

# The Structure of Liquid Alkali Metals Calculated by the Thermodynamic Perturbation Theory

H. Birtan KAVANOZ, İdris GÜMÜŞ  
*Department of Physics, Yıldız Technical University,  
80270 Istanbul-TURKEY*

Received 11.12.1996

## Abstract

The structure of a hard sphere fluid has been calculated numerically via the Percus-Yevick (PY) and hypernetted-chain (HNC) closure relations and used as a reference system to calculate the structure of liquid alkali metals under the optimized random-phase approximation (ORPA) using the effective ion-ion pair potential formed by the Heine-Abarenkov (HA), and the empty-core (EC) pseudopotentials.

The results are compared with experimental results. The calculations made by the reference system under the HNC closure relation are in better agreement with experimental results than those found under the PY closure relation.

## 1. Introduction

Over the last three decades, theories have been developed to calculate the thermodynamic and structural properties of liquid alkali metals. The hard sphere model [1], which is the first realistic conception for liquid metals, has been taken as a reference system for calculating their structure and thermodynamic properties in thermodynamic perturbation theories. A thermodynamic variation method based on and using the Gibbs-Bogoliubov inequality model [2-4] calculates the correct hard sphere diameter without any amendment in the structure functions. Later, Week-Chandler-Andersen (WCA) [5-8] showed that deviations of the true ion-ion pair potential from a hard sphere form may be taken into account by splitting the potential into a purely repulsive short-range term and a long-range oscillatory part. Therefore each treated by suitable perturbative techniques: the WCA “blip function” expansion for the repulsive term, and the optimized random-phase approximation (ORPA) for the oscillatory part. So far, the structure of liquid alkali metals has been calculated by these methods using the hard sphere reference system and empty-core pseudopotential taken as an interaction between and electron and ion [9,10].

Our aim in this paper is first to find the structure function of a hard sphere reference system by solving numerically the Ornstein-Zernike (OZ) integral equation under the PY and HNC closure relations, and then to calculate by the two methods the structure functions for liquid alkali metal: by taking into account a perturbed form of the reference system; and by having an ion-ion pair potential made by the HA and EC pseudopotentials.

## 2. Theory

The HA pseudopotential for an electron-ion interaction is defined as

$$v_{ei}(r) = \begin{cases} -Ze^2A/R_M & r < R_M \\ -\frac{Ze^2}{r} & r > R_M, \end{cases} \quad (1)$$

where  $Z$  is the valence of the ion and  $A$  and  $R_M$  are two potential parameters [11-14].

According to the linear response theory, the effective ion-ion pair potential is given as

$$\phi(r) = \frac{Z^2e^2}{r} \left(1 - \frac{2}{\pi} \int_0^\infty F_N(q) \frac{\sin qr}{q} dq\right), \quad (2)$$

where  $F_N(q)$ , the energy wave number characteristic, is of the form:

$$F_N(q) = \frac{v_{ei}(q)^2}{\left(\frac{4\pi Ze^2\rho}{q^2}\right)^2} \left[1 - \frac{1}{\epsilon(q)}\right]. \quad (3)$$

Here,  $v_{ei}(q)$  is the Fourier transform of the electron-ion pseudopotentials given by (1),  $\rho$  shows ion number density and  $\epsilon(q)$  is the dielectric function of the electron gas

$$\epsilon(q) = 1 - \frac{\frac{4\pi e^2}{q^2} \chi(q)}{1 + \frac{4\pi e^2}{q^2} G(q) \chi(q)}, \quad (4)$$

where  $\chi(q)$  is the Lindhard function

$$\chi(q) = -\frac{mk_F}{\pi^2 \hbar^2} \left[ \frac{1}{2} + \frac{4k_F^2 - q^2}{8k_F q} \ln \left| \frac{2k_F + q}{2k_F - q} \right| \right] \quad (5)$$

and  $G(q)$  is the local field correction term. In our study the  $G(q)$  form suggested by Ichimaru-Utsumi [15] is used.

The effective ion-ion pair potential given by relation (2) can be separated into two parts:

$$\phi(r) = \phi_0(r) + \phi_1(r) \quad (6)$$

Here,  $\phi_0(r)$  is the purely repulsive short range term

$$\phi_0(r) = \begin{cases} \phi(r) - \phi(r_0) & r < r_0 \\ 0 & r > r_0, \end{cases} \quad (7)$$

and  $\phi_1(r)$  is the long range oscillatory term

$$\phi_1(r) = \begin{cases} \phi(r_0) & r < r_0 \\ \phi(r) & r > r_0, \end{cases} \quad (8)$$

where  $r_0$  is that value of  $r$  for which  $\phi(r)$  is a minimum. Weeks et al.[5] showed that the hard sphere diameter  $\sigma$  is determined by the condition

$$\int B_\sigma(r) d\vec{r} = 0, \quad (9)$$

to optimize the convergence of the functional Taylor expansion of the free energy of a system interacting with a purely repulsive short range potential  $\phi_0(r)$ , in terms of the blip function  $B_\sigma(r)$

$$F = F_0 - \frac{\rho}{2\beta} \int B_\sigma(r) d\vec{r} + \dots \quad (10)$$

Here,  $B_\sigma(r)$  is given as

$$B_\sigma(r) = y_\sigma(r)[\exp(-\beta\phi_0(r)) - \exp(-\beta\phi_\sigma(r))] \quad (11)$$

and  $y_\sigma(r)$  is given as

$$y_\sigma(r) = g_\sigma(r)\exp[\beta\phi_\sigma(r)], \beta = 1/(k_B T), \quad (12)$$

and the pair potential of the hard sphere reference system is

$$\phi_\sigma(r) = \begin{cases} +\infty & r < \sigma \\ 0 & r > \sigma, \end{cases} \quad (13)$$

In our study, the pair correlation function is obtained by solving numerically the OZ integral equation [17] defined by

$$h(r) = c(r) + \rho \int c(r')h(|\vec{r} - \vec{r}'|)d\vec{r}', \quad h(r) = g(r) - 1 \quad (14)$$

with the approximations

$$c_{PY}(r) = g(r)[1 - \exp(-\beta\phi(r))] \quad (15)$$

$$c_{HNC}(r) = h(r) - \ln g(r) - \beta\phi(r). \quad (16)$$

Then the pair correlation function is given by

$$g_{WCA}(r) = g_\sigma(r) + B_\sigma(r) \quad (17)$$

from Equations (9) and (11) under the WCA approximation. In order to calculate the contribution of the long range term  $\phi_1(r)$ , the total correlation function  $h(r)$  and the direct correlation function  $c(r)$  are divided into two parts:

$$h(r) = h_0(r) + h_1(r) \quad (18a)$$

$$c(r) = c_0(r) + c_1(r). \quad (18b)$$

By substituting  $h_{WGA}$  for  $h_0(r)$  and  $c_{WGA}$  and using the OZ equation, the Fourier transform of  $h_1(r)$  is found to be

$$h_1(q) = \frac{S_\sigma(q)c_1(q)S_\sigma(q)}{1 - \rho c_1(q)S_\sigma(q)} \quad (19)$$

where  $c_1(q)$  is the Fourier transform of  $c_1(r)$  and the hard sphere static structure factor  $S_\sigma(q)$  is

$$S_\sigma(q) = 1 + \rho \int [g_\sigma(r) - 1] \exp[-i\vec{q} \cdot \vec{r}] d\vec{r}. \quad (20)$$

On the other hand, the ORPA is defined [7,8] as

$$c_1(r) = -\beta\phi_1^*(r) = \begin{cases} -\beta\psi(r) & r < \sigma \\ -\beta\phi_1(r) & r > \sigma, \end{cases} \quad (21)$$

with

$$h_1(r) = 0, \quad r < \sigma. \quad (22)$$

Here,  $\psi(r)$  is a function taken as

$$\psi(r) = \phi(r_0) + \sum_{n=1} a_n (r - \sigma)^n. \quad (23)$$

Now employing the ORPA, values of  $a_n$  that minimize the free energy function given by

$$F[\phi_1^*(q)] = \frac{1}{(2\pi)^3} \int \{ \rho\beta S_\sigma(q)\phi_1^*(q) - \ln[1 + \rho\beta S_\sigma(q)\phi_1^*(q)] \} d\vec{q} \quad (24)$$

as well as satisfy Equation (22) can be determined [17]. Thus by substituting  $c_1(r)$ , found from the equation (21) (and therefore  $c_1(q)$ ) in the equation (19), one obtains  $h_1(q)$  and hence  $h_1(r)$ . Consequently,  $g_{ORPA}(R)$  is given by

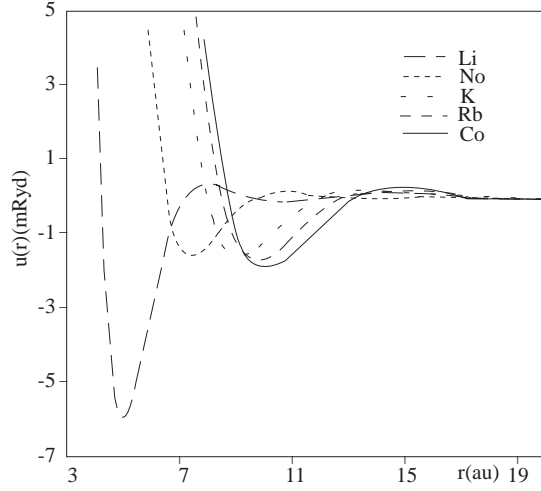
$$g_{ORPA}(r) = g_{(WCA)}(r) + h_1(r). \quad (25)$$

### 3. Results and Conclusions

The effective pair potential calculated by Equation (2), using the HA pseudopotential parameters, ion number densities and temperatures for alkali metals tabulated in Table 1 are shown in Figure 1.

**Table 1.** The HA pseudopotential parameters

Metal	A	$R_M(au)$	$\rho(1/au^3)$	T( $^{\circ}K$ )
Li	1.313	2.8	0.00648	523
Na	1.124	3.4	0.00350	473
K	1.068	4.2	0.00182	473
Rb	1.073	4.6	0.00145	473
Cs	1.066	4.8	0.00116	473


**Figure 1.** The pair potentials for liquid alkali metals

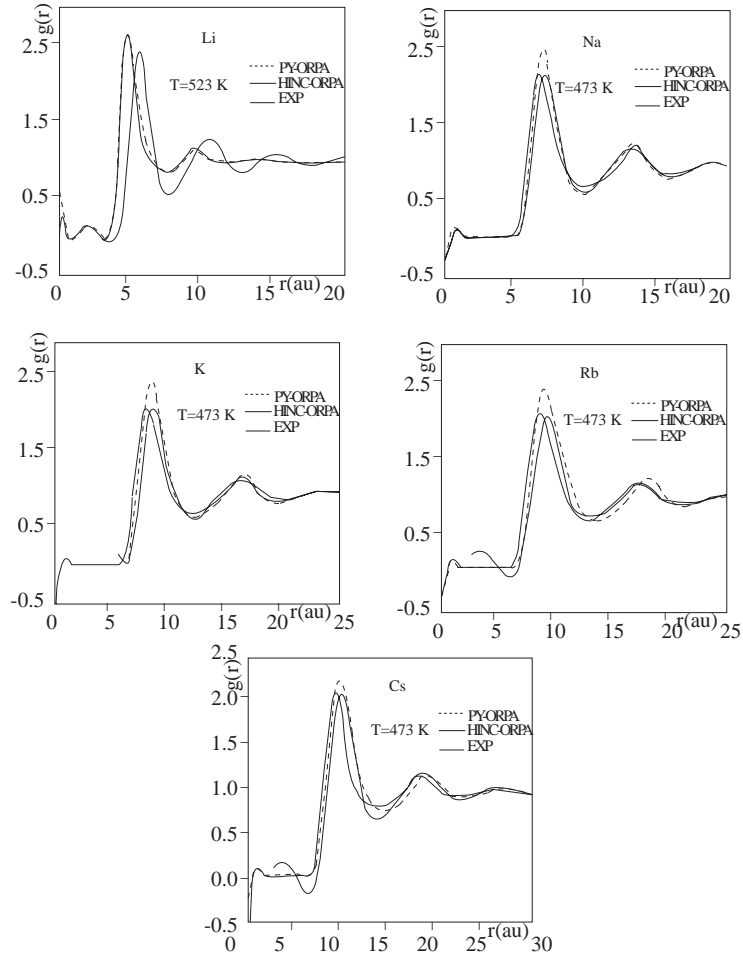
We calculated values of  $\sigma$  that satisfy condition (9) for each alkali liquid metal by taking the purely repulsive short range term of the effective pair potential that we formed. These results are given in Table 2 together with results found by other theories.

**Table 2.** Values calculated from WCA theory under the PY ( $\sigma_{PY}$ ) and HNC ( $\sigma_{HNC}$ ) closure relations.

Metal	$\sigma_{PY}(au)$	$\sigma_{HNC}(au)$	$\sigma^a(au)$	$\sigma^b(au)$	$\rho(1/au^3)$	T( $^{\circ}K$ )
Li	4.419	4.389	-	5.10	0.00648	523
Na	6.287	6.613	6.16	6.16	0.00350	473
K	7.747	7.575	7.54	7.62	0.00182	473
Rb	8.262	8.087	7.97	8.15	0.00145	473
Cs	8.555	8.418	8.52	9.02	0.00116	473

<sup>a</sup> Singh and Singh [18], <sup>b</sup> Hafner [4]

We also calculated the pair correlation functions  $g_{ORPA}(r)$  under the PY and HNC closure relation by using these more realistic  $\sigma$  values. These results for each liquid metal are shown in Figure 2 with the experimental results from [19].



**Figure 2.** Pair correlation functions  $g(r)$  for liquid alkali metals

Consequently, the ORPA results obtained by the reference system solved numerically under the HNC closure relation are more compatible with experimental results than those obtained by the PY reference system.

### References

- [1] N.W. Ashcroft and J. Lekner, *J.Phys.Rev.*, **145** (1966) 83.
- [2] H.D. Jones, *J.Chem.Phys.*, **55** (1971) 2640.
- [3] I.H. Umar, A. Meyer, M. Watabe and W.H. Young, *J.Phys.F*, **4** (1974) 1691.

- [4] J. Hafner, *Phys.Rev.*, **16A** (1977) 351.
- [5] J.D. Weeks, D. Chandler and H.C. Andersen, *J.Chem.Phys.*, **54** (1971) 5237.
- [6] H.C. Andersen and J.D. Weeks and D. Chandler, *Phys.Rev.*, **4A**. (1971) 1597.
- [7] H.C. Andersen and D. Chandler, *J.Chem.Phys.*, **57** (1972) 1918.
- [8] H.C. Andersen and D. Chandler and J.D. Weeks, *J.Chem.Phys.*, **56** (1972) 3812.
- [9] G. Kahl and J. Hafner, *Phys.Rev.*, **29A** (1984) 3310.
- [10] G. Kahl and J. Hafner, *Z.Phys.Cond.Matt.*, **58B** (1985) 283.
- [11] A.O.E. Animalu and V. Heine, *Phil.Mag.*, **12** (1965) 1249.
- [12] R.W. Shaw and W.A. Harrison, *Phys.Rev.*, **163** (1967) 604.
- [13] R.W. Shaw, *Phys.Rev.*, **174** (1968) 769.
- [14] O. Ese and J.A. Reissland, *J.Phys.*, **3** (1973) 2066.
- [15] S. Ichimaru and K. Utsumi, *Phys.Rev.*, **24B** (1981) 7385.
- [16] S. Labik, A. Malijevsky and P. Vonka, *Mol.Phys.*, **56** (1985) 709.
- [17] G. Kahl and J. Hafner, *Phys.Chem.Liq.*, **12** (1982) 109.
- [18] R.N. Singh and V.N. Singh, *Phys.Chem.Liq.*, **22** (1991) 235.
- [19] Y. Waseda, *The Structure of Non-Crystalline Materials*, (McGraw-Hill.1980) p.268-289.