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Screened Potential in a Reverse Monte Carlo (RMC) Simulation

M. Habchi, S. M. Mesli, M. Kotbi

Abstract**—**A structural study of an aqueous electrolyte whose experimental results are available. It is a solution of LiCl-6H_2O type at glassy state (120K) contrasted with pure water at room temperature by means of Partial Distribution Functions (PDF) issue from neutron scattering technique. Based on these partial functions, the Reverse Monte Carlo method (RMC) computes radial and angular correlation functions which allow exploring a number of structural features of the system. The obtained curves include some artifacts. To remedy this, we propose to introduce a screened potential as an additional constraint. Obtained results show a good matching between experimental and computed functions and a significant improvement in PDFs curves with potential constraint. It suggests an efficient fit of pair distribution functions curves.

Keywords**—**RMC simulation; Screened potential; partial and pair distribution functions; glassy and liquid state

I. Introduction

BY a structural modeling, the aqueous electrolyte LiCl6H2O is studied. This system presents the property of forming a glass in passing via the metastable supermelt state when the temperature decreases. The Reverse Monte Carlo (RMC) simulation [1-3] presents the interest being applicable without specifying intra/intermolecular interactions. It describes a three dimensional system on the atomic level based on the available experimental data and some geometric criteria's. This simulation method completes experiment by computing pair correlation functions between two species constituting the system.

Some artifacts appeared in PDF curves due to nonuniqueness problem of RMC or/and to the limited set of experimental data. To alleviate this problem, we introduce an additional constraint of potential.

Section 2 is reserved for the implementation of the RMC method; In section 3, the simulations details as performed here are described, section 4 provides obtained results and their discussion whereas in section 5, conclusion is drawn.

II. Implementation of the RMC Method

Details of the RMC method have been given before [4, 5] so we shall just give a brief summary. The aim is to produce three dimensional structural model of a disordered system consistent with the available diffraction data within fixed standard deviation. A modification of the Metropolis Monte Carlo (MMC) method is used [6]. Instead of minimizing the potential model as in the classical methods (Molecular Dynamic and Monte Carlo), the difference between the calculated and experimental partial distribution functions is minimized. Starting with a particular initial configuration, i. e. a set of coordinates in a box representing atomic positions, with periodic boundary conditions, we calculates the radial distribution function

$$g^{RMC}(r) = \frac{n_{RMC}(r)}{4\pi\, r^2 \rho\, \Delta r} \tag{1}$$

where ρ is the atomic number density and $n_{RMC}(r)$ is the number of atoms at a distance between r and $r+\Delta r$ from a central atom, averaged over all atoms as centre. It is the inverse Fourier transform of the structure factor depending of the wave vector Q and expressed as:

$$S^{RMC}(Q) = 1 + \rho \int_0^{\infty} 4\pi r^2 \left(g^{RMC}(r) - 1\right) \frac{\sin Qr}{Qr}\, dr \tag{2}$$

then the statistical parameter is:

$$\chi^2 = \sum_i \left[G^{RMC}(r_i) - G^{EXP}(r_i)\right]^2 / \sigma^2(r_i) \tag{3}$$

for any couples of partial distribution functions $G^{RMC}(r_i)$, $G^{EXP}(r_i)$ calculated by RMC method and experimental result, respectively. χ^2 is calculated by using the statistical measure error estimated by standard deviation $\sigma(r_i)$ supposed uniform, independent to distance r_i .

The validation or reject of a new χ^2 value is done following Metropolis Monte Carlo (MMC) principle, where the RMC parameter is minimized instead of potential energy. χ^2 will initially decrease until it reaches an equilibrium value about which it oscillates. The resulting configuration should be a three dimensional structure compatible with the experimental partial function within standard deviation σ. Further independent configurations may then be collected by continuing to run the simulation under the same conditions as the MMC principle.

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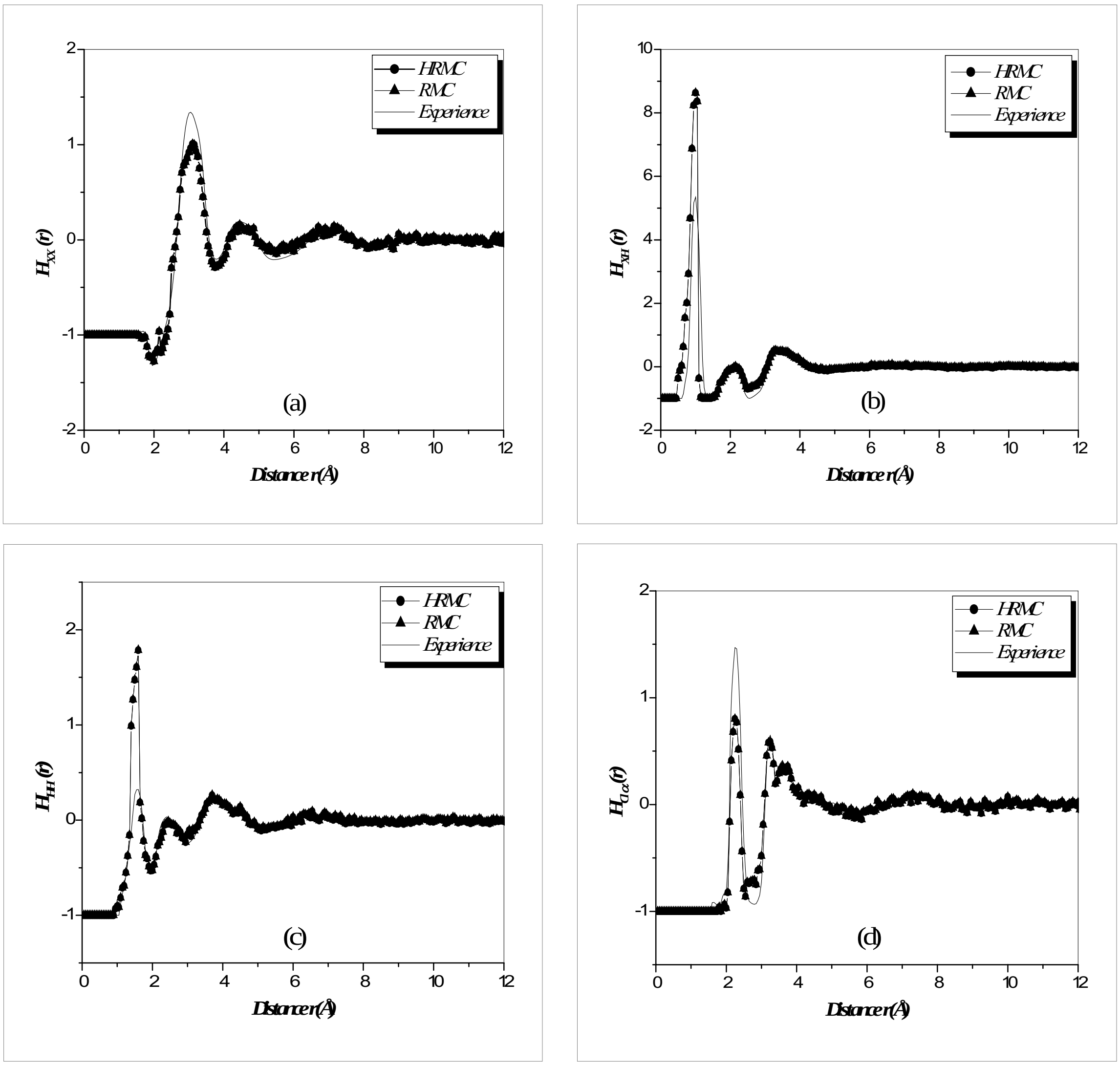

Fig. 1 Partial Distribution Functions $G_{ij}(r)$ of LiCl6H$_2$O at the glassy state: Correlation functions are represented $H_{ij}(r) = G_{ij}(r) - 1$

III. SIMULATION DETAILS

Some experimental results obtained by the neutrons scattering technique followed by that of isotopic substitution could be used [7, 8].

In order to improve the results obtained in RMC [9], we introduce an interaction potential model as additional constraint with a weight parameter ω chosen in this study to be unit. Then the parameter χ^2 is written as:

$$\chi^2 \propto \sum_l \sum_i \left\{ \left[G_l^{EXP}(r_i) - G_l^{RMC}(r_i) \right]^2 / 2\sigma(r_i)^2 \right\} + \omega U k_B T \qquad (4)$$

with U is the total potential energy. LiCl6H$_2$O structural study is taken using RMC modeling basing on four experimental partial distribution functions (PDF's).

These functions are $G_{XX}^{EXP}(r), G_{XH}^{EXP}(r), G_{HH}^{EXP}(r)$ and $G_{Cl\alpha}^{EXP}(r)$ [9] describing four types of correlations, X is all atoms species except the hydrogen atom and α correlation between any of species constituting the solution.

With the pair distribution functions and the angular correlation functions directly calculated by RMC, we can determine characteristic parameters as the coordination numbers and the correlation distances. The aqueous electrolyte thermodynamic states liquid/glass are contrasted with respect to the pure water at room temperature. Artifacts are appeared in curves representing some radial pair distribution functions $g_{ij}(r)$ (i,j=O, H, Li$^+$, Cl$^-$). To remedy to this, we introduced a screened potential for all the atomic species of the solution.

Since chlorine and lithium ions charged -1 and +1, respectively, the water molecule is represented by a flexible model [11] charged as -0.8476 for the oxygen and +0.4238 for each hydrogen atom [10, 11]. These charges whose values are defined by electronic unit, will be used to calculate the screened Coulomb potential [12] expressed as:

$$u_{ij} = C \frac{\alpha\, e^2 \exp(-\kappa\, r)}{r} \qquad (5a)$$

where one write for simplicity, respectively α and r , the charge fraction α_i corresponding to species and distance r_{ij} between two different species i and j. C is coulomb potential parameter and κ is the screen constant respectively being:

1. $C = \frac{1}{4\pi\pi}$ (5a) and $\kappa = \left(\frac{DK_BT}{\rho\, e^2}\right)^{-1/2}$ (5b)

D and K_B are the water dielectric constant at ambient temperature and Boltzman constant, respectively. T is the state temperature of the system, ρ the corresponding total species density and e electronic unit.

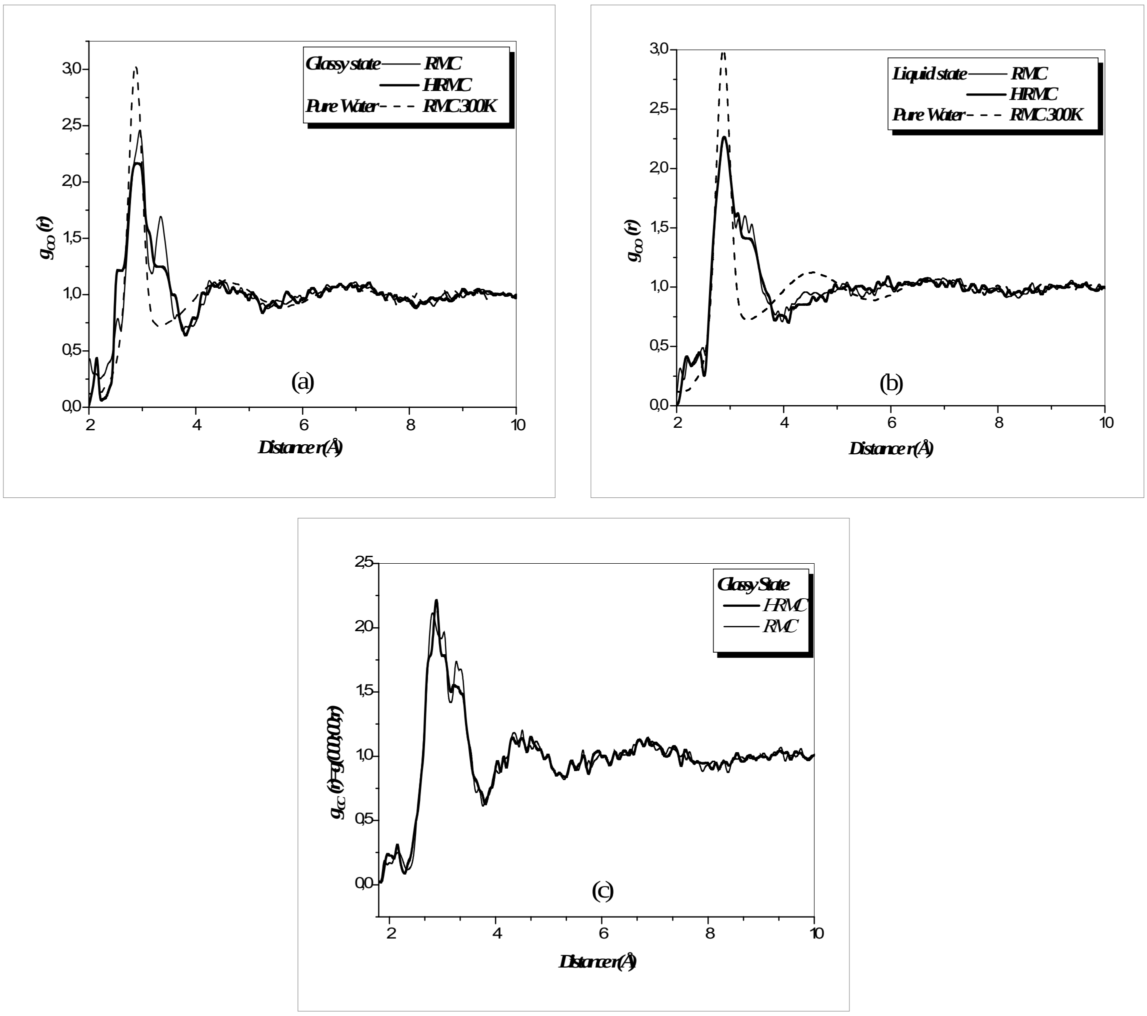

Fig. 2 (a)-(b) Pair distribution function $g_{OO}(r)$ at glassy and liquid states contrasted to the pure water at room temperature. (c) Center-center angular correlation function $g_{CC}(r)$

IV. RESULTS AND DISCUSSIONS

A. Partial Correlation Functions

We have judge more convenient to present only the curves corresponding to the glass state, because it shows a better structural organization than that of the liquid state. We can note that it is easy to represent the partial correlation functions instead the PDFs $H_{ij}(r) = G_{ij}(r) - 1$ (see *Fig.1*). The calculated partial distribution functions curves and the experimental ones are in good agreement. They show a net concordance, there is thus no mismatch between RMC with or without potential constraint.

So there is no conflict between the method used in our study and the introduced potential constraint.

This suggests that the model of potential is valid. It can be used to determine the structural properties and to describe the average correlations between the species constituting an aqueous electrolyte or a similar system.

B. Pair Correlations Water-Water and Water-Ions

Main intermolecular correlations of the H_2O molecule are observed in the figure 2; Oxygen–Oxygen in the pair distribution function $g\quad(r)$ (Fig.2.a) and the Center-Center in the angular distribution $g\quad(r)$ (Fig.2.b), describing water-water correlations.

The obtained results show a significant improvement of these functions, which shows an artificial peak, at distance 3.1 Å. Compared with previous work [13], this becomes practically smoothed. The pair correlation functions between two atoms of the water molecule in its two thermodynamic states are compared to those of the pure water. The principal peak of $g_{OO}(r)$ at 2.98Å is not affected by the presence of ions in the solution and has kept the same position.

The peak of the second coordination at 4.4Å (Fig.2.a/b) shows an interesting behavior. In the glassy state this pick oscillates in phase and practically with the same intensity of the pure water one showing a significant order, while no structure is visible in the liquid. We can also estimate that the correlation distances and the corresponding coordination numbers of water and the glassy solution are practically the same.

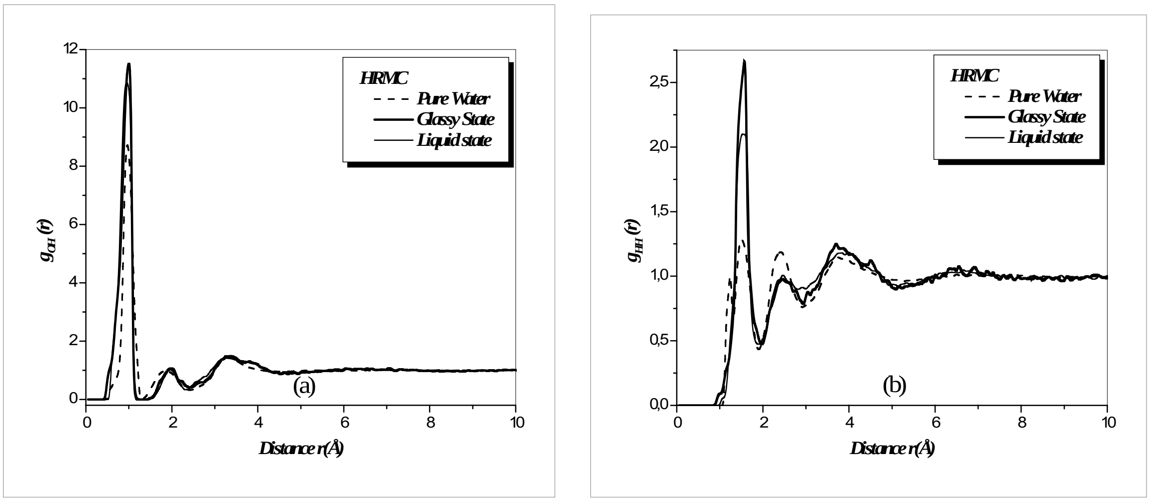

Fig. 3 Pair distribution function water-water: (a)g_{OH}(r), (b)g_{HH}(r) at glassy and liquid state contrasted to the pure water at room temperature

The glassy solution possesses a similar structure to the the pure water one at room temperature. It suggests that the lattice hydrogen bond is reorganized at the the glassy state. As the temperature decrease, the solution passes from a state where no meaningful order is observed, to another state more ordered. This suggests that this structure is broken when the temperature increases.

For the other functions, the first intramolecular peak of both $g_{OH}(r)$ (*Fig.3.a*) and that of $g_{HH}(r)$ (*Fig.3.b*) are identical in the two thermodynamic states, suggesting that the internal structure of the water molecule didn't change in any case.

Hence, neither the state changes nor the presence of ions affect the well know structure of the water molecule. However, a small shift has been observed for the first and the second coordination of $g_{OH}(r)$ (situated at 2Å and 3.4Å respectively) in the solution with respect to the pure water, probably due to the presence of ions. For the same reason the peak of the first and the second coordination in $g_{HH}(r)$ (located at 1.5Å and 2.4Å respectively) are raised in the pure water case. Otherwise, for the third coordination (situated at 3.7Å), the peak of the solution is more intense. This is synonym of the greater role of the ions in the raising of the long-range order.

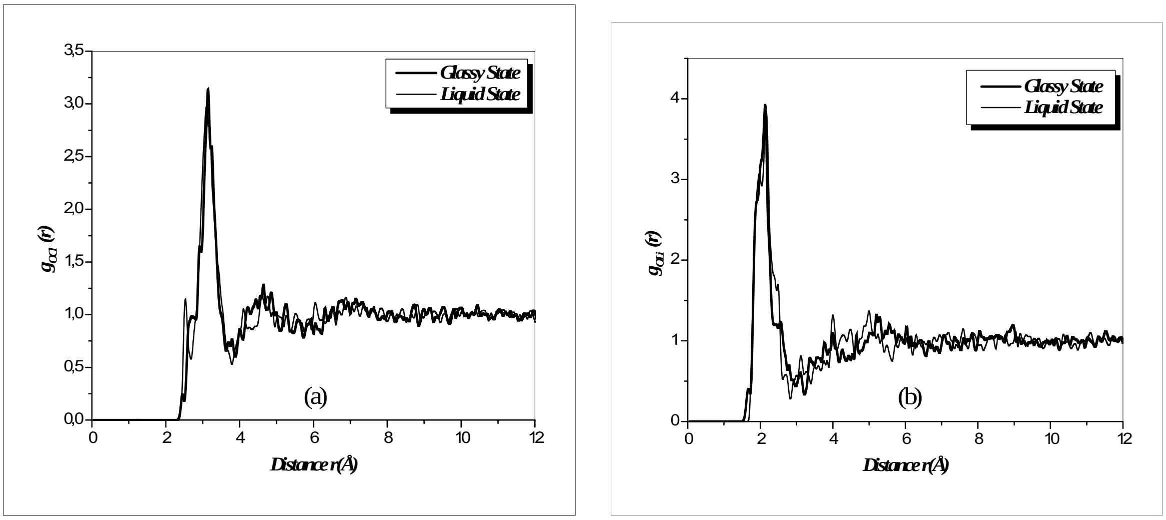

Fig. 4 Pair distribution function ion-Oxygen $g_{OCl}(r)$, $g_{OLi}(r)$ of LiCl6H_2O in glassy and liquid state

Finally, in the case of water-ions correlations, the $g_{Oi/Hi}(r)$ functions (i = Cl, Li) (*Fig.4/.5*) shows a relative more ordered structure for the Chlorine–Oxygen/Hydrogen (*Fig.4.a* and *Fig.5.a*) than for the Lithium-Oxygen/Hydrogen (*Fig.4.b* and *Fig.5.b*).

This can be assigned to the larger coherent scattering length in the Chlorine than in the Lithium as known in neutron experience.

The ion-ion pair radial distribution functions results, will be exploited and discussed in future works.

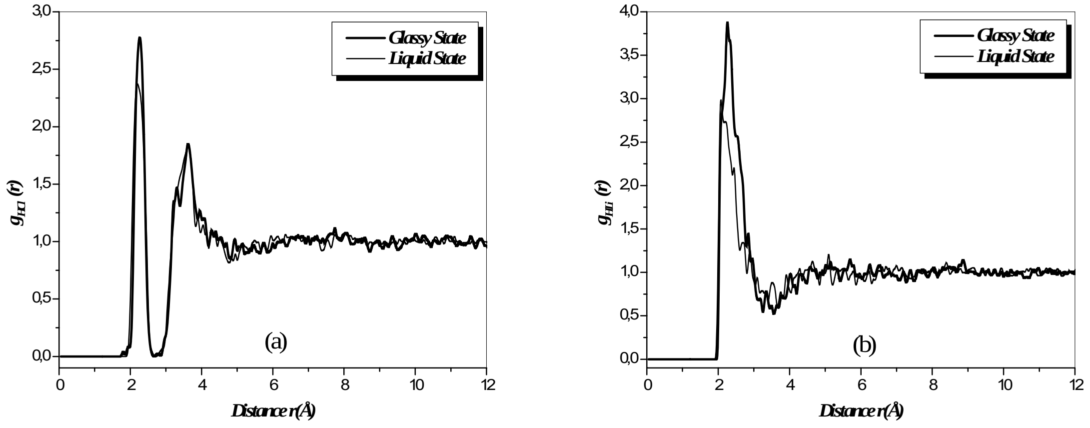

Fig. 5 Pair distribution function ion-Hydrogen $g_{HCl}(r)$, $g_{HLi}(r)$ of LiCl6H$_2$O in glassy and liquid state

V. CONCLUSION

The RMC method allows exploring a number of structural features of the system based on experimental data limited to four partial distribution functions (PDF). The obtained results include some artifacts. To remedy to this, we purpose to introduce a potential model as additional constraint. We must take into account the mismatch between the introduced potential and the RMC algorithm. Consequently, we could suggest that the choice of the interaction model as a function of atomic or molecular properties forming the system could bring a meaningful improvement to the results. This approach can be useful test for a defined interaction potential model used for conventional simulation methods as Monte Carlo (MC) and Molecular Dynamic (MD).

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