



A new reverse Monte Carlo simulation code combined with molecular mechanics simulation (RMC–MM) for molecular and ionic liquids

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ABSTRACT

A new reverse Monte Carlo (RMC) simulation code has been developed for molecular and ionic liquids, in which the molecular structure is constrained by the molecular mechanics (MM) method, while intermolecular correlations are simulated by the standard RMC algorithm. The present hybrid method (RMC–MM) has been successfully applied to a typical molecular liquid CCl₄ and to AlCl₃-1-ethyl-3-methylimidazolium chloride melt.

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1. Introduction

Liquids are essential materials in our life and are abundant in nature. Therefore understanding the structure of liquids is one of the important topics in chemical science, in order to understand their unique physicochemical properties.

Diffraction experiments are a powerful method of probing the structure of liquids. X-ray and neutron diffraction have been widely used to make direct measurements of coordination numbers and bond lengths by Fourier transformation of the total structure factor $S(Q)$ ($Q = 4\pi\sin\theta/\lambda$, 2θ : scattering angle, λ : wavelength of X-rays or neutrons) to a real-space function using the following equation:

$$g(r) = 1 + \frac{1}{2\pi^2\rho r} \int_{Q_{\min}}^{Q_{\max}} Q[S(Q) - 1] \sin(Qr)dQ, \quad (1)$$

where ρ is the atomic number density. However, recently developed room-temperature ionic liquids (RTILs) consist of organic materials as the cation, which prevents the determination of their structure at atomic and nanoscales from experimental diffraction data, because the real-space function obtained by diffraction experiments is dominated by the intramolecular correlation in the organic cation [1–4].

The computer simulation is one of the important methods for providing detailed information on the structure and dynamics of materials without carrying out experiments; thus, many computer simulation methods such as, molecular dynamics (MD), Monte Carlo

(MC) and *ab initio* simulations have been proposed. On the other hand, the reverse Monte Carlo (RMC) simulation [5] was developed by McGreevy and Pusztai in 1988 to model the atomic structure of disordered materials and disorder in crystalline materials on the basis of experimental data. RMC is a powerful tool for modeling structures, which makes it possible to generate a three-dimensional structure model without the use of interatomic potentials. In the RMC simulation, the Metropolis Monte Carlo method [6] is used to refine the agreement with neutron diffraction, X-ray diffraction and EXAFS data. Since the development of the RMC simulation, this method has been widely applied to analyze the structures of liquids, glasses, amorphous materials and disordered crystals. Recent publications and details of new techniques and problems related to the RMC simulation have been discussed and summarized in refs. [7–10]. Two of the technical problems in RMC are how to generate the initial atomic configuration and how to constrain the configuration of atoms in complicated molecules such as, ionic liquids. Pusztai *et al.* proposed a “fixed neighbor constraint” technique, which constrains the relative atomic positions in the molecules [9,10]. Keen *et al.* developed another technique to constrain the bond angles of structural units in the system [7,9]. More recently, these techniques have been integrated and installed in the new RMC simulation code “RMC++” [9–11].

In conventional RMC programs, a short-range structure has to be constrained by the bond lengths, bond angles, and coordination numbers; hence, geometric constraints can disturb convergence in the Monte Carlo algorithm. In addition, these geometric constraints are insufficient to maintain the configuration of a large molecule. Therefore, it is essential to introduce a more sophisticated method with a few parameters to constrain the structures of larger molecules and ions. In this study, we developed a new RMC code, reverse Monte

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Carlo modelling combined with molecular mechanics (RMC-MM), where the molecular structure can be constrained by the molecular mechanics (MM) technique and the intermolecular structure is modeled by the RMC method using diffraction data. As a first test of the present method, RMC-MM was applied to a typical molecular liquid CCl_4 and to a larger system, AlCl_3 -1-ethyl-3-methyl-imidazolium chloride (AlCl_3 -EMImC) melt.

2. Algorithm

The basic procedure for RMC-MM is the same as that for the standard RMC programme, known as RMCA. The partial pair distribution function, $g_{ij}(r)$, and partial pair structure factors, $S_{ij}(Q)$, (i and j define different atom types), and total structure factor, $S(Q)$, are defined by

$$Q[S_{ij}(Q) - 1] = 4\pi\rho \int_0^\infty r[g_{ij}(r) - 1] \sin(Qr) dr \quad (2)$$

$$S(Q) = \frac{1}{\langle \bar{b} \rangle^2} \sum_{ij} c_i c_j \bar{b}_i \bar{b}_j [S_{ij}(Q) - 1], \quad (3)$$

where ρ is the atomic number density of the system and the angular brackets represent averages over all atoms. The $S_{ij}(Q)$ are weighted by the scattering lengths, \bar{b}_i and \bar{b}_j (or X-ray form factors) and the molar concentrations c_i and c_j of each atomic species. A more detailed description of the basis of RMC is given in refs. [5,8]. To constrain the molecular structure, the RMC-MM program was developed by combining of the MM and Metropolis algorithms. The MM procedure was performed by employing the widely used TINKER code [12–17], since it gives the fastest convergence for the calculation of total potential energy. The total potential energy is expressed as a sum of the potential energy of each molecule, which takes the form

$$E_{\text{molecular}} = \sum E_{\text{bond}} + \sum E_{\text{angle}} + \sum E_{\text{torsion}}, \quad (4)$$

where the E_{bond} is the bond energy, E_{angle} is the energy of the angle, and E_{torsion} is the energy of the torsion. The details of RMC-MM algorithm are described elsewhere [18]. Fig. 1 shows the flowchart of the RMC-MM program algorithm.

3. RMC-MM simulation

3.1. Liquid CCl_4

First of all, the structure of a CCl_4 molecule was built using the equilibrium C–Cl bond distance of 1.791 Å and the equilibrium Cl–C–Cl angle of 109.5° together with the MM3 force field [19]. Then 1000 CCl_4 molecules were put into the simulation box at random, except that the closest C–C distance was constrained to be 4.0 Å. The edge of the simulation box was 53.92 Å, which corresponds to an atomic number density of 0.0319 Å⁻³. To constrain the exact structure of CCl_4 molecules, the MM procedure was performed at 10 K. The force-field parameters for CCl_4 were taken from the MM3 force field [19]. The simulation was run until χ^2 and the total potential energy calculated from the MM simulation reached equilibrium (χ^2 is the sum of the squares of differences between the experimental and calculated total structure factors).

3.2. AlCl_3 -EMImC melt

The total number of EMIm⁺ cations and AlCl_4^- anions was 512. The initial configurations were created by arranging randomly mixed and rotated ions in the simulation box with a corresponding atomic number density of 0.0672 Å⁻³. The force-field parameters for a 50 mol%

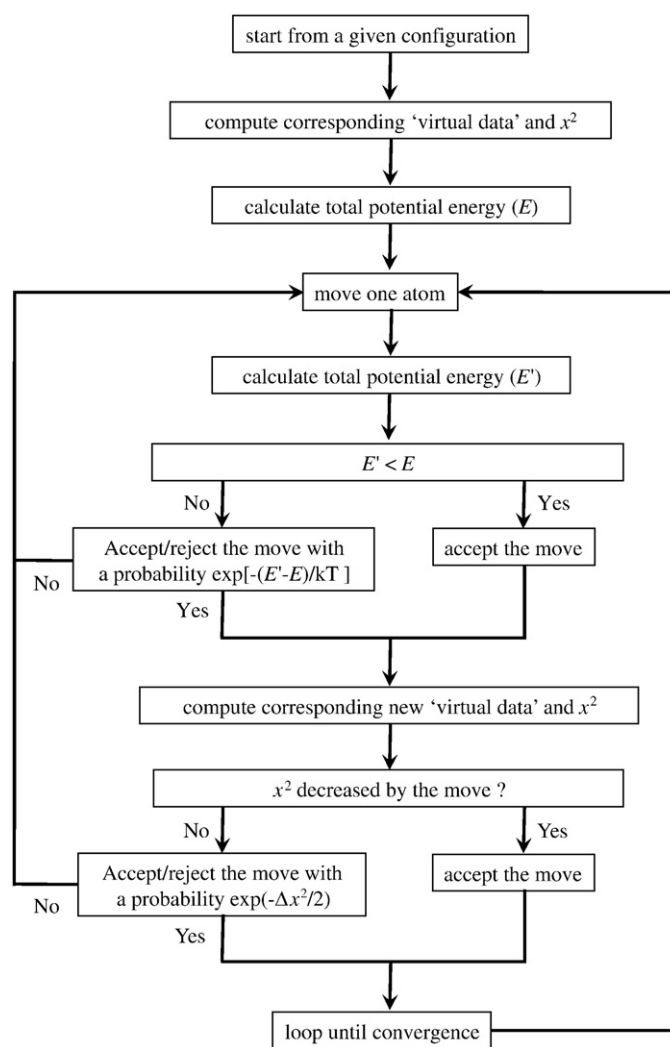


Fig. 1. Flowchart of the algorithm for the RMC-MM programme.

AlCl_3 -50 mol% EMImC system were taken from the AMBER and DREIDING parameters given in ref. [20].

4. High-energy X-ray diffraction experiment

The high-energy X-ray diffraction (HEXRD) experiment was carried out at the BLO4B2 beamline [21] at the SPring-8 synchrotron radiation facility, using a two-axis diffractometer dedicated to the study of disordered materials [22,23]. Liquid CCl_4 was sealed in a silica glass tube (2 mm in outer diameter, 10 μm in wall thickness). The diffraction patterns of the sample in a tube and an empty tube were measured in transmission geometry with a 2θ step scan method. The energy of the incident X-rays was 61.6 keV. The raw data were corrected for polarization, absorption, and background, and the contribution of Compton scattering was subtracted using standard analysis procedures [22,23].

5. Results and discussion

5.1. Liquid CCl_4

Liquid CCl_4 is a typical molecular liquid and its orientational correlation has been analyzed on the basis of the several structural models but is still under debate [24–26]. Fig. 2 shows the X-ray and neutron [27] total structure factors, $S^{\text{XN}}(Q)$, which obtained up to 30 Å⁻¹ using high-flux, high-energy X-rays and pulsed neutrons. The result of the RMC-MM simulation, plotted as solid lines, agrees well with the

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