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Comparative study of structure determination schemes: Application to liquid alkali metals

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The ionic structure of liquid alkali metals at their melting point is investigated with molecular dynamics, an optimized random phase approximation (ORPA), and a soft-core mean-spherical approximation (SMSA) as representative of, respectively, simulation, perturbation, and integral methods. The valence electron screening densities and the interionic pair potentials are derived from Shaw's optimized model of potential and are free of adjustable parameter. We take advantage of the central place of molecular dynamics to analyze the results and point out that the interionic potentials issued from Shaw's potential provide a correct description of the interactions in the whole set of alkali metals. By comparing simulation results to ORPA and SMSA predictions, it appears that the use of the last two methods has to be restricted to fluids with packing fractions of less than about 0.55. The results of the analytical methods are in rather good agreement with simulation and experimental data, except with lithium that turns out to have a remarkably high packing fraction. Taking advantage of the calculation of the structure and the screening charge, the electron-ion pair distribution functions are investigated and features characteristic of alkali metals are observed. [S0163-1829(97)04917-5]

I. INTRODUCTION

The prediction of the structure of metallic liquids remains a topical subject that combines two difficulties: (i) the description of the interactions between the components of the metal and (ii) the deduction of the ionic arrangement in the electron gas. Consequently, any attempt to calculate the structure of a real metallic fluid first requires one to model the interactions and, second, to deduce the structure factor by using the most appropriate theories. It is then often difficult to make allowance for the uncertainties resulting from each step.

So, the choice of a model potential as a starting point to study the structure of liquid metals is of prime importance. The optimized model potential (OMP, Shaw[1]) is an *ab initio* model since it is not fitted on any macroscopic property. It is as old as Ashcroft's, but has been less used because of the complexity induced by its nonlocality and its energy dependence. The OMP can be used to describe many properties of simple metals and it has already given good results for the polyvalent metals by allowing one to reproduce the shoulder on the first peak of the structure factor of Ga and Ge.[2,3] Nevertheless, no study of the whole set of alkali metals has ever been published to date with this potential.

Alkali metals are generally considered as the simplest metals since they possess a single electron in their external shell. Nevertheless, they are still the object of great interest (Gonzalez *et al.*,[4] Matsuda *et al.*[5]) for different reasons. Their chemical reactivity makes them valuable for researchers. For theoreticians, they constitute a set with ionic cores ranging from very simple (Li) to more complex (Cs), and are well adapted to test the field of application of an approach. This is reinforced by the fact that lithium exhibits a marginal behavior that often requires a specific treatment (Das and Joarder,[6] Gonzalez *et al.*,[7] Hoshino and Young[8]).

In this work, we call on the second-order perturbation theory and the local-field correction $G(q)$ to get the effective ion-ion pair potential. The behavior of the electron gas is still under investigation (Richardson and Ashcroft,[9] Moroni *et al.*,[10]) reflecting the unsettled status of $G(q)$, and different tractable expressions have been proposed. We use the expressions of $G(q)$ proposed by Ichimaru and Utsumi[11] (IU) and by Vashishta and Singwi[12] (VS), which are representative of two characteristic trends, with or without a hump at $2k_F$, and we use the effective pair potentials to predict the structure of alkali metals from Li to Cs. Three main kinds of approaches have been developed and applied to the prediction of the structure of liquid metals.

(i) Thermodynamic perturbations: they were historically first to be applied extensively to metallic liquids. Among them the optimized random phase approximation (ORPA) seems to be best suited for an analysis of these elements.

(ii) Integral equations, which are more or less suitable to deal with metallic interactions. For instance, the soft-core mean-spherical approximation (SMSA) has already provided promising results (Jakse and Bretonnet,[13] Bretonnet and Jakse[14]).

(iii) Numerical simulation methods such as Monte Carlo and molecular dynamics (MD) (cf. Heermann[15] for a review).

The first two approaches mentioned here are based on approximate relations between the interionic potential and the structure factor. The uncertainties of the potential are worsened by those arising from these approximations. On the contrary, MD simulation suffers limitations in its accuracy only in the numerical algorithm used to integrate the equations of motion and in the finite number of particles in the sample. Nevertheless, we have good knowledge of these parameters so that the MD results can be considered as experimental ones for a modeled or hypothetic fluid.

In this paper, we first take advantage of the great reliability of MD simulations to test the validity of the interionic potentials by comparing MD results of structure with the experimental ones. We also try to determine the incidence of the electron gas screening on the pair potential by comparing IU and VS local-field corrections. Second, we test the efficiency of two analytical methods for prediction of the structure, ORPA and SMSA, as representative of, respectively, perturbation methods and integral equations. The former was selected because the above-mentioned predisposition to deal with metal-like interactions, and the latter because it has been developed specifically for dense fluids at low temperature (Chihara,[16] Madden and Rice[17]) and does not require any adjustable parameter. Moreover, SMSA has already proved its ability to predict the structure of Rb and Cs near the critical point (Bretonnet and Jakse[14]). To test these methods, we compare their results with those of MD for the model fluid. Since the potential is the same in both cases, the differences that might appear stem from the only approximate schemes used. Third, we consider the electron-ion pair distribution function and structure factor. They can be obtained experimentally from x-ray and neutron-scattering experiments (Egelstaff *et al.*[18]) and have recently been the object of a great interest (Takeka *et al.*,[19] Hoshino and Watabe,[20] for instance). However, though an experimental assessment of these quantities is impaired by the uncertainties proper to experiments on scattering, it can easily be implemented on the basis of the ionic structure factor and the screening charge density. We can derive benefit of this advantage to investigate the spatial distribution of the screening cloud around an ion for the whole set of alkali metals.

After this introductory part, we describe, in Sec. II, the implementing of the effective potential with Shaw's OMP and the structure with the three methods ORPA, SMSA, and MD. Then, in Sec. III, we present our results that we analyze following the directions previously defined. Finally, we sum up and conclude in Sec. IV.

II. LIQUID STATE THEORY

A. Shaw's model of potential

The pseudopotential theory allows one to determine the effective interaction between two ions through a development of the energy of the metal to the second order of perturbations (Harrison[21]). This is a well-known approach for local and energy-independent potentials, but it is a more complex task in the case of potentials such as Shaw's. For these reasons, we remind the reader of the main steps in this calculation.

It was demonstrated that the real electron-ion potential should be replaced by a pseudointeraction provided the eigenvalues of the energy of the system are maintained. Shaw[1] proposed an optimization of the model of Heine and Abarenkov[22] developed in that sense. For the free ion, the expression of Shaw's model potential is $(e=\hbar=m=a_0=1)$

$$\hat{w}_0(\vec{r})=-\frac{Z}{r}-\sum_{l=0}^{l_0}\theta(R_l-r)\left(A_l(E)-\frac{Z}{r}\right)\hat{P}_l,$$

where Z is the valence of the ion, l_0 is the highest orbital momentum present among the core electrons, θ is the function of Heaviside, $\hat{P}_l$ is the projector on the l-momentum core orbitals responsible for the nonlocality, and $A_l(E)=Z/R_l$ are the parameters that reproduce the spectral lines of the free ion. Their energy dependence is assumed to be linear

TABLE I. Our values of the parameters of Shaw's model of potential and of the effective valence $Z^*=Z-\lambda$ as defined in the text. These values agree with those available in the literature [see, for instance, Cowley (Ref. 40)]. Let us notice that there is no A_2 parameter for alkali metals. While $l_0<2$ for Li, Na, and K, it appears that experimental spectral energies cannot be fitted for Rb and Cs.

		Li	Na	K	Rb	Cs
	$A_0(0)$	0.293	0.263	0.189	0.173	0.150
$l=0$	dA_0/dE	−0.183	−0.229	−0.312	−0.348	−0.389
	$A_0(E_F)$	0.342	0.319	0.255	0.243	0.224
	$A_1(0)$	—	0.343	0.228	0.198	0.170
$l=1$	dA_1/dE	—	−0.097	−0.166	−0.187	−0.215
	$A_1(E_F)$	—	0.367	0.262	0.234	0.209
	Z^*	1.082	1.081	1.117	1.128	1.151

$$A_l(E)=A_l(0)+E\times\frac{dA_l}{dE}.$$

We have calculated the free ion parameters and extrapolated them at the Fermi level of an electron in the metal following the prescriptions of Ballentine and Gupta.[23] Our results are presented in Table I; they are in good agreement with those available in the literature.

The main advantage of using pseudo- or model potentials is allowing an estimation of the energy of the electron gas, calling on a second-order perturbation development. The electron-electron interactions are accounted for by a screening method, which requires the charge density to be known, but a difficulty appears considering that the potential is energy dependent. The pseudo-wave function is no more normalized to unity and a correction, called a depletion hole, has to be introduced:

$$\lambda=-\sum_{k\leqslant k_F}\int_{\text{core}}\chi_{\vec{k}}^*(\vec{r})\frac{dw}{dE}\chi_{\vec{k}}(\vec{r})d\vec{r},$$

where $\chi_{\vec{k}}$ stands for the pseudo-wave function. This charge is located in the core, but its spatial distribution is unknown and we have assumed it to be uniform. Then, starting with the charge density, Poisson's equation allows one to get the screening potential. The expression is made more complex by the nonlocality of the potential, but we can write the screened form factor in an abridged form as follows:

$$w(\vec{k},\vec{q})=w_0(\vec{k},\vec{q})+\frac{1}{\varepsilon_H(q)}\left(1-\frac{G(q)}{\varepsilon(q)}\right)\times\{g^*(q)+v_d(q)+[1-\varepsilon_H(q)]v(q)\},\qquad(1)$$

where $w_0(\vec{k},\vec{q})=v(q)+f(\vec{k},\vec{q})$ is the bare form factor, $v(q)$ is its local part, $f(\vec{k},\vec{q})$ is its nonlocal part, $v_d(q)=\lambda\Omega_0M(q)$ is the correction introduced because of the depletion hole, $M(q)$ is a modulation function depending on the spatial distribution of λ, $\varepsilon_H(q)$ is the Lindhard-Hartree dielectric function, $G(q)$ is the local-field correction taking into account exchange and correlation effects between conduction electrons, and $\varepsilon(q) = 1-[1-G(q)][1-\varepsilon_H(q)]$; $g^*(q)$ follows from the screening of the nonlocal part of the potential,

$$g^*(q)=\frac{4}{\pi^2 q^2}\int_{k\leqslant k_F}\frac{f(\vec{k},\vec{q})}{k^2-\|\vec{k}+\vec{q}\|^2}d\vec{k}.$$

Once we have obtained the screened form factor, the expression of the energy of the electron gas follows and the total energy of the metal can thus be written as the sum of a volume-dependent part and a structure-dependent part. The latter can be expressed in terms of the normalized energy wave number characteristic $F_N(q)$ (Shaw[24])

$$F_N(q)=-\left(\frac{q^2}{4\pi Z^*}\frac{V}{N}\right)^2\left\{\frac{1-G}{\varepsilon}[g^*+v+v_d]^2+j\right.$$
$$\left.+2\frac{G}{\varepsilon}v(g^*+v+v_d)-(v+v_d)^2-\frac{\varepsilon_H G}{\varepsilon}v^2\right\}, \qquad (2)$$

where the q dependence has been omitted for typing convenience and where

$$j(q)=\frac{4}{\pi^2 q^2}\int_{k\leqslant k_F}\frac{f^2(\vec{k},\vec{q})}{k^2-\|\vec{k}+\vec{q}\|^2}d\vec{k}.$$

The other notations have already been defined with the form factor. Finally, the effective pair potential consists of a direct part and an indirect part, collected in the form

$$u(R)=\frac{Z^{*2}}{R}\left\{1-\frac{2}{\pi}\int_0^\infty F_N(q)\,\frac{\sin qR}{q}\,dq\right\},$$

where $Z^*=Z-\lambda$. Though they are obtained through the same approach as for local and energy-independent potentials, relations (1) and (2) do appear more complex.

B. The ionic structure determination schemes

In this paragraph, $c_{ii}(r)$ and $h_{ii}(r)$ are, respectively, the direct and total ionic correlation functions bound by the Ornstein-Zernicke relation

$$h_{ii}(r)=c_{ii}(r)+\rho\int_V c_{ii}(|\vec{r}-\vec{r}\,'|)h_{ii}(\vec{r}\,')d\vec{r}\,', \qquad (3)$$

where ρ is the density of the fluid. The Fourier transform of this relation introduces the ionic structure factor

$$S_{ii}(q)=\frac{1}{1-\rho c_{ii}(q)}$$

with

$$S_{ii}(q)=1+\rho h_{ii}(q)$$
$$=1+\frac{4\pi}{q}\rho\int_0^\infty r h_{ii}(r)\sin(qr)dr. \qquad (4)$$

1. Molecular dynamics

Deducing the structure of a fluid from the interactions between the particles can be undertaken following several methods. The easiest one in its principle is molecular dynamics in which the equations of motion of a finite number of interacting particles can be numerically integrated when the interaction forces are known. It allows one to get the microscopic description of a small sample of liquid immersed in a macroscopic one. Thus, the ionic-pair distribution function

$$g_{ii}(r)=h_{ii}(r)-1$$

is obtained by computing the probability $P(r)\cdot dr = \rho 4\pi r^2 g_{ii}(r)dr$ of finding a particle at a distance between r and $r+dr$ from a particle taken as origin and by averaging over independent configurations of the simulated system. This kind of approach is also applicable to analytical or tabulated potentials such as metallic ones. Our calculations were carried out with a large cubic cell containing 4394 particles subject to the standard periodic boundary conditions. A phase-space trajectory of this system was produced in the microcanonical ensemble by using Verlet's algorithm in the velocity form. After an equilibration time in which the temperature was constrainted periodically to the desired value, an averaged $g(r)$ over 300 configurations separated by 100 iteration steps of Δt (Δt typically from 10^{-15} to 10^{-14} s) was calculated.

In addition to the MD simulations, there exist analytical methods that are less time-consuming and usually founded on a special separation of the potential. Weeks *et al.*[25] (WCA) proposed to split up the pair potential into two contributions: a short-range part, $u_0(r)$, that is purely repulsive, and an attractive long-range part, $u_1(r)$, such as

$$u_0(r)=\begin{cases}u(r)-V_{\min} & \text{if } r<r_{\min},\\ 0 & \text{if } r>r_{\min},\end{cases}$$
$$u_1(r)=\begin{cases}V_{\min} & \text{if } r<r_{\min},\\ u(r) & \text{if } r>r_{\min},\end{cases} \qquad (5)$$

where $r_{\min}$ and $V_{\min}$ stand for the coordinates of the first minimum of $u(r)$. The repulsive part $u_0(r)$ is considered as predominant to determine the structure, whereas $u_1(r)$ is responsible for the liquid cohesion and governs its thermodynamical properties.

2. Integral equations

Integral equations are based on approximate closure relations connecting structure and interaction. In the case of the SMSA, this closure relation is (Chihara,[16] Madden and Rice[17])

$$c_{\mathrm{SMSA}}(r)=c_0(r)+c_1(r)$$
$$=\{1-\exp[\beta u_0(r)]\}g(r)-\beta u_1(r), \qquad (6)$$

where $\beta=1/k_BT$. It is obtained by splitting up $u(r)$ following Eq. (5). When $u_0(r)$ is taken as the hard-sphere potential, the SMSA becomes equivalent to the mean-spherical approximation (MSA, Lebowitz and Percus[26]):

$$c^{\mathrm{MSA}}(r)=c_1(r)=-\beta u_1(r).$$

Consequently, SMSA is a generalization of the MSA to soft-core potentials, and has already provided better results than HNC and PY in the case of metallic potentials and of Lennard-Jones fluid at its triple point (Madden and Rice[17]). The main difficulty in setting up the integral equations lies in solving the set of equations formed by Eq. (3) and Eq. (6). Because of the integral expression of Eq. (3), a self-consistent approach of this problem with classical algorithms, such as Picard's, converges very slowly and appears tiresome. In order to reduce the time of calculation and to improve the accuracy, we used the algorithm of Labik *et al.*[27] to deduce the pair correlation function $g(r)$ of liquid alkali metals.

3. Perturbation theories

The perturbation methods apply the WCA prescription to define an unperturbed system associated to the short-range potential $u_0(r)$, and a perturbing potential $u_1(r)$. Since the exact description of the unperturbed system is very complex, it is first replaced by a hard-sphere reference system, with diameter σ, which has been extensively studied especially by computer simulation (Verlet and Weis[28]). This amounts substituting a trial system for the true one (Andersen *et al.*,[29] Kahl and Hafner,[30] Bretonnet and Regnaut[2]) that is characterized by the potential $u_T(r)=u_\sigma(r)+u_1(r)$. Following the random phase approximation (RPA), when applied to the trial system, the total correlation function is $c_T(r)=c_\sigma(r)+c_1(r)$ [where $c_1(r)=-\beta u_1(r)$] so that the ionic structure factor is given by

$$S_T^{\mathrm{RPA}}(q)=\frac{S_\sigma(q)}{1-\rho S_\sigma(q)\beta u_1(q)}.$$

Since the trial system has a hard-sphere core, it requires $g_T(r)=0$ if $r<\sigma$. The condition, which is not met by the RPA, is fulfilled by the ORPA when $u_1(r)$ is replaced by an optimized potential $u_1^*(r)$:

$$\begin{aligned} u_1^*(r)&=u_1(r) \quad \text{if } r>\sigma \\ &=u_1(\sigma)+V_{\mathrm{opt}}(r) \quad \text{if } r<\sigma, \end{aligned}$$

where

$$V_{\mathrm{opt}}(r)=-\frac{1}{\beta}\times\left\{k_1+k_2\left(\frac{r}{\sigma}-1\right)+\left(\frac{r}{\sigma}-1\right)^2 \times\sum_{n=0}^{l}k_{n+3}P_n\left(\frac{2r}{\sigma}-1\right)\right\}.$$

In this relation, P_n stands for the nth Legendre polynomial and k_n for the parameters calculated requiring $g_T(r)=0$ if $r<\sigma$. This condition was fulfilled with $l=2$.

Having described the trial system, we now need to link it up to the real fluid. Using a perturbation development of the free energy, Weeks *et al.*[25] established that

$$S_0^{\mathrm{WCA}}(q)=S_\sigma(q)+\rho B_\sigma(q),$$

where

$$B_\sigma(r)=g_\sigma(r)\left[\exp\left\{\frac{u_\sigma(r)-u_0(r)}{k_BT}\right\}-1\right]$$

is the so-called blip function and where σ is defined such as

$$\int B_\sigma(r)d\vec{r}=0.$$

Finally, the ionic structure factor reads

$$S_{ii}^{\mathrm{ORPA}}(q)=\frac{S_\sigma(q)}{1-\rho S_\sigma(q)\beta u_1^*(q)}+\rho B_\sigma(q).$$

When the ORPA procedure is used after that of WCA, the value of the hard-sphere diameter is modified so that the WCA procedure has to be repeated in a self-consistent way until the stability of σ is reached. In the case of our potentials for alkali metals, the convergence was quite rapid except for Li.

C. The electron-ion structure factor

A liquid metal can be considered as an electron-ion mixture and, according to Egelstaff *et al.*,[18] the electron-ion correlation can be estimated from the difference between structure factors determined by x-ray and neutron diffraction experiments. The accuracy of these techniques is still far from being sufficient to give a precise quantitative electron-ion structure factor $S_{\mathrm{ei}}(q)$ even if Takeda *et al.*[19] have carried out some experiments on polyvalent liquid metals. However, $S_{\mathrm{ei}}(q)$ can also be calculated by a procedure described by Chihara,[31] Petrillo and Sachetti,[32] and more recently by Hoshino and Watabe.[20] According to these authors, the electron-ion structure factor can readily be expressed as

$$S_{\mathrm{ei}}(q)=\frac{1}{\sqrt{Z}}n_{\mathrm{sc}}(q)S_{ii}(q), \tag{7}$$

where $S_{ii}(q)$ is the ionic structure factor and $n_{\mathrm{sc}}(q)$ is the electron screening density. For Shaw's nonlocal OMP, $n_{\mathrm{sc}}(q)$ is written as follows, in terms of the quantities defined previously:

$$n_{\mathrm{sc}}(q)=\frac{q^2}{4\pi}\frac{\{v(q)[1-\varepsilon_H(q)]+\varepsilon_H(q)g^*(q)+v_d(q)\}}{\varepsilon(q)}.$$

In this expression, the nonlocality and the energy dependence are taken into account. If they had been omitted, we would have found the standard expression related to local energy-independent potentials. As will be seen later, the fact that $n_{\mathrm{sc}}(q)$ is the Fourier transform of the pseudoelectron density of the conduction electrons rather than the true one, has an incidence on the pair-correlation functions $g_{\mathrm{ei}}(r)$. We used our MD results of $S_{ii}(q)$ to calculate the electron-ion structure.

III. RESULTS AND DISCUSSION

A. Test of the potentials

We now test the effective pair potentials obtained with Shaw's OMP. Before dealing with our results of structure, we would like to investigate directly the pecularities of the effective pair potential curves. Data relative to the thermodynamical states of alkali metals near their melting temperatures are summarized in Table II.

TABLE II. Physical properties characteristic of the thermodynamical states under study. Ω_0 is the atomic volume and R_{WS} is the Wigner-Seitz radius.

Element	T (K)	Ω_0 (a.u.)^3	R_{WS} (a.u.)
Li	463	152.068	3.311
Na	378	277.623	4.047
K	343	530.432	5.022
Rb	313	661.388	5.405
Cs	303	810.227	5.783

TABLE III. Estimation of the hardness of the pair potentials.

	IU		VS	
	d (a.u.)	$d/r_{\min}$	d (a.u.)	$d/r_{\min}$
Li	5.643	0.888	5.681	0.888
Na	6.366	0.890	6.432	0.887
K	7.700	0.890	7.776	0.889
Rb	8.184	0.889	8.270	0.889
Cs	8.837	0.888	8.918	0.892

The first feature of the pair potentials that we look at is the assumption of universality of the shape for alkali metals. Figure 1 shows the potentials for the five alkali metals on reduced scales, with the local-field correction of VS. If we consider the short-range part, we observe that, except for Li, the curves are almost identical. Differences only appear after the first maximum, but the amplitude of oscillations is rather small. In order to compare the hardness of the repulsive part of the potentials, we consider the following quantity (Tanaka[33]):

$$\frac{d}{r_{\min}}=\frac{1}{r_{\min}}\int_0^{r_{\min}}\left[1-\exp\left(-\frac{u_0(r)}{k_BT}\right)\right]dr. \tag{8}$$

The values of $d/r_{\min}$ corresponding to our potentials (Table III) show a striking similarity for the whole set of alkali metals and the universality of the shape of the pair potentials (Singh and Holz,[34] Gonzalez *et al.*[4]) seems rather confirmed by our calculations, indicating that liquid alkali metals are scaled versions of each other.

The second feature we examine is the influence of the screening. MD results of the pair distribution function are insensitive to whatever local-field correction is used, whereas the potentials appear to be rather affected, especially in the first minimum region. This insensitivity was already observed for liquid alkali metals by Bretonnet and Jakse[14] with the integral equation hybridized mean-spherical approximation. A study of the interatomic forces $[-du(r)/dr]$ for both local-field corrections show (Fig. 2) that they are quite identical in that range. The differences between both screenings are noticeable only in the range between first and second neighbors. This confirms the idea according to which the structure is rather conditioned by the short-range repulsive interactions. Such differences, which are perceptible exclusively in the medium range, are specific to alkali metals. With polyvalent metals, larger differences between VS and IU appear in the repulsive part of $u(r)$ (Bretonnet and Regnaut[2]), responsible for the shoulder at the right side of the principal peak of $S(q)$ for Ga and Ge.

We now compare the curves of $g(r)$ obtained by MD simulations and the experimental ones. The experiments by Waseda[35] are taken into account since they were carried out with the same experimental protocols for the whole set of alkali metals. No general trend emerges when going from the lighter to the heavier elements [Figs. 3(a)–3(e)]. It appears that MD calculations yield a good prediction of the pair distribution function of Na and Cs. Two main discrepancies can be pointed out for the other elements. For Li, it appears that the predicted oscillations are fuller than the experimental ones. Nevertheless, the position of the first two peaks coincide exactly. In the cases of K and Rb, we observe leading oscillations of MD compared with experiments, but the amplitudes are of the same order.

We would like to point out that Shaw's model of potential is an *ab initio* one and has to be distinguished from those with adjustable parameters. With the latter, some authors achieved excellent agreement between simulation and experiment. Gonzalez Miranda and Torra[36] obtained very good results for Na with Ashcroft's empty core model potential.

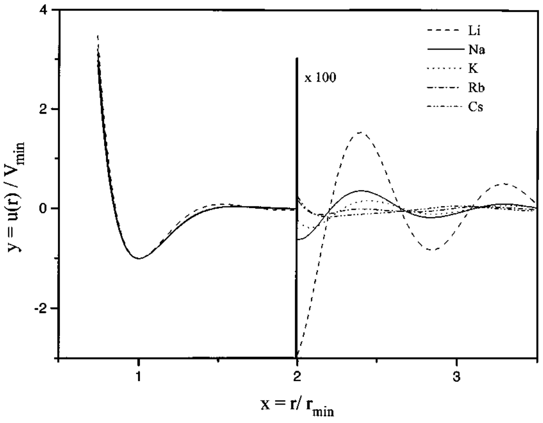

FIG. 1. Pair potentials for alkali metals, in reduced units, for VS screening. The curve of lithium is slightly shifted from the others that are indiscernible in the short distance region. With IU screening, the differences between the set of curves are smaller.

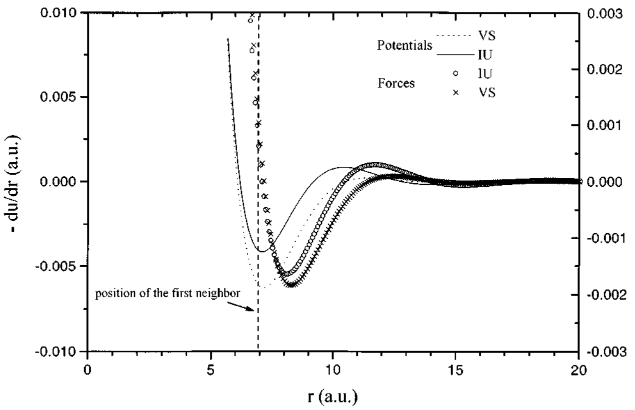

FIG. 2. Pair potentials and forces for Na with both IU and VS screenings. The position of the first neighbors is indicated. In the region of the first neighbors, potentials show differences and the forces are quite identical.

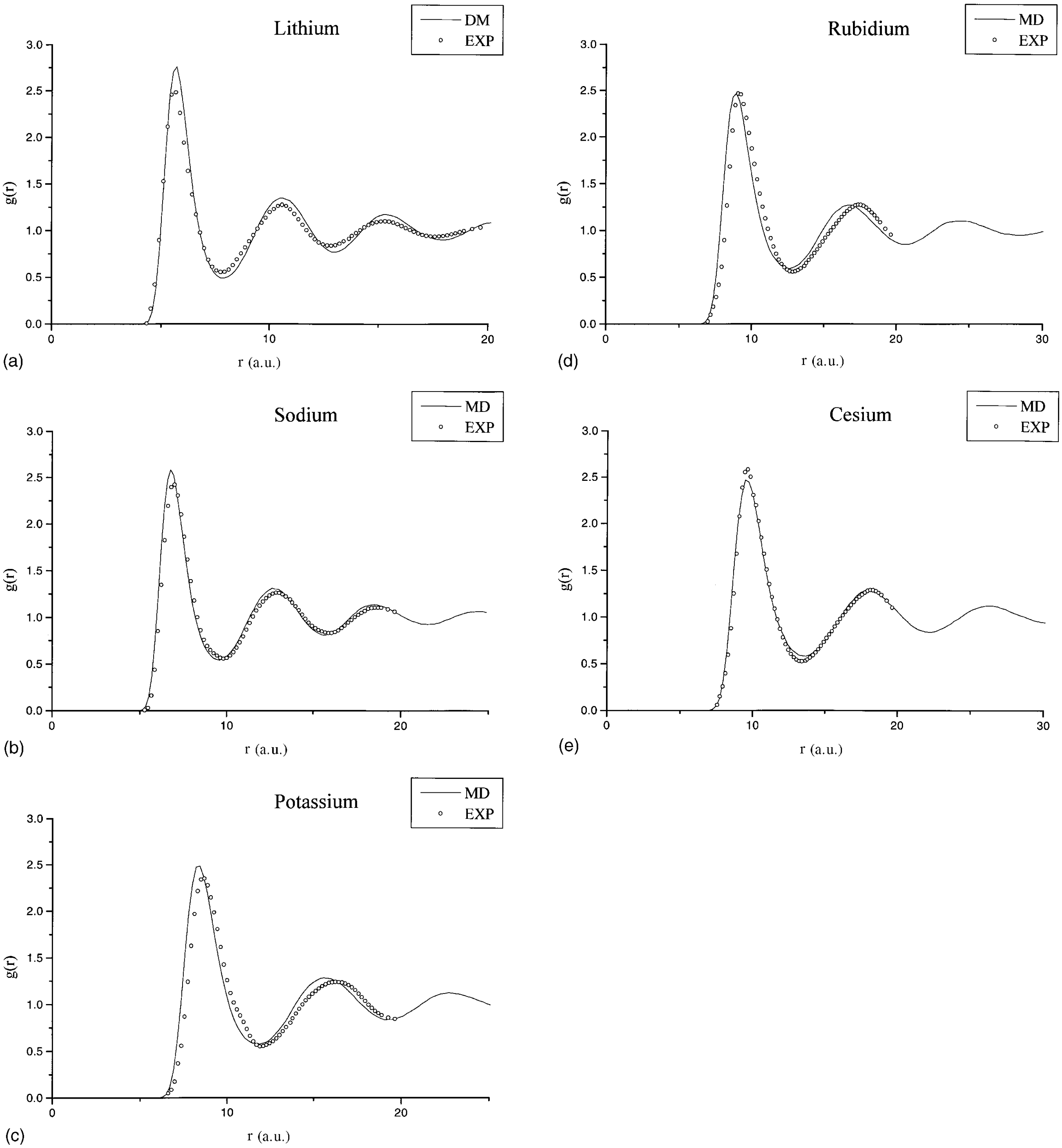

FIG. 3. Pair distribution functions. Circles represent experimental results of Waseda (Ref. 35). Full curves show our MD results with IU local-field corrections.

Some others were not so lucky, though having adjustable parameters at their disposal: Matsuda *et al.*[5] for Na, K, and Rb with the model potential of Hasegawa *et al.*[37] and Gonzalez *et al.*[38] for the whole set of alkali metals with Ashcroft's model. In our case, it is worth noting that K and Rb are the elements that raise the most problems with the shift of $g(r)$ oscillations towards small distances. It is found that $g(r)$ of Li is very acceptable when calculated with the OMP and does not require the kind of special treatment that is usually devoted to it. Consequently, the pair potentials determined with the nonlocal *ab initio* model potential of Shaw are very realistic and appropriate to describe the structure of liquid alkali metals.

B. Comparison of the analytical approaches with molecular dynamics

In this subsection, we compare the curves of $g(r)$ obtained by MD with those obtained by SMSA and ORPA in order to test their ability to predict the structure of liquid metals. Whereas Na, K, Rb, and Cs are similarly well described by each method, Li displays a completely different pattern. We discuss separately the case of Li and take Rb as representative of the remaining four elements.

Figure 4 shows simultaneously the curves of $g(r)$ for Rb obtained with the three different methods. A striking feature is the very good concordance between the predictions of ORPA and of SMSA, even though the repulsive part of $u(r)$ is treated differently. Only little deviations appear in the position of the first peak of $g(r)$. When compared with MD results, both methods underestimate the height of the first peak. Analytical methods present a slight packing down of the left side of the second peak. So, both methods show a similar and suitable ability in deducing the structure of Na, K, Rb, and Cs from the interactions obtained with Shaw's OMP.

On the contrary, as shown in Fig. 5, lithium is an exception. The results of SMSA and ORPA are not in agreement with MD predictions, as the oscillations of $g(r)$ are amplified. Besides, considering the two analytical methods, a substantial difference exists between both curves of $g(r)$ in the region of the first two peaks, i.e., (i) a shift of the principal peak, (ii) a severely distorted second peak given by ORPA and marked by an original triangular shape.

This situation reveals an interesting feature of the analytical methods and a criterion to use them. If we define a packing fraction

$$\eta=\left(\frac{d}{2R_{\mathrm{WS}}}\right)^3,$$

where d is a core radius given by the prescription of Tanaka[33] [Eq. (8)], this quantity is much higher for Li than for the other alkali metals (0.631 for Li, 0.502 for Na, 0.464 for K, 0.448 for Rb and 0.458 for Cs). This specificity of Li was already observed by Kummaravadivel and Evans[39] and it could be responsible for the above-mentioned difficulties encountered by the ORPA and the SMSA. In order to test this assumption, we can calculate the structure of a fluid with an adjustable packing fraction. We obtained such hypothetical fluids by keeping the effective potential unchanged (and so d) and by varying the density (and so R_{WS}). When decreasing η with the potential of Li, we observed an agreement of the same quality as that presented in Fig. 4 for Rb between MD, ORPA, and SMSA for values of η inferior to about 0.55. The differences only appeared with greater values of η. When increasing η with the potential of Na, we drew the same conclusions. Thus, we have pointed out that the use of the ORPA and the SMSA has to be restricted to fluids with a packing fraction of less than about 0.55.

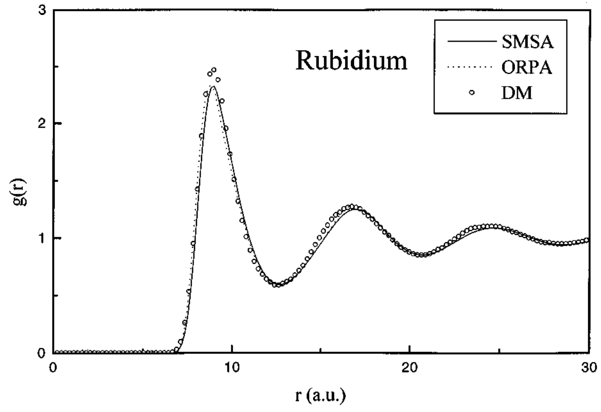

FIG. 4. Pair distribution functions of Rb with IU screening. Rb is representative of the other alkali metals, except Li.

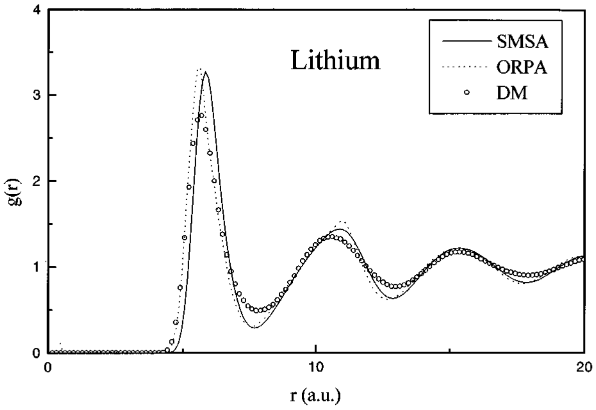

FIG. 5. Pair distribution function of Li.

According to our MD results, we hold the opinion that the interionic pair potentials calculated with Shaw's OMP can be used for all alkali metals, including Li. We only have to use the analytical approximations with the utmost care to determine the structure because they do not apply properly when the packing fraction is greater than 0.55.

C. Electron-ion correlation function

In this subsection, we present our results of the electron-ion correlation in showing first the electron-ion structure factor plotted vs q/k_F for all alkali metals. The curves of $S_{\mathrm{ei}}(q/k_F)$ (Fig. 6), which are conditioned by $n_{\mathrm{sc}}(q)$ and $S_{ii}(q)$ [Eq. (7)], show rather similar features, namely, (i) an abrupt dip at the position $q/k_F \simeq 2.2$ corresponding to the principal peak of $S_{ii}(q)$, (ii) small oscillations around zero at large q, and (iii) a low-q region specified by a positive electron-ion structure factor. These features are in accordance with the experimental results of Takeda *et al.*,[19] even if the dip deduced from the ionic-structure factors measured

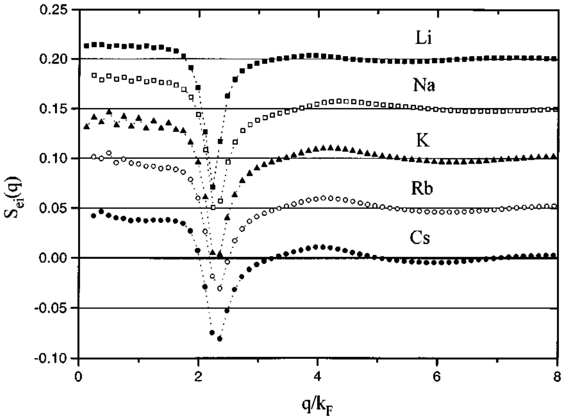

FIG. 6. Electron-ion structure factors vs q/k_F obtained with VS screening. From Cs to Li, the successive curves are vertically shifted by an amount of 0.05.

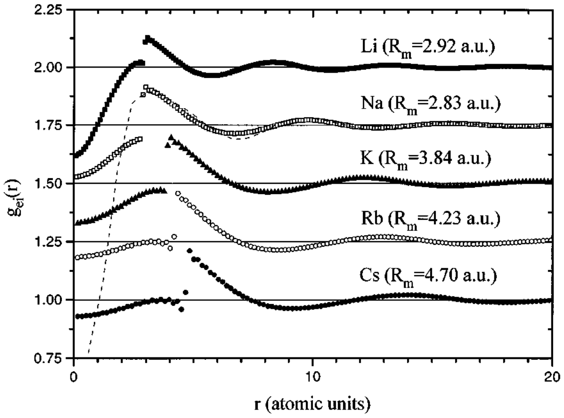

FIG. 7. Electron-ion pair distribution functions. R_m stands for the core-radius within which the depletion hole is confined. From Cs to Li the curves are shifted by an amout of 0.25. The dashed curve has been obtained for Na with Ashcroft's potential to point out the influence of the depletion hole.

by x ray and neutron scattering is substantially deeper. There is not much more to be done, given the uncertainties of diffraction experiments.

In Fig. 7, we also compare the electron-ion pair correlation functions $g_{\mathrm{ei}}(r)$ drawn from $S_{\mathrm{ei}}(q)$ by the Fourier transform

$$g_{\mathrm{ei}}(r)=1+\frac{\sqrt{Z}}{\rho}\frac{1}{8\pi^3}\int S_{\mathrm{ei}}(q)\exp(i\vec{q}\cdot\vec{r})d\vec{q}.$$

For all elements under study, small oscillations of $g_{\mathrm{ei}}(r)$ around unity at large distances can be pointed out. The most striking feature of our results is the discontinuity that occurs at a position ranging from 3 a.u. for Li to 5 a.u. for Cs. These positions coincide with the radius of the sphere containing the depletion hole at each ionic site. It is worth bearing in mind that, when replacing the true potential by a pseudo one, the true wave function is replaced by a pseudo one too. Consequently, $g_{\mathrm{ei}}(r)$ does not describe the true electron-ion pair distribution function inside the ionic cores, but rather the pseudo one. When dealing with energy-dependent pseudopotentials, the pseudo-wave function has to be kept normalized. This is achieved by introducing the depletion holes into each core. We assumed it to be uniformly distributed in the core volume; this accounts for the discontinuity observed. In order to check that it is really related to the energy dependence of Shaw's OMP, we performed a calculation of $g_{\mathrm{ei}}(r)$ for Na with Ashcroft's potential (Fig. 7). In contrast to our results obtained on the basis of Shaw's OMP and also to the rather jagged outline of $g_{\mathrm{ei}}(r)$ in the ionic core obtained by Gonzalez *et al.*,[4] using the neutral pseudoatom method, the curve smoothly slopes down to zero. Moreover, if the value of the depletion hole λ is artificially set to zero, the discontinuity disappears.

The behavior of $g_{\mathrm{ei}}(r)$ inside the ionic core should be regarded with caution. Outside the core, it is interesting to note that the first peak of $g_{\mathrm{ei}}(r)$ is located at half the distance of the first peak of $g_{ii}(r)$, which coincides with the first minimum of $g_{\mathrm{ei}}(r)$. This was qualitatively observed from experimental data with alkali metals but not with polyvalent ones. Thus, as expected, the first peak of the electron-ion pair distribution function corresponds to the maximum position of the screening valence electron density around an ion and the successive peaks to the next maxima of the charge density of the valence electron cloud.

IV. SUMMARY

We applied the nonlocal and energy-dependent Shaw OMP, using the atomic number as the only input data, to derive an effective interionic pair potential with all alkali metals. We found that these pair potentials show a universal shape for all the alkali metals, including Li.

Then, the evaluation of the ionic structure was carried out by calling on MD, ORPA, and SMSA techniques. We have proved the reliability of the analytical theories of the liquid state by comparing the corresponding predictions with the results obtained for the structure with the MD method. ORPA and SMSA results are of the same quality and are in good agreement with those of MD provided that the packing fraction is less than about 0.55.

Finally, we performed the calculations of the electron-ion correlation function applying a consistent approach, without any fitted parameter, starting from the sophisticated Shaw OMP to determine the screening valence electron density and the ionic structure factor via the interionic pair potential. Various results are given and discussed in connection with Shaw's OMP.

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