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COMPARATIVE STUDIES OF STRUCTURE FACTORS OF SOME SIMPLE LIQUID ALKALI METALS

Abstract

In the present work, the comparison of the structure factors produced by using four different theoretical models based on the One-Component Plasma (OCP), Optimized Random Phase Approximation (ORPA), Generalized Mean Spherical Approximation (GMSA) and Perckus-Yevick (PY) models for liquid alkali metals viz. Li, Na, K, Rb and Cs are carried out. The empty core (EMC) model pseudopotential of Ashcroft is used with Taylor (TY) screening function in the present computation of the structure factor. The comparison of the various theoretical models of the structure factor are found consistent with each other and show good agreement with experimental data of the structure factor.

Keywords: *liquid alkali metals, Structure factor, Perckus-Yevick Hard Sphere (PYHS) method, One component Plasma (OCP) method, Generalized mean spherical approximation (GMSA) method, Optimized random phase approximation (ORPA) method reference systems.*

1. Introduction

Amid the most recent couple of decades, there has been an enthusiasm for the examination of auxiliary properties of liquid metals utilizing distinctive models as reference frameworks. Perckus-Yevick hard sphere (PYHS)(Patel et al. 2015; A. M. Vora 2007, R. C. Malan and A. M. Vora 2018), one component plasma (OCP) (Bretonnet and Regnaut 1985; Thakor, Sonvane, and Jani 2011), genralized mean spherical approximation (GMSA) (Arai, Naito, and Yokoyama 1993; Waisman and Lebowitz 1972, M. H. Jani and A. M. Vora 2018, M. H. Jani and A. M. Vora 2017), hard sphere Yukawa (HSY)(Denton, Kahl, and Hafner 1999; Ginoza and Yasutomi 1999), soft sphere (SS)(Badirkhan et al. 1992; Ross 1979), optimized random phase approximation (ORPA)(Akinlade, Badirkhan, and Pastore 2000; Senatore and Tosi n.d.), charged hard sphere (CHS)(Baria 2003; Thakor, Gajjar, and Jani 2002), mean spherical approximation (MSA) (Kalyuzhnyi, Cummings, and Cummings 2006) are some of the methods to calculate the structure factor of liquids. With due all earlier attempts and interfaces , in the present paper we have represented four reference systems, i.e. PYHS, GMSA, OCP and ORPA are employed to investigate the structure factor of some simple liquid alkali metals viz., Li, Na, K, Rb and Cs. The structure factor is one of the most important properties to study the various electronic, magnetic, static and dynamic properties of material in liquid states. Therefore, one has to know very precisely the arrangement of atoms and ions. For this reason, the knowledge of the structure factor is the most essential part. The structure factor is a measurement of particle correlations in the reciprocal space and from the graphical presentation one can answer the question, what structural feature changes as material passes through a transition. Hence, accurate knowledge of this quantity is vital for studying numerous properties of liquid metals. The structure of liquid metals can be easily understood with the help of the model of a mixture of hard spheres. It is also possible to study the structure of a liquid metal in terms of the electron-electron, electron-ion and ion-ion structure factors by treating the liquid metal as a two-component, i.e. ion and electron fluid based on the perturbation theory employing pseudopotential.

To incorporate the electron-ion interaction, well established model pseudopotential of Ashcroft is used. The form of the model potential in real space is given by (Foiles, Ashcroft, and Reatto 1984)

$$\bar{V}(q) = \frac{-4\pi Z e^2}{q^2} cosqr_c$$

Here $Z, e\ \Omega, q$ and r_c are the valency, electronic charge, atomic volume, wave vector and the parameter of potential respectively.

2. Theory

The hard-sphere reference system is largely justified because it provides analytical representation in terms of a single parameter, σ, known as hard-sphere diameter, and reproduces the basic profile of the structure of liquid metals.

The Structure factor $S_{PYHS}(q)$ due to PYHS model is given by (Thakor, Sonvane, and Jani 2009)

$$S_{PYHS}(q) = [1 + \frac{24\eta}{(1-\eta)^4 y^6}((1+2\eta)^2 y^3(siny - cosy) - 6\eta\left(1+\frac{\eta}{2}\right)^2 y^2[2ysiny - (y^2-2)] + \frac{\eta}{2}(1+2\eta)^2[(4y^3-24y)siny - (y^4-12y^2+24)cosy + 24])]^{-1}$$

With $y = q\sigma$

The OCP reference system is an ideal system of point like charges moving in a neutralizing uniform background of opposite charges. An equilibrium state of the OCP system with the number density ρ and the temperature T may be characterized by a dimension less plasma parameter $\Gamma = (Ze)^2/(ak_BT)$, which measures the ratio between the average potential energy and the average kinetic energy per particle, where Ze is the charge of an ion and $a = [3/4\pi\rho]^{1/3}$ represents the ion-sphere radius whose volume equals to the volume per electron.
If the assumption is made that ionic liquid and electron gas are weakly coupled to each other through pseudopotential as in the liquid metals, the electron gas screening can be taken in to account by employing the random phase approximation. In the OCP system the structure factor $S_{OCP}(q)$ is given by (Bretonnet and Regnaut 1985; Khanna and Bretonnet 1986; Thakor et al. 2011)

$$S_{OCP}(q) = \frac{S_O^{OCP}(q)}{1 + \rho\beta u^*(q) S_O^{OCP}(q)}$$

In this equation, $\rho = 1/\Omega$ is the number density, $\beta = 1/(k_BT)$, where k_B and T are the Boltzman constant and temperature of the system, respectively $S_O^{OCP}(q)$ is the static structure factor of the bare OCP reference system (Thakor, Sonvane, and Jani 2011) with the screening function of Taylor(Taylor 1978)

For the GMSA due to Waisman(Arai, Arisawa, and Yokoyama 1999), the Fourier transform of the direct correlation function, $C(q)$, is given by

$$\rho C(y) = -\frac{24\eta}{y^6}\Big\{ay^3[siny - ycosy] + by^2[2ysiny - \{y^2-2\}\times cosy - 2] + \frac{a\eta}{2}[\{4y^3-24y\}siny - \{y^4-12y^2+24\}cosy + 24] + \frac{v}{z}y^5\left[\frac{1-cosy}{y} + \frac{(zsiny + ycosy)e^{-z} - y}{z^2+y^2}\right] + \frac{v^2y^5}{2Kz^2e^z}\left[\frac{(zsinhz)siny - (ycoshz)cosy + y}{z^2+y^2} - \frac{1-cosy}{y}\right] - \frac{Ky^5}{z^2+y^2}(zsiny + ycosy)\Big\}$$

here, $y = q\sigma$

where the coefficients a, K , v, z and b are all density dependent and must be numerically determined by thermodynamic requirements. However, the procedure employed by Waisman (Waisman and Lebowitz 1972) is considerably difficult to solve the simultaneous algebraic equations. The detailed simplification of the equations were described by Arai *et al.* (Arai, Naito, and Yokoyama 1993). Since the structure factor $S(y)$ is given by,

$$S(y) = \frac{1}{1 - \rho C(y)}$$

For, the ORPA due to Senatore (Senatore and Tosi n.d.)the structure factor of these liquid metals provide good first order solution of these approach. The linear screening theory leads to the following equation for the Fourier transform of the effective ion-ion potential in the liquid alkali metal

$$V(q) = \frac{4\pi e^2}{q^2} + \check{v}(q)$$

The first term in this equation represent ion-ion Coulomb repulsion, which is the OCP structure, while the screening correction $\check{v}(q)$ is given by

$$\check{v}(q) = \frac{\bar{V}(q)}{4\pi e^2/q^2}\left[\frac{1}{\epsilon(q)} - 1\right]$$

in terms of bare electron ion pseudopotential $\bar{V}(q)$ and of dielectric function $\epsilon(q)$ of electron gas. The term $\check{v}(q)$ generates a purely attractive interaction between the ions. The only source of repulsive interionic forces is such an approach is thus the bare Coulomb term. The following expression derived by linear screening theory for the structure factor $S(q)$ of the liquid metal.

$$S(q) = \frac{S_0(q)}{\left[1 + \frac{\rho\check{v}(q)}{k_B T} S_0(q)\right]}$$

where, $S_0(q)$ is the structure factor for the OCP. In the common language of liquid structure theory this equation can be seen as combining with OCP with Optimized random phase approximation (ORPA) on the attractive screening correction $\rho\check{v}(q)$. This system is appropriate and accurate in the small angle scattering region.

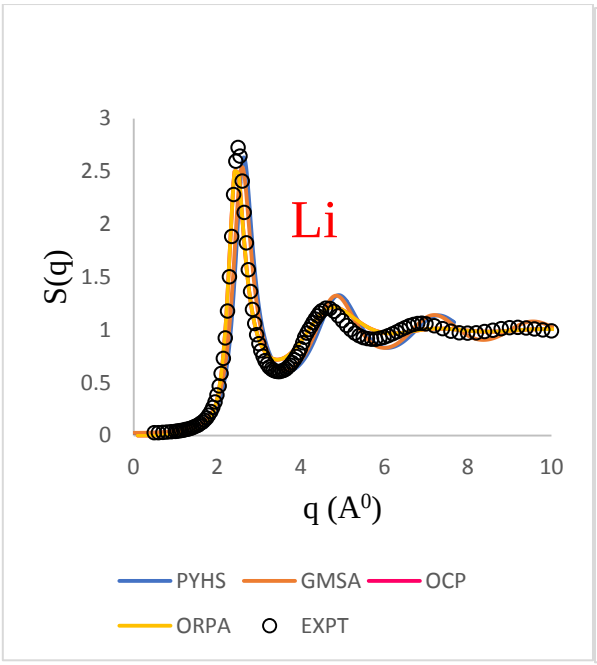
3. Results and Discussion

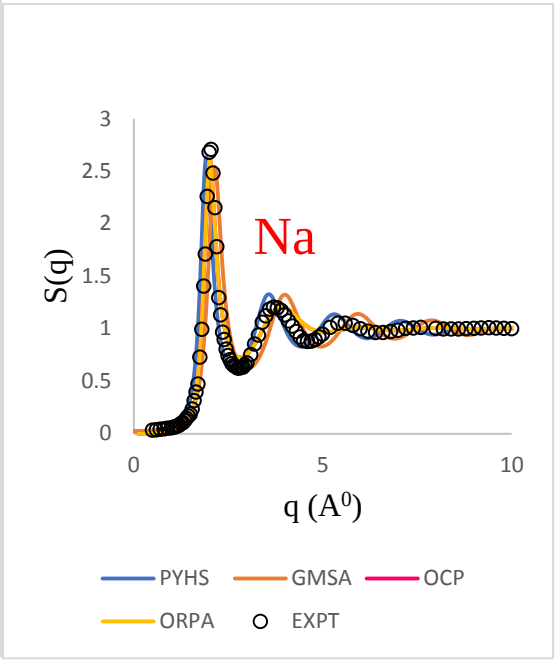
In the present article an attempt has been made to perform a detailed study of the comparison and analysis of peak positions of some simple liquid metals: Li, Na, K, Rb, and Cs at melting temperatures. The input parameters used to investigate the comparison and calculation of the structure factor of liquid metals are tabulated in Table. 1. The plasma parameter Γ have been chosen in such a way that the result due to the OCP reference system are obtained in good agreement with the experimental results (A. M. Vora 2008).

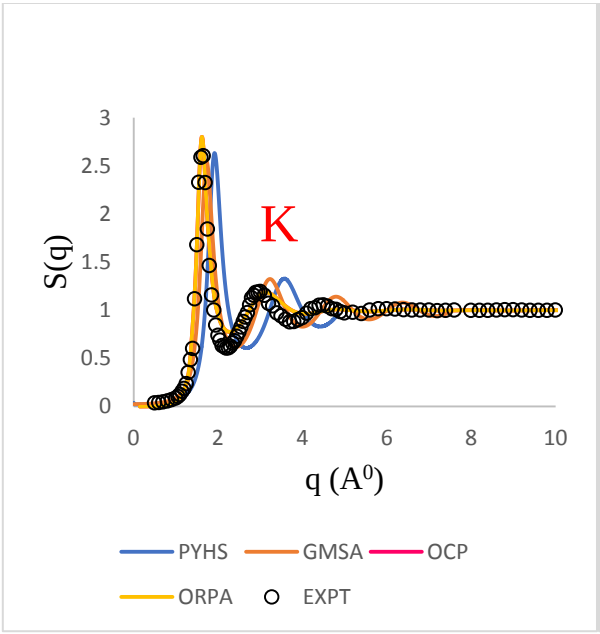
Table. 1 Input parameters and constants used to obtain the structure factor

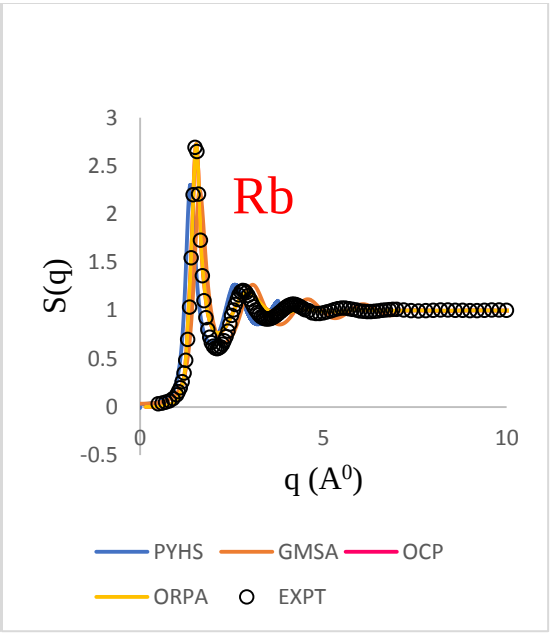
Metal	Z	Ω (au)	T (K)	η	Γ
Li	1	151.82	453	0.46	210.62
Na	1	277.52	378	0.46	206.45
K	1	529.63	343	0.46	183.35
Rb	1	648.68	313	0.43	187.86
Cs	1	810.06	303	0.43	180.21

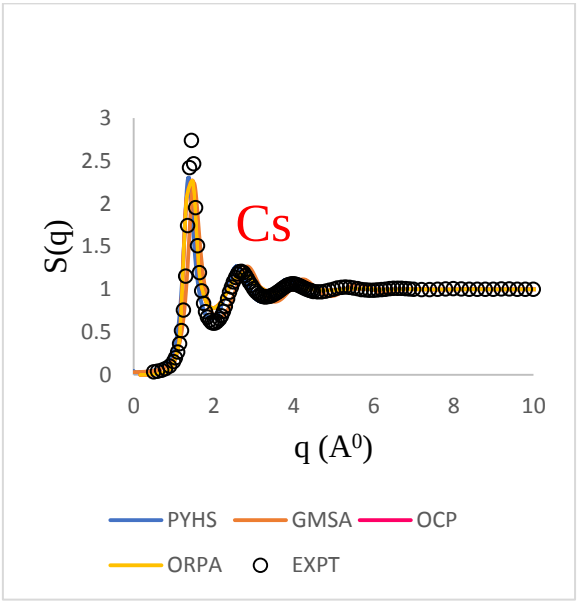
The comparison for the structure factors from different reference systems for liquid metals: Li, Na, K, Rb and Cs are plotted in Figs. 1-5 respectively.


Li
S(q)
q (A0)
PYHS
GMSA
OCP
ORPA
EXPT


Na
S(q)
q (A0)
PYHS
GMSA
OCP
ORPA
EXPT


K
S(q)
q (A0)
PYHS
GMSA
OCP
ORPA
EXPT


Rb
S(q)
q (A0)
PYHS
GMSA
OCP
ORPA
EXPT


Cs
S(q)
q (A0)
PYHS
GMSA
OCP
ORPA
EXPT

Tables 2, 3 and 4 represents the first peak positions, second peak positions and (q_2/q_1) ratio of the structure factor $S(q)$.

Table. 2 First Peak position and Related magnitude in $S(q)$

Metal	First Peak position and Related magnitude in *S(q)*									
	Peak position q_1 in $(A^0)^{-1}$					Related magnitude				
	PYHS	OCP	GMSA	ORPA	EXP.	PYHS	OCP	GMSA	ORPA	EXP.
Li	2.67	2.51	2.60	2.50	2.50	2.61	2.48	2.54	2.47	2.72
Na	1.92	2.01	2.15	2.02	2.05	2.63	2.62	2.54	2.62	2.70
K	1.94	1.61	1.75	1.61	1.65	2.61	2.79	2.51	2.79	2.60
Rb	1.36	1.53	1.62	1.57	1.5	2.24	2.73	2.20	2.64	2.69
Cs	1.36	1.48	1.47	1.48	1.45	2.29	2.26	2.25	2.26	2.73

Table. 3 Second Peak position and Related magnitude in $S(q)$

Metal	Second Peak position and Related magnitude in S(q)									
	Peak position q_2 in (A^0)-1					Related magnitude				
	PYHS	OCP	GMSA	ORPA	EXP.	PYHS	OCP	GMSA	ORPA	EXP.
Li	4.94	4.8	4.91	4.81	4.6	1.31	1.17	1.32	1.17	1.20
Na	3.57	3.85	3.9	3.8	3.70	1.33	1.19	1.32	1.17	1.20
K	3.64	3.1	3.28	3.12	3.0	1.31	1.55	1.32	1.57	1.19
Rb	2.60	2.85	3.08	2.9	2.75	1.27	1.20	1.27	1.18	1.19
Cs	2.61	2.65	2.87	2.64	2.65	1.27	1.20	1.26	1.21	1.20

Table. 4 The ratio (q_2/q_1) of structure factor $S(q)$.

Metal	PYHS	OCP	GMSA	ORPA	EXP.
Li	1.85	1.91	1.88	1.92	1.84
Na	1.86	1.91	1.93	1.88	1.80
K	1.87	1.92	1.87	1.93	1.81
Rb	1.91	1.86	1.90	1.84	1.83
Cs	1.91	1.79	1.95	1.82	1.82

It is seen from the structure factor from different reference systems that ORPA method are in much agreement with the experimental data in comparison with the PYHS, GMSA and OCP. The discrepancy in the outcome of ORPA with experimental observations is found higher than those PYHS and GMSA. Then the structure of monovalent metals is better described by the PYHS and GMSA than by the OCP reference system. Our study is lead to the conclusion that GMSA reference system is better than PYHS and OCP in explaining the structure of liquid metals. The results also confirm the use of Ashcroft empty core potential, in the aforementioned study.

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Mayank H. Jani
Department of Physics
University School of Sciences
Gujarat University
Ahmedabad

A. M. Vora
Department of Physics
University School of Sciences
Gujarat University
Ahmedabad