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Abstract. The main objective of this paper is to present a method to fully determine the six degrees of freedom regarding position and orientation of a neighboring molecule around a central one, i.e. the $g(r_{CM},\omega)$ distribution function. This is accomplished by completely determining the short range structure of liquid carbon tetrachloride, while employing results from two different methods, Molecular Dynamics (MD) [1] and Reverse Monte Carlo (RMC) [2]. Exclusively, the structural ordering of the first four molecules will be detailed.

1. Introduction

Due to the unavailability of a consensus on how to extract the detailed intermolecular structure of liquids made up of symmetric top molecules, we have sought to provide a method as to completely determine the structure of carbon tetrachloride (CCl_4), one of the first and most studied such molecular liquids [3-10].

Since this method is able to detect the slightest change in molecular ordering, we have also used it to compare the molecular orderings obtained both by MD and RMC [5, 7] methods. The former is a simulation requiring *a priori* information concerning intermolecular interaction potentials, whereas the latter method is a maximum entropy analysis of experimental diffraction patterns which needs no initial information aside from macroscopic density, as the most probable molecular ordering is obtained directly from experimental measurements.

2. Experiment

Neutron diffraction experiments were performed at the two-axis diffractometer D1B at Institut Laue Langevin (ILL) using a wavelength of 1.28 Å. Standard and Placzek corrections were performed to the obtained data. The chemical CCl_4 with purity higher than 99% was obtained from Across and was used as such.

3. Structural ordering

3.1. Positional ordering

Firstly, to describe the positional ordering a coordinate system has been defined on a central molecule. The origin is at the center of mass (CM), the z-axis has been placed along a carbon chloride (C-Cl) bond, the x-axis is co-planar with the z-axis and another bond, and finally the y-axis is the cross product of the previous two axes.
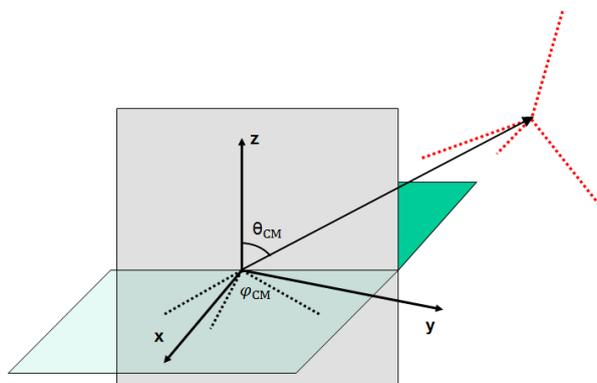
Figure 1. Using the newly defined coordinate system, a surrounding molecule's center of mass is determined by spherical coordinates (θ_{CM} and Φ_{CM}).

The 3D probability distribution graphs plotting the spherical coordinates ($\cos \theta_{CM}$ - Φ_{CM}) of the positions of the first four adjacent molecules are displayed in figure 2, which show the areas of highest probability of a molecular position.
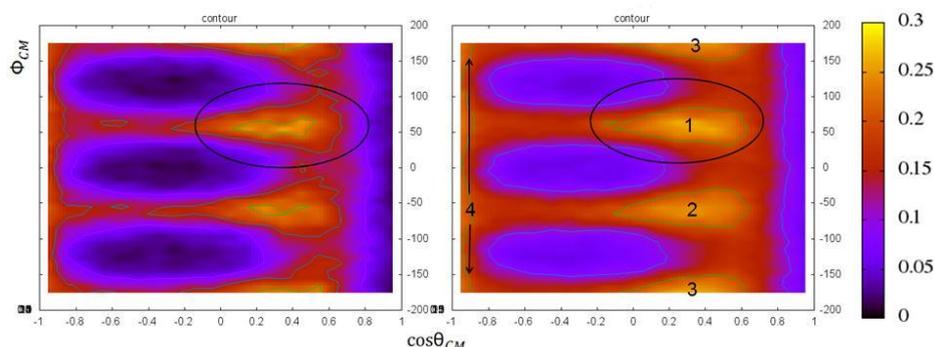

Figure 2. Graph from MD data is shown left and RMC on the right. Numbers are placed upon each probable position of a neighboring molecule.

The neighboring molecules present a tetrahedral arrangement around a carbon tetrachloride molecule. This central tetrahedral molecule has a neighboring molecule upon each of its 'faces', as can be seen in figure 3.
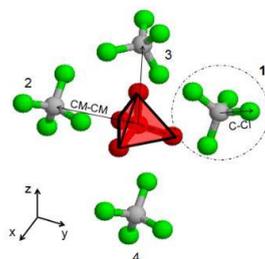

Figure 3. Most probable arrangement of four neighboring molecules around a central one.

3.2. Orientational ordering

In order to gather the orientational ordering of the first four molecules, the data of the molecule labeled as one (1) in figure 3 has been selected for further analysis and through symmetry the three remaining orientational configurations are deduced. In figure 4 we plot the probability map of the first two Euler angles in the ZY'Z'' convention (φ, θ, Ψ angles respectively) related to the orientation of any C-Cl vector of a neighbor molecule in regard to the central one.
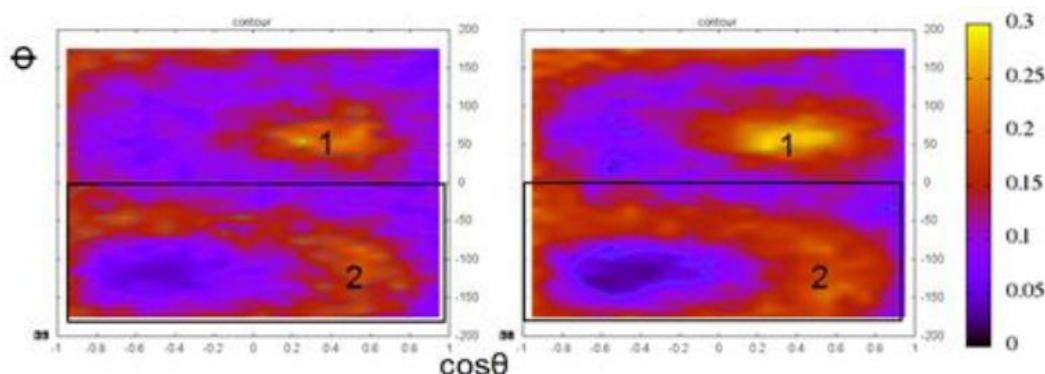
Figure 4. Two main high-probability orientational tendencies can be observed in the cosθ-φ graph. MD (left), RMC (right).

The area numbered as 1 in the figure at approximately cosθ=0.4, φ=60 is related to a C-Cl vector which is pointing opposite and perpendicular to a face of the central molecule. The other somewhat undefined area (2) which surrounds a point at about cosθ=-0.4, φ=-60, is caused by the three other C-Cl vectors, which are not perpendicular to the face of the tetrahedron. These results agree with previous studies of CCl_4, for which the face to face configuration is the most probable for closest molecules [4].
The remaining Euler angle ψ concerns the probability of a rotation around each C-Cl vector of the neighboring molecule: either around the C-Cl vector perpendicular to the face of the central tetrahedral molecule (area (1) in figure 4) or around the remaining three C-Cl vectors (area (2) in figure 4). Therefore, in order to further analyze these two different orientations, the cosθ-Ψ graph concerning each area of the graph above has been plotted.

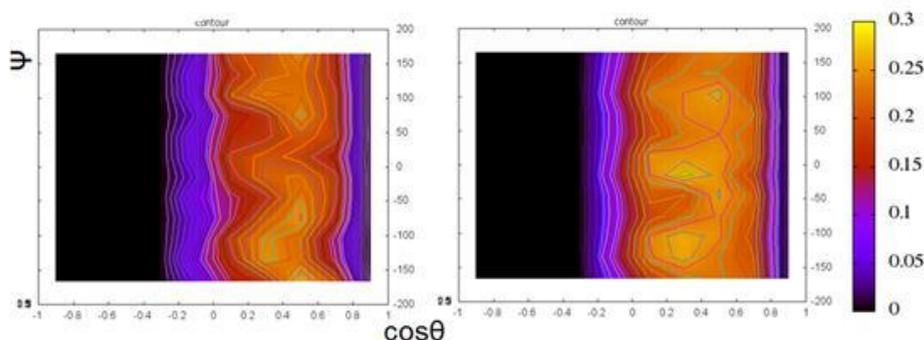**Figure 5.** The cosθ-Ψ graph employing data from area (1). MD (left), RMC (right).

The cosθ-Ψ graphs (figure 5) do not display any clear probable orientations. Since in this case ψ determines a rotation around the antiparallel C-Cl bond, any orientation set around this axis is possible. However, three slightly discernible areas on these graphs, due to interatomic repulsion, favor a face to face inverted configuration such as that showed in figure 6.
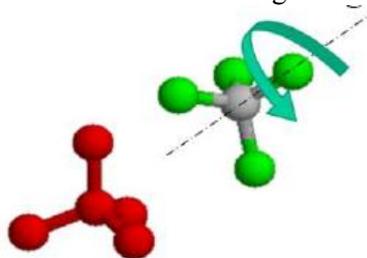

Figure 6. Face to face orientational configuration. Axis set at C-Cl bond perpendicular and opposite to a face of the central molecule.
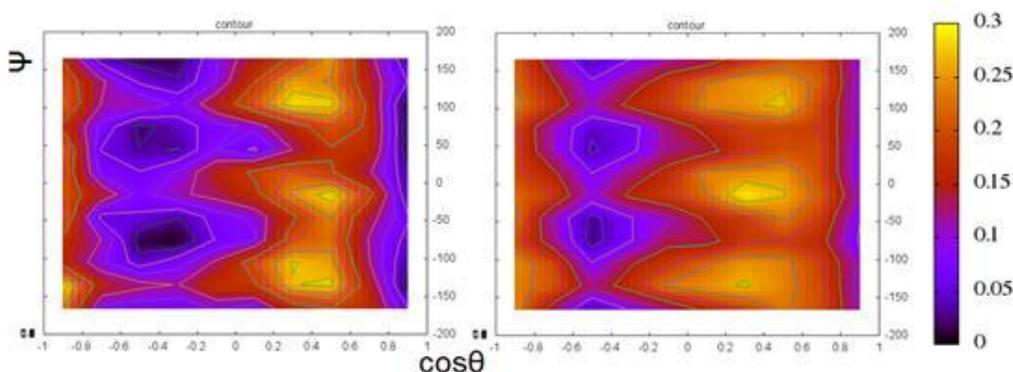
Figure 7. The cosθ-Ψ graph using data from area (2). MD (left), RMC (right)

Now if only the information from area (2) is taken into account, three main orientations can be discerned from the graph (figure 7). These correspond to three equilibrium orientations set 120° apart around an axis directed along any of the three remaining C-Cl bonds; due to the tetrahedral symmetry of the molecule, each of these orientations are essentially the same.

4. Conclusions

The short range order has been successfully determined assessing the six degrees of freedom, three positional and three orientational, describing the molecular order within liquid carbon tetrachloride. The obtained structure is coherent with the geometry of the molecule, as each molecule is set on the faces of the tetrahedral central molecule.

Concerning the relative orientation of two molecules, a face to face configuration is the most probable. Aside from small interferences due to interatomic interaction, the orientation of the molecule around the axis defined by the C-Cl bond perpendicular to a face of the central tetrahedron (Ψ angle) remains unclear. Similar conclusions have been recently obtained for quasi-tetrahedral molecules [5].

Finally, we conclude that for simple tetrahedral molecules both RMC and MD methods provide accurate and similar results regarding short range order. RMC, nevertheless, manages a better fit for experimental data.

5. Appendix

The Euler angles denote a series of rotations around the axes of a coordinate system, in order to describe an orientation. The angles are calculated with the following formulae (ZY'Z'' convention about mobile frame axes):

$$\varphi = \frac{z_y}{|z_y|} \arccos \frac{z_x}{\sqrt{1-z_z^2}} \quad (1) \qquad \theta = z_z \quad (2) \qquad \psi = -\frac{y_z}{|y_z|} \arccos \frac{-x_z}{\sqrt{1-z_z^2}} \quad (3)$$

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