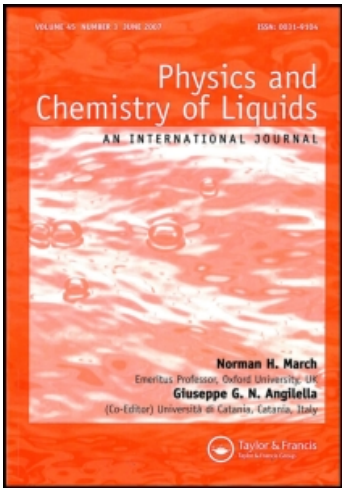

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

Unified Pair Potential for the Structure Factor of Liquid Alkali Metals

S. K. Nigam[a]; K. N. Khanna[a]
[a] Department of Physics, V.S.S.D. College, Kanpur, India

To cite this Article Nigam, S. K. and Khanna, K. N.(1993) 'Unified Pair Potential for the Structure Factor of Liquid Alkali Metals', Physics and Chemistry of Liquids, 25: 2, 75 — 79
To link to this Article: DOI: 10.1080/00319109308030348
URL: http://dx.doi.org/10.1080/00319109308030348

Phys. Chem. Liq., 1993, Vol. 25, pp. 75–79
Reprints available directly from the publisher
Photocopying permitted by license only

UNIFIED PAIR POTENTIAL FOR THE STRUCTURE FACTOR OF LIQUID ALKALI METALS

S. K. NIGAM and K. N. KHANNA

Department of Physics, V.S.S.D. College, Kanpur, India

(Received 5 January 1992)

An analytical expression for the direct correlation function (dcf) is presented based on a unified pair potential to calculate the structure factor of soft liquid metals in the random phase approximation. A similar expression for the dcf as proposed by Colot *et al.*[7] can be derived as a particular case of our proposed expression. The results show good agreement between the structure factors of liquid alkali metals and experiment.

KEY WORDS: Direct correlation function, Yukawa interaction, inverse screening length

1 INTRODUCTION

Softness in the pair potential plays a significant role in the determination of the structure factor of the liquid alkali metals[1]. The fact that the one-component plasma (OCP)[2] works better than the hard sphere reference system for the liquid alkali metals suggests that the softness in the pair potential is an essential factor for the liquid metals. Another soft reference system is the hard sphere Yukawa (HSY) reference system proposed by Waisman[3]. The HSY was first applied by Hayter *et al.*[4] to fit the structure factors of liquid alkali metals. The main advantage of the HSY over the HS system fluid is that it accounts not only for the effective size of atoms, but also for the softness of the interatomic interaction at close contact. This reference system has recently been applied for the determination of the structure factors of liquid alkali and transition metals[5,6]. However, their application of HSY does not include the long-range Friedel oscillations. Colot *et al.*[7] have also presented a semi-empirical expression for the direct correlation function (dcf) obtained by mixing the PY approximation with Yukawa tail. We have recently shown that the soft reference system[8] when combined with the Cummings potential[9] in the random phase approximation (RPA) leads to good structure factors for the alkali metals. However, the exact matching of two potentials while mixing the Cummings potential with the Yukawa-type reference system could not be achieved as the analytical expression for the dcf bears no direct relationship to the Fourier transform of the Yukawa potential. In the present work, we propose to combine the two potentials in a unified way.

2 FORMULATIONS

We proceed, basically, with two observations. The first concerns the choice of the reference system. The best choice of the reference system appears to be the combination of the Percus–Yevick (PY) hard sphere together with expression for the Yukawa potential. The second concerns the long-range Friedel oscillations. We propose that with a composite system of the Yukawa repulsion and Friedel-type Cummings potential, softness both in the core and in the long-range interactions, can be accounted for in a unified way. This is done by matching the potentials of HSY and Cummings potential and their derivatives at a distance where the Friedel-type of oscillation comes into play through the Cummings potential[9]. Such optimization yields a smooth potential and avoids any kind of kink or discontinuity in the system. The pair potential $u(r)$, of the hard sphere Yukawa fluid is defined by

$$\begin{aligned} u(r) &= \alpha && r < \sigma \\ &= A\frac{e^{-z(r-\sigma)}}{r} && \sigma < r < \lambda\sigma \\ &= -\frac{e^{-z_1(r-\lambda\sigma)}}{r}\,[B\ \mathrm{Cos}\ \mu(r-\lambda\sigma) + C\ \sin\ \mu(r-\lambda\sigma)] \\ & && r > \lambda\sigma \end{aligned} \tag{1}$$

Here σ is the diameter of the hard sphere, $A = \varepsilon\sigma$ where ε is the strength of the Yukawa interaction at hard contact, Z is the Yukawa inverse screening length and Z_1 is the inverse screening length of the Cummings potential. The parameters A, B and C are determined by the conditions:

$$[Uy(r)]_{r=\sigma_1} = [Uc(r)]_{r=\sigma_1} \tag{2}$$

$$\left[\frac{d}{dr}(Uy(r))\right]_{r=\sigma_1} = \left[\frac{d}{dr}(Uc(r))\right]_{r=\sigma_1} \tag{3}$$

with $\sigma_1 = \lambda\sigma$ and Uy and Uc represent the Yukawa and Cummings parts of the potentials. Solving Eqs. (2) and (3), we find the following relations:

$$Ae^{-Z\sigma(\lambda-1)} = B \tag{4}$$

$$B[Z - Z_1] = C\mu = C * 2k_F \tag{5}$$

In Eqs. (4) and (5) B, C and Z_1 are Cummings potential parameters and are the same as used in earlier work[8]. Hence Z can be determined using Eq. (5).

The Fourier transform of the direct correlation function of hard sphere part is well known[10]. The Fourier transform of the direct correlation function of Yukawa

part of the potential is derived as:

$$Cy(q) = -\frac{24\eta}{(Z\sigma^2\sigma^2 + q^2)}\frac{A}{q(\sigma K_B T)} \times [e^{-Z\sigma(\lambda-1)}(Z\sigma \sin \lambda q + q \cos q) - (Z\sigma \sin q + q \cos q)] \quad (6)$$

where $q = Q\sigma$. By substituting $\lambda = \infty$ and therefore extending the range of Yukawa:

$$Cy(q) = \frac{24\eta}{(Z^2\sigma^2 + q^2)}\frac{A}{q(\sigma K_B T)}[Z\sigma \sin q + q \cos q]. \quad (7)$$

Assuming $z\sigma = d$ and $(A/\sigma K_B T) = b$. We find

$$Cy(q) = \frac{24\eta b}{(q^2 + d^2)}\left[\cos q + \frac{d}{q}\sin q\right] \quad (8)$$

which is the Yukawa part proposed by Colot *et al.* The structure factor can now be calculated as

$$S(q) = \frac{1}{1 - (C_h + C_Y + C_c)} \quad (9)$$

where C_h, C_y and C_c are the dcf of the hard sphere, Yukawa and Cummings parts of the pair potential. The dcf of the Cummings potential is written in earlier work[1]. The long wavelength limit of the Yukawa part is given by

$$C_y(0) = -\frac{24\eta}{Z^2\sigma^2}\left(\frac{1}{K_B T\sigma}\right) * [B(Z\sigma\lambda + 1) - A(Z\sigma + 1)] \quad (10)$$

3 RESULTS AND DISCUSSION

We have calculated the structure factors of liquid alkali metals using Eq. (9). In the calculation, the parameters B and C and Z_1 are the same as in our earlier work[8].

Table 1 Input parameters for Cummings and hard sphere Yukuwa potential.

Metal	*Temp.* (*K*)	η	$\frac{B}{\sigma K_B T}$	$\frac{C}{\sigma K_B T}$	Z_1	ε $\times 10^{-3}$ (*Ryd*)	Z (*a.u.*)
Na	378	0.460	−0.2378	0.3887	0.337	1.32	1.885
K	343	0.451	−0.5049	0.7418	0.404	1.40	1.525
Rb	313	0.455	−1.4215	1.8993	0.650	1.81	1.600
Cs	303	0.442	−2.2638	3.3929	0.815	2.60	1.809

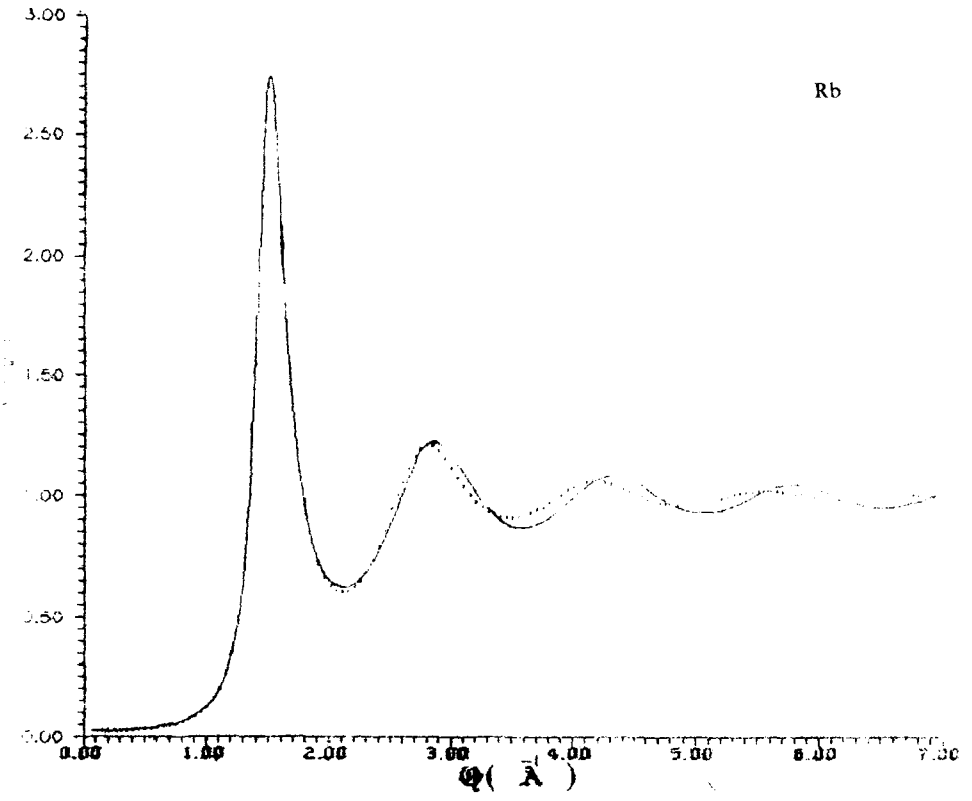

Figure 1 Structure factors for (a) Rb (b) Cs at melting temperature. The full curves are theoretical results while the dots are experimental values.

The value of screening length of Yukawa part Z is determined by using Eq. (5). The strength of Yukawa potential at hard contact occurs in Eq. (1) as $A = \varepsilon\sigma$. The Yukawa part of the repulsive potential mainly modifies the height of the first peak in the composite system and we treated ε as a variable parameter in fixing the height of the first peak of the structure factor. This value of ε is found to be very versatile and a small variation in ε changes the peak height sharply. The range of operation of Yukawa potential is automatically fixed through Eq. (4), once ε is fixed. The parameter η is used to fit the position of the first peak of the structure factor. The values of the inverse screening length (z) are found to be close to the values obtained by Hausleitner and Hafner[5] for the alkali metals. The values of ε in our work show a systematic trend. A comparison of b in the Colot expression with ours through $A/K_B\sigma T = b$ shows that our calculated values of b are of the same order as occurring through Colot's expression for 'b'[7]. However, the values of Z used in our expression ($Z\sigma = d$) differ considerably from Colot's 'd', our values of Z being lower. However, a larger value of inverse screening length and a larger region of Yukawa potential operation in Colot's case suggests an effective short range operation of the Yukawa form, which we have already taken into account by limiting its operation up to $\lambda\sigma$ only. The results for Rb and Cs are displayed in Figs 1a and b. We find that our

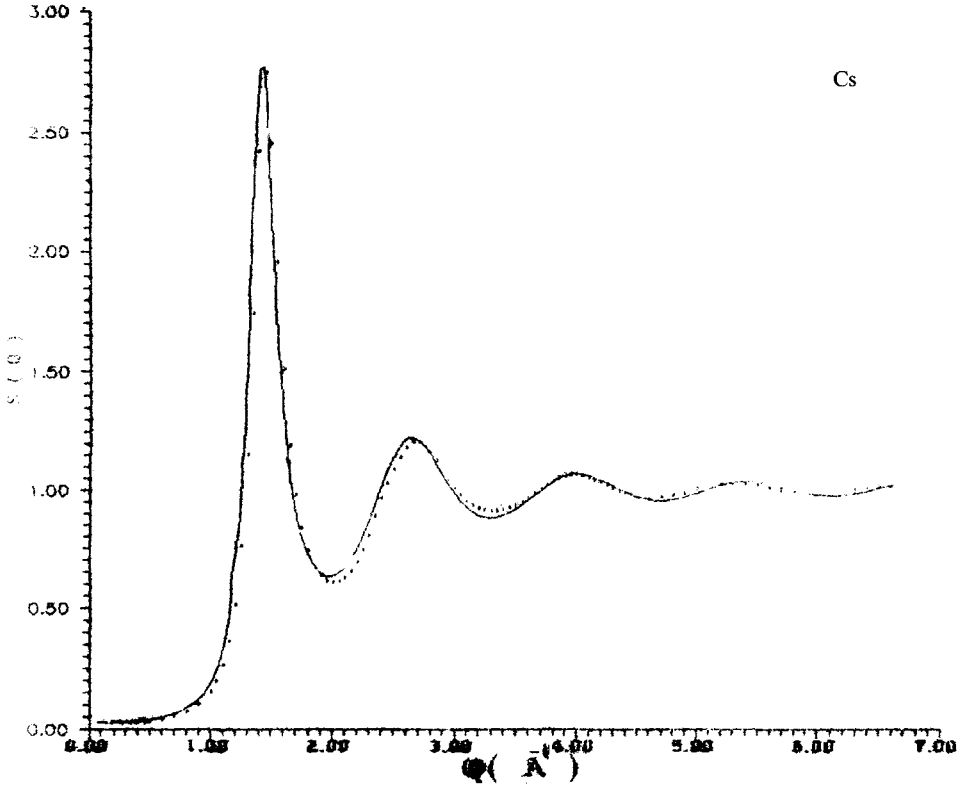

Figure 1(b)

model shows a more realistic form of the first peak, phase shift and a slight damping of the higher order oscillations in comparison with the hard-sphere system.

There are several observations which deserve emphasis. The low q values are extremely good by using the Cummings potential. We also see that the magnitude of the main and subsequent peaks are in excellent agreement with experiment[11]. As regards the phase shift, we observe it to be almost negligible in Rb and fairly small in Cs.

References

1. K. N. Khanna and I. L. Mclaughlin, *J. Phys. Cond. Matt.* **1**, 4155 (1989).
2. K. K. Mon, R. Gann and D. Stroud, *Phys. Rev.* **A24**, 2145 (1981).
3. E. Waisman, *Mol. Phys.* **25**, 45 (1973).
4. J. B. Hayter, R. Pynn and J. B. Suck, *J. Phys. F.* **13**, L1 (1983).
5. C. Hausleitner and J. Hafner, *J. Phys.* **F18**, 1013, 1025 (1988).
6. D. H. Li, R. A. Moore and S. Wang, *Phys. Letters* **118A**, 405 (1986).
7. J. L. Colot, M. Baus and H. Xu, *Mol. Phys.* **57**, 809 (1986).
8. S. K. Nigam and K. N. Khanna, *Phys. Stat. Sol.* **167**, 11 (1991).
9. J. L. Bretonnet, *Solid State Comm.* **47**, 395 (1983).
10. M. S. Wertheim, *Phys. Rev. Letters* **10**, 321 (1963).
11. Y. Waseda, *The Structure of Non-Crystalline Material*: New York (1980).