argue here that the reason for this is the fact that the screening cloud around a Na^+ ion in a finite cluster depends on the cluster size, and even for clusters with about ten thousand atoms it has not yet converged to its bulk form. The same can be said for the effective interionic potential and cluster structure. PACS: 36.40 + d 61.50.Lt 61.50.Cj.

KEY WORDS: Na clusters, screening, effective potential.

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1 INTRODUCTION

Clusters of alkali metals have been the subject of intense investigation[1–5]. The atomic structure and electronic properties of small clusters of these elements are dominated by electronic shell effects: the electrons move in a smooth effective potential (which can be simulated using the jellium model[1,4]) and are delocalized over the whole volume of the cluster. Electronic shell effects are apparent up to sizes of a few thousand atoms[4,6,7]. The closing of the cluster electronic shells leads to very stable (magic) clusters with high relative abundance in the mass spectra and to sharp variations in the ionization potential and other electronic properties. On the other hand, Martin and coworkers[8–10] have recently found for large Sodium, Calcium and Magnesium clusters that beyond a critical size N_c a new modulation emerges in the mass spectra which can be interpreted as revealing onion-like atomic structure and growth. For Sodium, N_c is in the range 1500–2000 atoms. The new magic numbers correspond to the successive filling of "atomic shells" in structures that could *a priori* be icosahedral or face-centered-cubic (fcc) -cuboctahedral. In the case of Magnesium and Calcium, the experimental analysis of sub-shell filling has shown that the clusters are icosahedral[9,10]. Although an analogous analysis has not been yet possible for Sodium, theoretical calculations suggest also an icosahedral growth[11,12]. The atomic-shell modulation is observed in Sodium clusters up to very large sizes (more than twenty thousand atoms).

The crystal structure of the alkali elements in the bulk metallic phase is body-centered-cubic (bcc), and that of the alkaline-earths is close-packed (hexagonal-close-packed for Mg and fcc for Ca)[13]. This indicates that even for very large clusters the atomic structure is still different from that of the bulk solid metal. The question of the transition to the bulk crystallographic structure is therefore open for this class of materials. This is, on the other hand, a fundamental question in condensed matter physics.

In this paper we attempt to shed some light on this problem. The experience accumulated on the treatment of bulk metals indicates that arguments based on the effective interionic potentials derived within the context of second order perturbation theory are able to explain the crystal structure of non-transition metals in the bulk phase[14,15]. For a typical interionic potential the main principle governing the atomic structure of the solid is well understood: a close-packing structure is favoured if the nearest neighbors fall on the minimum of the potential. On the other hand, if the nearest neighbors in a close-packed structure fall on a peak of the potential, then the crystal can lower its energy by moving some neighbors closer and others further away, leading to a more open structure. This argument rests on the fact that the interionic potential is a well defined concept in the bulk. We can say that the form of the potential determines the crystal structure.

A convenient way to calculate the effective interionic potential in a metal can be established by combining the Neutral Pseudo Atom (NPA) method[16–21] and second order perturbation theory[15]. This is explained in Section II. The interionic potentials so obtained show oscillations around zero after the first minimum. These oscillations are a consequence of the Friedel oscillations of the electronic charge screening the ion. Our intention in this paper is to study the evolution of the screening charge around a Na^+ ion placed in a finite electron gas, or more precisely at the center of a Na cluster modelled by the spherical jellium approximation, as a function of the cluster radius. We will show that this screening cloud depends on the cluster size, and that for the largest clusters studied (around ten thousand atoms) the screening cloud is still far from converging to the result for the infinite (bulk) system. This is evidently due to the presence of the cluster surface. The conclusion is that even for those large clusters we are still far from obtaining a converged interionic potential having the property of being independent of the cluster size. Such a converged potential would be required to have a lattice structure characterized by "long range" periodicity, like that characteristic of the bulk metal. We propose this qualitative argument as the reason why the bcc structure of the Na metal has not yet been observed [illegible] cluster studies.

2 NEUTRAL PSEUDOATOM METHOD AND EFFECTIVE INTERIONIC POTENTIALS IN A METAL

In a zeroth-order approximation, a metal can be described as a homogeneous electron gas of mean density n_0 neutralized by a uniform positive background (this is the jellium model). However this model is too simple to describe the electronic

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structure of a real liquid or solid metal, because the true positive charge is concentrated on the ions, and these attract the valence electrons, which pile up around them screening the ions. A pseudoatom in a metal is then formed by the nucleus, the core electrons and the screening cloud. With these considerations in mind, we can decompose the total electron density in the metal $n_e(\vec{r})$ as a sum of individual electron densities localized around the ions

$$n_e(\vec{r}) = \sum_i n(|\vec{r} - \vec{R}_i|) = \sum_i [n_c(|\vec{r} - \vec{R}_i|) + n_v(|\vec{r} - \vec{R}_i|)] \tag{1}$$

where $\vec{R}_i$ denote the ionic positions, $n_c(r)$ is the core electron density and $n_v(r)$ the valence electron density or screening cloud. The first step in the Neutral Pseudoatom (NPA) method is to calculate the screening cloud $n_v(r)$ around an ion. This computation is briefly explained in Section III below. The final goal of the method is the construction of a pseudopotential that, in linear response, reproduces the NPA displaced valence electron density. However, the very definition of pseudopotential makes impossible the appearance of orthogonality oscillations in the valence density, since no bound states can exist. Therefore, before constructing the pseudopotential, the NPA valence electron density is pseudized, eliminating the orthogonality oscillations in a region of radius R_M[20,21]. From the pseudized density $n_{\mathrm{ps}}(r)$ so obtained, application of linear response theory leads to an effective local pseudopotential, $\tilde{v}_{\mathrm{ps}}(q)$, given by

$$\tilde{n}_{\mathrm{ps}}(q) = \chi(q)\,\tilde{v}_{\mathrm{ps}}(q) \tag{2}$$

where the tilde denotes Fourier Transform, and $\chi(q)$ is the density response function. Finally, application of standard second order perturbation theory leads to an effective interionic pair potential between two pseudoatoms in the metal as[15]

$$\varphi(r) = \frac{Z_v^2}{r} + \varphi_{\mathrm{ind}}(r) \tag{3}$$

where Z_v is the valence and the Fourier Transform of the indirect part of the interionic potential is given by

$$\tilde{\varphi}_{\mathrm{ind}}(q) = \chi(q)|\tilde{v}_{\mathrm{ps}}(q)|^2. \tag{4}$$

In summary, from Eqs. (2)–(4) we can conclude that the screening cloud around an ion, $n_v(r)$, determines the interionic pair potential in the metal. As stated in the introduction, the work of Hafner and Heine[14] showed that the trends in the structural stability of non-transition metals, that is, the change from close-packed structures at the left of the periodic table, to open structures with low coordination number on the right, can be explained from the detailed form of the interionic pair potentials, and therefore of the screening cloud.

3 SCREENING OF AN ION IN A FINITE CLUSTER AND IN AN INFINITE JELLIUM

A metallic cluster with N atoms is modelled by a spherical jellium background of constant positive charge density $n_+(r)$ numerically equal to n_0 and radius $R=(3Z_vN/4\pi n_0)^{1/3}$, in which the valence electrons (Z_v per atom) are immersed. An atom is then placed at the center of the sphere, which provides an extra contribution to the valence electron cloud, and we calculate the selfconsistent electronic distributions $n^j(r)$ and $n^{ja}(r)$ corresponding, respectively, to the sphere and sphere plus atom systems. Then we form the screening cloud by taking the difference

$$n_v(r)=n_v^{ja}(r)-n^j(r) \tag{5}$$

where $n_v^{ja}(r)$ results from removing the electronic core contribution from $n^{ja}(r)$.

The method used to calculate the densities is the Kohn-Sham version of the Density Functional formalism[22]. Within this scheme the electron density $n(\vec{r})$ for a generic system is written as (Hartree atomic units are used)

$$n(\vec{r})=\sum_i^{\text{occ}}|\psi_i(\vec{r})|^2 \tag{6}$$

where the ψ_i represent the solutions of the one-electron Kohn-Sham equations

$$\left[-\frac{\nabla^2}{2}+V_{\text{eff}}(\vec{r})\right]\psi_i(\vec{r})=\varepsilon_i\psi_i(\vec{r}) \tag{7}$$

and the summation in (6) runs over occupied states. The effective potential V_{eff} is composed of a coulombic part V_C and the exchange-correlation contribution. We have the following expressions for V_C in the cases of the sphere and sphere plus atom systems respectively,

$$V_C^j(r)=\int\frac{n(r)-n_+(r)}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,' \tag{8}$$

and

$$V_C^{ja}(r)=\int\frac{n(r)-n_+(r)}{|\vec{r}-\vec{r}\,'|}d\vec{r}\,'-\frac{Z}{r} \tag{9}$$

with Z being the atomic number of the atom placed at the cluster centre. The local density approximation[22] is assumed for the exchange-correlation effects.

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The electron level ordering is determined by minimizing the total energy of the system. Some differences exist between the electronic configurations of the sphere and sphere plus atom systems, which are mainly due to the stabilization of the low angular momentum states when the Z/r term is present.

Since our intention is to study if the screening cloud $n_v(r)$ around an ion in a large cluster converges towards its limit for a cluster of macroscopic size, let us now turn to the infinite system. When the "central" atom is not present the electron density is just a constant n_0 equal to the mean electron density. Therefore, the screening cloud is now

$$n_{v\infty}(r) = n^{ja}_{v\infty}(r) - n_0 \tag{10}$$

where, as before, the inner core electrons have been removed from the total electron density of the jellium plus atom case, $n^{ja}_{\infty}(r)$, in order to form the valence contribution $n^{ja}_{v\infty}(r)$.

Equations (6–9) are again used for the calculation of $n^{ja}_{\infty}(r)$ with the only difference that the summation includes both bound states and scattering states, whose eigenvalues form a continuum, and their contribution is included up to the Fermi level,

$$n^{ja}_{\infty}(r) = \sum_{nl} 2(2l+1)|R_{nl}(r)|^2 + \frac{1}{8\pi^3}\int_0^{k_F} 4\pi k^2 dk \sum_l 2(2l+1)|R_{kl}(r)|^2 \tag{11}$$

The Kohn-Sham equations for the scattering states are integrated up to a distance r large enough for the radial functions $R_{kl}(r)$ to attain their asymptotic behavior,

$$R_{kl}(r) \sim \sin\left[kr - l\frac{\pi}{2} + \delta_l(k)\right] \tag{12}$$

in terms of the phase shifts $\delta_l(k)$.

4 RESULTS

The formalism outlined above has been applied to Sodium clusters ($Z = 11$, $Z_v = 1$) of sizes $N = 556$, 1516, 3690 and 9882 atoms, as well as to the infinite system. The radius per electron, r_s, related to n_0 by the equation $r_s = (3/4\pi n_0)^{1/3}$, has been fixed to its bulk value, $r_s = 3.94$ a.u.

The screening clouds corresponding to the immersion of an additional Na atom inside jellium clusters with those different sizes have been plotted in Figures 1 and 2. The radius of the positive background is indicated in each case. It can be observed that the small-r wiggles, which are due to the orthogonality condition between core and valence wavefunctions, converge rapidly. The next, main, oscillation with a maximum at $r = 3.6$ a.u. can be considered as coverged to the bulk value for the system with $N = 3690$. The Friedel oscillations, however, show a non-converging behavior as the system size increases. The oscillations for $N = 3690$ and $N = 9882$

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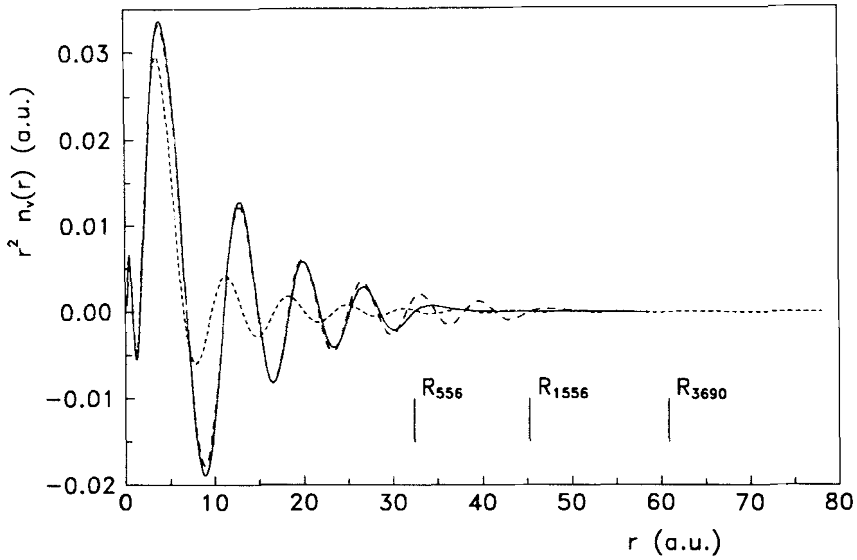

Figure 1 Screening clouds, $n_v(r)$, corresponding to the immersion of one additional Na atom in jellium clusters with $N = 556$ particles (continuous line), 1516 particles (long-dashed line) and 3690 particles (short-dashed line).

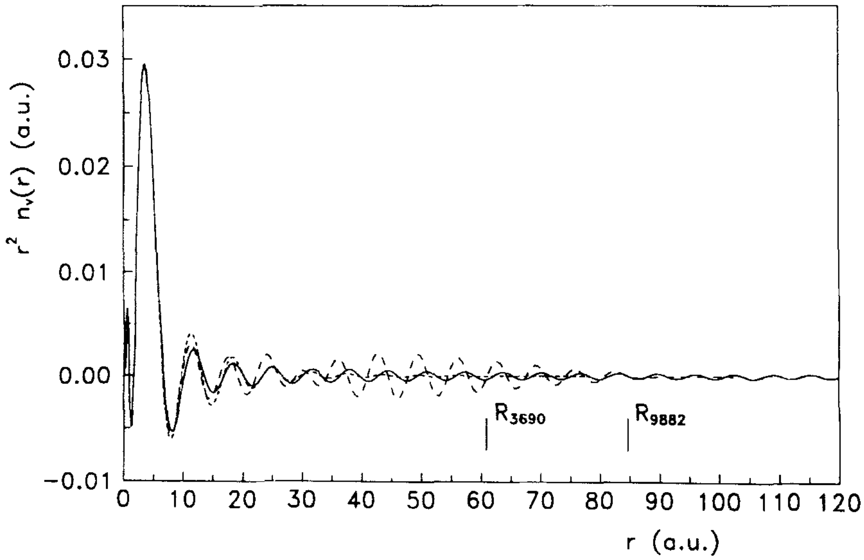

Figure 2 Screening clouds, $n_v(r)$, corresponding to the immersion of one additional Na atom in jellium clusters with $N = 3690$ particles (short-dashed line), 9882 particles (long-dashed line) and the infinite system (continuous line).

are not in phase with those for the infinite system, that is, the position of the maxima (or minima) of the screening clouds do not coincide. An interesting effect is observed for $N = 9882$. In this case, after a region where the amplitude of the Friedel oscillations displays the usual decay with increasing distance r (this region ends at $r \approx 30$ a.u.) there is an increase in the amplitude of the oscillations followed, finally, by the normal asymptotic decay. We interpret this modulated behavior of the amplitude of the Friedel oscillations as being due to the interference between the Friedel oscillations induced by the screening of the Na^+ ion at the cluster centre and the Friedel oscillations induced inside the metal (in our case a finite cluster) by the presence of the surface[15,23].

By observing the decay of the Friedel oscillations around the Na^+ ion in the infinite system, one can realize that those oscillations are still significative at a distance r equal to the radius R of the cluster with $N = 9882$. This, of course, just indicates that this cluster is still "not too large", and that much larger sizes appear to be required to avoid the interference with the surface effects. Based on the relation between screening cloud and interatomic potential we then conclude that even for such a large Na cluster, having $N = 9882$, a converged interionic potential does not exist. We propose this argument to justify the fact that the bcc structure of bulk Na has not yet been experimentally observed even in the largest clusters studied (more than twenty thousand atoms). This conclusion is, of course, restricted to Na and the other alkali elements. Higher electron densities induce a more efficient screening, and the convergence of the screening cloud to that of the bulk can be faster. The fact that large Na clusters appear to be icosahedral is consistent with the above arguments. The icosahedral structure is mainly reflecting the short-range repulsive part of the interionic interaction, which is likely to be not very sensitive to the long-range details of the screening cloud.

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References

1. W. A. DeHeer, W. D. Knight, M. Y. Chou and M. L. Cohen, *Solid State Physics*, ed. H. Ehrenreich, F. Seitz and D. Turnbull, **40**, p. 93 (Academic, New York) (1987).
2. V. Kresin, *Phys. Rep.*, **220**, 1 (1992).
3. V. Bonačić-Koutecký, P. Fantucci and J. Koutecký, *Chem. Rev.*, **91**, 1035 (1991).
4. M. Brack, *Rev. Mod. Phys.*, **65**, 677 (1993).
5. W. A. DeHeer, *Rev. Mod. Phys.*, **65**, 611 (1993).
6. T. P. Martin, S. Bjørnholm, J. Borgreen, C. Bréchignac, Ph. Cahuzac, K. Hansen and J. Pedersen *Chem. Phys. Lett.*, **186**, 53 (1991).
7. H. Nishioka, K. Hansen and B. Mottelson, *Phys. Rev.*, B **42**, 9377 (1990).
8. T. P. Martin, T. Bergman, H. Göhlich and T. Lange, *Chem. Phys., Lett.*, **172**, 209 (1991).
9. T. P. Martin, T. Bergman, H. Göhlich and T. Lange, *Chem. Phys. Lett.*, **176**, 343 (1991).
10. T. P. Martin, U. Naher, T. Bergman, H. Göhlich and T. Lange, *Chem. Phys. Lett.*, **183**, 119 (1991).
11. J. Mansikka-aho, M. Manninen and E. Hammanén, *Z. Phys.*, D **19**, 25 (1991).
12. Q. Wang, M. D. Glossman, M. P. Iñiguez and J. A. Alonso, *Philos. Mag.*, B **67**, 1045 (1994).
13. Ch. Kittel, *Introduction to Solid State Physics*, 5th edition (Wiley, New York) (1976).
14. J. Hafner and V. Heine, *J. Phys.*, F **13**, 2479 (1983).

15. See, for a review, J. A. Alonso and N. H. March, *Electrons in Metals and Alloys* (Academic, London) (1989).
16. J. M. Ziman, *Proc. Phys. Soc.*, **91**, 701 (1967).
17. L. Dagens, *J. Physique*, **36**, 525 (1975).
18. F. Perrot, *Phys. Rev.*, A **42**, 4871 (1990).
19. F. Perrot and N. H. March, *Phys. Rev.*, A **41**, 4521 (1990).
20. L. E. González, A. Meyer, M. P. Iñiguez, D. J. González and M. Silbert, *Phys. Rev.*, E **47**, 4120 (1993).
21. L. E. González, D. J. González, M. Silbert and J. A. Alonso, *J. Phys: Condens. Matter*, **5**, 4283 (1993).
22. R. G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, New York) (1989).
23. N. D. Lang, *Solid State Physics*, ed. H. Ehrenreich, F. Seitz and D. Turnbull, **28**, p. 225 (Academic, New York) (1973).

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