Molecular Dynamics Study of the Structural and Dynamical Properties of Liquid Tetrahydrofuran

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A molecular dynamics simulation has been performed to investigate the structural and dynamical properties of liquid tetrahydrofuran. In particular, we have calculated six radial distribution functions, translational and rotational autocorrelation functions and their associated frequency spectra.

Key words: Structural and dynamical properties, Molecular dynamics, Simulation, Tetrahydrofuran.

Tetrahydrofuran (THF) is often used as solvent for luminescent molecules. We have therefore undertaken a molecular dynamics (MD) simulation of this liquid. The simulation was carried out for planar THF molecules in the form of pentagons without inclusion of pseudorotation, i.e. motions in the form of puckering deformations moving around the ring. This motion has been neglected since it proved to be negligible in the calculation of the intermolecular structure and thermodynamic properties [1].

1. Interaction Potential

The molecular structure of THF is shown in Figure 1. The bond lengths and angles were taken from [1].

Each of the molecules is assumed to consist of five interaction sites: an oxygen atom and four CH_2 groups. The short-range interaction was described by a Lennard-Jones potential. The calculations of the structural and dynamical properties of THF were based on transferable intermolecular potential functions (TIPF). These functions have proven particularly successful in simulations of a variety of pure organic liquids [1, 2].

The total potential is expressed as a sum of a Lennard-Jones and a Coulomb term [1]:

$$V_{ij}^{kl} = \frac{A_k A_l}{(r_{ij}^{kl})^{12}} - \frac{C_k C_l}{(r_{ij}^{kl})^6} + \frac{q_k q_l}{r_{ij}^{kl}}. \qquad (1)$$

k and l denote sites on different molecules. A, C and the partial charges q were taken from [2]. In Table 1 the coefficients A and C are presented. The q's are expressed in electronic charges. The charge on the oxygen atom is -0.5 e. The adjacent CH_2 groups were assigned $+0.25$ e, while the remaining two CH_2 groups are neutral [1].

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2. Computational Details

For the simulations, 64 rigid THF molecules were placed in the periodic cube of edge length 20.5665 Å. The simulations were carried out at 298 K and a density of 0.881 g cm^{-3}. The intermolecular potential was a multicentre Lennard-Jones potential augmented with fractional charges to model the electrostatic part of interaction [2]. The cutoff radius was slightly less

Table 1. Parameters of the 5-site potential of THF.

Site	$A^2 \times 10^{-4}$ (kcal Å^{12}/mol)	C^2 (kcal Å^6/mol)
O	50	600
CH_2	729	1825

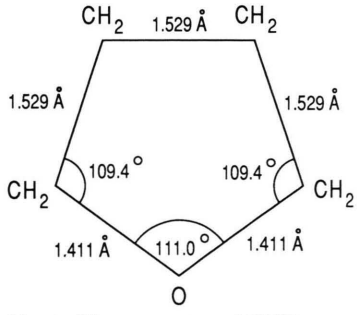

Fig. 1. The geometry of THF.

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than half of the edge length of the cell for the short-range forces. The Coulomb interactions were calculated by the Ewald sum technique [3]. As starting configuration, the centers of mass of the molecules were placed with random orientations on a cubic lattice matching the desired density. The translational and angular velocities of the molecules were chosen randomly but such that the system as a whole had no resultant translational or angular momentum. The temperature was adjusted by scaling the linear and angular velocities. Molecular orientations were expressed by means of the quaternion parameters [4]. Coupled Newton-Euler equations served to describe the time evaluation of the system. A fourth-order Adams-Bashforth predictor and the third-order Adams-Moulton corrector algorithm were used to integrate the equations of motion [5, 6]. The time step was 5×10^{-4} ps. In the course of the simulation the components of the linear and angular velocities were stored every 5 time steps for the evaluation of the correlation functions. 7500 time steps were allowed for equilibration and then the simulation was carried out for another 7500 steps. The initial temperature was set at 298 K. The mean temperature of the system in equilibrium was 299.4 K. The fluctuations of the temperature was ± 6 K.

3. Structural Properties

The structure of liquid THF is represented by the following six radial distribution functions (RDFs): $g_{O\text{-}O}$, $g_{O\text{-}C1}$, $g_{O\text{-}C2}$, $g_{C1\text{-}C1}$, $g_{C1\text{-}C2}$, and $g_{C2\text{-}C2}$. The indexes O, C1 and C2 correspond to the oxygen and the two CH_2 groups, respectively. C1 is adjacent to the oxygen. The computed RDFs are displayed in Figs. 2 and 3. We compared the RDFs calculated from the present MD simulations with previous Monte Carlo (MC) results [1]. In general the results agree. However, some differences can be observed. The peak and the minimum in $g_{O\text{-}O}$ are located about 0.5 Å further than according to the MC results. From the area under the peak up to the minimum of $g_{O\text{-}O}$ the average number of nearest neighbours is found to be 13. The MC calculation yielded 12 neighbours [1]. Marked differences have been found in the shape of the first and second peak of $g_{C1\text{-}C1}$. The second peak in all RDFs is more pronounced than in the MC results. In the MC calculations a spherical cutoff radius of 11 Å was used, whereas in the present calculations this radius was 10.26 Å.

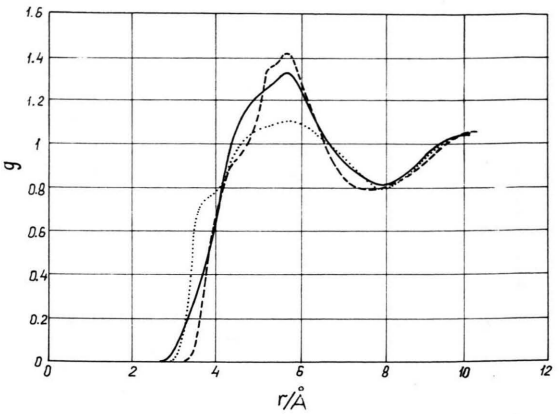

Fig. 2. Site-site radial distribution functions, (——) $g_{O\text{-}O}$, (– – –) $g_{O\text{-}C2}$, (· · · · ·) $g_{C2\text{-}C2}$.

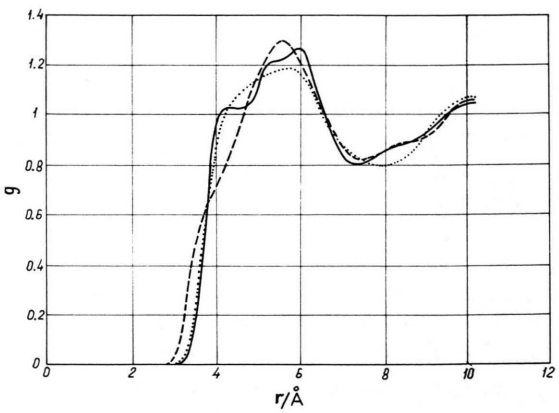

Fig. 3. Site-site radial distribution functions, (——) $g_{C1\text{-}C1}$, (– – –) $g_{O\text{-}C1}$, (· · · · ·) $g_{C1\text{-}C2}$.

4. Dynamical Properties

Translational and rotational motions of the molecules can be characterized by normalized center of mass, $Z(t)$, and angular, $C(t)$, velocity autocorrelation functions:

$$Z(t) = \frac{\langle \boldsymbol{V}_i(t_0) \cdot \boldsymbol{V}_i(t+t_0) \rangle}{\langle |\boldsymbol{V}_i(t_0)|^2 \rangle}, \tag{2}$$

$$C(t) = \frac{\langle \boldsymbol{\omega}_i(t_0) \cdot \boldsymbol{\omega}_i(t+t_0) \rangle}{\langle |\boldsymbol{\omega}_i(t_0)|^2 \rangle}. \tag{3}$$

The angular brackets denote averages over all molecules in the system and over a suitable range of initial times t_0. As shown in Fig. 4, $Z(t)$ becomes negative after 0.15 ps and remains essentially negative as the

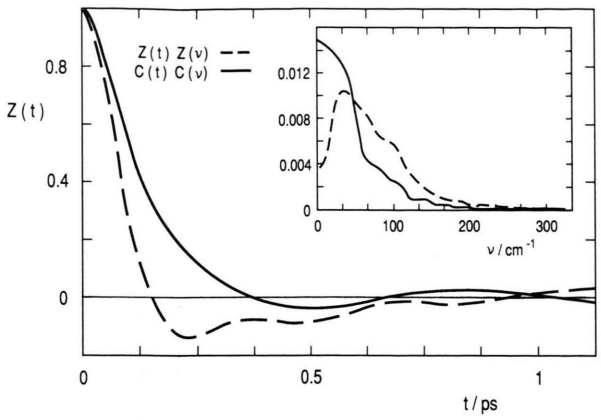

Fig. 4. Center of mass (– – – –) and angular (———) velocity autocorrelation functions. The corresponding spectral densities are shown in the insertion.

decay goes to zero at 1.04 ps. The negative correlation indicates a cage effect, where the molecule is trapped by its nearest neighbours and partially reverses its direction of motion during this time. Small undulations in $Z(t)$ reflect deviations of the molecule from being spherical. Figure 4 shows also $C(t)$. This function becomes negative at 0.38 ps and has shallow negative lobe. In liquids for which the potential is noncentral, there is an interval of time for which $C(t)$ is negative. The negative region indicates that on the average, a molecule suffers a sufficiently strong collision with the cage formed by its nearest neighbours so that the torque acting on it is large enough to reverse the direction of its angular velocity.

The corresponding spectral densities $Z(\nu)$ and $C(\nu)$ are the Fourier transforms

$$Z(\nu) = \int Z(t) \cos(\omega t)\, \mathrm{d}t, \tag{4}$$

$$C(\nu) = \int C(t) \cos(\omega t)\, \mathrm{d}t. \tag{5}$$

Contributions to the functions $Z(t)$ and $C(t)$ were accumulated every 0.0025 ps. These small steps have been chosen to resolve the fine details of the correlation functions. The Fourier transform $Z(\nu)$ represents the frequency spectrum of $Z(t)$ and is presented in the insert of Figure 4. It consists of a well developed not very broad peak at 33 cm^{-1} with a high frequency tail. The nonzero value of $Z(0)$ indicates the existence of low frequency diffusive modes. The frequency spectrum of $C(\nu)$ is essentially diffusive in character and is also shown in the insertion of Figure 4. Both spectra span almost identical frequency ranges, indicating remarkable coupling between translational and rotational modes. Generally, in most liquids translations and rotations are strongly coupled [7].

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