Journal of Molecular Liquids 225 (2017) 160–166

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Intermolecular orientations in liquid acetonitrile: New insights based on diffraction measurements and all-atom simulations

Szilvia Pothoczki *, László Pusztai

Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, Hungarian Academy of Sciences, Konkoly-Thege M. út 29-33, 1121 Budapest, Hungary

ARTICLE INFO

Article history:
Received 14 October 2016
Received in revised form 8 November 2016
Accepted 17 November 2016
Available online 18 November 2016

Keywords:
Molecular liquid
Liquid structure
Orientational correlations
Molecular dynamics simulation
Reverse Monte Carlo modelling

ABSTRACT

Intermolecular correlations in liquid acetonitrile (CH_3CN) have been revisited by calculating orientational correlation functions. In the present approach, hydrogen atoms are included, so that a concept applicable for molecules of (nearly) tetrahedral shape can be exploited. In this way molecular arrangements are elucidated not only for closest neighbours but also extending well beyond the first coordination sphere. Thus a complementary viewpoint is provided to the more popular dipole-dipole correlations. Our calculations are based on large structural models that were obtained by applying diffraction data and partial radial distribution functions from potential-based (all-atom) molecular dynamics simulation simultaneously, within the framework of the Reverse Monte Carlo method.

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1. Introduction

Liquid acetonitrile has attracted a continuous interest [1–24] over the past nearly 40 years, due to its physical properties (high dipole moment, high dielectric constant, miscibility with protic solvents) that allow for a wide range of applications [1]. Its structure has been investigated both by X-ray [2–4] and neutron [5–6] diffraction methods. In these early studies even the (intermolecular) partial radial distribution functions were not determined. Thus it became clear that for detailed analyses of molecular-level correlations, the application of computational methods, such as molecular dynamics (MD) [7–15], Monte Carlo (MC) [16–20] and Reverse Monte Carlo (RMC) simulation [18], and/or various theoretical calculations based on statistical mechanics [21–24], would be necessary. For determining mutual orientations of the molecules in the liquid, structural models containing thousands of molecules would be essential.

Unfortunately, it is difficult to assess statements and findings arising from these calculations because the majority of the works mentioned above [7,9–13,15–17,19–24] have not considered any comparison with any diffraction measurements [2–6] (as direct information of the structure). As a reminder, we wish to point out here that just one type of diffraction data, either X-ray or neutron, cannot provide the appropriate information necessary for determining even all the two-body intermolecular correlations [14,18]: X-ray diffraction is mainly sensitive to carbon-carbon and nitrogen-nitrogen correlations, whereas neutron diffraction is most sensitive to pair correlations involving hydrogen atoms.

Accordingly, *our first aim is to generate large structural models that are consistent with both neutron- and X-ray diffraction data*. For this purpose we apply the Reverse Monte Carlo (RMC) technique [25]. We note here that one RMC based study can be found in the literature [18], from the early years of the method, using only X-ray diffraction data and molecules of only three sites, i.e., without explicitly including H atoms. Similarly, most of the previous structural models (except for Refs. [7, 8, 11–13]) do count hydrogen atoms separately but just a 'united atom type' methyl group. One of the novelties of the present study is that *our approach, while making use of also neutron diffraction data, considers hydrogen atoms of the methyl group explicitly*, with the aim of gaining information about intermolecular correlations, including orientations, between realistic molecules. This allows acetonitrile molecules to be taken as elongated tetrahedra, with the nitrogen and the three hydrogen atoms as the four corners. Distance-dependent orientational correlation functions can be calculated to describe mutual orientations of these distorted tetrahedra, similarly to the case of liquid chloroform [26]. This is a possible way of revealing orientational correlations between molecules that are most frequently handled as linear bodies (possibly with dipolar vectors defined along their axes).

A more traditional way of determining mutual arrangements of dipolar molecules is to calculate correlation functions using the angle confined between two dipole vectors [8,16–20]. Here we also provide distance dependent dipole-dipole correlation functions, for comparison with earlier findings [8,16–20]. Furthermore, we aim to introduce two additional characteristic angles [27,28], in order to complement the standard description of dipole-dipole correlations so that, for instance,

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* Corresponding author.
E-mail address: pothoczki.szilvia@wigner.mta.hu (S. Pothoczki).

http://dx.doi.org/10.1016/j.molliq.2016.11.056
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within antiparallel arrangements 'head-to-head' and 'tail-to-tail' type orientations may become distinguishable. These orientations are hardly identifiable without this extra.

In addition, one further question emerges: can we say anything about *mutual orientations beyond the first coordination shell*? The present study reports an attempt to address this issue.

A general difficulty concerning multi-component systems (in our case, at least the three constituents, N, C and H, need to be taken as 'components') is encountered here: due to the 'all-atom' approach the number of available independent diffraction data sets is lower than the number of partial radial distribution functions. To handle this kind of a lack of information, partial radial distribution functions from MD simulations have been utilized as input data, together with the experimentally determined total scattering structure factors (TSSF) of neutron and X-ray diffraction. Perfect agreement (within experimental uncertainties) with diffraction data was required from the RMC calculations. The expectation against partial radial distribution functions (PRDF) from MD was to see how well the potential-based PRDF-s can be approached while fitting experimental data perfectly. A combined RMC + MD scheme, suggested some years ago [29] and described in more detail recently [30], is, apart from potentially improving the quality of RMC structures, also a possible tool for a detailed validation of interaction potentials used in MD.

The initial configuration of our RMC calculations has been constructed by means of 'all-atom' Molecular dynamics simulation using a 6-site potential model for acetonitrile. Every molecular site in the MD corresponded to an atom in RMC. During the RMC simulation all atoms were treated separately from each other. Particle configurations from RMC and also from MD simulations could later be analysed in detail; here, correlation functions mentioned above have been computed (see Section 2.3 for details).

It was found important to provide comparison with the most relevant findings of earlier studies [8,13,14,16,18], especially of the work of Böhm et al. [8], as this latter work formulated objectives fairly to close our intentions.

The paper is organized as follows. In Section 2, we briefly introduce our method for the preparation of structural models exploited in this study, accompanied by a detailed description of the three different orientational correlation functions that our results are based on. The evaluation of the models can be found in Section 3. Results regarding intermolecular correlations are summarized in Section 3, and conclusions are presented in Section 4.

2. Computational details

We obtained our final ('ready-for-analyses') model in two steps: (1) first a potential based Molecular dynamics simulation has been performed; (2) then the final configuration of the MD simulation became the initial configuration of Reverse Monte Carlo (RMC) modelling, by which we wished to refine the MD structure.

Partial radial distribution functions coming from the initial MD simulation were used as input data for RMC, just as measured total scattering structure factors from diffraction experiments. Due to chemical considerations, the two carbon atoms within the CH_3CN molecule were distinguished and therefore in practice—with the N and H atoms—we had a four-component system. Consequently, the number of partial contributions (10) was much larger than the number of available diffraction data sets (2), leading to the information deficiency mentioned earlier.

2.1. Molecular dynamics simulation

Molecular dynamics simulations have been performed in the NVT ensemble using the GROMACS 4.0 program package [31] at $T = 293$ K. The temperature was controlled by the Berendsen thermostat [32], with the temperature coupling time constant τ set to 0.1 ps. The initial configuration contained 2000 molecules (12,000 atoms), with randomly placed molecular centres, in a cubic simulation box with periodic boundary conditions. The edge length of the simulation box was 55.837 Å, corresponding to the experimental density (0.786 g/cm^3). The OPLS all-atom force field [33] was selected for representing interactions between molecules. σ parameters of the Lennard-Jones (LJ) potential were 3.3 Å (C_{methyl} and C), 2.5 Å (H) and 3.2 Å (N), whereas LJ ε-s were 0.276144 kJ/mol (C_{methyl} and C), 0.06276 kJ/mol (H) and 0.711280 kJ/mol (N). The partial charges were distributed, so that they bring about the correct dipole moment (3.92D): -0.08 (C_{methyl}); 0.46 (C); 0.06 (H); −0.56 (N). The calculation of the non-bonded interactions was optimized by a grid-based neighbour list algorithm (the lists were updated in every 10 steps). Both electrostatic and van der Waals interactions were truncated at 0.9 nm, and the particle mesh Ewald method was employed for the long-range electrostatic interactions. Bond lengths and angles were kept flexible using the LINCS algorithm [34], allowing for an integration time step of 2 fs. Initial bond lengths were set to 1.47 Å (C_{methyl}-C), 1.157 Å (C-N), and 1.09 Å (C_{methyl}-H), accompanied by initial bond angles of 180° (C_{methyl}-C-N), and 107.8° (H-C_{methyl}-H).

The total simulation time was 2000 ps. A steepest-descent gradient method was applied prior to the simulations for energy minimization and to avoid atomic overlaps in the system. The total energy reached its equilibrium value within 100 ps. Data from the last 1500 ps were used for further analyses, e.g., for calculating partial radial distribution functions, and comparison with scattering data. For the latter, the *g_rdf* software of the GROMACS package was modified; details of the calculation can be found in Ref [35].

2.2. Reverse Monte Carlo modelling

The Reverse Monte Carlo method [25,36–38] is a way to generate large structural models that are consistent with experimental data within their errors. In this study we applied partial radial distribution functions arising from MD simulation (see previous section) simultaneously with total scattering structure factors from X-ray and neutron diffraction experiment during the fitting procedure. Although earlier X-ray diffraction data can be found in the literature [2–4], we took results from a new experiment [39] that has been carried out at the SPring-8 synchrotron radiation facility (Japan), using the single-detector diffractometer setup of the BL04B2 (high-energy X-ray diffraction) beamline [40]. Neutron diffraction measurements were taken from Ref. [5].

Our RMC simulations were started from particle configurations resulting from the preceding MD simulation (see previous section). In this way, RMC calculation may be considered as a "refinement" of the MD results. The basics of RMC modelling can be found in, e.g., Refs. [36–38], therefore only the relevant details are provided here. The atomic number density (0.06893 atom/Å^3) and the simulation box lengths (55.837 Å) were identical in MD and RMC simulations. Molecules have been kept together by means of 'fixed neighbours constraints' (fnc) [37], which keep atoms within a molecule within prespecified minimum and maximum distances; in our case, specifically: 1.44–1.48 Å (C_{methyl}-C), 0.987–1.187 Å (C_{methyl}-H), 1.99–2.19 Å (C-H), 1.665–1.875 Å (H-H), 2.57–2.69 Å (C_{methyl}-N), 1.15–1.19 Å (C-N), 3.1–3.22 Å (H-N). In addition, the C_{methyl}-C-N bond angle has been required to be 180° with a small tolerance.

To prevent overlaps of the atoms, the following closest approach values were enforced: 3.0 Å (C_{methyl}-C_{methyl}), 3.0 Å (C_{methyl}-C), 2.5 Å (C_{methyl}-H), 2.8 Å (C_{methyl}-N), 2.9 Å (C-C), 2.4 Å (C-H), 2.7 Å (C-N), 2.0 Å (H-H), 2.2 Å (H-N), 3.0 Å (N-N).

The essence of the present study is the analyses based on four different kinds of orientational correlation functions (see the next section for details); all these characteristics have been calculated directly from particle coordinates.

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