

Liquid structure of the alkaline-earth metals

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(Received 8 September 1992; revised manuscript received 10 March 1993)

We present *ab initio* calculations of the liquid structure of the alkaline-earth metals. Our approach is based on the neutral-pseudoatom method to obtain the interionic pair potential and on the variational-modified-hypernetted-chain integral-equation theory of liquids [Y. Rosenfeld, *J. Stat. Phys.* **42**, 437 (1986)] to obtain the liquid structure. This combination results in a whole theory that is free of adjustable parameters. We find that our pair potentials follow the expected trends for these metals. The predicted static structure factors are in good agreement with the available experimental data [Y. Waseda, *The Structure of Non-Crystalline Materials* (McGraw-Hill, New York, 1980)].

PACS number(s): 61.20.Ne, 61.25.Mv

I. INTRODUCTION

This paper concerns the calculation of the liquid structure of a particular class of simple *s-p* bonded metals, the alkaline-earth metals. These are carried out using a recently developed very accurate integral-equation theory of liquids, the variational-modified-hypernetted-chain equation (VMHNC) [1] and an effective interionic pairwise additive interaction obtained from the neutral-pseudoatom (NPA) method [2, 3]. The ensuing combination results in a body of theory that is free of adjustable parameters.

Trends in the liquid structure have been analyzed through the shapes of the main peaks of the structure factor $S(q)$ [4], model potentials [5], effective interionic potentials [6], and thermodynamics [7]. Hence, with the exception of the liquid alkali metals, the tendency has been to study the liquid structure across a row rather than along a column of the table of the elements.

It has been shown [6] that a good qualitative, and in some cases quantitative, description of $S(q)$ for liquid simple metals is obtained using effective interionic potentials based on the Ashcroft empty-core form [8] by making a judicious choice for the core radius R_c and a thermodynamic perturbation theory of the liquid structure, the optimized random-phase approximation (ORPA). However, as we shall see below (Sec. IV), these potentials do not yield good qualitative results for the liquid structure of the divalent alkaline-earth metals. These shortcomings have been the subject of close scrutiny over the past few years. Recent calculations of the liquid structure of the divalent elements [9], using optimized pseu-

dopotentials originally developed by Harrison [10], result in a good agreement for the pair distribution functions $g(r)$ deduced from experiment and those obtained from molecular dynamics (MD) within the range defined by the simulation box.

In this work we present an alternative, and in our view promising, approach based on effective interionic pair potentials derived from the NPA method, which has been recently extended by Perrot [11] to finite temperatures. The philosophy of the NPA is similar to that of the pseudopotential theory, and so is its domain of applicability. In conjunction with density-functional theory (DFT) it is entirely *ab initio* and has the advantage of handling true, rather than pseudodensities (Sec. III).

The NPA has been recently applied to study the interionic pair potentials of liquid Na, Be, and Al [11–13] and to evaluate the thermodynamic properties of several liquid simple metals [14]. Here we adopt an approach similar to that developed by Perrot, which we discuss briefly in Sec. III.

The VMHNC theory used in the evaluation of the liquid structure belongs to a new generation of accurate integral-equation theories of liquids. Its derivation ensures the thermodynamic consistency between the energy and virial routes to the equation of state, a consistency also enjoyed by the hypernetted-chain approximation (HNC), from which it originates [15]. Moreover, and unlike the HNC, the variational procedure ensures in the VMHNC a reasonably good thermodynamic consistency between the compressibility and virial routes, without enforcing it, which has some advantages in the case of liquid metals for reasons we have discussed in detail else-

where [16, 17]. We have recently verified the accuracy of the VMHNC by comparing the predicted $g(r)$ for the liquid alkali metals with computer simulation results [16]. We discuss the VMHNC in Sec. II.

In Sec. IV we present the results of our calculations. First, we present the effective interionic potentials derived from the NPA to show that as we progress down the column of the alkaline-earth metals we find the expected trends. Then we present the results for the liquid structure, including beryllium for which there is no experimental diffraction data at present. We also include, for comparison, the liquid structure obtained by using the effective interionic potentials derived from Ashcroft's empty-core model. We complete the paper in Sec. V with a brief discussion of our results.

II. LIQUID-STATE THEORY

Most of the integral-equation theories of liquids stem from the Ornstein-Zernike equation, which for a homogeneous, isotropic system reads

$$h(r) = c(r) + \rho \int d\mathbf{r}' h(|\mathbf{r} - \mathbf{r}'|) c(r'), \quad (2.1)$$

which defines the direct correlation function $c(r)$ in terms of the total correlation function $h(r) = g(r) - 1$, where $g(r)$ denotes the pair distribution function and ρ is the number density. This equation is supplemented by the exact closure relation

$$c(r) = h(r) - \ln \left[g(r) e^{\beta\phi(r) + B(r)} \right], \quad (2.2)$$

where $\beta = (k_B T)^{-1}$ is the inverse temperature times the Boltzmann constant, $\phi(r)$ is the pairwise additive potential of interaction, and $B(r)$ is the so-called bridge function, for which some approximation must be made. Following the universality assumption of the bridge functions [18], we have chosen those obtained within the Percus-Yevick (PY) approximation for hard spheres, $B_{PY}(r, \eta)$. These functions only depend on one parameter, the packing fraction, and the procedure to determine it has led to different, though closely interwoven, approaches [18, 19]. We briefly describe below the VMHNC theory used in this work, and we refer the interested reader to Refs. [1, 17].

Let us start by considering the modified-hypernetted-chain (MHNC) expression for the configurational part of the reduced Helmholtz free energy, $f^{\text{MHNC}} \equiv F'_{\text{MHNC}}/Nk_B T$, which is a function of the thermodynamic state, and a functional of the bridge function [1, 17]. If we choose the above $B_{PY}(r, \eta)$, then the MHNC free energy becomes a function of β , ρ , and η . In order to choose η as a function of the thermodynamic state, that is, $\eta = \eta(\beta, \rho)$, the VMHNC criterion takes the form

$$\frac{\partial f^{\text{VMHNC}}(\beta, \rho, \eta)}{\partial \eta} = 0, \quad (2.3)$$

where

$$f^{\text{VMHNC}}(\beta, \rho, \eta) = f^{\text{MHNC}}(\beta, \rho, \eta) - f_{\text{PY}}^{\text{MHNC}}(\eta) + f_{\text{CS}}(\eta), \quad (2.4)$$

where $f_{\text{PY}}^{\text{MHNC}}(\eta)$ is the value of the MHNC reduced Helmholtz free energy when the PY hard-sphere (HS) distribution and bridge functions with packing fraction η are used, and $f_{\text{CS}}(\eta)$ is the empirical HS Carnahan-Starling Helmholtz free energy.

III. EFFECTIVE INTERIONIC POTENTIALS: THE NPA

The calculations leading to the effective interionic pair potentials incorporate two distinct steps. In the first one, we compute the electronic valence density displaced by an ion embedded in a homogeneous electron gas using the NPA; in the second step we construct an effective local pseudopotential which, used in conjunction with linear-response theory (LRT), reproduces the same displaced density as in the first step. Finally this pseudopotential is used to construct the pair interaction. In this section we briefly discuss both steps. We shall use atomic units throughout the rest of the paper.

Within the NPA method it is assumed that the total electron density $\rho(\mathbf{r})$ of the metal can be decomposed as a sum of localized electronic densities, $n(r)$, that follow the ions in their movement,

$$\begin{aligned} \rho(\mathbf{r}) &= \sum_i n(|\mathbf{r} - \mathbf{R}_i|) \\ &= \sum_i n_c(|\mathbf{r} - \mathbf{R}_i|) + \sum_i n_v(|\mathbf{r} - \mathbf{R}_i|), \end{aligned} \quad (3.1)$$

where \mathbf{R}_i denote the ionic positions, $n_c(r)$ is the core electronic density, and $n_v(r)$ the valence-electron density. It must be stressed that Eq. (3.1), which is based on the superposition approximation, is an approximate relation, particularly with regard to $n_v(r)$. Nevertheless this approximation is consistent with the binary character of the interatomic forces and, therefore, compatible with the usual analysis of the simple metals in terms of pair interactions.

In order to improve the validity of the superposition approximation (3.1), we consider the difference between the real external potential acting on the valence electrons (arising from their interaction with the ions) and the external potential arising from a homogeneous background of positive charge density ρ_0 (jellium)

$$\mathcal{V}_0(\mathbf{r}) = \sum_i V_{\text{ion}}(|\mathbf{r} - \mathbf{R}_i|) - \left\{ -\frac{1}{r} \circ \rho_0 \right\}. \quad (3.2)$$

In Eq. (3.2) the symbol \circ denotes the convolution integral, and V_{ion} stands for the bare ionic potential. Now, we rewrite Eq. (3.2) as

$$\mathcal{V}_0(\mathbf{r}) = \sum_i V'_{\text{ion}}(|\mathbf{r} - \mathbf{R}_i|) + \mathcal{V}''(\mathbf{r}), \quad (3.3)$$

where

$$V'_{\text{ion}}(r) = V_{\text{ion}}(r) - \left[-\frac{1}{r} \circ \nu(r) \right], \quad (3.4)$$

$$\mathcal{V}''(\mathbf{r}) = \frac{1}{r} \circ \left[\rho_0 - \sum_i \nu(|\mathbf{r} - \mathbf{R}_i|) \right] \equiv \frac{1}{r} \circ \rho_r(\mathbf{r}), \quad (3.5)$$

and $\nu(r)$ is a cavity screening function that integrates to the ionic valence Z_v , and is introduced so as to render both V'_{ion} and \mathcal{V}'' as weak as possible. In fact, the choice of $\nu(r)$ is mainly determined by requiring that the residual density $\rho_r(\mathbf{r})$ be small everywhere, in order to render \mathcal{V}'' weak throughout the metal.

Now the difference between the true valence density and the corresponding jellium density may be approximately, but fairly accurately, given by

$$\rho_v(\mathbf{r}) - \rho_0 = \sum_i n'_v(|\mathbf{r} - \mathbf{R}_i|) + \rho''_v(\mathbf{r}). \quad (3.6)$$

Given that \mathcal{V}'' is small everywhere, $\rho''_v(\mathbf{r})$ is computed via LRT yielding

$$\rho''_v(\mathbf{r}) = -\rho_0 + \sum_i n''_v(|\mathbf{r} - \mathbf{R}_i|). \quad (3.7)$$

Here $n''_v(r)$ is the electron density that screens, in linear response, the charge distribution given by $\nu(r)$, that is,

$$\tilde{n}''_v(q) = -\frac{4\pi}{q^2} \chi(q) \tilde{\nu}(q), \quad (3.8)$$

where $\chi(q)$ is the density response function and $\tilde{\nu}(q)$ is the Fourier transform of $\nu(r)$. Substitution of (3.7) in (3.6) gives the desired superposition approximation for $\rho_v(\mathbf{r})$

$$\rho_v(\mathbf{r}) = \sum_i n_v(|\mathbf{r} - \mathbf{R}_i|) \quad (3.9)$$

with $n_v(r) = n'_v(r) + n''_v(r)$. For the computation of $n'_v(r)$ the LRT is not adequate, as V'_{ion} is not weak inside the core; moreover, the contribution of the core electrons to V'_{ion} is influenced by the presence of the valence electrons. Consequently V'_{ion} and $n'_v(r)$ must be evaluated self-consistently. This is carried out in the manner described below.

We use DFT so that $n'_v(r)$ —together with V'_{ion} and $n_c(r)$ —is found by computing the electron density for a system of $(Z_{\text{at}} - Z_v)$ core electrons, plus a continuum of valence electrons, placed in an external field given by the nucleus at the origin, a cavity, and a positive background to neutralize the valence electrons. We specifically use the Kohn-Sham formalism [20] and the local-density approximation (LDA) for the exchange and correlation effects. This completes the calculation of $\rho_v(\mathbf{r})$.

We now turn to the calculation of a local pseudopotential $\tilde{v}_{\text{ps}}(q)$ that within LRT reproduces the nonlinear screening charge determined by the NPA method. This is achieved by first pseudizing $n_v(r)$ in the way described

in Ref. [21], so as to eliminate the core orthogonality oscillations leading to a displaced valence-electron pseudodensity $n_{\text{ps}}(r)$, from which the local pseudopotential is obtained by

$$\tilde{n}_{\text{ps}}(q) = \chi(q) \tilde{v}_{\text{ps}}(q). \quad (3.10)$$

Now a discussion of some of the assumptions made to obtain the pseudopotential is in order. The present approach is based on the physical picture of a simple liquid metal where the ions are diffusively free and the electronic response to them is treated as a superposition of single responses to one ion. The Kohn-Sham equations are solved for a bare nucleus, surrounded by a spherical cavity of charge Z_v , embedded in a jellium with a given mean density ρ_0 . The self-consistent ion together with the screening charge corresponding to the cavity produce a weak scattering potential (note that its Friedel sum is zero at the Fermi level). Thus the superposition approximation of single-site densities should be a very good approximation for the metal. Furthermore, the spherical symmetry reduces the calculation to a one-dimensional integration of the radial Kohn-Sham equations, thus rendering into a simple problem the calculation of the different physical properties of the system.

Next, we consider the choice of the screening function $\nu(r)$ in the calculation of $\mathcal{V}''(\mathbf{r})$. In a solid, where the structure is known, it is possible to evaluate explicitly the residual density for different shapes of $\nu(r)$ and to choose the one that minimizes $\rho_r(\mathbf{r})$. Actually, Dagens [3] has shown, using this approach, that for the most common crystal structures a trapezoidal form for $\nu(r)$ is the most suitable one. In a liquid, however, the structure is not known *a priori*; actually it is one of the properties that a theory of liquids is expected to predict. In the liquid state, what really matters is the ensemble average of the residual density, $\rho_r(\mathbf{r})$, and it turns out that this average value is zero, irrespective of the particular shape adopted for $\nu(r)$, provided it integrates to Z_v . Hence we have chosen for $\nu(r)$ the simplest approximation, that is, a spherical shape. In the calculation of $\mathcal{V}''(\mathbf{r})$ via the LRT, it is important to notice that it is possible to compute the density displaced by a set of many vacancies—one for each ion—in terms of the density displaced by just one vacancy. This is not possible in an all order theory, like DFT, where the many vacancies problem is in fact intractable. Of course, we could treat one vacancy within the DFT to obtain $n''_v(r)$ [21], but then the superposition approximation can no longer be justified.

The displaced valence density has been evaluated within the LDA. This is the simplest approximation we could use and the sole reason why we have done so. It is possible to improve upon it, and we are currently exploring several avenues in this direction, although it is unclear as to whether these refinements will yield much improved potentials.

The choice of a local effective pseudopotential, as defined by Eq. (3.10), is an ansatz made to avoid the introduction of adjustable parameters while, at the same time, preserving the full information contained in the calculated NPA displaced valence electronic density, $n_v(r)$. In

this way a pseudopotential in the linear-response regime is built up so as to generate a nonlinear screening charge determined by the NPA method. The assumption of a particular pseudopotential model would imply to use only that part of the NPA $n_v(r)$ consistent with that particular model. Finally, note that a local effective pseudopotential is uniquely given by Eq. (3.10); this would no longer be the case for a nonlocal pseudopotential.

IV. RESULTS

A. Calculation of the effective interionic potentials

As already indicated in the preceding section, the evaluation of the interionic potentials requires, as a first step, the calculation of the displaced valence density, $n_v(r)$, which has been decomposed into two parts, $n'_v(r)$ and $n''_v(r)$.

For $n'_v(r)$ we have solved the Kohn-Sham equations [20], in which the exchange and correlation potential has been evaluated within the LDA, using the very accurate expression proposed by Vosko, Wilk, and Nussair [22] which closely matches the computer-simulation results of Ceperly and Alder [23] for the electron correlation energy. In the solution of the Kohn-Sham equations we have used a Herman-Skillman [24] mesh consisting of 11 blocks with 40 intervals for each block. Technical details of the choice of the stepsize and iteration procedure are discussed in detail elsewhere [25].

For the calculation of $n''_v(r)$ we have used a density response function $\chi(q)$ which takes into account the electronic exchange and correlation effects via a local-field factor. In order to be consistent with the level of approximation used in the evaluation of $n'_v(r)$ we have adopted the LDA version of the local-field factor using the correlation energy of Vosko, Wilk, and Nussair [22].

Once $\tilde{v}_{ps}(q)$ has been obtained, the effective interionic pair potential $\phi(r)$ follows from

$$\phi(r) = \frac{Z_v^2}{r} + \phi_{ps}(r), \quad (4.1)$$

where the Fourier transform of $\phi_{ps}(r)$ is given by

$$\tilde{\phi}_{ps}(q) = \chi(q) |\tilde{v}_{ps}(q)|^2. \quad (4.2)$$

The present method has been applied to the liquid alkaline-earth metals at conditions near the triple point and in Table I we show the corresponding thermodynamic states for which the present study has been carried out.

The inset in Fig. 1(b) shows an example of the kind of results obtained, within the NPA, for the displaced valence electronic density $n_v(r)$ and its two components, $n'_v(r)$ and $n''_v(r)$. Note that, within the present method, $n'_v(r)$ screens a total zero charge, whereas $n''_v(r)$ screens a total Z_v charge. This explains the strong difference between both displaced densities, particularly around the core region. Both $n'_v(r)$ and $n''_v(r)$ show an oscillatory behavior although the physical mechanisms below the occurrence of the oscillations are different. The oscilla-

TABLE I. Thermodynamic states (ρ , T) for which the present calculations have been carried out. R_c and D_{CP} denote the Ashcroft empty-core radius and the nearest-neighbor distance for close packing.

System	ρ (\AA^{-3})	T (K)	R_c (a.u.)	D_{CP} (a.u.)
Be	0.11293	1521	0.76	4.38
Mg	0.03829	953	1.30	6.29
Ca	0.02058	1123	1.84	7.74
Sr	0.01636	1053	2.08	8.35
Ba	0.01456	1003	2.10	8.69

tions of $n_v(r)$ around the core region are mainly due to $n'_v(r)$ and they are related to the orthogonality condition between the valence electronic wave functions and the core electronic ones. At large values of r the oscillations in $n_v(r)$ are the Friedel oscillations, and their behavior is mainly determined by $n'_v(r)$. The oscillations in $n'_v(r)$ are related to the phase shifts of the valence electronic wave functions whereas in $n''_v(r)$ they are due to the structure of the density response function $\chi(q)$. In conclusion, our results show that the main features of the total displaced valence electronic density $n_v(r)$ are mainly driven by $n'_v(r)$.

The displaced valence electronic pseudodensities $n_{ps}(r)$, obtained for Be, Mg, Ca, Sr, and Ba, are plotted in Fig. 1 and show the typical oscillatory behavior. The principal oscillation is located just outside the core region, and is followed by oscillations of decreasing amplitude. The increasing atomic volume, going down the IIa column, is not corresponded by a similar increase in the size of the ionic core. This is reflected in a wider and lower height for the main peak, as well as a shift of the position of its maximum towards values which are larger than the atomic radius.

The calculated interionic pair potentials for the alkaline-earth metals are shown in Fig. 2. The variations found within this group follow rather well the trends suggested by Hafner and Heine [26], including the small change in the depth of the minimum seen between Ca and Sr. Starting from Be it is observed that as we go down the IIa column the repulsive part of the potential increases and becomes harder, the depth and width increases, and the position of the principal minimum is displaced to larger values of r . As for the long-range behavior, it is observed that the Friedel oscillations are rather marked in Be, slightly damped for Mg, and very similar for Ca, Sr, and Ba, although they increase in magnitude as the atomic number increases.

Those trends suggested by Hafner and Heine [26] for the interionic pair potentials of the nontransition metals were derived within the framework of second-order perturbation theory and using the empty-core model potential for the electron-ion interaction. Although our NPA-derived interionic pair potentials do follow those trends, it does not imply that the use of second-order perturbation theory along with a local model pseudopotential would be enough theoretical tool in order to explain the observed structural properties of the liquid alkaline-earth elements.

In Fig. 1 we also show the corresponding linear-response displaced valence electronic densities obtained by using Ashcroft's empty-core model potential, $\tilde{v}_{ps}(q) = -4\pi Z_v \cos(qR_c)/q^2$, with the R_c values given in Table I that have been chosen so as to match the first peak position of the experimental static structure factor. Comparison with the previous NPA results shows that both ap-

proaches lead to rather different results for the displaced valence electronic densities (the only exception is Mg). The charge densities calculated via Ashcroft's empty-core model always give values which are smaller in the core region (actually they are smaller than those obtained from the jellium model) and bigger around the core. The magnitude of the Friedel oscillations is very similar in both

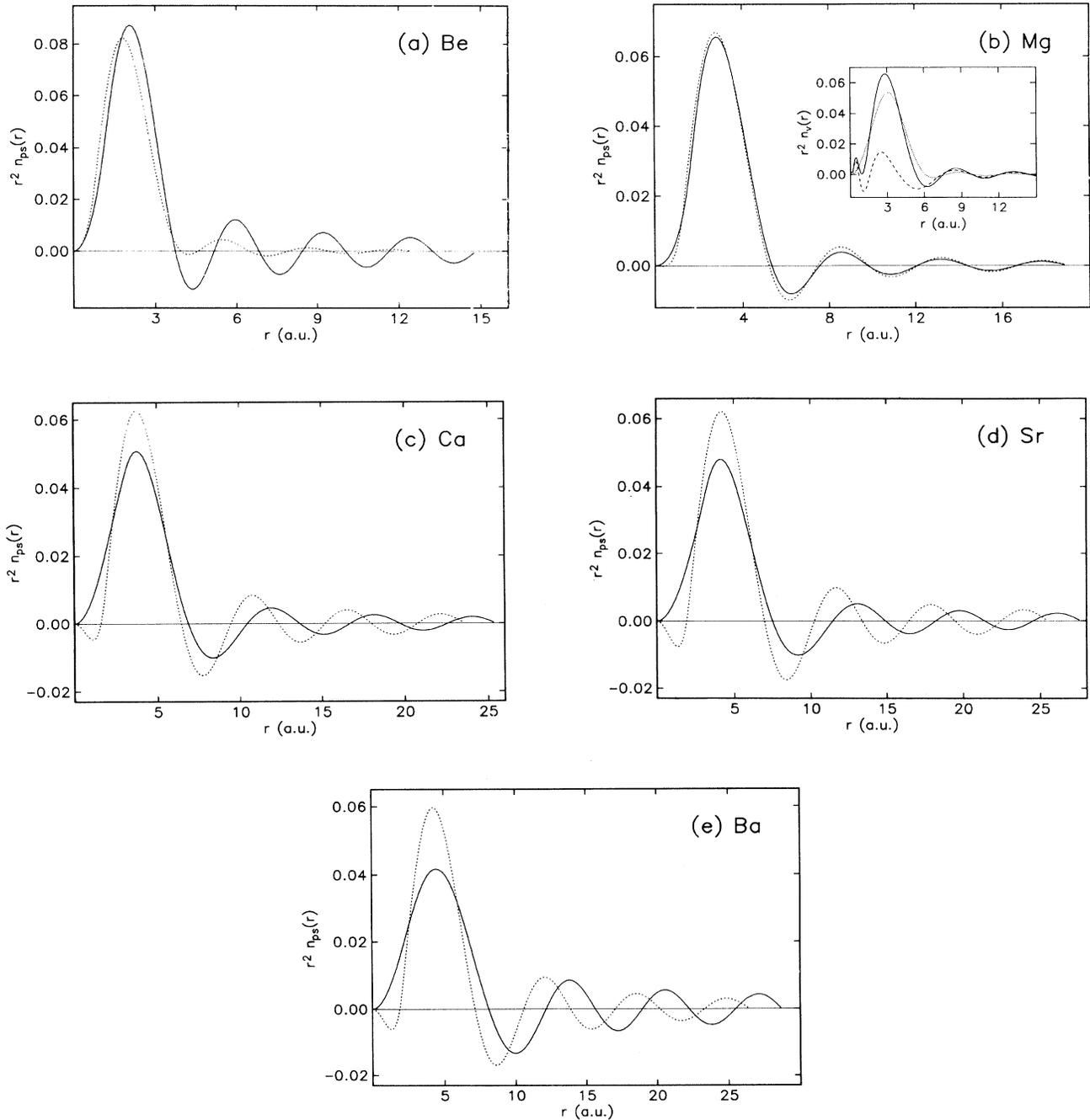


FIG. 1. Displaced valence electronic pseudodensities (a.u.) for the alkaline-earth metals. The continuous line shows the NPA results, and the dotted lines are the results obtained using Ashcroft's empty-core model. The inset in (b) shows the Mg total displaced valence electronic density, $r^2 n_v(r)$ (full line), and its two components, $r^2 n'_v(r)$ (dashed line) and $r^2 n''_v(r)$ (dotted line).

approaches, although they are out of phase. The only exception is Be, where the empty-core pseudopotential leads to strongly damped Friedel oscillations, but it is well known that Be has a very nonlocal pseudopotential with a strongly attractive p component, so it is not likely that the empty-core model be appropriate for this element.

In Fig. 2 we have also plotted, for comparison, the in-

terionic pair potentials derived from the empty-core model. These are very different from those obtained from the NPA, particularly so for Be. The principal minimum in the former is narrower and shallower, and the Friedel oscillations are stronger. Nevertheless, the trends within each set of pair potentials are rather similar.

A characteristic feature of the alkaline-earth-metal elements is the strong increase of the atomic volume (and a

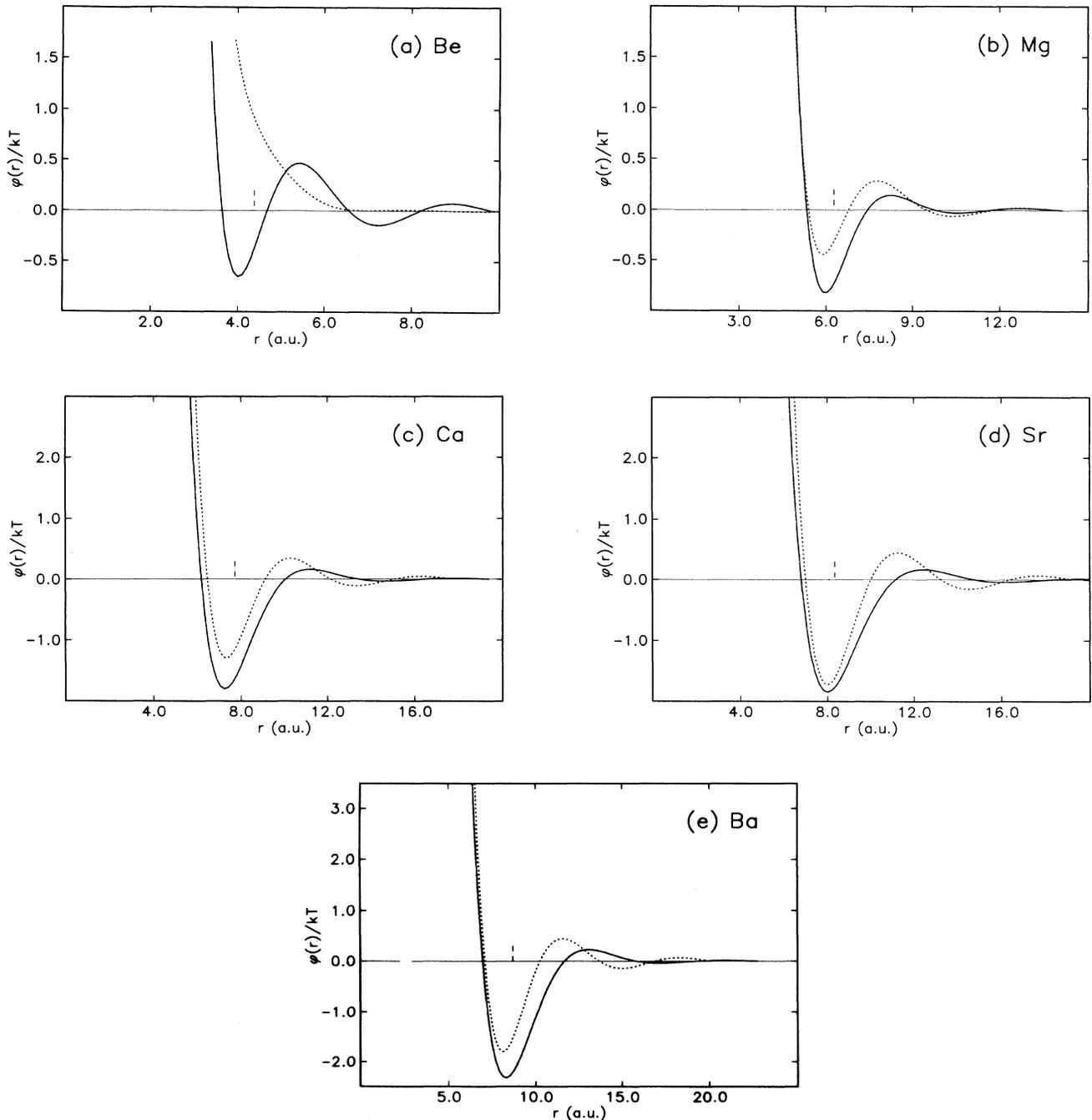


FIG. 2. Interionic pair potentials for the alkaline-earth metals. The continuous line shows the NPA results, and the dotted lines are the results obtained using Ashcroft's empty-core model. The vertical broken lines show the nearest-neighbor distances for close packing (D_{CP}).

corresponding decrease of the valence electronic density) with the principal quantum number. Amongst this group Be has the smallest atomic volume and the strongest ion-electron interaction, leading to a rather high density which, according to the present results, implies that the first attractive minimum is partially covered by the repulsive core, yielding a pair potential with a narrow and fairly shallow first minimum, comparable in magnitude to the first maximum. Going down the column, it is observed that the corresponding increase in the principal quantum number results in a progressive weakening of the effects shown by Be, with the first attractive minimum being progressively more exposed and becoming wider and deeper.

The main features shown by our NPA pair potentials are also shared with the pair potentials obtained by Jank and Hafner [9] through the use of the first-principles optimized pseudopotentials (OPW) of Harrison. In fact, these authors suggest that relativistic effects for the core electrons are important for the understanding of the properties of the heavy alkaline-earth elements (Ca, Sr, and Ba) and their results show that the inclusion of these effects into their pair potentials leads to a deepening of the first attractive minimum and a shifting of the pair potential towards larger r values (for Ba the shifting is about one atomic unit). Comparison between their nonrelativistic-core pair potentials and the present ones shows that (with the exception of Mg for which both approaches lead to very similar results) the NPA interionic pair potentials are always deeper and their positions shifted towards smaller values of r . In fact, the present NPA interionic pair potentials are rather similar to those obtained by Moriarty [27] via the generalized pseudopotential perturbation theory (GPPT). We illustrate this point in Fig. 3 where the NPA result for Ca is compared with the OPW results [9] (including and excluding relativistic core interactions) and with the GPPT result [27].

The solid-crystalline structures of the alkaline-earth-metal elements are of close-packed type, ranging from

hexagonal (Be, Mg) to face-centered cubic (Ca, Sr) and body-centered cubic (Ba). The experimental structure factors for the liquid state near melting suggest that a close-packed arrangement is conserved, in accord with the observed trend that most of the features in the crystalline structure also persist in the liquid. For a liquid (as well as for a solid) the typical nearest-neighbor distances usually lie within the region where the pair potential changes gradually from repulsive to oscillatory behavior. In Figs. 2 and 3 we have also plotted the nearest-neighbor distances (D_{CP}) for close packing, which for our NPA as well as for Moriarty's pair potentials are close to the first minimum. A similar agreement is shown by the nonrelativistic-core pair potentials of Jank and Hafner [9]. When these authors include relativistic-core corrections into their OPW-derived pair potentials it is found that D_{CP} is now located at the repulsive part of the pair potential, and this tendency becomes more marked when going down the column from Ca to Ba; we will comment below on its consequences when the liquid structure is calculated using these relativistic-core pair potentials.

B. Liquid structure

The calculation of the liquid structure for the alkaline-earth metals has been carried out by combining the interionic pair potentials obtained in Sec. IV A with the VMHNC theory presented in Sec. II.

Figure 4 shows our calculated static structure factors $S(q)$, along with the corresponding x-ray-diffraction experimental results of Waseda [4], excepting Be, for which, as far as we know, $S(q)$ has not yet been experimentally measured. Our results predict a sharp first peak for the static structure factor of Be at a position of about 3.5 \AA^{-1} in good accord with the calculations of Jank and Hafner [9] and with their observation about the minimum shown by the electronic density of states at the Fermi energy. In all other cases, we find good agreement between our calculated $S(q)$'s and the experimental data; the positions and amplitudes of the oscillations are accurately predicted. The only discrepancy with the experimental results is in the height of the main peak of $S(q)$, for which our theoretical results predict systematically higher values than the experimental data, and we discuss below two possible reasons for this discrepancy. First, it appears that the procedure used by Waseda in the analysis of his x-ray diffraction data gives lower values for the height of the principal peak of $S(q)$. In the case of the liquid alkali metals, for which comparison with other experimental data is possible (obtained by either x-ray or neutron diffraction [28–31]), the values obtained by Waseda are systematically lower by an average of about 10%. We note, however, that at least for the heavy alkaline-earth elements (Ca, Sr, and Ba) our results tend to slightly overestimate the height of the principal peak of $S(q)$.

Second, some years ago Mon, Ashcroft, and Chester [32] studied the effects of the dynamically screened fluctuating dipole interactions between ion cores on the structure of simple metals. Their results for liquid Ga showed that one of these effects was to lower the height of the

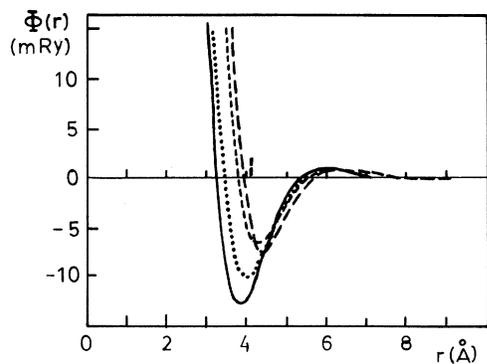


FIG. 3. Interionic pair potentials for Ca. Long-dashed line, relativistic core OPW results (Ref. [9]); short-dashed line, nonrelativistic core OPW results (Ref. [9]); dotted line, GPPT results (Ref. [27]); continuous line, present NPA results. The vertical broken line shows the nearest-neighbor distance for close packing (D_{CP}).

main peak of $S(q)$. Taking into account that the ionic polarizabilities of the heavy alkaline-earth elements are comparable to that of Ga, it can be inferred that the inclusion of these polarization forces in our calculations could lead to a better agreement with the experimental static structure factor.

We have also included in Fig. 4 the $S(q)$'s obtained

by using the interionic pair potentials obtained from Ashcroft's empty-core model [8]. The values of the core radius parameter (R_c) have been determined by fitting the position of the principal peak of $S(q)$. We find that, with the exception of Mg, this pseudopotential is unable to give a proper description of the liquid structure. It gives too high main peaks and overestimates the ampli-

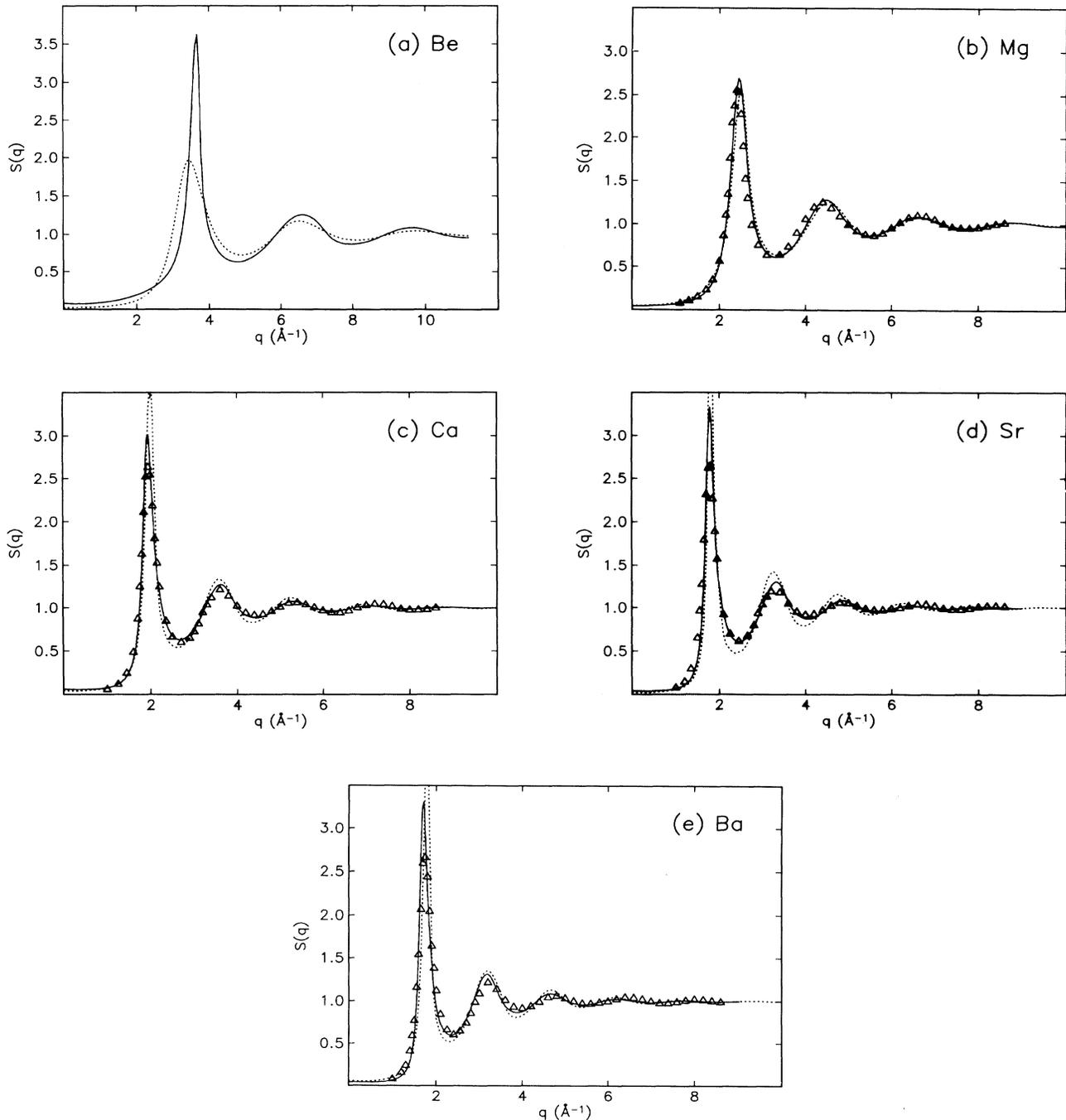


FIG. 4. Static structure factors of the alkaline-earth metals. Continuous lines, present VMHNC results using the NPA interionic pair potentials; dotted lines, VMHNC results using the interionic pair potentials derived from Ashcroft's empty-core model; open triangles, experimental results (Ref. [4]).

tude of the oscillations. Had we chosen to determine R_c to fit the height of the principal peak of $S(q)$, we would find that its position is shifted towards larger q values and the oscillations would be completely out of phase vis-à-vis the experimental data. Given the accuracy of the VMHNC as a liquid-state theory [16, 17, 25] we conclude that Ashcroft's empty-core model is not really adequate to use in describing the liquid structure of the alkaline-earth metals.

Finally, in Fig. 5 we present our results for the pair distribution function $g(r)$, together with those deduced from the experimental data. We find overall good agreement between the calculated and measured $g(r)$'s; the agreement is excellent for Mg and Ca. We have also included, for comparison, the molecular-dynamics (MD) simulation results of Jank and Hafner [9], where OPW-derived interionic pair potentials are used in the simulations. The agreement between our $g(r)$'s and those obtained by MD is also good. We note, however, that the height of the main peak in the simulated $g(r)$'s are systematically higher than those deduced from the experimental data.

Jank and Hafner [9] have also suggested that a proper account of the structure may require the inclusion of relativistic effects for the core electrons in the calculation of the interionic pair potentials. Our results do not appear to lend support to this suggestion. We note, in passing,

that in those cases where they have actually included relativistic effects the simulated $g(r)$'s exhibit a poor agreement with the experimental results. Our conclusion does not exclude the need to incorporate relativistic effects in the calculation of, say, the band structure of the heavy alkaline-earth metals.

It is our view that, given the relatively large values of the static atomic polarizability in the heavy alkaline-earth metals (particularly so for Sr and Ba), it is likely that such an effect will play a more prominent role than the relativistic-core electrons effect in characterizing the liquid structure of the alkaline-earth metals. We are currently exploring this idea and the results will be reported in due course.

Some authors [9, 33, 34] have suggested that Ba shows a transition-metal behavior. In his study of the crystalline-phase stability and phonon spectra of the heavy alkaline-earth-metal elements, Moriarty [33] found that while a simple metal treatment is rather adequate for Ca and Sr, an $sp-d$ hybridization contribution was necessary in order to lower the Ba phonon frequencies close to experiment. Also, self-consistent linear muffin-tin orbital calculations [34] suggest that there is nearly one d electron per atom in solid Ba whereas Jank and Hafner calculations [9] lead to a number of 0.87 d electrons per atom in liquid Ba. The present calculations, in which the Kohn-Sham equations have been solved for all electrons, do allocate within the

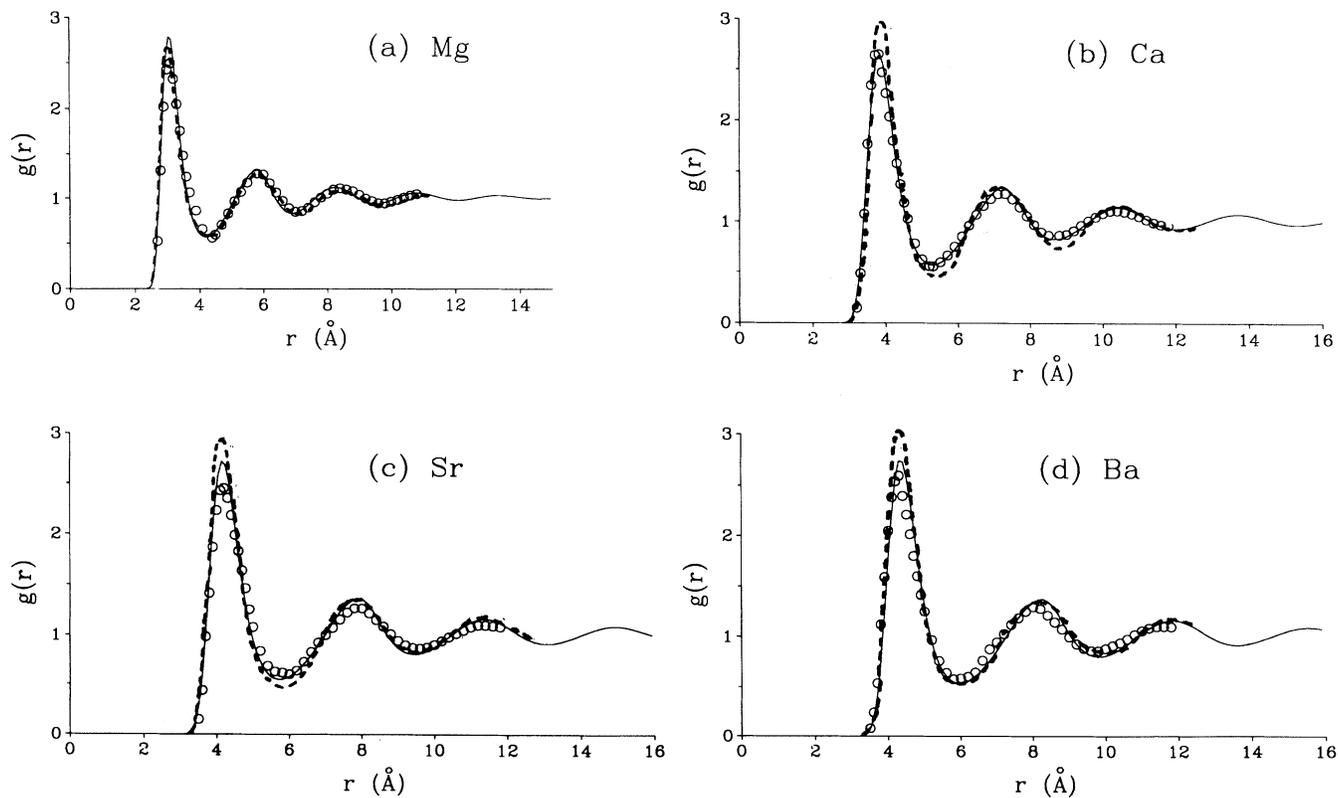


FIG. 5. Pair distribution functions of Mg, Ca, Sr, and Ba. Continuous lines, present VMHNC results using the NPA interionic pair potentials; broken lines, molecular-dynamics results using nonrelativistic core OPW interionic pair potentials (Ref. [9]); open circles, experimental results (Ref. [4]).

core region all the electrons excepting the two outer ones which now are not bound by the self-consistent potential. Although the present model does not allow us to compute the partial densities of states (from which the occupation of the d band could be obtained), we find that the d -type phase shifts of the valence electronic wave functions do take appreciable values in comparison with the s - and p -type ones. This result suggests some incipient occupation of the d band, but as the corresponding electronic states are delocalized ones, we cannot conclude from the present calculations whether liquid Ba shows some kind of transition-metal behavior.

V. SUMMARY

We have calculated the liquid atomic structure of the alkaline-earth metals near their triple point, by combining the NPA theory for computing the interionic pair potentials, with the VMHNC theory of liquids.

The calculated interionic pair potentials show, going down the second column of the Periodic Table, similar trends to those already found by other authors [9, 27].

Our results confirm and extend the general analysis of Hafner and Heine [26] about the variations of the interionic pair interactions and their relation to both solid and liquid structures.

The results obtained for the liquid structure show a good agreement with experiment, which we consider very rewarding given that our calculations are completely free of adjustable parameters. Our results do not appear to lend support to the suggestion concerning the need to include relativistic effects in the calculation of the interionic pair potentials. However, we do suggest that the inclusion of polarization effects of the core electrons may be significant.

ACKNOWLEDGMENTS

This work was supported by the EEC under Contract No. ERSC1*-CT910754 and the DGICYT of Spain under Grant No. PB89-0352-C02-01. D.J.G. and M.S. acknowledge additional support from the British-Spanish Joint Research program (Acciones Integradas), and LEG from the Universidad de Valladolid (Programa de Estimulo a Grupos Jovenes).

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