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Structure studies of alkaline-earth metals: evaluation through the charged hard sphere approximation

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The present article deals with the liquid alkaline-earth metals are treated as a system of Coulombically interacting charged hard spheres (CHS) in the background of conduction electrons. The structure factor is evaluated on the basis of the linear scattering optimization approximation by considering the weak coupling of the valance electrons to the ions. To describe electron-ion interaction, it is used the well known Ashcroft's empty core (EMC) single parametric model potential along with the most recent local field correction function due to Sarkar et al. Qualitative agreement between presently computed data and experimental findings is established.

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1. Introduction

The static structure factor $S(q)$ is one of the principal properties characterizing a metal in its liquid state, which is a measure of the particle correlation in reciprocal space. The charged hard sphere (CHS) model is very useful to evaluate the structure factor of metals in the liquid state [1-8]. Such a system of the CHS in a uniform background of the electrons has been solved exactly in a mean spherical approximation by Palmer and Weeks [5]. According to the CHS model the reference system consists with coulombian interaction positively charged point charges in a uniform background of conduction electrons. Though the CHS method is proved very useful for explaining structural properties of the liquid metals, the study of liquid alkaline-earth metals using the CHS is very limited [3]. Rao and Bandyopadhyay [3] have reported the structure factor $S(q)$, radial distribution function $g(r)$ and interatomic distance r_1 of nearest neighbour atoms for liquid alkaline-earth metals by employing CHS reference fluid with Ashcroft empty core model potential [9]. Recently Thakore et al. [6] have been reported the structural studies of various liquid metals. The present article deals with the structural studies of liquid alkaline-earth metals, which reports the structure factor $S(q)$, radial distribution function $g(r)$ and interatomic distance r_1 of nearest neighbour atoms for liquid alkaline-earth metals viz. Ba, Sr and Ca. The important aspect of the present investigation is to use the most recent local field correction function of Sarkar et al. [10].

2. Computational methodology

The charged hard sphere (CHS) model was studied within the framework of mean spherical approximation inside the core and outside the core, a perturbation in the form of Coulomb interaction is assumed to act by Palmer and Weeks [5]. In the CHS approximation, the direct correlation function is given by [3, 4, 6]

$$C_0(r) = A + B\left(\frac{r}{\sigma}\right) + C\left(\frac{r}{\sigma}\right)^2 + D\left(\frac{r}{\sigma}\right)^3 + E\left(\frac{r}{\sigma}\right)^5 \qquad r < \sigma,$$
$$= -\frac{\gamma}{\left(\frac{r}{\sigma}\right)} \qquad r > \sigma. \tag{1}$$

The coefficients involved in equation (1) are given by,

$$A = -\frac{(1+2\eta)^2}{(1-\eta)^4} + \frac{Q^2}{4(1-\eta)^2} - \frac{(1-\eta)QK}{12\eta} - \frac{(5+\eta^2)^2}{60\eta}. \tag{2}$$

$$B = 6\eta M^2 \tag{3}$$

$$C = \frac{K^2}{6} \tag{4}$$

$$D = \left(\frac{\eta}{2}\right)\left(A - K^2 U\right) \tag{5}$$

and

$$E = \frac{\eta K^2}{60} \tag{6}$$

with

$$Q = \frac{(1+2\eta)}{(1-\eta)}\left[1-\left\{\frac{1+2(1-\eta)^3 K}{(1+2\eta)^2}\right\}^{1/2}\right], \qquad (7)$$

$$M = \frac{Q^2}{24\eta} - \frac{(1+0.5\eta)}{(1-\eta)^2}, \qquad (8)$$

$$U = \frac{\left(1+\eta-\dfrac{\eta^2}{5}\right)}{12\eta} - \frac{(1-\eta)Q}{12\eta K}, \qquad (9)$$

$$\gamma = \beta\frac{(Ze)^2}{\varepsilon_O \sigma}, \qquad (10)$$

$$K = (24\eta\gamma)^{1/2}, \qquad (11)$$

and

$$\eta = \left(\frac{\pi}{6}\right)\rho\sigma^3. \qquad (12)$$

Where, γ, K and η are the dimensionless variables, which are representing the Coulomb interaction potential, the inverse screening length due to the Debye-Huckel and packing fraction, respectively. Here, σ is charged hard sphere diameter, Ze the ionic charge, $\beta = 1/k_B T$, k_B is the Boltzmann constant, T the absolute temperature of the system, ε_O the dielectric constant of the medium. Since the electron background is uniform, its dielectric constant is unity.

The static structure factor $S_O(q)$ of the present CHS reference system is related to its direct correlation function in the following form [3, 4, 6].

$$S_O(q) = \frac{1}{[1-\rho C_O(q)]}. \qquad (13)$$

The mathematical expression for $\rho C_O(q)$ is given by [3, 4, 6]

$$\begin{aligned}\rho C_0(q) = \left(\frac{24\eta}{q^6}\right)\Big[& Aq^3(\sin q - q\cos q) \\ & + Bq^2\left\{2q\sin q - (q^2-2)\cos q - 2\right\} \\ & + Cq\left\{(3q^2-6)\sin q - (q^2-6)\right\} \\ & + D\left\{(4q^2-24)q\sin q - (q^4-12q^2+24)\cos q + 24\right\} \\ & + E\left\{6(q^4-20q^2+120)q\sin q - (q^6-30q^4+360q^2-720)\cos q - 720\right\}/q^2 \\ & - \gamma q^4\cos q\Big]\end{aligned} \qquad (14)$$

Here q is expressed in units of σ^{-1}.

The effect of responding electrons on the ionic motion is taken into account by assuming weak coupling between valence electrons and ions which is also the basis of standard pseudopotential approach. Within a linear screening approximation, the structure factor of a liquid metal is given by [3, 4, 6]

$$S(q) = \frac{S_O(q)}{\left[1+\rho\beta\bar{V}(q)S_O(q)\right]}, \qquad (15)$$

with,

$$\bar{V}(q) = \left[\frac{W_B{}^2(q)}{\phi(q)}\right]\left[\frac{1}{\varepsilon(q)}-1\right], \qquad (16)$$

is the attractive screening correlation to the direct ion-ion potential. $\Phi(q) = \dfrac{4\pi e^2}{q^2}$ is the Fourier transform of bare Coulombic interaction between two electrons and $W_B(q)$ the bare ion pseudopotential. $\varepsilon(q)$ be the modified dielectric function.

$$\varepsilon(q) = 1 + [1-f(q)][\varepsilon_H(q)-1]. \qquad (17)$$

$\varepsilon_H(q)$ is the static Hatree dielectric function represented by

$$\varepsilon_H(q) = 1 + \frac{me^2}{2\pi h^2 k_F Y^2}\left[1+\frac{(1-Y^2)}{2Y}\ln\left|\frac{1+Y}{1-Y}\right|\right], \qquad (18)$$

where, m is the ionic mass, h the Planck's constant, k_F the Fermi wave vector, e the electronic charge and $Y = \dfrac{q}{2k_F}$.

Here we use the well known Ashcroft's empty core (EMC) single parametric model potential [9] is of the form

$$W_B(q) = \frac{-8\pi Z}{\Omega_O q^2}\cos(qr_C). \qquad (19)$$

where, Z, Ω_O and r_C are the valence, atomic volume and parameter of the model potential of metals, respectively. The model potential parameter r_C is expected to be close to the actual ionic radius given by Pauling [11].

The most recent local field correction $f(q)$ due to Sarkar et al. [10] is used to incorporate the exchange and correlation among the conduction electrons in the dielectric screening.

$$f(q)=A_S\left\{1-\left(1+B_S\left(\frac{q}{k_F}\right)^4\right)\exp\left(-C_S\left(\frac{q}{k_F}\right)^2\right)\right\}. \quad (20)$$

Sarkar et al. [10] have recently proposed local field correction function using the quantum Monte Carlo data of Ceperley-Alder for the correlation energy of electron gas in both the "para" and "ferro" states, in the given density range. The details of the constants A_S, B_S and C_S are discussed in the respective paper [10].

The expression for the radial distribution function $g(r)$ is given by [3, 6]

$$g(r)=1+\left(\frac{1}{2\pi^2\rho r}\right)\int_0^\infty q\,\{S(q)-1\}\sin(qr)\,dq\,. \quad (21)$$

Using this radial distribution function $g(r)$, we obtain the interatomic distance r_1 of the nearest neighbour atoms. The interatomic distance r_1 corresponds to the maximum peak of $g(r)$ curve.

3. Results and discussion

The constants and parameters used in the present computations of the structure factor $S(q)$, radial distribution function $g(r)$ and interatomic distance r_1 of nearest neighbour atoms for liquid alkaline-earth metals viz. Ba, Sr and Ca are taken from Rao and Bandyopadhyay [3].

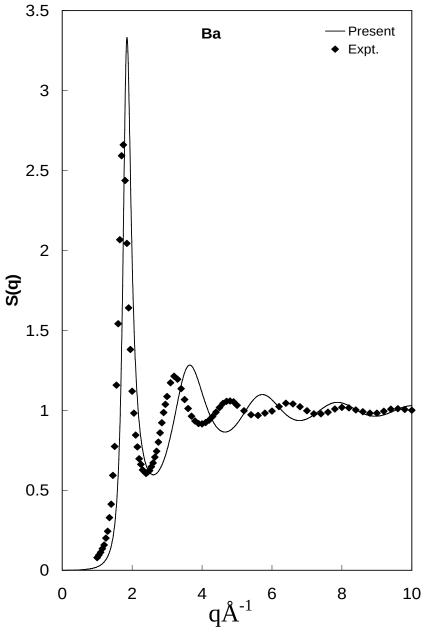

Fig. 1. Structure factor $S(q)$ *for Ba.*

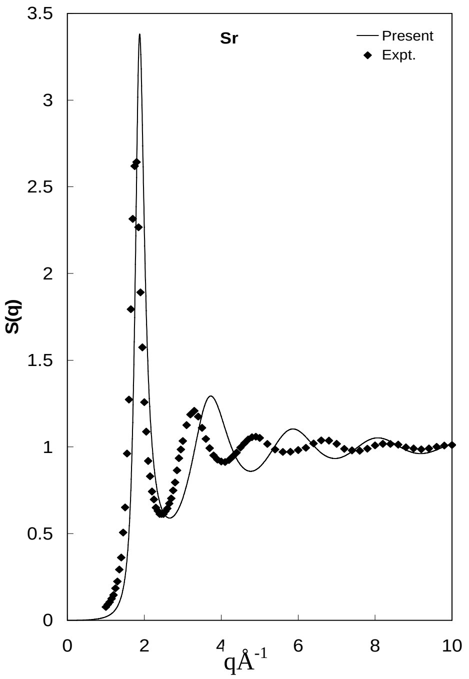

Fig. 2. Structure factor $S(q)$ *for Sr.*

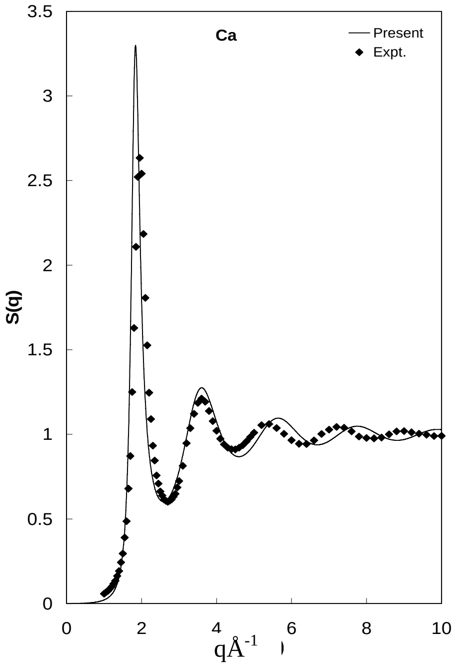

Fig. 3. Structure factor $S(q)$ *for Ca.*

The structural feature of the Ba, Sr and Ca liquid alkaline-earth metals are furnished in Figs. 1-3. These results have been compared with those obtained by Waseda [12, 13] experimentally and Rao and Bandyopadhyay [3] theoretically. All the results are tabulated in Table 1. The radial features have been plotted in Figs. 4-6.

Table 1. Position of first and second peak in $S(q)$, $g(r)$ *(Å^{-1}) and interatomic distance (* r_1 *) (Å).*

Metal	Peak positions in $S(q)$ (Å^{-1})						Interatomic distance r_1 (Å)		
	First			Second					
	Present	Others [3]	Expt. [12]	Present	Others [3]	Expt. [12]	Present	Others [3]	Expt. [13]
Ba	1.850	1.750	1.750	3.650	3.500	3.200	4.18	4.0	4.30
Sr	1.880	1.850	1.800	3.730	3.650	3.300	3.92	3.8	4.20
Ca	1.840	1.950	1.950	3.750	3.850	3.600	3.76	3.7	3.80

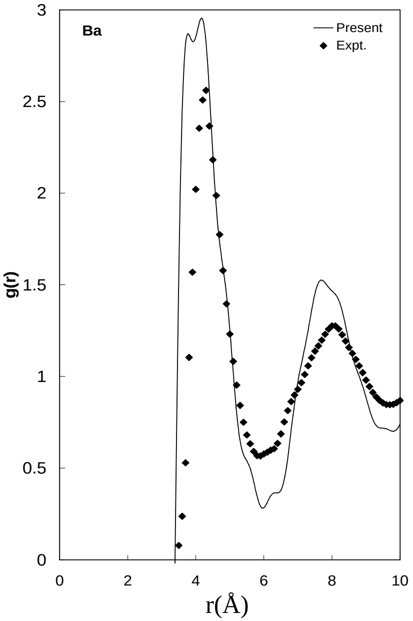

Fig. 4. Radial distribution function $g(r)$ *for Ba.*

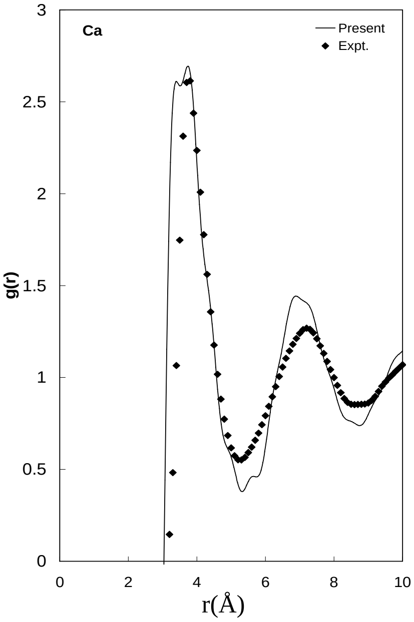

Fig. 6. Radial distribution function $g(r)$ *for Ca.*

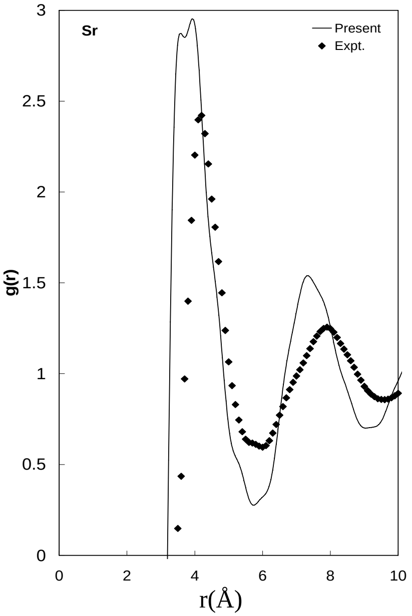

Fig. 5. Radial distribution function $g(r)$ *for Sr.*

The overall agreement with the theoretical and experimental data, considering the simplicity of the model, is quite encouraging. Further in this approximation the hard sphere diameter σ is the only adjustable parameter which is treated as a “free parameter” as was done by Singh and Holtz [4]. All the other coefficients and parameters are related to it.

In the present paper we follow the fitting procedure of the hard sphere diameter σ of Rao and Bandyopadhyay [3]. They have noted that, initially, the hard sphere diameter σ is equal to that given by Pauling [11]. Then it was varied in small steps. But, possible fit is obtained for the hard sphere diameter σ , which is slightly grater than the Pauling value.

From the Figs. 1-6, we observe that the agreement is particularly good in the low q-region and near the principal peak. This region is of vital importance in determining the transport properties of liquid metals [3]. It may farther seen from Figs. 1-3 that even though there is good agreement near first peak position, there is divergence near the second peak more so in the case of ‘Sr’ while the disagreement is lesser in the case of ‘Ca’. The height is, however, well matched in all the three cases.

In the case of radial distribution function $g(r)$, the distortions are found in the first peak and second minima may be due to the topological disorder of the atoms in the liquid states of the metallic elements. The present results of the radial distribution function $g(r)$ for Ba, Sr and Ca liquid alkaline-earth metals are found qualitative agreement with the experimental data [12, 13].

Thus, the charged hard sphere (CHS) method based on the one component plasma approximation can be utilized successfully to understand in a simple way the structure of liquid metals.

4. Conclusions

At the end we conclude that, Ashcroft's empty core (EMC) single parametric model potential is useful in deriving the properties of liquid metals belonging to the second group (IIA) of the periodic table. Also, the effect of the most recent local field correction function due to Sarkar et al. is found successful. Hence the reported data are more meaningful and will provide better source for further comparison either with theoretical or experimental data, which conforms the applicability of EMC model potential and CHS method for predicting the structural studies of the liquid metals.

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