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Structural Modelling of the LiCl Aqueous Solution: Using the Hybrid Reverse Monte Carlo (HRMC) Simulation

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***Abstract*—**The Reverse Monte Carlo (RMC) simulation is applied in the study of an aqueous electrolyte $LiCl6H_2O$. On the basis of the available experimental neutron scattering data, RMC computes pair radial distribution functions in order to explore the structural features of the system. The obtained results include some unrealistic features. To overcome this problem, we use the Hybrid Reverse Monte Carlo (HRMC), incorporating an energy constraint in addition to the commonly used constraints derived from experimental data. Our results show a good agreement between experimental and computed partial distribution functions (PDFs) as well as a significant improvement in pair partial distribution curves. This kind of study can be considered as a useful test for a defined interaction model for conventional simulation techniques.

***Keywords*—**RMC simulation, HRMC simulation, energy constraint, screened potential, glassy state, liquid state, partial distribution function, pair partial distribution function.

I. Introduction

AQUEOUS Aqueous electrolyte solution of lithium chloride LiCl presents interesting properties which is studied by different methods at different concentration and thermodynamical states [1-5]: This system possesses the property to become a glass through a metastable supercooled state when the temperature decreases [6-9]. Several 3-dimensional configurations are generated to study the aqueous electrolyte LiCl6H2O by means of the Reverse Monte Carlo "RMC" simulation method [10]. This technique has the advantage to be applied without any specified inter-atomic and/or intermolecular interactions. It allows the construction of a 3-dimensional model on the atomic level based on both experimental data and some geometric constraints. This simulation method completes the experiment by computing the pair correlation functions between each two components of the studied system. Unrealistic features [14-18] appear in different pair distribution functions due to the limited set of experimental data and/or to the nonuqueness problem [19] of RMC. In order to overcome this problem and improve the obtained results by the conventional (RMC) [14,15], we apply a modified simulation protocol based on reverse Monte Carlo (RMC) algorithm, which introduces an energy constraint in addition to the commonly geometrical constraints derived from the experimental data (see table2). This method is called Hybrid Reverse Monte Carlo (HRMC) [15-17].

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In section 2, the details of the simulations performed here are described; Section 3 provides obtained results and their discussion whereas in section 4, conclusion is drawn. To insert images in *Word*, position the cursor at the insertion point and either use Insert | Picture | From File or copy the image to the Windows clipboard and then Edit | Paste Special | Picture (with "Float over text" unchecked).

II. Simulation Details

The Reverse Monte Carlo (RMC) method has been described elsewhere in detail [9-12], we will only give a brief summary. The aim is to produce three dimensional structural models of ordered or disordered systems consistent with the available diffraction data within fixed standard deviation. A modification of the Metropolis Monte Carlo (MMC) method is used [19]. Instead of minimizing the potential term as in the classical methods (Molecular Dynamics and Monte Carlo), the difference between the calculated and the experimental partial distribution functions $G(r_i)$ is the quantity to be minimized, χ^2, which is given by

$$\chi^2 = \sum_i \left[G^{RMC}(r_i) - G^{EXP}(r_i) \right]^2 / \sigma^2(r_i) \qquad (1)$$

where $G^{RMC}(r_i)$ and $G^{EXP}(r_i)$ are the partial distribution functions obtained from the RMC configurations and experiment, *i=1* to is the number of experimental data point and $\sigma(r_i)$ is an estimate of the experimental error .

The RMC simulation starts with an appropriate initial configuration of atoms. When modeling crystalline materials, this configuration will have atoms in their average crystallographic positions, and will contain several unit cells. If modeling non-crystalline materials, an initial algorithm will be required to generate a random distribution of atoms without unreasonably short inter-atomic distances. Atoms are selected and moved randomly, to obtain a new configuration, after each move, the $G(r_i)$ of the new configuration is calculated as well as the χ^2 . If χ^2_{new} is less then χ^2_{old} ; the agreement between experimental and the current configuration is improved by the move, thus the move is accepted and another move is made, if χ^2_{new} is increased, it is not rejected outright but accepted with a probability the process is then repeated until

$$\exp\left[-\left(\chi^2_{new} - \chi^2_{old} \right) / 2 \right] \qquad (2)$$

 fluctuates around an equilibrium value. The resulting configuration should be a three-dimensional structure

compatible with the experimental partial function within the fixed standard deviation. In this work, The RMC modeling of $LiCl6H_2O$ is taken on the basis of the four experimental partial distribution functions (PDF's): $G_{XX}^{EXP}(r)$, $G_{XH}^{EXP}(r)$, $G_{HH}^{EXP}(r)$ and $G_{Cl\alpha}^{EXP}(r)$ obtained by the neutrons scattering technique from the isotopic substitution [5-8]. Experimental PDF's describe four types of correlations, where the subscript X defines all atom species except the hydrogen one, while $Cl\alpha$ represents the correlation between Cl and all the other species constituting the solution. From the direct calculated radial pair distribution functions and those of angular correlation, characteristic parameters as the coordination numbers and the correlation distances can be determined. The obtained results include some unrealistic features [13,14]. Artifacts appeared in the curves of pair distribution functions $g_{ij}(r)$ (*i,j=O, H, Li, Cl*), to remedy this problem, we use the Hybrid Reverse Monte Carlo (HRMC) simulation. The HRMC method [15,16] consists in introducing an energy penalty term in the acceptance criteria. The energy of the system is calculated, in this study, by using the screened Coulomb potential [20].

$$u_{ij} = C\frac{\alpha_i \alpha_j e^2 \exp(-\kappa r_{ij})}{r_{ij}} \quad (3)$$

where q is the charge fraction corresponding to the species i and r_{ij} is the distance between two different species i and j respectively. $C = 1/4\pi\varepsilon$ is the coulomb potential parameter while $\kappa = (DE_{th}/\rho e^2)^{-1/2}$ is the screen constant. D corresponds to the water dielectric constant at ambient temperatures and ρ the corresponding total species density. e corresponds to the electronic charge.

The agreement factor χ^2 becomes:

$$\chi^2 \propto \sum_{lj}\left\{\left[G_l^{EXP}(r_i) - G_l^{RMC}(r_i)\right]^2 / 2\sigma(r_i)^2\right\} + \omega U / E_{th} \quad (4)$$

where U denotes the total potential energy and $E_{th} = k_B T$ is the thermal energy, while ω is a weighting parameter. *T* represents the temperature of the system. The conditional probability is now given as:

$$\exp\left[-\left(\chi^2_{new} - \chi^2_{old}\right)/2\right]\exp(U_{new} - U_{old}) \quad (5)$$

where U_{new} and U_{old} are the energies of the new and old configurations, respectively.

Since chlorine and lithium ions charges are -1 and +1, respectively, the water molecule is represented by a flexible model [21,22] charged as -0.8476 for the oxygen and +0.4238 for each hydrogen atom [21-23]. These charges, whose values are defined by electronic unit, will be used to calculate the Screened Coulomb potential

With this in mind, the aqueous electrolyte thermodynamic states liquid/glass will be contrasted with respect to pure water at room temperatures.

III. Results and Discussions

A. Partial Correlation Functions

It is more convenient to present the curves of the glass state, as it shows a better structural organization compared to the liquid state. Note that it is easy to use partial correlation functions equivalent to PDF's $H_{ij}(r) = G_{ij}(r) - 1$

A comparison between the experimental and calculated PDF's by RMC with and without the energy constraint is displayed in *Fig.1*. All of the obtained results show good agreement and a clear concordance. There is no discrepancy between RMC with or without the screened potential constraint and consequently, no conflict can be reported between the system studied and the introduced potential model. The used potential model is valid and thus can be used to calculate the structural properties and to describe the average correlations between the species in an aqueous electrolyte or a similar system.

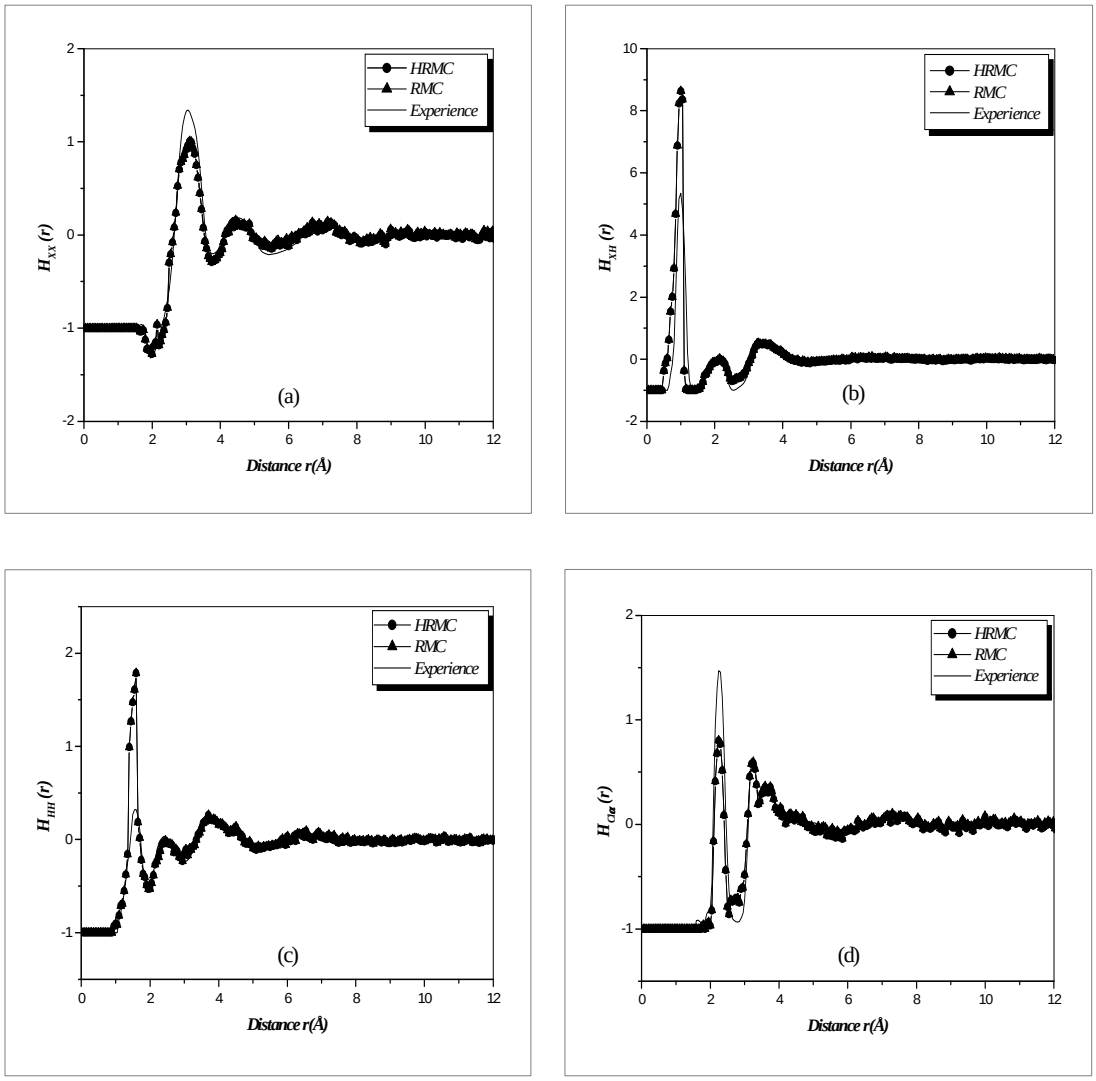


Fig. 1 Partial Distribution Functions $G_{ij}(r)$ of $LiCl6H_2O$ at the glassy state: Correlation functions are represented $H_{ij}(r) = G_{ij}(r) - 1$

B. Pair Correlations Water-Water and Water-Ions

The main intermolecular correlations of the H_2O molecule are described through the radial pair distribution function Oxygen–Oxygen $g_{OO}(r)$ (*Fig.2*) for both the glassy (*Fig.2.a*) and the liquid (*Fig.2.b*) states, and through the angular correlation function Center-Center $g_{CC}(r)$ (*Fig.2.c*).

We can notice that they are accompanied by an artificial satellite peak. This can be due to the limited set of experimental data to only four functions.

Using the inter-atomic energy term penalizes against physically unrealistic local structure**.** The obtained results show a significant improvement of $g_{OO}(r)$ with the quasi disappearance of the artifact peak located at 3.1Å. Other artificial structures have also been corrected within the same process. In fact, the pair correlation functions of water-water and water–ions have been suitably smoothed where many other artifacts disappear.

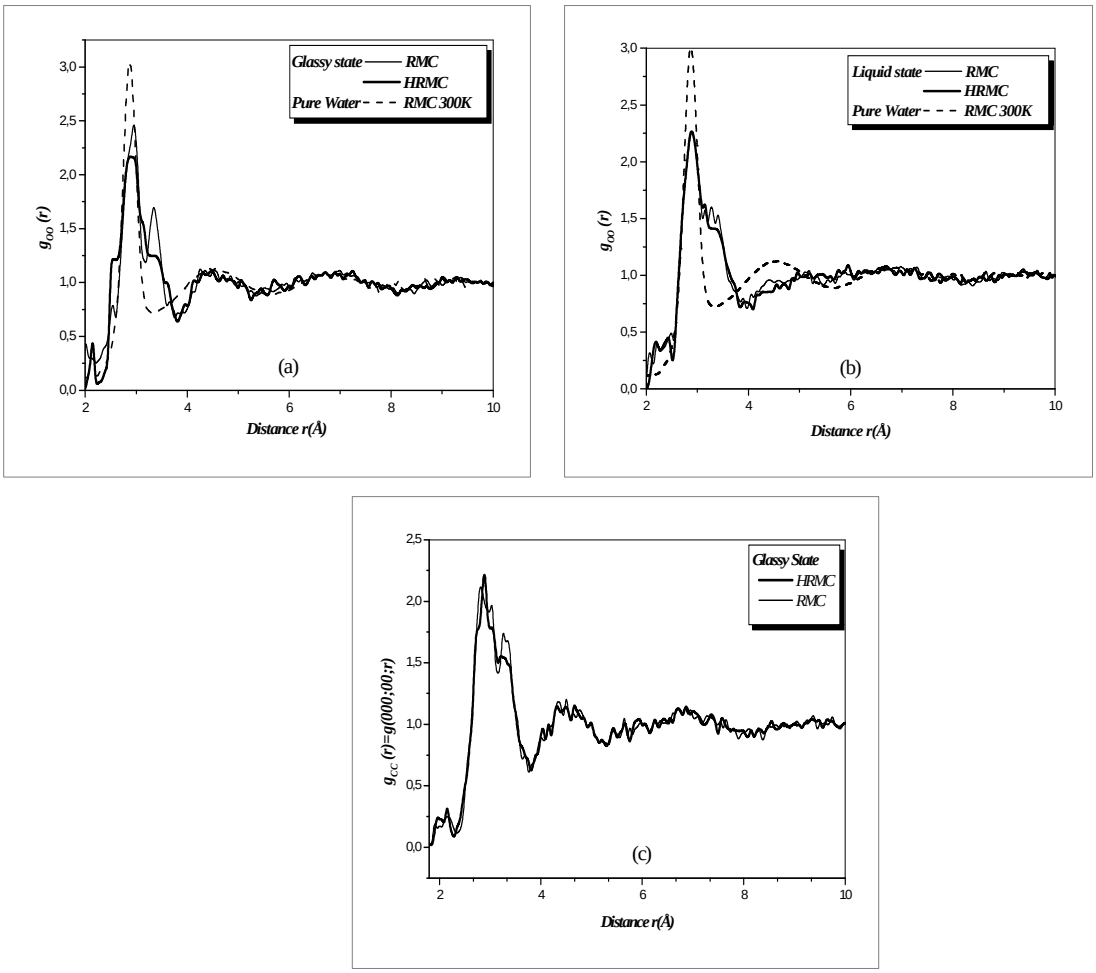


Fig. 2 (a)-(b) Pair distribution function $g_{00}(r)$ at glassy and liquid states contrasted to the pure water at room temperature (c)Center-center angular correlation function $g_{cc}(r)$

On the other hand, the radial pair distribution functions between two atoms of the water molecule in its two thermodynamic states are compared to those of pure water (*Fig.3*). The main peak of $g_{oo}(r)$ located at 2.98Å is not affected by the presence of ions in the solution. The second coordinence peak situated at 4.4Å shows an interesting behavior: In the glass state, the peak intensity oscillates with the same manner as in pure water, showing the presence on a significant order until 10Å while no structure is visible in the liquid case. We can also estimate that the correlation distances of the peak and the corresponding coordinence number for water and the glassy are practically the same.

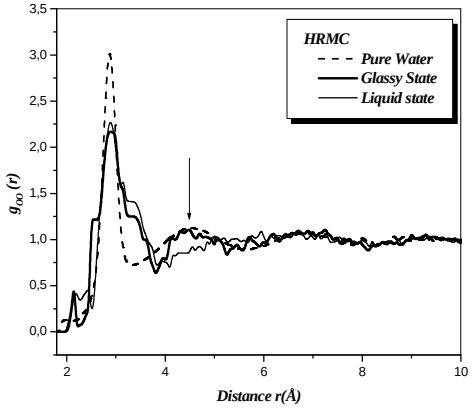


Fig. 3 Pair distribution function $g_{00}(r)$ at glassy and liquid states contrasted to the pure water at room temperature

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

For the other functions, the first intra-molecular peak of both $g_{OH}(r)$ (*Fig.4.a*) and that of $g_{HH}(r)$ (*Fig.4.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 known structure of the water molecule. However, a small shift has been observed for the first and the second coordinence of $g_{OH}(r)$ (situated at 0.8Å and 2Å respectively) in the solution with respect to pure water, probably due to the presence of ions. For the same reason the peak of the first and the second coordinences in $g_{HH}(r)$ (located at 1.5Å and 2.4Å respectively) are raised in the pure water case. Otherwise, for the third coordinence (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.

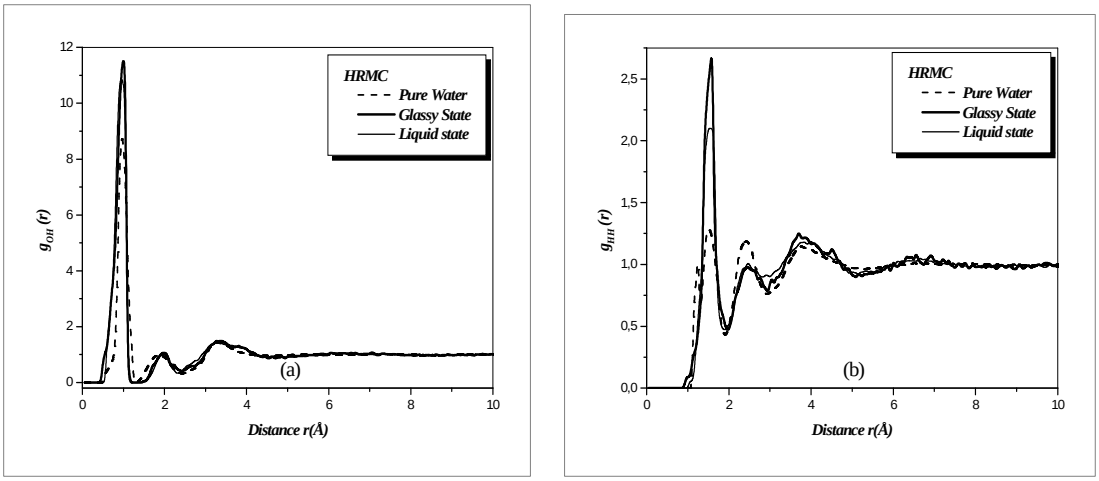
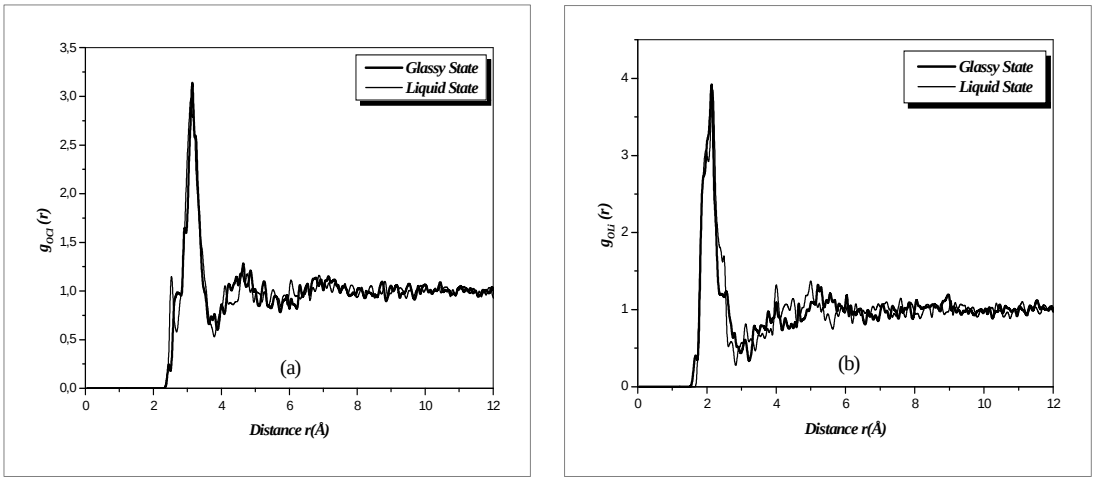


Fig. 4 Pair distribution function water-water: (a)$g_{OH}(r)$, (b)$g_{HH}(r)$ at glassy and liquid state contrasted to the pure water at room temperature

In the case of water-ions correlations, the $g_{Oi/Hi}(r)$ functions (i = Cl, Li) (*Fig.5*) show a relative more ordered structure for the Chlorine-Oxygen/Hydrogen (*Fig.5.a* and *Fig.5.c* respectively) compared to the Lithium-Oxygen/Hydrogen (*Fig.5.b* and *Fig.5.d* respectively). This can be assigned to the larger coherent scattering length in the Chlorine than in the Lithium as known in neutron experience.



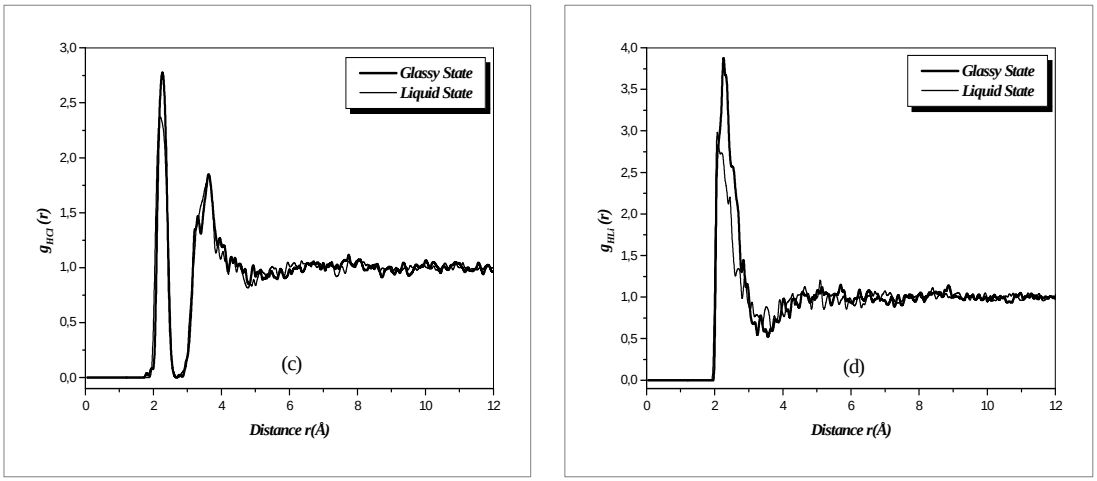


Fig. 5 Pair distribution function ion-oxygen/hydrogen $g_{Oi/Hi}(r)$ (i = Cl, Li)

IV. Conclusion

The reverse Monte Carlo method describes and examines a number of structural features of the system based on available experimental data, limited, in our case, to four partial distribution functions (PDF). The obtained results include some artifacts in peaks of many pair distribution functions. To alleviate this problem, we use an extension of the RMC algorithm, referred to as the Hybrid RMC. It introduces an energy term calculated, in our study, from a screened Coulomb potential model, as additional constraint. One must take into account the discrepancy between the interaction potential model and the RMC simulation method. The choice of the interaction model, as a function of the chemical and physical properties of atoms and molecules forming the system bring a meaningful improvement to the obtained results. The use of the energy constraint in RMC simulation can be, at the same time, a useful test for defined interaction potential model used in conventional simulation methods as Monte Carlo and Molecular Dynamics and an efficient fit to the pair distribution curves.

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