



# Studying structural properties of rubidium and cesium liquid metals using an effective hard-core Yukawa potential



Hossein Nikoofard<sup>\*</sup>, Leila Hajiashrafi

Faculty of Chemistry, Shahrood University, Shahrood 36199-95161, Iran

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## ABSTRACT

In this work, we investigate the applicability of a modification of the random phase approximation (RPA) theory with an effective hard-core Yukawa potential to the static structure factor for the rubidium and cesium liquid metals. Based upon the perturbation theory, we assume that the core contribution of the direct correlation function is related to the geometric effects via a linear form for a hard-sphere fluid, in which the molecular diameter is obtained at any temperature and, its tail contribution is related to the long-range intermolecular interactions of the system via a linear form. We use the long-range Yukawa potential in the modeling of liquid alkali metals (LAMs) with the decay parameter  $\lambda = 1.8$  and a well depth potential that is state-dependent. The linear isotherm regularity (LIR) equation of state (EOS) is applied to obtain the long-range interactions. The results obtained show that the proposed approach for LAMs can predict the behavior of the structure factor,  $S(k)$ , at a wide range of  $k$  values with a good accuracy, as compared to the experimental data, over the whole liquid states. The interaction model used is also successful in the presentation of the Ornstein–Zernike (OZ) behavior of  $S(k)$  at the low- $k$  region including the  $S(0)$  values.

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## 1. Introduction

Alkali metals, in the liquid state, are promising for both the fundamental and technological applications due to their physical and thermodynamic properties such as high heats of vaporization, extended liquid range, and thermal conductivities, which make them good heat transfer fluids in the reactors operating at high temperatures and at high energy rates, as high as nuclear power reactors. Liquid alkali metals (LAMs) are widely under investigation for use in the nuclear energy, emission electronics, new power-intensive chemical current sources, medicine, and a number of other fields [1–7]. These applications require having the knowledge of high-temperature thermodynamic and structural properties of LAMs. As the critical point is approached, the conductivity drops sharply, thus showing a metal–nonmetal transition. Near the critical point, LAMs gradually turn to insulators, and their thermodynamic behaviors would be different from those at low temperatures and high densities [8,9]. In this regard, a quantitative description of the structural properties of LAMs is an important subject in the

theory of condensed matter.

Alkali metals, in comparison with normal fluids, do not follow the law of corresponding state, in which the interactions between particles at the solid, liquid, and gaseous phases are supposed to have the same form. In fact, the interatomic interactions in these fluids are strongly dependent on the thermodynamic state of the system [10,11]. The structure of a solid metal is usually considered to be a collection of ions, fixed in a solid matrix, and thus creating an ionic lattice. A conclusion is that the valence electrons are delocalized over the lattice, and hence have little correlations with the core electrons [12]. For liquid densities near the melting point, the interatomic pair potentials of alkali metals are the same as those in the solid state, and may be described by the pseudo-potential obtained from the first-order perturbation theory based on the nearly free electron (NFE) model. This potential consists of a direct coulomb potential (repulsion) between the ions plus the attraction of each ion to the screening charge distribution induced by the pseudo-potential of the second ion [13,14]. This effective pair potential describes the interatomic potential and structure of the metals with a relatively high accuracy, only when the density of the fluid is more than twice the critical density [15]. For lower densities, the free electron belongs to its ion, and thus the NFE model fails to give a reasonable pair potential, especially near the critical point. In

<sup>\*</sup> Corresponding author.

E-mail address: [hnikoofard@shahroodut.ac.ir](mailto:hnikoofard@shahroodut.ac.ir) (H. Nikoofard).

these states, alkali metal fluids consist of neutral atoms, molecules, and some small clusters, and the interaction potentials between these atoms and molecules may be described, in some cases, by a simple potential without an oscillating tail [16,17]. With a further decrease in density in the gaseous phase, the fluid is in an atomic form, and the interactions between these atoms are van der Waals forces, and may be considered as the Lennard–Jones (LJ)-type pair potentials [17]. In fact, the interatomic interactions for alkali metals change from a screened columbic potential to the LJ-type interactions with decrease in density. Therefore, the interatomic interactions at moderate densities are very complex, and there is no theoretical method available to obtain them.

Fortunately, studies on the experimental structure factor,  $S(k)$ , of alkali metals provide an important source of information for the interatomic interactions. The structure factor at low- $k$  values is very sensitive to the intermolecular interactions at the long-range limit [18], whereas the short-range potential has a central role in the large  $k$  values [19]. In our previous works, using the linear isotherm regularity (LIR) equation of state (EOS), the accuracy and role of different parts of the effective pair potential functions have been extensively studied for nonmetal fluids [20,21]. However, a number of EOSs and different potential functions have been used to predict and reproduce the thermodynamic properties of ALMs [22–24]. Some of these attempts are restricted to a limited range of temperatures and pressures, and the low- $k$  values for  $S(k)$ , and the results obtained show different degrees of accuracy. In this work, based on a modification of the random phase approximation, we investigated the structural properties of the liquid alkali metals rubidium and cesium in term of the direct correlation function (DCF) and structure factor. The Yukawa potential function was used to model the long-range attractions. In our proposed approach, the contribution of all interactions was considered via a definition for the effective pair potential, whose intermolecular parameters vary with the thermodynamic states. Using the LIR equation of state, we evaluated the behavior of  $S(k)$  for rubidium and cesium over the whole liquid ranges within the temperature range of 500–1000 K.

## 2. Theory

### 2.1. Equation of state

It has been found that the linear isotherm regularity equation of state (LIR-EOS) is derived as the following form:

$$(Z - 1)v^2 = A + B\rho^2 \quad (1)$$

where  $Z$  is the compressibility factor,  $\rho = 1/v$  is the number density, and  $A$  and  $B$  are the temperature-dependent parameters; the details can be found elsewhere [25]. This regularity is experimentally valid for all types of fluids including polar, non-polar, hydrogen-bonded, and quantum fluids, for the densities greater than the Boyle density, and the temperatures less than twice the Boyle temperature [26–29]. The temperature dependency of the LIR parameters can be considered as:

$$A = A'' - \frac{A'}{RT} \quad (2)$$

$$B = B'' + \frac{B'}{RT} \quad (3)$$

where  $A'$  and  $B'$  are related to the attraction and repulsion terms of the applied potential function, respectively.  $A''$  is related to the non-ideal thermal pressure, and  $B''$  is a constant that is equal to zero for simple dense fluids. The experimental  $pVT$  data can be used to

determine the  $A$  and  $B$  parameters in the LIR equation of state for the Rb and Cs liquid metals over the whole liquid range.

### 2.2. Direct correlation function and structure factor

A more common route toward the structure factor is via the perturbation theory and is known as the random phase approximation (RPA). The RPA in the theory of simple liquids suggests a combination of a linear function related to the long-range attraction interaction,  $\varphi(r)$ , with the representation of the direct correlation function,  $c(r)$ , of the reference system owing to the short-range repulsion interaction in the form of  $c_0(r)$ :

$$c_{RPA}(r) = \begin{cases} c_0(r), & r < d \\ -\beta\varphi(r), & r \geq d \end{cases} \quad (4)$$

where  $\beta = 1/(k_B T)$  is the inverse temperature and  $d$  is the hard-core diameter, in which the Mayer cluster function was used for a reasonable choice of  $d(T)$  at any temperature  $T$  [30]. In this work, we approximated  $c_0(r)$  by the Henderson-Grundke correction to the direct correlation function of the hard-sphere fluids [31]:

$$c_0(r) = c_{HS}(r) \left(1 - 0.127\rho^2 d^6\right) \quad r < d \quad (5)$$

where  $c_{HS}(r)$  is DCF of the hard-sphere reference fluid, which is expressed using the Percus-Yevick (PY) equation for hard-sphere fluids [32]. In the general case, the pair potential with a hard-core,  $\varphi_{HC}(r)$ , can be written as:

$$\varphi_{HC}(r) = \begin{cases} \infty, & r < d \\ w(r), & r \geq d \end{cases} \quad (6)$$

where  $w(r)$  is a pair potential in the long-range interactions. Here, on account of the Yukawa potential playing an important role in classical simple liquid metals and combined versatility and simplicity, we selected it to describe the long-range interactions in ALMs:

$$w(r) = -\varepsilon \frac{\exp[-\lambda(r/d - 1)]}{r/d}, \quad r \geq d \quad (7)$$

where  $\varepsilon$  is the well depth and  $\lambda$  is a decay parameter that measures the intermolecular attraction range. We may account for the contribution of many-body interactions using an effective pair intermolecular potential,  $w_{eff}(r)$ , which is dependent on the thermodynamic state. Therefore, the final expression for DCF is:

$$c(r) = \begin{cases} c_{HS}(r) \left(1 - 0.127\rho^2 d^6\right), & r < d \\ -\beta w_{eff}(r), & r \geq d \end{cases} \quad (8)$$

In order to predict the behavior of  $S(k)$  over different thermodynamic states, we used the Ornstein–Zernike (OZ) equation, as:

$$S(k) = (1 - \rho c(k))^{-1} \quad (9)$$

where  $c(k)$  is the Fourier transform (FT) of  $c(r)$ . In all the calculations used to predict  $S(k)$ , we need to have the molecular parameters in DCF (Eq. (8)). In this way, the well-known thermodynamic relationship for the reduced bulk modulus  $B_r$  can be used as:

$$B_r = \beta \left( \frac{\partial P}{\partial \rho} \right)_T = 1 - 4\pi\rho \int_0^\infty c(r)r^2 dr \quad (10)$$

where  $P$  is the pressure. Based on the perturbation approximation

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