Ionic Motion in CuI: A Molecular Dynamics Simulation

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Molecular dynamics simulation was used to study the structural properties and charge transport in ionic (γ-phase) and super-ionic (α-phase) phases of CuI material. The first order $\gamma-\alpha$ phase transition was analysed. The diffusion constant and its temperature dependence are in quite good agreement with experiments.

I. Introduction

Fast-ion conductors or superionic conductors are solids that show high ionic conductivity. These materials are usually divided into classes of cation or anion conductors, and can generally be described as two interpenetrating sub lattices. Among the families of superionic conductors there are simple silver salts, fluorites, β-aluminas, and copper halides.[1,2]

Among the classes of superionic materials cooper iodine (CuI) is considered to be a unique material with respect to its various phases structures. While those materials have in general different crystalline structures in both ionic and superionic phases, CuI, has the same crystalline structure. Copper iodine can be found in three different phases named α, β, and γ-phases. In both low-temperature γ-phase and high-temperature superionic α-phase, the anions are arranged in the face-centered cubic (fcc) structure. Below 642 K, the γ-phase, it has a zinc blend structure, space group F$\bar{4}$3m, where the anions I^- are distributed in a fcc sub lattice while the cation Cu^+ sits on a fcc sub lattice shifted by (1/4,1/4,1/4) from the anion sub lattice. At 642 K CuI undergoes a structural phase transition to the β-phase with the hexagonal structure, space group $p\bar{3}m1$, similar to the wurtzite structure. At 680K another structural phase transformation takes place (α-phase) where CuI transforms back to the fcc sub lattice of I^-, with the cations Cu^+ randomly distributed over the tetahedrally coordinated sites (space group $Fm\bar{3}m$).[3-7] Upon further heating, the fcc superionic phase melts at 873K.[3] Recently, a series of tracer diffusion experiments[8-12] has been carried out in the copper halide family of such materials. Those data give the diffusion constant of the order 10^{-7} cm^{2}s^{-1} for the γ-phase, 10^{-6} cm^{2}s^{-1} for the β-phase and 10^{-5} cm^{2}s^{-1} for the α-phase.

The microscopic description of the mechanism of diffusion can be obtained through molecular dynamics (MD) simulations. The central key of those techniques is the model of the interaction potential between the particles from which all the relevant structural and dynamical properties are obtained. Vashishta and Rahman[13,14] have proposed a two-body interaction potential based on a simple prescription that only considers the bulk properties of the solid. Even though the calculations using this model predicts the $\gamma-\alpha$ transition and the results agree qualitatively well with the experimental data, the constants of self-diffusion were much higher than the experimental ones in both phases. Furthermore, the transition $\gamma-\beta$ was prevented because the computer experiment was done in a fixed volume.

In this work we employ the same functional form of the effective interaction potential proposed by Vashishta and Rahman[13,14] to describe structural and dynamical properties of the superionic conductor CuI. However, a rigorous choice of the potential parameters allows us to obtain a better agreement with the experimental results. We also use the MD simulation in a fixed volume (micro canonical ensemble), which means that the transition $\gamma-\beta$ is not allowed. We compare our results with MD simulations by Johansson et al.,[15,16] who have used a similar interaction potential to study this system. We show that the ionic-superionic transition region is in quite good agreement with experiments and the temperature dependence of the self-diffusion coefficient reproduces the results of trace-diffusion experiments satisfactorily.

II. Effective potential model and molecular dynamics calculations

The effective pair potential proposed by Vashishta and Rahman,[13,14] which has been used to describe other several systems,[17–26] is comprised of three terms:

$$\begin{aligned} V &= \frac{Z_i Z_j}{r_{ij}} + A\left[\frac{\sigma_\alpha + \sigma_\beta}{r_{ij}}\right]^{\eta_{\alpha\beta}} \\ &+ -\frac{1}{2}(\alpha_i Z_j^2 + \alpha_j Z_i^2)\exp(-r_{ij}/r_s). \end{aligned} \qquad (1)$$

The first term corresponds to Coulomb interaction due to the charge transfer between ions with Z_i being the effective charge of the i^{th} ion and r_{ij} their separation; the second term comes from the steric repulsion to balance the attractive interaction between cations and anions at short distances; and the third one is the charge-dipole interaction, due to the large polarizability of the anions I^-, where α_i is the electronic polarizability of the i^{th} ion and $r_s = 4.5$Å is a screening length chosen in order to cut off the-long tail of this term of the potential. The exponents $\eta_{\alpha\beta}$, as used for other simulations,[18,23,25,26] were set to be 7, 9, and 11, respectively for I-I, Cu-I, and Cu-Cu interactions. The electronic polarizability was taken from Kittel.[27] The effective charges are adjusted in such a way that the energy scale is comparable with the experimental results. The ionic radii are taken from Shannon.[28] Finally, the repulsive term A was chosen to get the correct Cu-I bond length. Table 1 summarises the parameters used in the effective interaction potential.

Table 1: Constants in the effective interaction potential used in this simulation. e is the elementary charge.

	Cu	I
Z_α	$0.62e$	$-0.62e$
m_α	2.107×10^{-22} g	1.055×10^{-22} g
σ_α	0.520 Å	2.174 Å
α_α	0.0 Å^3	6.52Å^3
A	$1.65 \times 10^{-20} J$	
η_{CuCu}	11	
η_{CuI}	9	
η_{II}	7	

The MD calculations were performed in the micro canonical ensemble (NVE) with 512 particles (256 Cu + 256 I) in a MD-simulation cubic box of size L. The experimental value 3.439×10^{28} m^{-3} of the number density at the α-phase (T=720 K) corresponds to L = 26.6Å. Periodic boundary conditions were imposed and the equations of motion were integrated by using the Beeman algorithm[29] with a time step of $\Delta t = 1.0 \times 10^{-14}$ s. The long-range Coulomb interaction was handled through the Ewald summation method. All other interactions are summed up to L/2. For each temperature the system was first thermalized for 40,000 time steps and the averages performed over additional 20,000 time steps.

In this paper we are interested in the dynamical behavior of the system, in particular, in the calculation of the constant of self diffusion in the ionic as well in the superionic phases. From the positions and velocities of all particles, as a function of time, we can easily compute the mean square displacement

$$\langle u^2 - (t)\rangle = \frac{1}{N}\sum_{n=1}^{N}\langle (r_n(s+t) - r_n(t))^2\rangle \qquad (2)$$

for each type of ions, and the velocity autocorrelation function,

$$Z_\alpha(t) = \frac{\langle \vec{\nu}_{i\alpha}(0)\cdot\vec{\nu}_{i\alpha}(t)\rangle}{\langle \vec{\nu}_{i\alpha}(0)^2\rangle} \qquad (3)$$

where $\vec{\nu}_{i\alpha}(t)$ is the velocity of particle i of type α at time t, and <> denotes the ensemble average as well as the summation over the α-type particles.

The coefficient of self diffusion is given by

$$D = \lim_{t\to 0}\frac{\langle u^2(t)\rangle}{6t} \qquad (4)$$

or in terms of the velocity autocorrelation $Z(t)$ as

$$D_\alpha = \frac{k_\beta T}{m_\alpha}\int_0^\infty Z_\alpha(t)dt \qquad (5)$$

We obtain the same self-diffusion constant both from the mean square displacement and from the velocity autocorrelation function.

III. Results and discussion

In this simulation, we analyse the two phases in which we are interested, γ-ionic, and α-superionic phases of CuI from the thermodynamics point of view. The temperature dependence of the total energy per particle is shown in Fig. 1. It can be observed that there is a discontinuity in the energy, around T=670K, in good agreement with the experimental results. Fig. 2 displays the specific heat at constant volume as a function of temperature. The discontinuity in energy and the peak in the specific heat are the signature of a first order transition from the γ- to α-phase. These results are in reasonable agreement with previous MD simulation[13,14] and the experimental values reported by Miyake et. al..[3]

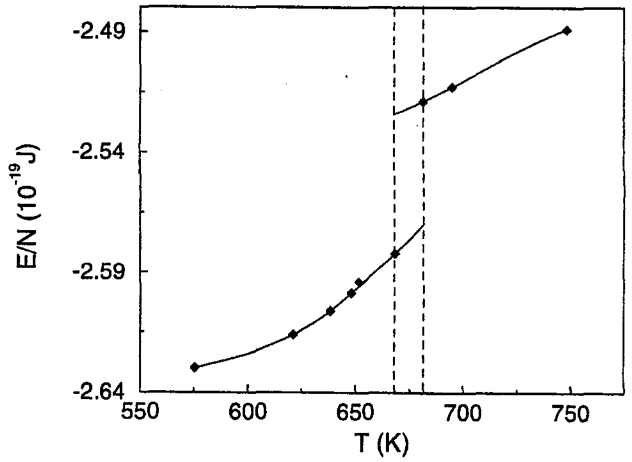

Figure 1. Total internal energy per particle as a function of temperature. The transition temperature from γ- to α-phase is found to be 670K.

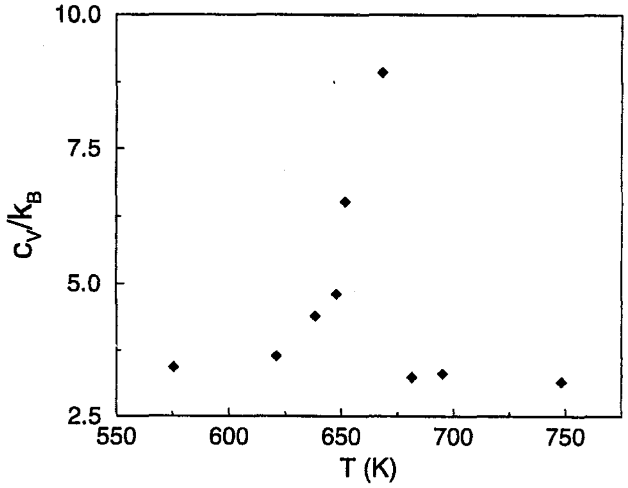

Figure 2. Heat capacity in units of K_B as a function of temperature.

From the phase space trajectories obtained in the MD simulation, we calculated the partial pair correlation functions. For all temperatures studied, the iodines continue to form a well defined fcc structure which are surrounded in average by 12 atoms of Cu. Figs. 3 and 4 show the partial pair correlation functions at two temperatures, for the ionic (576K) and the superionic (680K) phases respectively. As we can see in Fig. 3(c) the Cu ions also form a fcc structure with 12 nearest neighbors. In the high-temperature phase, the Cu ions are diffusing while the I ions still remain in thermally activated but stable fcc structure. In both phases we observed that the charge neutrality occurs around 5.3Å.

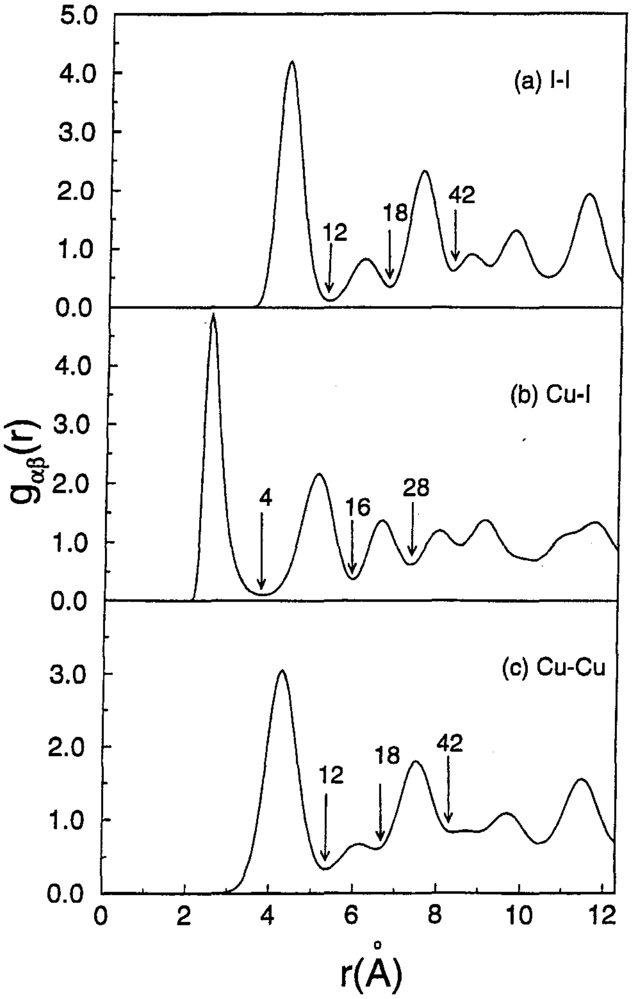

Figure 3. Partial pair-distribution function for the ionic γ-phase at 576K. The arrows show the coordination of 12, 18, and 42 as in a fcc lattice. Charge neutrality is observed around 5.3Å.

Better ascertain of the structural correlations can be made by examining the bond- angle distribution as defined in ref. 25. All the six bond-angle distributions, at two different temperatures, are shown in Fig. 5, for the ionic or γ-phase and superionic or α- phase, respectively.

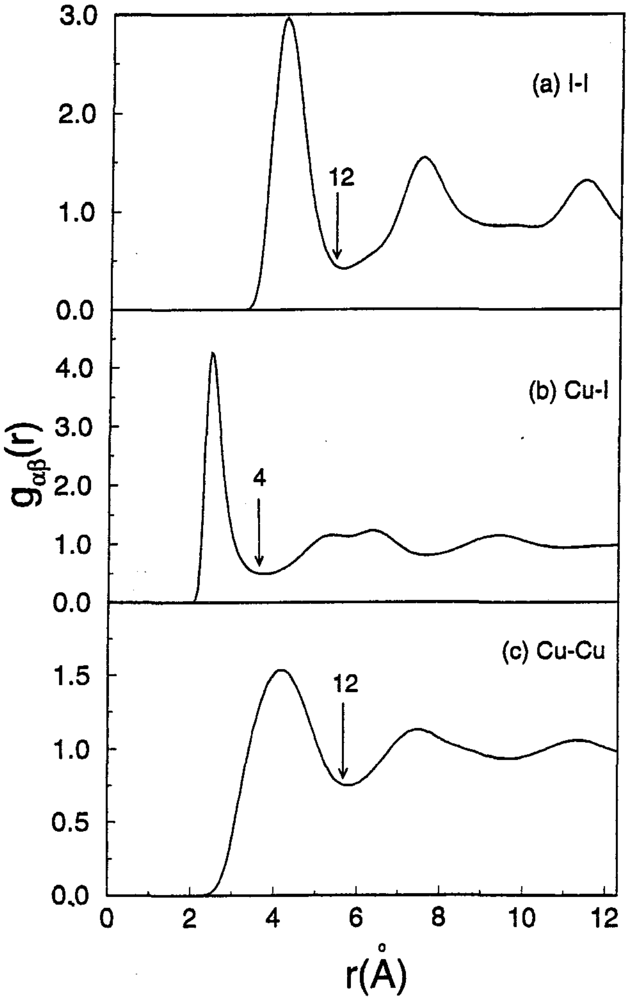

Figure 4. Partial pair-distribution function for the superionic α-phase at 680K.

In the low temperature phase (γ-phase) both I-I-I and Cu-Cu-Cu bond-angle distributions show very well defined peaks at 60°, 90°, 120°, and 180°, which are the angles the fcc structure. The distributions of Cu-I-Cu and I-Cu-I, and I-Cu-Cu and I-I- Cu also exhibit the same form because the crystallographic structure at low temperature consists of two intercalated fcc structures. On the other hand, in the high temperature superionic phase (α-phase), the distributions involving Cu cations are broader. The Cu-Cu-Cu angle distribution is very broad indicating the melting of this sub lattice and the diffusive character of the Cu ions. However, the I-I-I angle distribution display peaks at the same angles as before indicating that the anions remais in a fcc lattice. The decrease in intensity and broadening come from the thermal effects.

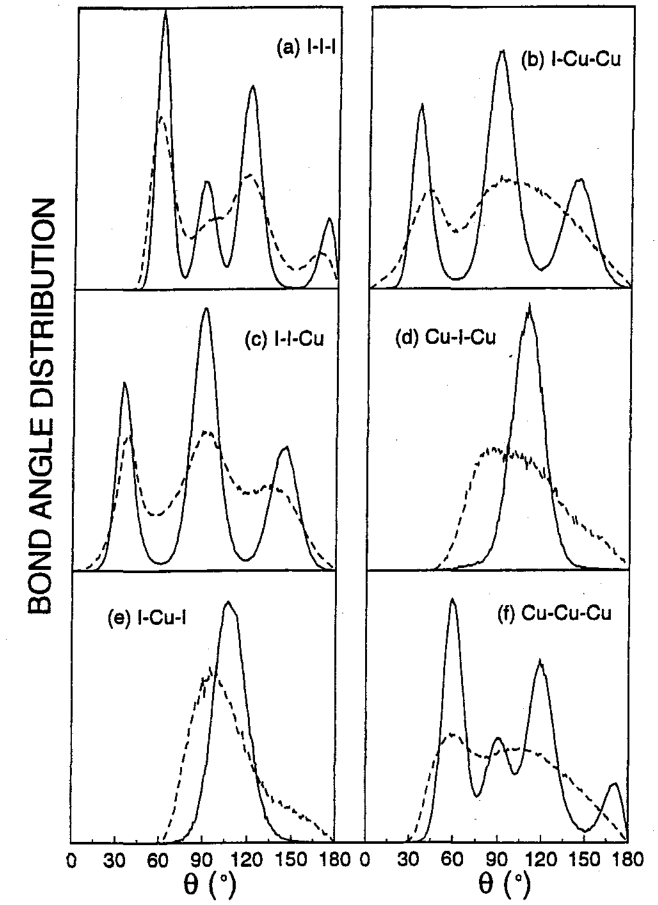

Figure 5. Bond angle distributions for ionic γ-phase at 576K (continuous line) and superionic α-phase at 680K (dashed line). The four peaks in I-I-I, in both phases, confirm that iodines form a fcc lattice.

The diffusion path of the Cu ions can also be found by using the bond-angle distributions. In the time averaged sense, it is possible to get information about the cations preference to stay along their self-diffusion motion. In Fig. 6 we represent the I^- in a fcc structure an its tetrahedral and octahedral symmetric positions. The broad peak around 100°, in the I-Cu-I bond-angle distribution can be explained by the presence of Cu ions in the octahedral point of symmetry. The peaks around 60° and around 109° in the Cu-Cu-Cu angle distribution can also be explained if Cu^+ visit the octahedral position. These results are in agreement with the density-map for a-CuI obtained by Vashishta et al.,[13,14] but in disagreement with the simulation done by Johansson et al.,[16] where the same functional form for the two-body interaction plus the van der Waals interaction were used as a model potential. In conclusion, the diffusion path of the Cu ions occurs not only from occupied tetrahedral positions to unoccupied tetrahedral positions (from (+) to (-) in the Vashishta notation) along the 100 direction, but also from tetrahedral to octahedral positions along the 111 direction.

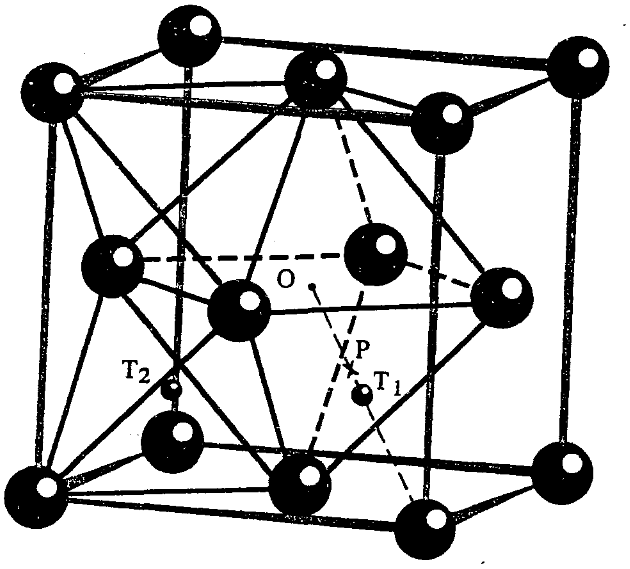

Figure 6. Representation of the fcc anion sub lattice. The big spheres denote the I^-. Tetrahedral (T_1 and T_2) and octahedral (O) sites. The point P is on the triangular interface sharing a octahedron and a tetrahedron.

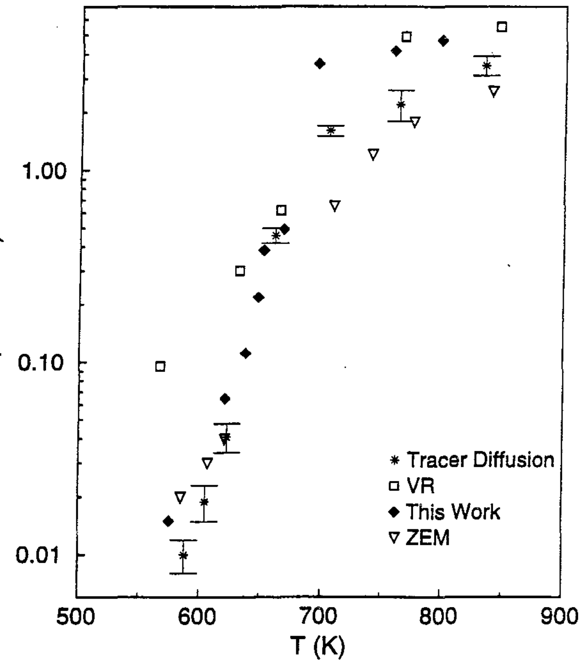

Figure 7. Temperature dependence of the self-diffusion constant for Cu^+ in ionic and superionic phases. Tracer diffusion experimental result are taken from reference 8. VR are the molecular dynamics results from Vashishta and Rahman,[13,14] and ZEM the molecular dynamics results from Zheng-Johansson, Ebbsjo, and Mcgreevy.[15]

The dynamical behavior of the system is shown in Fig. 7, where the self-diffusion constant D_{Cu} is depicted as a function of the temperature. We also display the experimental radioactive-trace-diffusion measurement[8] and the previous MD results obtained by Vashishta and Rahman[13,14] and by Johansson et al..[15] It is clear from the figure that there is a substantial increase in the diffusion just before the $\alpha - \beta$ transition, which is in excellent agreement with the experimental observation. Although our result for the self-diffusion coefficient in the ionic phase agrees very well with the results of other simulation and the experimental ones, and simulation shows the same overall description of the superionic phase as compared with the experimental data, we observe that self-diffusion constant is overestimated in our simulation, while it is subestimated in the previous simulation.[15] This is a consequence of different effective charge of ions used in different simulations. We conclude that the diffusion constants are extremely sensitive to the effective charges.

In conclusion, we have studied the structural and dynamics properties of the CuI material in the ionic and superionic phases by the MD technique. We showed that the effective two-body interaction potential proposed by Vashishta et al. provide a satisfactory description for CuI, like other several superionic conductors and glasses, as shown in Refs [13,14,17-21,23-26]. As suggested by Rahman and Vashishta,[14] larger values of the effective charge of the Cu ions lead to better agreement with experimental results. The transition region from ionic to a superionic conductor for CuI was obtained in quite good agreement with experiments. The diffusion path of Cu ions was found to occur not only through jumps from tetrahedral to tetrahedral positions along the 100 direction, but also through jumps from tetrahedral to octahedral positions along the 111 direction. The temperature dependence of the self-diffusion coefficient reproduces satisfactorily the trace diffusion experiments.

References

1. J. B. Boyce and B. A. Huberman, Phys. Rep. **51**, 189 (1979).
2. M. Aniya, *Liquid-Like Model of Superionic Conductor: Toward an United Understanding of Liquid and Superionic phases* (Niigata University, Japan, 1991), and the references there in.

3. S. Miyake, S. Hoshino and T. Takenaka, J. Proc. Soc. Japan **7**, 19 (1952).
4. W. Buhrer and W. Halg, Electrochim. Acta **22**, 701 (1977).
5. L. Merril, J. Phys. Chem. Ref. Data **6**, 1205 (1977).
6. S. Hull and D. A. Keen, Europhys. Lett. **23**, 129 (1993).
7. D. A. Keen and S. Hull, Phys. Rev. **B 50**, 5868 (1994).
8. R. Dejus, K. Sköld and B. Graneli, Sol. State Ionics **1**, 327 (1980).
9. J.X.M.Z. Johansson and K. Sköld, Sol. State Ionics **50**, 247 (1992).
10. J.-E. Jørgensen, J.X.M.Z. Johansson and K. Sköld, J. Sol. State Chemistry **98**, 263 (1992).
11. J.X.M.Z. Johansson, K. Sköld and J.-E. Jørgensen, Sol. State Ionics **70/71**, 522 (1994).
12. J.-E. Jørgensen, J.X.M.Z. Johansson and K. Sköld, Phys. Rev. **B52**, 1004 (1995).
13. P. Vashishta and A. Rahman, in *Fast Ion Transport in Solids* (eds. P. Vashishta, J.N. Mundy & G.K. Shenoy, G.K.) 527-533 (Elsevier North-Holland Inc., 1979).
14. A. Rahman and P. Vashishta, in *The Physics of Superionic Conductors and Electrode Materials* (eds. J. W. Perram) 93-142 (Plenum Publishing Corporation, 1983).
15. J.X.M.Z. Johansson, I. Ebbsjo and R. L. McGreevy, Sol. State Ionics (1995(submitted)).
16. J.X.M.Z. Johansson and R.L. McGreevy, Sol. State Ionics (1995 (submitted)).
17. P. Vashishta and A. Rahman, Phys. Rev. Lett. **40**, 1337 (1978).
18. J. P. Rino, et al. J. Chem. Phys. **89**, 7542 (1988).
19. J. P. Rino, et al. Solid State Ionics **32-33**, 968 (1989).
20. I. Ebbsjö , P. Vashishta, R. Dejus and K. Sköld, J. Phys. C **20**, L441 (1987).
21. J. P. Rino, R. K. Kalia and P. Vashishta, in *Condensed Matter Theories* (eds. S. Fantoni, & S. Rosati, S.) 171-187 (Plenum Press, New York, 1991).
22. J. P. Rino, I. Ebbsjö, R. K. Kalia, A. Nakano and P. Vashishta, Physical Review B **47**, 3053 (1993).
23. P. Vashishta, I. Ebbsjö, R. Dejus and K. Sköld, J. Phys. C **18**, L291 (1985).
24. P. Vashishta, R. K. Kalia, G. A. Antonio and I. Ebbsjo, Phys. Rev. Lett. **62**, 1651 (1989).
25. P. Vashishta, R. K. Kalia, J. P. Rino and I. Ebbsjö, Physical Review B **41**, 12197 (1990).
26. P. Vashishta, R. K. Kalia and I. Ebbsjö, Phys. Rev. Lett. **75**, 858 (1995).
27. C. Kittel, in *Introduction to Solid State Physics* (Willey, New York, 1971).
28. R. D. Shannon, Acta Cryst. A**32**, 751 (1976).
29. D. Beeman, J. Comp. Phys. **20**, 130 (1976).