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Competing structures within the first shell of liquid C_2Cl_6 : A molecular dynamics study.

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Abstract

We present a detailed study on the liquid structure of hexachloroethane (C_2Cl_6) within the first shell using the proper Euler-angles convention. Molecular dynamics is used and the van der Waals picture of a liquid is taken as the main phenomenology. Particular attention is paid to the first neighbour structure studying the distance of the center of mass (CM) and relative orientation arrangements. The distance dependence of the orientation and location of closer neighbours is studied up to the fourth neighbour (the maximum of first peak of the CM radial distribution function). An unusual arrangement in the first neighbour is seen.

1. Introduction

Liquids (although a common state of matter) are not understood completely and their structure, as opposed of that of crystals, lacks of a simple description [1]. This has been a matter of discussion since long time ago. In 1962 Bernal [2] introduced the concept of hard spheres packing for the structure of simple liquids on his Bakerian lecture. A later review by Chandler in 1978 [3] underlined the importance of the idea, originated with the work of Van der Waals long ago, that repulsive forces dominate the liquid structure. The shape of molecules then determines the intermolecular correlations (this is not always the case, Berthier and Tarjus addressed the role of attractive forces for the viscous regime of a liquid [4]). The problem of locally ordered packing is important for the stability of liquids and it has been discussed in metallic liquids and glasses [5]. Recently Ingebrigtsen et.al [6] discussed the definition of a (Roskilde) simple

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liquid regarding whether or not the long-range interactions can be ignored and quantified this via the virial potential-energy correlation. Computational techniques have become an essential tool in condensed matter research: molecular dynamics (MD) [7], Reverse Monte Carlo (RMC) [8, 9] and Empirical Potential Structure Refinement (EPSR) [10, 11] are some of the widely used methods to study disordered systems. These, along with the experimental data (Light scattering, dielectric constant measurements, neutron and X-ray scattering), give us the tools to unravel the principles behind the ordering of these structures. Hexachloroethane (C_2Cl_6) is an interesting material to study since we can consider it as a nonassociated liquid (it is well described by the van der Waals picture) and therefore steric effects are the most important ones to understand the structure. The intramolecular geometry of C_2Cl_6 was investigated by means of electron diffraction in the gaseous and solid states by Morino and Iwasaki [12] revealing the staggered disposition (chloride shells have a gauche relationship). Sasada and Atoji [13] determined the atomic parameters of orthorhombic C_2Cl_6 with x-ray methods and Hohlwein et.al [14] refined them using neutron experiments. For the structure of the plastic phase Gerlach et.al [15] conducted a neutron powder and Single-Crystal investigation and later Gerlach et.al [16] compared the previous results to a model structure of the plastic phase from a Monte Carlo (MC) method. In 1988 Gerlach and Prandl [17] studied the orientational ordering in the plastic phase using diffuse X-ray scattering and later (Gerlach et al. [18]) with elastic and quasielastic neutron scattering. Criado and Muñoz [19] used MD to simulate the plastic phase of C_2Cl_6 and used the results to interpret an inelastic neutron scattering experiment [20]. No experimental studies on the structure of liquid C_2Cl_6 have been performed (to our knowledge) due to its van der Waals symmetry (as explored by Slovokhotov et al. [21]), the boiling temperature is 1K above the melting point under ambient pressure (C_2Cl_6 sublimates easily). Therefore a simulation study is ideal to gain knowledge on this liquid to further comparisons to the plastic phase.

2. Computational details

2.1. Simulation details

We did an MD simulation using the Gromacs 4.5 [22] package. The potential parameters were chosen from the Gromos53a6 [23] force field, those values are presented in table 1. Although we have not found reported simulations on the liquid state of C_2Cl_6 , there are previous works on the crystalline and plastic phases using MC [16, 24] and MD [19] methods, which we use as a check for the potential in an auxiliary simulation on the known BCC structure before proceeding. The simulation was made on a 2000 molecules system using the NPT ensemble at the thermodynamics conditions of the liquid [25], namely $T = 458\text{K}$ and $P = 1\text{atm}$. Other general conditions were: $\Delta t = 2\text{fs}$ (during 500ps), shifted cut-off from 16 to 17Å for Lennard-Jones interactions and 20Å for coulomb pairs. We used the Particle Mesh Ewald (PME) method beyond the

Table 1: Forcefield parameters

Atom	$\sigma(\text{\AA})$	$\epsilon(KJmol^{-1})$	charge in e	mass(a.m.u)
C	3.5812	0.27741	-0.735	12.011
Cl	3.4689	1.25556	0.245	35.453

electrostatic cut-off for the reciprocal space sum. Finally the last uncorrelated 300 configurations, one each ps are taken as the raw data for the subsequent analyses.

2.2. From plastic to liquid

There are no previous reports on the simulation of the liquid state of C_2Cl_6 . Therefore, we validate our computational model on the well known BCC plastic phase. A supercell of 10x10x10 unit cells was used. The result for the lattice parameter (exposing the density) after equilibration at $T = 400K$ and $P = 1atm$ was $7.54\text{\AA}$, which is a good result compared to the experimental value of $7.58\text{\AA}$ [15] at $T = 413K$ (the difference due to temperature expansion). We proceeded then to simulate the liquid state (from a random disordered initial configuration). The Mean-square displacement (MSD) is shown in Fig. 1, a negligible positional motion (only thermal agitation) is seen for the plastic phase (thick line) as for the liquid phase (dotted line) the characteristic MSD slope shows the diffusion of the molecules through the lattice, a fluid like property.

Figure 1: (color online). Mean-square displacement for the plastic (thick line) and liquid (dashed line) temperatures.

In order to characterize the structure of the liquid we obtained the center of masses radial distribution function g_{CM} and the running coordination number

n_{CM} in the short range order, which are shown in Fig. 2. The analysis will be carried out for the first 4 neighbours (first g_{CM} maximum: $6.525\text{\AA}$ and $n_{CM} = 3.2$) rather than in the first coordination shell (FCS: g_{CM} $9.225\text{\AA}$ and $n_{CM} = 13$).

Figure 2: (color online). Short range order for the center of mass (CM) in the liquid C_2Cl_6 . The radial distribution function g_{CM} (thick line) and the running coordination number n_{CM} (dashed line) are plotted as a function of the distance. The arrow at the first peak of g_{CM} marks $n_{CM}=3.2$ molecules and the first coordination shell (FCS) arrow shows that $n_{CM}=13$ molecules.

2.3. Euler angles and axes definition

This study is based on the complete knowledge of the six degrees of freedom for the rigid molecule model, only the translational and orientational dispositions are taken into account. For that manner we used the proper Euler angles convention [26], this analysis is ideal to study the short range order, see for instance [27] and [28], here we used our own written code for that analysis. The C_2Cl_6 molecule defines a coordinate system as shown in Fig. 3). The origin of this coordinate system is used to position a pseudo-atom named the center of mass (CM). Having defined the coordinate system for each molecule we proceed to the structure characterization, namely the position and orientation ordering. The position of any molecule relative to another one is defined between their CM's taking the vector between their CM's (v_{CM}). The distance is the vector norm and the relative position is known within the sphere coming from the equatorial and polar locations. The equatorial position is given by the angle between the vector v_{CM} and the y -axis (ϕ_{CM}). For the polar location it

Figure 3: (color online). Reference axis definition for the Euler angles study on the molecule C_2Cl_6 . Angles θ_{CM} and ϕ_{CM} describe the position of any molecule relative to a reference molecule (with darker chlorides in the figure) using the vector v_{CM} that joins their centers of masses.

is the angle formed with the z -axis (θ_{CM}) that defines it. The orientation is uniquely defined under three rotations of the coordinate system, we used here the $Z - Y' - Z''$ convention and the function *atan2* for the degeneracy of the Euler angles.

The above defines unambiguously the geometrical arrangement of the molecules since it takes into account the six degrees of freedom needed for orientational and translational operations. We must recall that this analysis was done over the raw data obtained (300 configurations) from the MD simulation.

3. Results and Discussion

3.1. Positional ordering

Let us begin then with the positional ordering (θ_{CM} , ϕ_{CM}) of the very first neighbour molecule. The probability distribution of θ_{CM} and ϕ_{CM} is given in the left region of Fig. 4, with several local maxima, originated by two distinct main dispositions. First, from all the possible dispositions for the first neighbours, the most probable are in the equatorial region ($-0.8 < \cos(\theta_{CM}) < 0.8$) and some other in the polar (above and below of the reference molecule) region ($0.8 < |\cos(\theta_{CM})| < 1$). Having established this, from now on we will consider both kind of positions, namely equatorial molecules (EQM) and polar molecules (PM). The EQM are arranged most likely around 72 and 107 degrees with respect to θ_{CM} . For ϕ_{CM} it is interesting to note that it does not prefer any location but some defined positions (0, ± 60 , ± 120 , ± 180 degrees). This analysis

Figure 4: (color online). Bivariate maps for the Euler-Angles of the first neighbour. Left: Bivariate map for the position of the center of masses (CM) (θ_{CM} , ϕ_{CM}). Middle: Up the orientational bivariate map (θ_{ori} , ϕ_{ori}) for the equatorial molecules (EQM) marked at Left. Down the orientational bivariate map (θ_{ori} , ϕ_{ori}) for the polar molecules (PM) marked at Left. Right: (a). Bivariate map (θ_{ori} , Ψ_{ori}) for the EQM labeled as $ori_{||}$ (highlighted in the middle-up figure). (b). Bivariate map (θ_{ori} , Ψ_{ori}) for the EQM labeled as $ori_{\perp}$ (highlighted in the middle-up figure). (c). Bivariate map (θ_{ori} , Ψ_{ori}) for the PM labeled as $ori_{\perp}$ (highlighted in the middle-down figure).

was extended for the first four neighbours obtaining the same result as indicated for the first neighbour.

3.2. Orientational ordering

With the position being defined we moved on the orientational ordering of the first neighbour. In Fig. 4 we highlight one of the most probable regions and analyze the bivariate distribution (θ_{ori} , ϕ_{ori}) for EQM (center-up of Fig. 4) and PM (center-down of Fig. 4). All the information is contained in this spot since the locations are equiprobable and correspond to the symmetry of the system. Looking at the orientations (θ_{ori} , ϕ_{ori}) of EQM (middle-up of Fig. 4), two main regions are found in this probability map. One corresponds to the two areas centered at $\cos(\theta_{ori}) = \pm 0.3$, ($\phi_{ori} = 120, -60^\circ$) and the other is the wrapping region ranging all possible θ_{ori} . Yet, we are missing one more degree of freedom related to the orientation, Ψ_{ori} . This is analyzed in the right region of fig. 4. The wrapping area is seen at the right-top and is labeled as **(a)**. There, it can be observed that all the values of θ_{ori} appear with probability $\neq 0$ although the preferred ones are centered around 0 and 180 degrees, while there are discrete

orientations for Ψ_{ori} that are (± 30 , ± 90 , ± 150 degrees). It is interesting to note the jumps of 60 degrees, similar to those of the position (ϕ_{CM}). The second region of the middle-up map of Fig. 4 is seen at the right-middle of the figure and is labeled as **(b)**. Unlike the first region here only a narrow range of θ_{ori} values is relevant with a maximum at 107 degrees (by symmetry it will also be around 72 degrees). Again Ψ_{ori} shows some discrete values (0 and ± 120 degrees). Recalling that ϕ_{ori} and Ψ_{ori} contain the relative orientations of chlorides, we interpret this as a fact of the molecular symmetry. The chloride shell form a pyramid and it is energetically favourable to locate other chlorides in spaces between the vertices, having to give jumps of 60 degrees to reach those spaces. We can already see two different preferred orientations labeled as **(a)** and **(b)** in Fig. 4. **(a)** shows the chloride shell pointing in the same direction and we will label them as ($ori_{\parallel}$), while **(b)** shows the chloride shell pointing in perpendicular directions and we will label it as ($ori_{\perp}$). These orientations can be seen for the molecules rather than for the Euler-angles in Figs. 5a and 5b. The same analysis on the PM (center-down in Fig. 4) shows two big areas

Figure 5: (color online). Molecular orientation for the three possible arrangements seen in Figs. 4a, 4b and 4c. The reference molecule is highlighted with darker chlorides. (a). Parallel orientation ($ori_{\parallel}$) for equatorial molecules (EQM), the coordinate system and the angles convention are also shown. (b). Perpendicular orientation ($ori_{\perp}$) for EQM. (c) Perpendicular orientation ($ori_{\perp}$) for polar molecules (PM).

centered about $\cos(\theta_{\text{ori}}) = \pm 0.2$ and $\phi_{\text{ori}} = 60$ and -120 degrees. The bivariate distribution ($\theta_{\text{ori}}, \Psi_{\text{ori}}$) labeled as **(c)** in Fig. 4 reveals an equivalent arrangement to that of **(b)**, being the PM also of the perpendicular ($ori_{\perp}$) class. Again the

discrete values for Ψ_{ori} appear. The molecular disposition of the PM is given in Fig. 5c. We made the orientational analysis for the first four neighbours and we found the same characteristics. This shows a print of the local order in the positional and the orientational structure of the C_2Cl_6 liquid model and brings out the question about to what extent the short range order of the plastic phase is persistent.

Now we compare the probability distributions of the $\text{ori}_{\parallel}$ and $\text{ori}_{\perp}$ structures in order to investigate up to what extent they are equivalent structures. We started by analyzing the population (percentages) in each configuration and the characteristic distance for each neighbour. As usual, we isolate the first neighbour. We computed the distribution of distances for the CM in the $\text{ori}_{\parallel}$ and $\text{ori}_{\perp}$ classes. The result is a gaussian distribution plotted in Fig. 6a. The dotted and solid lines correspond to $\text{ori}_{\parallel}$ and $\text{ori}_{\perp}$ molecules respectively, showing that the two structures appear at different distances. The most probable values are $d_{\parallel} = 5.92\text{\AA}$ and $d_{\perp} = 6.045\text{\AA}$. Regarding to the population of each class it was found that 52% of the molecules are oriented as the class $\text{ori}_{\parallel}$ and 14% are $\text{ori}_{\perp}$, which clearly presents that one of them is more probable. We conclude then that they are non-equivalent structures. This is a strange feature given that both orientations belong to different distances. The study was again extended to the first four neighbours and the results are summed up in the Figs. 6b and 6c. Panel b shows the distance at which the close neighbour appears for the $\text{ori}_{\parallel}$ and $\text{ori}_{\perp}$ classes (dotted and solid lines respectively). The behaviour of the first neighbour is repeated here but the distances get closer as n_{CM} increases. Regarding to the population of each class the values are plotted in Fig. 6c. A similar tendency is seen, both classes approach to the same population as we go from the first to the fourth neighbour. The amount of molecules living in a given orientation is dependent on the distance, which can be related to the minimal configuration energy. And the non-equivalency of both structures is strong in the first neighbours and disappears as n_{CM} grows. Finally for the fourth neighbour the common pattern in liquids is recovered where co-living structures are equiprobable and they are characterized by the same distance.

4. Summary and conclusions

We have studied the structure of the C_2Cl_6 defining unambiguously the operations over translational and rotational states using the proper Euler-angles. The four closest neighbours are more likely to sit in the equatorial plane of a reference molecule, but there are also some of them in the polar region. The EQM present two classes of orientations: $\text{ori}_{\parallel}$ and $\text{ori}_{\perp}$. On the contrary, the PM only show the $\text{ori}_{\perp}$ class. These structures are strongly non-equivalent for the first neighbour, the two possible orientations (parallel and perpendicular) correspond to different characteristic distances. This is a non-common feature of liquids. The structures merge as the coordination number increases, being almost equivalent at the fourth neighbour in both probability and characteristic distance, being this the common case of the short range order in the liquids. A complete understanding on the structure of liquids is still missing. Taking the

Figure 6: (color online). Differences of the $ori_{\parallel}$ (dotted line) and $ori_{\perp}$ (solid line) classes. (a). Distance distribution of the center of mass CM for the first neighbour. (b). Most probable value of distance of CM for the $ori_{\parallel}$ and $ori_{\perp}$ classes (filled and empty squares respectively) as a function of the number of neighbours. (c). Fraction of molecules populating each $ori_{\parallel}$ and $ori_{\perp}$ class (filled and empty circles respectively) as a function of the number of neighbours.

present study as a basis, it seems interesting to investigate the relation of the structure of the liquid to that of BCC plastic phase. Work in this direction is in progress.

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