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LIQUID STRUCTURE OF SOME RARE-EARTH METALS USING AN ANALYTIC PAIR POTENTIAL

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The analytical Pettifor-Ward (PW) pair potential with the Ashcroft empty core model for the pseudopotential is employed to obtain structural properties of some liquid rare-earth metals. The liquid structure is calculated using the variational modified hypernetted chain (VMHNC) approximation. Recently proposed the modified Harrison model potential (MH) of Karmakar and Joarder has been calculated using the PW pair potentials for s electron contribution for comparison. A good agreement with the experimental data for structural properties has been found. However, VMHNC calculations using MH potential fail to yield reasonable results if one used Karmakar's data set.

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1. Introduction

The structure and thermodynamics of the s-p bounded simple metals in their liquid state was described using the effective inter-ionic interaction which is derived from the pseudopotential theory [1]. The pseudopotential, a weak effective interaction between a valence electron and an ion core, brings an useful simplification to condensed matter physics and quantum chemistry at some cost in accuracy. However, the difficulties arise when this method is applied to non-simple like transition and rare-earth metals because of the hybridisation of d or f states. The pseudopotential theory was reformulated and generalised by Harrison to include d-band metals [2]. Generalised pseudopotential method has been extended and applied by Moriarty [3, 4] to calculate the dynamic properties of noble and alkaline earth metals, possessing either completely filled or empty d-bands. Most theoretical works on liquid transition metals are based on a study of Wills and Harrison (WH)[5] who used a separate treatment of s-p and d states and, in addition, take account of the effect of s-p-d hybridisation. Here the former are treated within the empty core local model pseudopotential (EC) [6], for s-like contribution, which depends on the only one adjustable parameter r_c that is generally obtained by fitting the minimum of the free energy at observed volume of the solid phase. WH model potential is sufficiently simple to be use in the liquid state calculations and applied to liquid transition metals by most number of workers [7-9]. One of the main result of WH calculations for transition metals is that the applicability of WH model for the elements at the beginning and at the end of the 3d series is ascertained. In previous theoretical works it has been noted that some accurate liquid state theories fail to produce results for structure factor S(q) of the d transition metals with half-and-less than half filled d band.

Recently, the Harrison model potential [5] for liquid 4f metals using the Gibbs – Bogolyubov variational calculation with charge hard sphere (CHS) reference system to obtain the thermodynamic properties has been modified and employed by Karmakar and Joarder [10]. On the other hand, some earlier calculations for the liquid properties of rare-earth metals based on hard sphere (HS), one component plasma (OCP), a charged hard sphere models (CHS) have been produced quite successful results [11-14].

In the literature [15] the simple metal theory [1, 5] has been used to apply directly to describe the liquid structure using the Ashcroft empty core pseudopotential in conjunction with a one component plasma. Then, following a proposal of Wills and Harrison [5] it has been assumed that the effective valence $Z_{eff} = Z - Z_0$, electrons per ion are in the free electron like states, where Z valence electrons per ion, Z_0 electrons are incorporated in the non-overlapping ion core and their coupling is considered to be weak [15]. It is not explicitly taken into account for the contribution from d or f electron here. In this work, this proposal is used for our pair potential calculations. Pettifor and Ward (PW) pair potential form [16] using the EC pseudopotential is well described the structure and thermodynamic properties of liquid sp bonded metals and alloys [17]. Our main aim in this work is to apply PW potentials to liquid rare-earth metals in order to derive the liquid state properties using the VMHNC approximation. Hence, the results presented below are crucial test for PW pair potentials. On the other hand, to the present time, MH model has not been applied to predict the structural and thermodynamic properties of liquid 4f metals using the integral equations. For this purpose we have shown the validity of an accurate theory of liquids VMHNC [18-20] for structural calculations of liquid rare-earth metals using the MH model potentials.

We have found that PW pair potentials using the standard pseudopotential theory in conjunction with VMHNC reproduced the experimental structure data quite well. However, VMHNC calculations using MH potential fail to yield reasonable results if one uses Karmakar’s data set. We believe that these difficulties encountered with the use of the MH potential because of the very deep first minimum of its potential well.

The layout of the paper is as follows; in section 2, we outline the theoretical basis of our work. The inter-atomic pair potentials using the standard pseudopotential formalism, PW analytic pair potential form and the modified Harrison potential for 4f liquid metals are described. The main features of the liquid state theory used in our calculations are given in the same section. The results of structural calculations for some liquid rare-earth metals, lanthanides are presented in Section 3, together with a brief discussion of our results. Finally, in Section 4, we sum up and briefly comment on the results of our work.

2. Theory

The effective inter-atomic pair potential in simple metals $\phi(r)$ is based on the use of pseudopotentials to describe the interaction between an ion and a second ion and its screening cloud of electrons from second order pseudopotential perturbation theory

$$\phi(r) = \frac{Z_{eff}^{\;2}}{r}\left(1 - \frac{2}{\pi}\int_0^\infty \frac{F_N(q,\rho)}{q}\sin qr\,dq\right), \tag{1}$$

where

$$F_N(q,\rho) = \left(\frac{q^2\omega(q)}{4\pi Z_{eff}}\right)^2 \left(1 - \frac{1}{\varepsilon(q,\rho)}\right) \tag{2}$$

where Z_{eff} for the effective number of valence electrons per ion and ρ the density of ions. Here $\omega(q)$ is the local pseudopotential and $\varepsilon(q)$ is the dielectric screening function. In the present work we use the Ashcroft empty core pseudopotential as,

$$\omega(q) = -(4\pi Z_{eff}/q^2)\cos(qr_c) \tag{3}$$

where r_c is the core radius.

In this paper we employ the well known local field corrections G(q) of the Ichimaru-Utsumi (IU) [21] and the local density approximation (LDA) with the parametrization of Vosko - Wilk and Nussair (VWN) [22] to describe the electron gas.

PW used an analytic fit to the dielectric function $\varepsilon(q)$ in Eq. (1) as,

$$\varepsilon^{-1}(q) = \sum_m \frac{D_m q^2}{(q^2 - q_m^2)} \quad . \tag{4}$$

which yields

$$\phi(r) = \frac{Z_{eff}^2}{R}\sum_m A_m \cos(k_m R + \alpha_m) e^{-\chi_m R} \tag{5}$$

where the parameters $A_m = 2d_m|M_m(q)|^2$, $\alpha_m = \delta_m + \arg|M(q_m)|$ are related to the poles q_m, $q_m = k_m + i\chi_m$ and the weight D_m as, $D_m = d_m \exp(i\delta m)$. Note that D_m and q_m depend only the density of the free electron gas representative of the system, while A_m and α_m depend also on the pseudopotential used. $M(q)$ is the normalised bare-electron ion interaction as, $M(q) = \cos(qr_c)$ for EC electron-ion potential.

Recently, Harrison's model potential for 4f metals in the solid state applicable to the liquid state has been modified by Karmakar and Joarder [10]. The effective pair potential for the electron configuration $5d^1 6s^2 4f^n$, with n=0,1,2 etc. can be written as ,

$$\phi(r) = \phi_s(r) + \phi_d(r) + \phi_f(r) + \phi_{ff}(r) \tag{6}$$

where $\phi_s(r)$ denotes the s contribution to the pair potential which can be calculated here from Eqs. (1) and (5) replacing the number of s electrons Z_s, by Z_{eff}. $\phi_d(r)$ is the one d state contribution which can be written as in Ref. [10]

$$\phi_d(r) = -\frac{28.1}{\pi}\left(\frac{12}{N_c}\right)^{1/2} Z_d\left(1-\frac{Z_d}{10}\right)\frac{r_d^3}{r^5} + \frac{225}{\pi^2} Z_d \frac{r_d}{r^8} \tag{7}$$

where r_d is the d-state radius, N_c is the coordination number and Z_d is the number of d electrons. In Eq. (7), first term is a bonding term proportional to the width of the d band and the repulsive term corresponds to the shift of the centre of gravity of the d band. The f-state contribution due to coupling that broadens the f-states into bands taking a simple rectangular model of density of f-states suggested by Friedel [23-24] can be written

$$\phi_f(r) = -Z_f\left(1-\frac{Z_f}{14}\right)\left(\frac{1}{N_c}\right)^{1/2}\frac{(5.06r_f)^5}{r^7} \tag{8}$$

if the ions interact with only nearest neighbours. Here r_f is the f-state radius, Z_f is the number of the electrons in the f-band. The last term corresponds to the shift in the f-band centre. The fourth-order shift in the band centre can be represented in terms of an overlap matrix element between perturbed states and an atomic sphere approximation for f-f matrix elements of different ion sites. Thus the nonorthogonal potential due to f-states as in Ref. [5,24] is

$$\phi_{ff}(r) = 2Z_f\frac{(3.11r_f)^{10}}{r^{12}} \tag{9}$$

The effective pair potential for the electron configuration $5d^0 6s^3 4f^n$, n = 0, 1, 2 can be written as a sum of the pseudopotential term for s contribution and additional terms due to the f state contributions.

With the effective pair potential known, integral equations are able to provide us the liquid structure for metals. For the structural calculations, one of the the integral equation theory which has been shown to be very reliable theory of liquids is VMHNC, has been carried out [18-20]. The starting point of most of the integral equation theories of liquids is the Ornstein-Zernike(OZ) equation, which for a homogeneous, and isotropic system can be written as

$$h(r) = c(r) + \rho\int d\vec{r}\,' h(|\vec{r} - \vec{r}\,'|)c(\vec{r}\,') \tag{10}$$

The equation defines the direct correlation function c(r), in terms of the total correlation function, h(r)=g(r)-1, where g(r) is the pair distribution function and ρ is the atomic density. This equation is supplemented by the exact closure relation involving the effective pair potential $\phi(r)$,

$$g(r) = \exp[h(r) - c(r) - \beta\phi(r) - B(r)] \tag{11}$$

where $\beta = (k_B T)^{-1}$, and B(r) the bridge function. In this work B(r) is approximated by the use of the analytic solution of the Percus-Yevick (PY) equation for hard sphere (HS), namely $B(r) = B_{PY}(r, \eta)$ [18]. The packing fraction $\eta = \eta(\beta, \rho)$ is variationally determined by minimising the VMHNC configurational free energy at a temperature T, as

$$\frac{\partial fVMHNC(\beta, \rho, \eta)}{\partial \eta} = 0 \tag{12}$$

3. Results and discussion

The rare–earth metals were investigated in thermodynamic states just above the melting point. The thermodynamic states studied in this work specified by the temperatures and number densities taken from Waseda [25] are given in Table 1. In order to calculate the pair potentials, we shall use a couple of sets of Z and r_c values [10, 15]. First, Z_{eff}, r_c values for liquid La, Ce, Pr and Nd based on OCP are used in our simple metal calculations. The second data set for MH potentials are from Karmakar and Joarder [15]. In Table 1, r_c^{KJ} shows the r_c values for MH potentials which are generally determined by fitting to some physical properties of the system of interest: for example, bulk modulus or structural data. As we are interest in a study of structures, r_c values are taken from [15, 5]. Following Singh et al. [15, 26] and Karmakar, d-state radius is taken equal to that for lanthanum (r_d=1.286 a.u) (in solid state) for all members of the series.

Table 1. Input parameters for effective pair potentials of 4f liquid metals.

Metal	T(°K)	ρ(atoms/Å^3)	Z_{eff}	r_c(a.u.)	Z_s	Z_f	Z_d	N_c	r_c^{KJ}(a.u.)	r_f(a.u.)
La	1243	0.0258	1.12	1.787	2	0	1	12	1.98	1.12
Ce	1143	0.0287	1.05	1.726	2	1	1	12	1.99	1.10
Pr	1223	0.0283	1.13	1.734	-	-	-	-	-	-
Nd	1323	0.0289	1.2	1.721	-	-	-	-	-	-
Eu	1103	0.0183	-	-	2	7	1	8	2.22	1.19
Gd	1603	0.0265	-	-	2	8	1	12	1.97	1.17
Tb	1653	0.0274	-	-	2	9	1	12	1.94	1.16

3.1. Effective pair potentials

First we consider the interatomic pair potential $\phi(r)$ for liquid rare – earth metals, using a standard pseudopotential theory with EC pseudopotential. We have used the Z_{eff} values as given by Yokoyama et al. [15] estimated from OCP. The value of r_c was determined from the position of the first node of EC pseudopotential in q space, namely q_o. The calculated PW pair potentials $\phi(r)$ using EC pseudopotential are shown in Fig. 1.

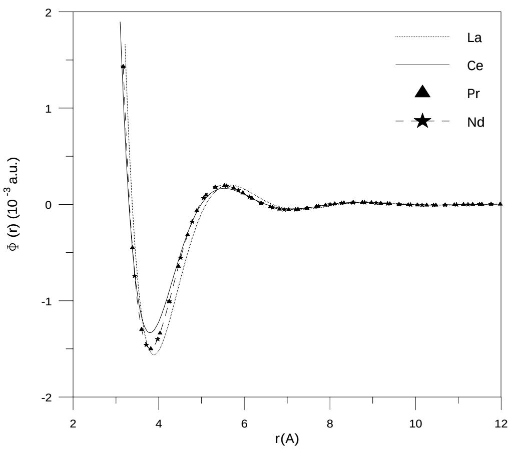

Fig. 1. PW pair potentials $\phi(r)$ for liquid La, Ce, Pr and Nd near the melting point.

It is seen in Fig. 1 that the minimum of the $\phi(r)$ gets deeper and repulsive part of the $\phi(r)$ gets harder when the atomic number changes from Ce to Nd but the size of the ion-core remains almost unchanged. The core size of La is the largest one. We agree with others [15], the 5d electron is responsible for this. We should say that the repulsive part of the potentials corresponds to the energies of the order of the mean kinetic energy $\left(E_{kin} = 3k_BT/2\right)$. In Fig. 2 we have also compared the pair potential of La which has been calculated using different commonly used local-field corrections G(q), as already mentioned.

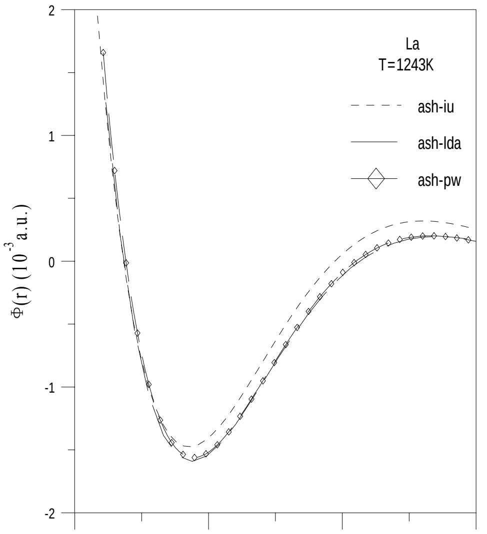

Fig. 2. Effective pair potential of La using different screening functions
iu – Ichimaru – Utsumi [21]; lda – local density approximation; pw – Pettifor and Ward [16].

It appears that the IU gives rise to a shallow potential well, while the others yield a deep potential well. PW and LDA forms almost the same which is observed for all rare-earth metals with more marked difference as we go toward the heaviest metals. The calculated modified Harrison model potentials with the EC electron-ion potential for s contribution, using the PW dielectric screening function are shown in Fig. 3. The depth of the MH model potential is larger than those obtained by standard pseudopotential theory. The MH potential is sum of three distinct contributions s electron like term and attractive potential proportional to both the d-band and f-band width; and a repulsive potential arising from the shift of the centre of gravity of both the d-band and f-band. The last term are responsible for the fairly hard repulsive behaviour of $\phi(r)$ and for the rather flat bottom in the first minimum. It has been noted that the s electron contribution affects the attractive part of the MH model effective potential most and Friedel oscillations are observed at large r region as in simple metals. Fig. 3 shows that the depth of the potential is larger and core diameter affected is mostly in the middle of the series. It may be said that the hardness of the repulsive part of $\phi(r)$ is very sensitive to variations of $r_{c.}$ We should say some improvements can be made by increasing the value of $r_{c,}$ thus shifting the position of the well and making it shallower.

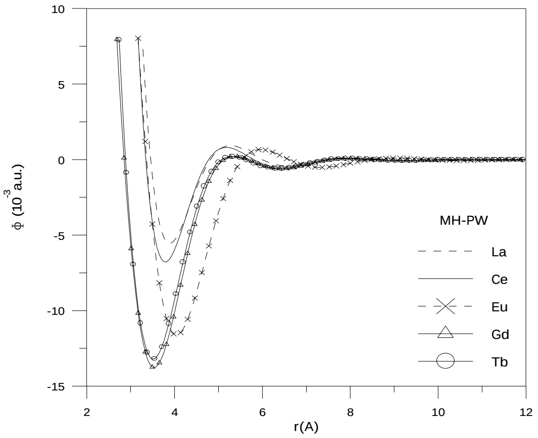

Fig. 3. MH potentials for liquid rare-earth metals using PW pair potentials for s contribution..

We have shown the effect of s contribution to the effective pair potential in Fig. 4, for liquid Eu. Fig. 4 shows that the effective pair potential of Eu shows one additional positive minimum at short distances where is observed by others [10]. It shows still solid state character so that the parameters used in the calculations for d or f state contributions are based on solid state properties. Another important point is that, the total MH pair interaction is considerably stronger than a typical simple – metal pair potential. That means the depth of the MH potentials is larger than k_BT .

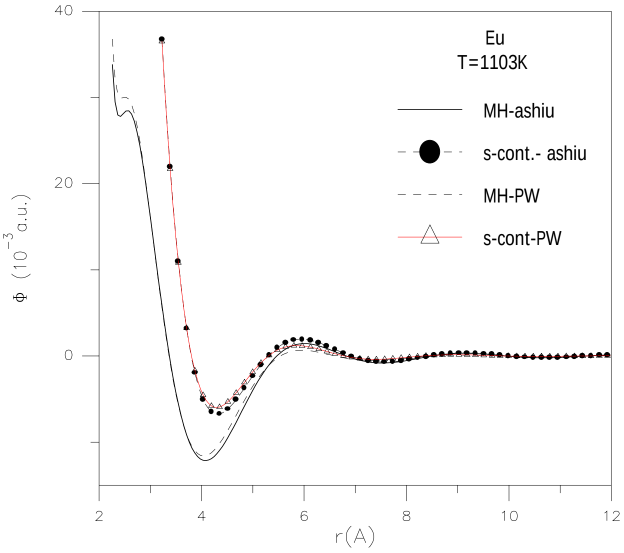

Fig. 4. The effective pair potential of liquid Eu using different screening functions.

3.2. Structure factors and pair distribution functions

The VMHNC approximation is employed to calculate the liquid state structure factors S(q) and pair distribution functions g(r). The calculated results using PW pair potentials in Figure 1 are shown in Figs. 5 and 6 along with experimental data of x-ray diffraction [25]. In our calculations, for the numerical solution of the Ornstein-Zernike equation (10) and the closure relation (11) we have used Zerah's algorithm [27]. In all cases we use 2048 points with a step size $\Delta r = 0.0523$ Å.

As can be seen from these figures, both S(q) and g(r) are rather well described by these potentials, namely PW pair potentials for s-p bonded metals. There are some discrepancies in detail, such as the second peak region in S(q) and distinct Friedel oscillations in large q region are less than experimental data [25] and those obtained by others [15]. The positions of the second peak of S(q) have shifted to the left relative to those of the experimental data. It is seen that the calculated values, both S(q) and g(r), correctly reproduce the position of the experimental first peak for all systems but the peak values are larger than that of the experimental data in La, Ce, and Nd, except Pr. We believe that Z_{eff} increases the height of the peaks of g(r) without altering their positions.

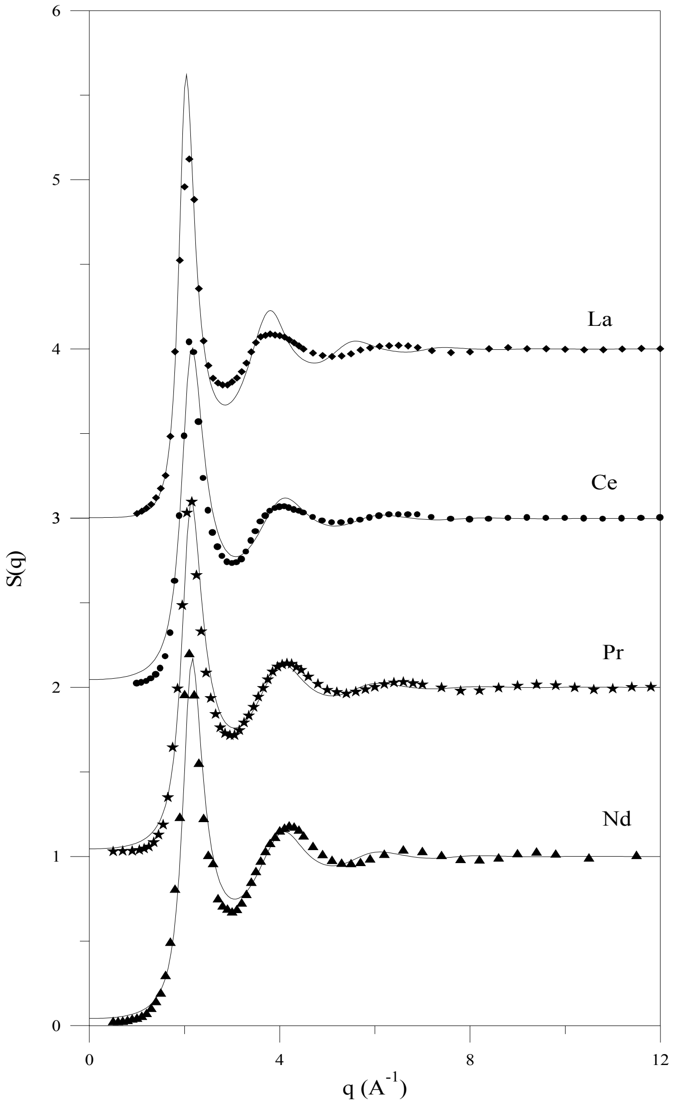

Fig. 5. Structure factors S(q): ♦,●, , ▲ experimental data, —— PW-VMHNC

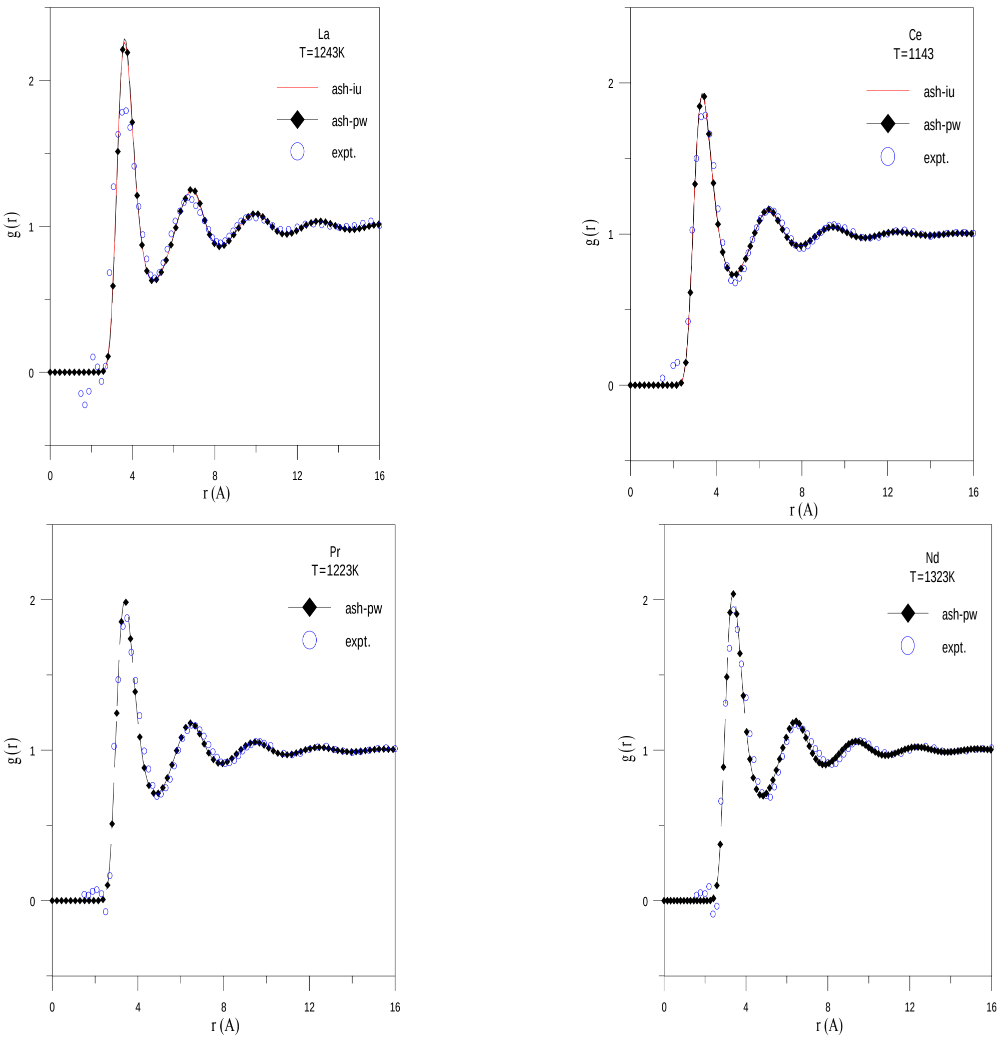

Fig. 6. Pair distribution functions g(r) for liquid La, Ce, Pr and Nd using simple metal theory.

In Fig. 7 we have shown the calculated S(0) values using PW potentials in conjunction with VMHNC comparing with the values those obtained by Yokoyama et al. [15] and experimental data. A very good agreement is found, except La. As seen in Fig. 7 the S(0) values increase with temperature and across the lanthanide series.

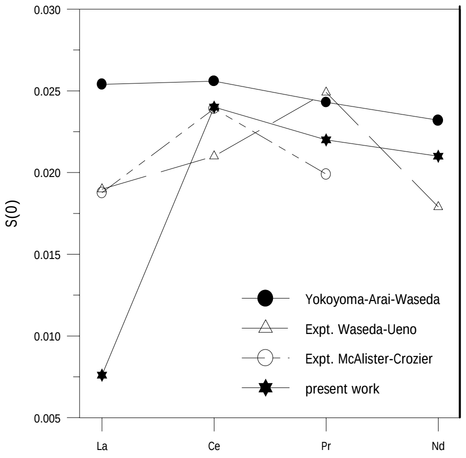

Fig. 7. The long-wavelength limit of the static structure factors of some lanthanides.

4. Conclusions

In this paper, we have calculated PW and MH pair potentials for some liquid rare-earth metals. We have analysed the structure of some liquid lanthanide's using the VMHNC liquid state theory. We have also checked the validity of VMHNC in structural calculations using PW and MH potentials. A good agreement of our calculated structural properties (the isothermal compressibility, static structure factor S(q) and the pair distribution function g(r)) shows that PW potentials using standard pseudopotential theory can be applicable for other liquid rare-earth metals namely actinides. This work will progress on this line. On the other hand, it has been noted that regardless of the parametrization used the VMHNC theory which has previously proven to be successful for simple liquids and alkali metals, transition metals, always converges the solution. However our results show that VMHNC fails to describe the structural properties of lantanide's using MH potentials if one uses the Karmakar's data set. It needs improvement for quantitave results for structure. This work is in progress.

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