

SEMI-EMPIRICAL POTENTIALS FOR CuI

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We have investigated the prospects for developing semi-empirical model potentials for use in the studies of structural properties of CuI with integral equation theories. The point of view adopted requires that only short range two atom and three atom interactions appear. A three-body potential of Tersoff has been tested with the hypernetted chain integral equation by calculating the pair correlation function for CuI at 710 K. The two-body and three-body Kohen -Tully-Stillinger empirical interatomic potential has been applied. The structural results of liquid CuI have been compared with experiment and those obtained by rigid ion potentials.

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1. Introduction

Recently, the possibility of producing microcrystals [1] of copper halides have received much attention. Other interesting materials (chalcogenide glasses) applicable to optical devices and fibres [2-5] have been also intensively studied. The copper halides (CuCl, CuBr, CuI) can be considered as the last number of series of tetrahedrally coordinated semiconductors. It is known that these systems are not purely ionic and the polarizability of ions, and the small size of the cation, fast ions conduction. Among them CuI has the smallest ionicity on the Phillips scale [6]. This shows its ability to form more covalent bonds. A clear understanding of the physical properties of copper halides is known to depend heavily upon their structure and pair potential at a microscopic level. For this reason there has been a great interest in developing the simple model potentials for these systems.

Up to now the two-body interatomic potentials based on the rigid-ion model potentials have been used to describe the microscopic mechanisms of ionic conduction of CuI using molecular dynamics simulation and integral equation theories. Zheng-Johansson et al. [7, 8] and Trullas et al. [9] have used the interionic potential proposed by Vashishta and Rahman (VR) [10]. Within the framework of statistical mechanics of liquids, inverse potentials for such liquid ionic systems have been studied by number of workers. Belashchenko and co-workers [11] have constructed the computer models of these systems using experimental diffraction data. Mitev et. al. [12] has been calculated the effective pair potentials from measured structural data using a solution of the modified hypernetted-chain equation coupled with the predictor-corrector method. It has been found that the theoretical approach is difficult to extend to describe the structure and the physical properties of more complex liquids, such as non-ideal ionic melts. Molten CuI are included in this category. Another point of view has been developed on semi-empirical model potentials for copper halides by Sekkal and co-workers [13-15]. They have been interested in testing the transferability of a three-body empirical potential model, (Tersoff potential (TP) [16]) for these systems. They have concluded that an empirical three body potential with MD method reproduces well the structural properties of copper halides in their different high pressure phases.

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On the other hand, a Tersoff type potential [17] was extended to describe interatomic interactions in the Si-H system by some researchers [18-20]. An alternative potential for these systems have been developed by Kohen- Tully- Stillinger (KTS) [21] where a Stillinger-Weber (SW) potential [22], was designed to describe interactions in both solid and liquid forms of silicon systems [23].

However, no structural calculations have been performed on copper halides using TP and a two or three-body KTS potentials coupled with integral equations, to our knowledge.

The main point of the present work is the test of the transferability of semi-empirical potential models to predict structural properties of molten CuI coupled with integral equations. For this purpose, first we have calculated the inter-ionic interactions for Cu using three body TP and two body KTS (KTS-V2) potential models which are used as input data in its structural calculations with the hypernetted chain (HNC) integral equation theory [24]. Then, the two and three body KTS potential models have been applied to CuI system in order to describe interionic interactions of the system. These potentials' accuracy has been tested in the structural calculations for CuI at two different temperatures. The computed partial structure factors and pair distribution functions of CuI have been compared with experiment and each other. We have shown that the KTS model potentials can be applied to copper halides successfully. In addition to this the results of KTS-V2 potential model are in good agreement with the experimental data than others.

2. Theory

2.1 Semi empirical potentials

2.1.a Tersoff Potential

Among the many empirical model potentials that have been developed for tetrahedral semiconductors, that of Tersoff has been applied to many of the semiconductors successfully. The interatomic potential is taken to have the form as [16]

$$E = \sum_i E_i = \frac{1}{2} \sum_{i \neq j} V_{ij}, \quad (1)$$

$$V_{ij} = f_C(r_{ij})[a_{ij} f_R(r_{ij}) + b_{ij} f_A(r_{ij})], \quad (2)$$

where E is the total energy of the system, which is decomposed for convenience into a site energy E_i and band energy V_{ij} . The indices i and j ion over the atoms of the system and r_{ij} is the distance from atom i to atom j . The function f_R represents a repulsive potential and f_A represents an attractive pair potential associated with bonding given as

$$f_R(r) = A \exp(-\lambda_1 r), \quad (3)$$

$$f_A(r) = -B \exp(-\lambda_2 r). \quad (4)$$

The term f_c is merely a smooth cut of function to limit the range of potential taken as,

$$f_C(r) = \begin{cases} 1 & r < R - D \\ \frac{1}{2} - \frac{1}{2} \sin\left[\frac{\pi}{2} \frac{(r - R)}{D}\right] & R - D < r < R + D \\ 0 & r > R + D \end{cases} \quad (5)$$

where b_{ij} is the many-body order parameter describing how the bond-formation energy is affected by local atomic arrangement due to the presence of other neighboring atoms (the k atoms). It is a many-body function of the positions of atoms i , j and k given as

$$b_{ij} = (1 + \beta^n \zeta_{ij}^n)^{-1/2n}, \quad (6)$$

$$\zeta_{ij} = \sum_{k(\neq i,j)} f_C(r_{ik}) g(\theta_{ijk}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3], \quad (7)$$

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos \theta)^2}, \quad (8)$$

$$a_{ij} = (1 + \alpha^n \eta_{ij}^n)^{-1/2n}, \quad (9)$$

$$\eta_{ij} = \sum_{k(\neq i,j)} f_C(r_{ik}) \exp[\lambda_3^3 (r_{ij} - r_{ik})^3], \quad (10)$$

where ζ is defined as the effective coordination number and $g(\theta)$ is a function of the angle between r_{ij} and r_{ik} . Following others [13], we assume that λ_3 and α are maintained to be zero, thus $a_{ij}=1$. Other adjustable fitting parameters, A , B , n , c , d , h , λ_1 and λ_2 are determined by fitting to the cohesive properties of the material.

2.1.b Kohen-Tully-Stillinger Potential (KTS)

We have chosen to use the extended SW potential, namely KTS potential. It has been tested successfully for its accuracy in describing the Si:H system in recent studies [23]. The KTS potential energy V is a sum of two and three body interactions given by,

$$V = \sum_{\substack{i,j \\ i < j}} V_2(i, j) + \sum_{\substack{i,j,k \\ i < j < k}} V_3(i, j, k), \quad (11)$$

where the two-body term given as

$$V_2(r_{ij}) = \begin{cases} \xi_{ij} (C_{ij} r_{ij}^{-p} - 1) \exp[\kappa_{ij} / (r_{ij} - \ell_{ij})], & r_{ij} < \ell_{ij} \\ 0, & r_{ij} \geq \ell_{ij} \end{cases}, \quad (12)$$

and the three-body term as

$$V_3(r_{ij}, r_{jk}, r_{ki}) = H(r_{ij}, r_{ik}, \theta_{jik}) + H(r_{jk}, r_{ji}, \theta_{ijk}) + H(r_{ki}, r_{kj}, \theta_{jki}) \quad (13)$$

Here H is taken as

$$H(r_{ij}, r_{ik}, \theta_{jik}) = \begin{cases} \varepsilon_{jik} (1 + \mu_{jik} \cos \theta_{jik} + \nu_{jik} \cos^2 \theta_{jik}) \exp[\Gamma(\gamma, r\chi)], & \text{if } r_{ij} < \chi_{jik}, r_{ik} < \chi_{jik} \\ 0, & \text{otherwise} \end{cases}, \quad (14)$$

where $\Gamma(\gamma, r\chi)$,

$$\Gamma(\gamma, r, \chi) = \frac{\gamma_{ij(k)}}{r_{ij} - \chi_{jik}} + \frac{\gamma_{ik(j)}}{r_{ik} - \chi_{jik}} \quad (15)$$

where r is the distance between a pair of atoms, ℓ_{ij} and χ_{jik} are the cut-off distances of the two-body and the three-body potentials, respectively, and θ_{ijk} is the vertex angle at j subtended by i and k . ξ_{ij} , C_{ij} , p , and κ_{ij} are fixed parameters chosen by fitting to the cohesive properties of the material. Parameters ε_{jik} , μ_{jik} , ν_{jik} , $\gamma_{ij(k)}$, and $\gamma_{ik(j)}$ are constants chosen to give best possible values for the structure.

2.2 Liquid state theory

With the effective pair potential known, integral equations are able to provide us the liquid structure for systems. The calculations were performed by solving numerically the hypernetted chain (HNC) integral equation theory of liquids. The starting point of most of the integral equation theories of liquids is the Ornstein-Zernike (O-Z) equation, which for a homogenous; an isotropic system can be written as

$$h(r) = c(r) + \rho \int d\bar{r} \bar{h}(|\bar{r} - \bar{r}'|) c(\bar{r}'), \quad (16)$$

which defines the direct correlation function $c(r)$, in terms of the total correlation function, $h(r) = g(r) - 1$ where $g(r)$ is the pair distribution function and ρ is the number density. This equation is supplemented by the HNC closure relation involving the pair potential $\phi(r)$,

$$g(r) = \exp[h(r) - c(r) - \phi(r)/k_B T]. \quad (17)$$

In this work, Zerah's algorithm is used to solve the O-Z equation [24,25]. The partial structure factors and pair distribution functions are calculated within the HNC approximation which is used in the variational modified HNC (VMHNC) calculations while the bridge function $B(r)$ is zero.

3. Results and discussion

Firstly, we have presented the interatomic pair potentials for liquid Cu based on the semi-empirical potential functions of TP and KTS-V2. In the present work, the all parameters of potential functions are determined by fitting to cohesive energy and taking into account for the cut-off procedure together with the HNC structural calculations. The cohesive energy for liquid Cu is taken as 3.11 eV which is calculated from the Rose equation of state (EOS) and used in the liquid state calculations within the embedded atom method (EAM) [26]. For this calculation we need the input parameters, such as the ionic number densities and thermodynamic states for liquid Cu which are taken from Waseda [27], namely $\rho = 0.0755$ (atoms/Å³) and $T=1423$ K. The value of the cohesive energy for CuI is 2.66 eV taken from Harrison [28]. The set of potential parameters have been chosen to give the best possible values for the structure comparing with the experimental data. We have noted that Sekkal and co-workers have obtained the TP parameters for CuI by fitting the results of total energy versus volume to the Murnaghan equation of state. The adjusted potential parameters for TP and KTS model potentials are presented in Tables 1-3 respectively. In Table 1, the fitting parameters for CuI, except B , λ_1 , λ_2 , R and D values, are the same as given in Ref. [13]. In this work, the angle θ is taken as 109.45° in TP and KTS-V3 potential calculations. For simplicity, $H(r_{ij}, r_{ik}, \theta_{jik}) = H(r_{jk}, r_{ji}, \theta_{ijk}) = H(r_{ki}, r_{kj}, \theta_{jki})$, is taken in Eq. (13) for the KTS-V3 model potential.

Table 1. The adjusted TP parameters for Cu and CuI.

	Cu	CuI
\dot{A} (eV)	690.136	688.00
B(eV)	85.463	65.50
$\lambda_1(\text{\AA}^{-1})$	3.04923	3.2210
$\lambda_2(\text{\AA}^{-1})$	1.5511	1.6105
n	20.00	21.45
h	-0.333	-0.333
β	0.321	0.333
c	228987	69219.5
d	0.1154	0.15
R(\AA)	4.163	3.02
D(\AA)	0.6	0.3

Table 2. The adjusted KTS potential parameters for two body interactions.

	ξ (eV)	$C(A^p)$	$k(\text{\AA})$	$\ell(A)$	P
Cu	75.215	3.535	9.431	4.763	1.8003
CuI	100.000	55.626	9.1281	4.110	4.800

Table 3. The three body KTS potential parameters.

	ϵ (eV)	μ	ν	$\gamma_{ij(k)}(\text{\AA})$	$\gamma_{ik(j)}(\text{\AA})$	$\chi(\text{\AA})$
CuI	135.544	-19.897	0.0125	9.128	9.128	4.11

Fig. 1 shows the calculated effective pair potentials of Cu using the TP and KTS-V2 models together with the potentials those obtained from different embedded atom methods (EAM) [26,29,30]. The present results of the Cu pair potentials show deeper minima when compared with the EAM based potential cases. However the semi-empirical potentials are similar in the short r-range. The position of the principal minimum is almost the same for these two. It appears that TP potential is wider than others such as the rigid ion model (RIM) potentials.

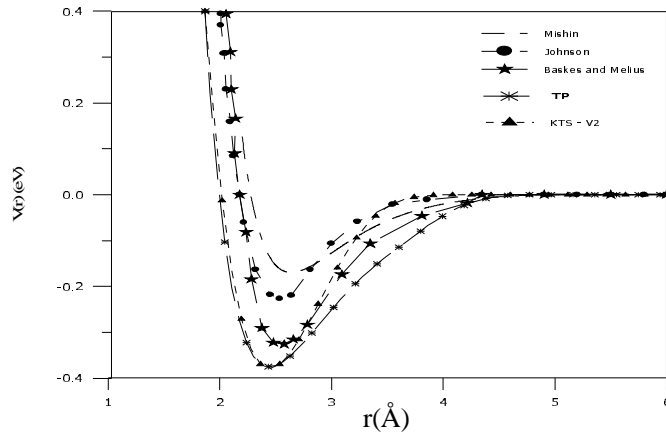


Fig. 1. Pair interaction potentials for Cu.

In Fig. 2, we present our HNC results of $S(q)$ for liquid Cu along with the experimental data of Waseda [27]. We notice that the position of the main peak of $S(q)$ obtained by semi-empirical potentials is in excellent agreement with the experimental value of $3(\text{\AA}^{-1})$. However the results using the KTS-V2 potential are better agreement than TP model. The results of $S(q)$ for TP model are shifted slightly towards greater q values as compared with experimental data.

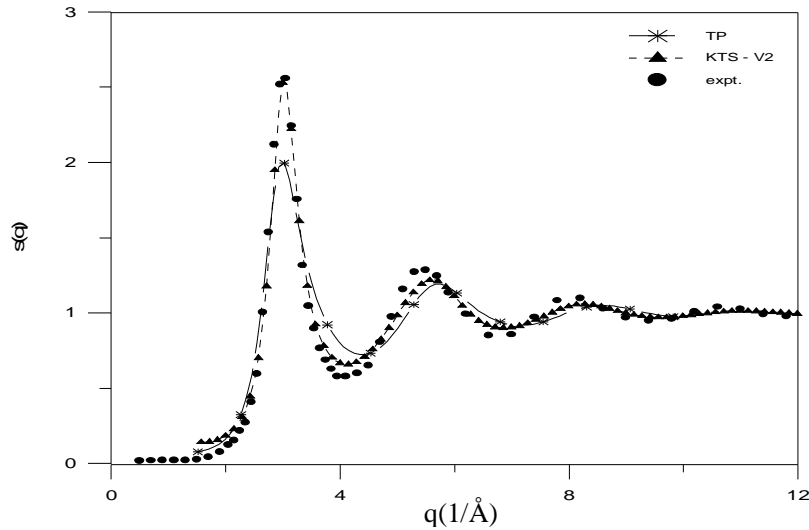


Fig. 2. Static structure factors for liquid Cu at 1423 K.

The calculated effective interatomic potentials of CuI are shown in Fig. 3. The TP potential is flatter and deeper than the KTS potentials. When r is less than the cutoff distance r_c , all three potentials except KTS-V3, almost coincide with each other. However the KTS-V3 potential takes repulsive pair potential format in this region.

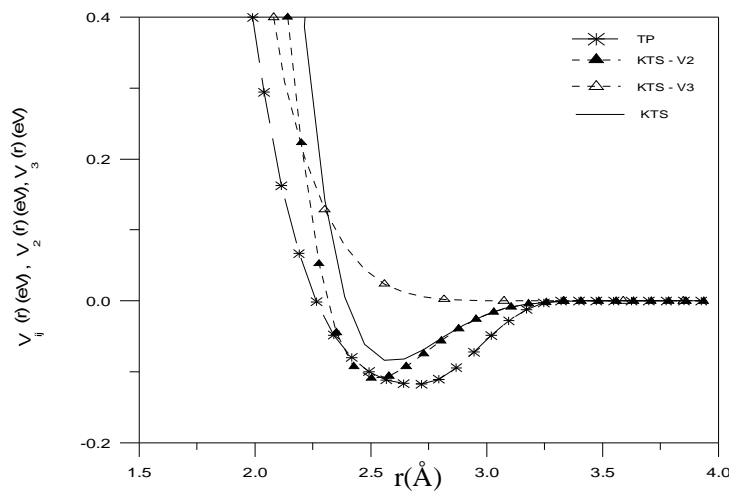


Fig. 3. Pair interaction potentials for CuI.

In the present paper, HNC calculations for CuI were carried out at two temperatures $T = 710$ K and 923 K. The partial structure factors and pair distribution functions calculated from the potentials presently obtained are shown in Figs. 4 and 5, respectively for the case of CuI at 710 K. In Fig. 5, we also present the results of Sekkal using the TP potential at 710 K for comparison [13].

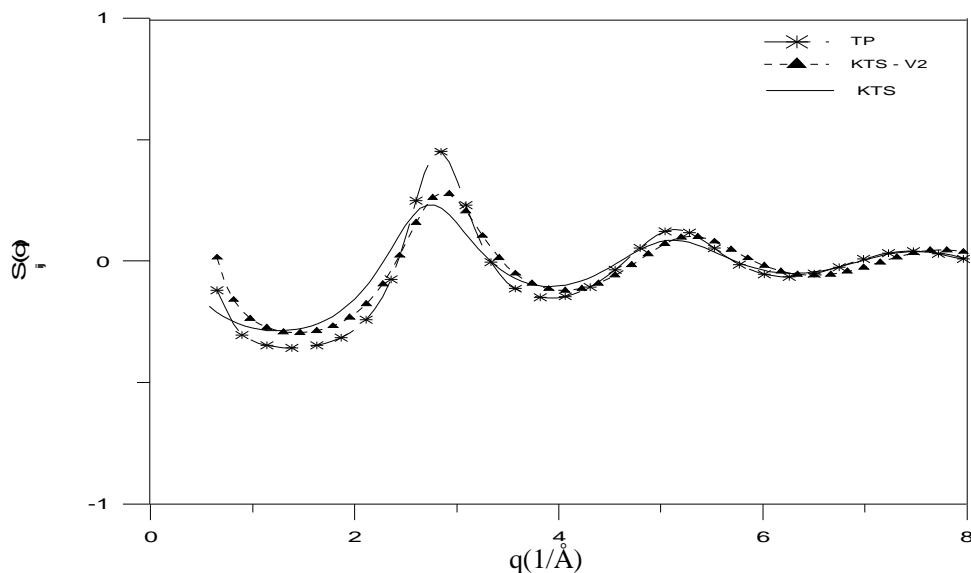


Fig. 4. Partial structure factors of CuI at 710 K.

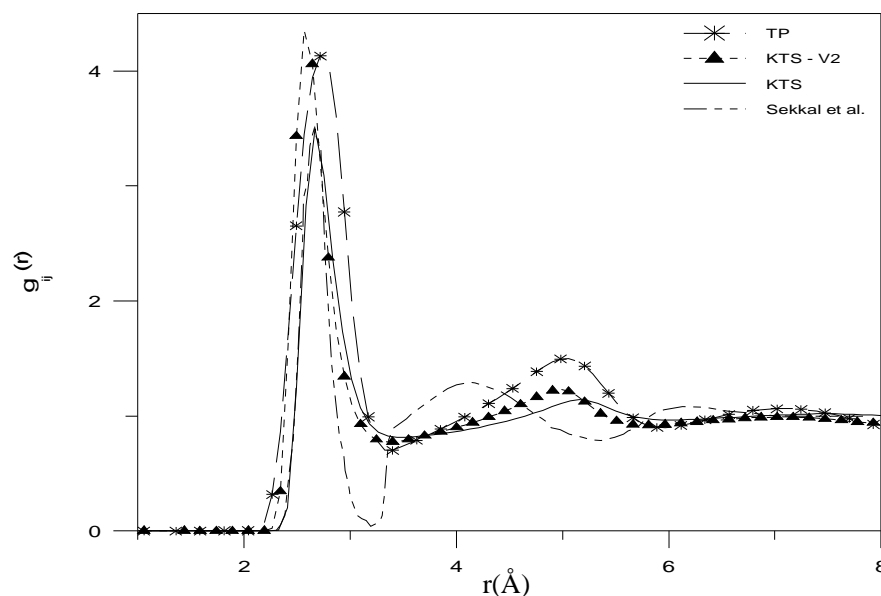


Fig. 5. Pair distribution functions for CuI at 710 K.

It is seen in Fig. 4, the partial structure factors of the TP and KTS-V2 potentials have a principal peak located at the same position. However the present result for KTS potential is flatter than others. We notice that the results of TP potentials are similar to those of KTS in the large q region.

It is seen in Fig. 5 that the HNC results presently obtained clearly differs from the Sekkal data in the medium range region. However both the position and height of the first peak of KTS agree well with the values determined by Sekkal. We note that the HNC results are qualitatively similar in the first neighbour region. As reported by Sekkal the distribution is quite liquid like where the first peak position of experimental $g(r)$ is at 2.5 \AA . Our results are also excellent agreement with this experimental value. It would also be noted a particular feature can be easily seen in the depth of

first minima of the pair distribution function obtained by Sekkal. This is the evidence of the structurless feature of Cu ions in this liquid system. In order to confirm the validity of our adjusted potential parameters we have calculated the partial structure factors and pair distribution functions of CuI at 923 K. The value of alloy number density is 0.0304 as taken from Ref. [12]. The HNC results obtained in this case are presented in Figs. 6 and 7, respectively together with the experimental data of Waseda [12]. In Fig. 7, we have compared our results with those obtained using the RIM potential proposed by Tatlipinar et al. (TAPT) [31] which was parameterized for Cu-I by S. S. Dalgic and co-workers [32]. The TAPT calculations were performed by solving numerically the HNC theory of liquids at the same thermodynamic state.

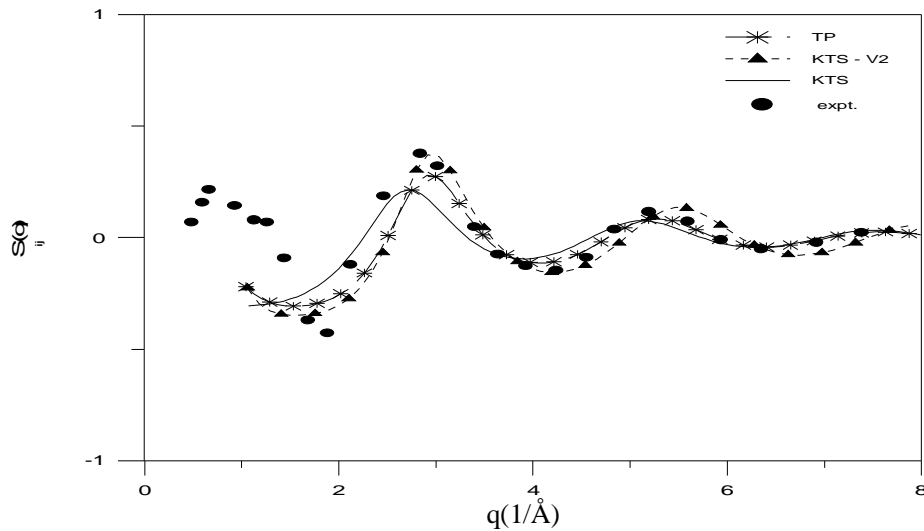


Fig. 6. Partial structure factors of CuI at 923 K.

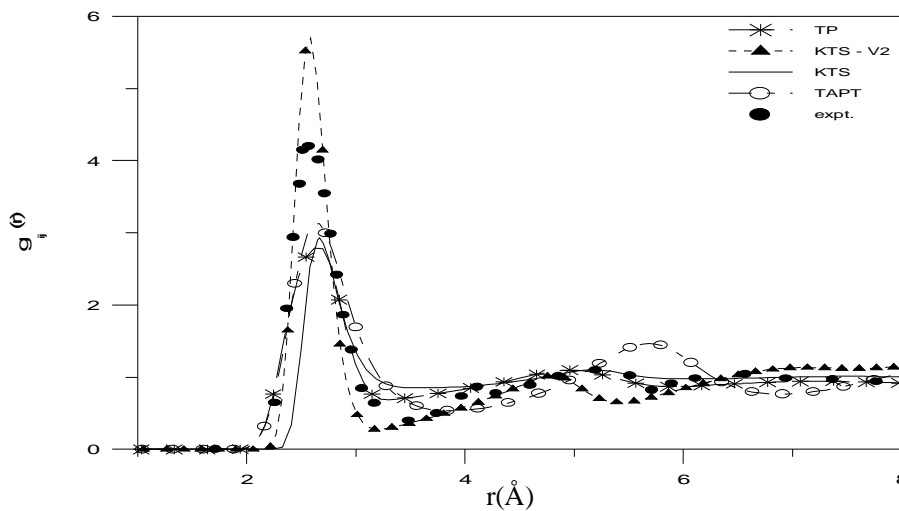


Fig. 7. Partial pair distribution functions of CuI at 923 K.

We notice from Fig. 6 that our HNC results except KTS are in good agreement with the position of the main peak of experimental data [12] and seem to be much more accurate than those of others using the Vashishta-Rahman model [7,8]. The position of main peak of $S(q)$ is same for TP and KTS-V2 potentials. It is seen in Fig. 7 that the results obtained by using the semi-empirical potentials follow the main features of the experimental distribution function better than those obtained using the TAPT potential. It has also noticed that there is no a significant difference found

in the interatomic distance for the nearest neighbour Cu-I pair between the presently obtained potentials, except KTS-V2 one. The first peaks of $g(r)$ presently obtained by TAPT and TP model potentials are located at the same position while the calculated $g(r)$ using the KTS potential shifted slightly towards larger r values. This could be attributed to the difference detected in the position of the minimum for the pair potential. The HNC result using the TP model is in good agreement with experiment than those presently obtained potentials, except the height of the first peak.

4. Conclusions

First, the presented semi-empirical three body TP potential provides a realistic description of the pair interactions in liquid Cu and CuI. These calculations were performed for the functions not only fit to solid data but also liquid state properties. We have improved the parameterization of the KTS potentials which gives a good description of the liquid and still describe the solid accurately. In summary, we conclude that an empirical two-body KTS potential with the HNC method reproduces well the structural properties of molten CuI than the presented three-body. However the presented KTS formalism can be extended which is capable of providing a good description of copper halides in their liquid state. This method is easy to be applied to the CuBr and CuCl alloy cases. The validity of these potentials can be resulted after that. This work will progress on this line.

References

- [1] D. Frohlich, E. Mohler, P. Weisner, *Phys. Rev. Lett.* **26**, 554 (1971).
- [2] J. Tauc, A. Menth, *J. Non Cryst. Solids* **8-10**, 569 (1972).
- [3] V. M. Mitsa, R. M. Holomb, *J. Optoelectron. Adv. Mater.* **6**, 1177 (2004).
- [4] N. Mehta, R. K. Shukla, A. Kumar, *J. Optoelectron. Adv. Mater.* **6**, 1185 (2004).
- [5] M. Popescu, *J. Optoelectron. Adv. Mater.* **6**, 1147 (2004).
- [6] J. C. Phillips, *Rev. Mod. Phys.* **42**, 317 (1970).
- [7] J. X. M. Zheng-Johansson, I. Ebbjö, R.L. McGreevy, *Solid State Ion* **82**, 115 (1995).
- [8] J. X. M. Zheng-Johansson, I. Ebbjö, R.L. McGreevy, *Solid State Ion* **83**, 35 (1996).
- [9] J. Trullas, A. Giro', R. Fontanet, M. Silbert, *Phys. Rev.* **B50**, 16279 (1994).
- [10] P. Vashishta, A. Rahman, *Phys. Rev. Lett.* **40**, 1337 (1978).
- [11] D. K. Belashchenko, O. I. Ostrovskii, *Rus. J. Phys. Chem.* **77**, 627 (2003).
- [12] P. D. Mitev, S. Masatoshi, Y. Waseda, *J. Non Cryst. Solids* **312-314**, 443 (2002).
- [13] W. Sekkal, A. Zaoui, M. Certier, *J. Phys. Chem Solids* **59**, 1293 (1998).
- [14] W. Sekkal, A. Zaoui, A. Laref, M. Certier, H. Aourag, *J. Phys: Condens. Matter* **12**, 6173 (2000).
- [15] F. El Haj Hassan, A. Zaoui, W. Sekkal, *Mat. Sci. Eng.* **B87**, 40 (2001).
- [16] J. Tersoff, *Phys. Rev.* **B37**, 6991 (1988).
- [17] J. Tersoff, *Phys. Rev.* **B39**, 5566 (1989).
- [18] T. Ohira, O. Ukai, M. Noda, *Surf. Sci.* **458**, 216 (2000).
- [19] M. V. R. Murty, H. A. Atwater, *Phys. Rev.* **B51**, 4889 (1995).
- [20] T. Ohira, O. Ukai, T. Adachi, Y. Takeuchi, M. Murata, *Phys. Rev.* **B52**, 8283 (1995).
- [21] D. Kohen, J. C. Tully, F. H. Stillinger, *Surf. Sci.* **397**, 225 (1998).
- [22] F. H. Stillinger, T. S. Weber, *Phys. Rev.* **B31**, 5262 (1985).
- [23] T. Hawa, M. R. Zachariah, *Phys. Rev.* **B69**, 035417 (2004).
- [24] S. S. Dalgic, S. Dalgic, S. Sengul, M. Celtek, G. Tezgor, *J. Optoelectron. Adv. Mater.* **3**, 831(2001).
- [25] G. Zerah, *J. Comput. Phys.* **61**, 280 (1985).
- [26] S. S. Dalgic, S. Dalgic, U. Domekeli, *J. Optoelectron. Adv. Mater.* **5**, 1263 (2003).
- [27] Y. Waseda, *The Structure of Non – Crystalline Materials* (McGraw – Hill Publ. Co., New York, 1980).

- [28] W. A. Harrison, *Electronic Structure and the Properties of Solids* (CA: Freeman, San Francisco, 1989).
- [29] R. A. Johnson, *Phys. Rev.* **145**, 423 (1966).
- [30] M. I. Baskes, C. F. Melius, *Phys. Rev.* **B20**, 3197 (1979).
- [31] H. Tatlipinar, Z. Akdeniz, G. Pastore, M. P. Tosi, *J. Phys.: Condens. Matter* **4**, 8933 (1992).
- [32] S. S. Dalgic, M. Caliskan, H. Gurbuz, C. Canan (unpublished results).