Structural study of $C_2Cl_6$ by Molecular Dynamics

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Abstract

A Molecular Dynamics study of hexachloroethane $C_2Cl_6$ was done in order to study the structure at different temperatures, varying from 300K to 480K. The system at 480K showed a liquid phase, as reported in the literature. A comparison with an experimental neutron scattering structure factor was made obtaining good agreement. A simulated annealing was carried out in a range of 300 to 480K. The radial distribution functions were compared studying the thermal dependence of the structure, the mean square displacements and self diffusion coefficients were also analyzed to complete an image of the structural changes. The transition to the liquid phase is observed above 450K, this is in agreement with the reported melting temperature for this system of 458K.

Keywords: hexachloroethane, structure factor, radial distribution functions, molecular dynamics.

I. INTRODUCTION

Molecular dynamics simulations have been used for the study of condensed-phases since long time ago [1], [2]. These studies are not only able to characterize the structure and static properties of systems at the molecular level, but to describe the dynamical processes that undergo in these systems. Hexachloroethane ($C_2Cl_6$), is an interesting material with three different solid phases [3], [4] (orthorombic between 4 and 318K, monoclinic between 318 and 344K and a plastic phase stable from 344K up to the melting temperature $T_m = 458K$ [5]). In this study we will investigate the structural properties of the $C_2Cl_6$ liquid phase at 480K and the solid region in the range of temperatures between 300 and 450K. We will use classical molecular dynamics simulations to study radial distribution functions, structure factors, mean square displacements and self diffusion coefficients.

This work is divided as follows, Section II. explains the details of the force field, the molecular model employed and the simulation procedure. Section III. shows the results and discussion of static and structural properties, divided in subsections A. for the liquid phase at 480K and subsection B. with the same properties for the simulated annealing starting from a solid structure at 300 K. Section IV. is devoted to analyze the mean square displacement and diffusion coefficients in all the range of temperatures simulated, comparing and relating them to the results of the Section III. Section V. is devoted to the concluding remarks and future work possibilities.

II. MOLECULAR MODEL AND COMPUTATIONAL DETAILS

The Gromos53a6 force field [6] was used, where the description of the system energy results from the sum of intramolecular interactions (bond stretching $U_{strecht}$, angle bending $U_{bend}$, dihedral torsion $U_{torsion}$) and intermolecular interactions that come from Van der Waals (Lennard-Jones $U_{LJ}$) and electrostatic (Coulomb $U_{coulomb}$) terms:

$$U = U_{strecht} + U_{bend} + U_{torsion} + U_{LJ} + U_{coulomb}$$  (1)

where the functional forms of these potentials are:

$$U_{strecht} = \sum_{n=1}^{N} \frac{1}{4} K_{bn} \left[ b^2 - b_0^2 \right]^2$$  (2)

$$U_{bend} = \sum_{n=1}^{N} \frac{1}{2} K_{\phi n} \left[ \cos \theta - \cos \phi_0 \right]^2$$  (3)

$$U_{torsion} = \sum_{n=1}^{N} K_{\phi n} \left[ 1 + \cos (m\phi_0 \phi) \right]$$  (4)

$$U_{LJ} = \sum_{pairs \ i, j} \left( \frac{C_{12}_{ij}}{r_{ij}^{12}} - \frac{C_{6}_{ij}}{r_{ij}^{6}} \right)$$  (5)

$$U_{coulomb} = \sum_{pairs \ i, j} \frac{q_i q_j}{4 \pi \varepsilon_0 r_{ij}}$$  (6)

Force field parameters [7] are given in Table I. A geometric view of the initial configuration of the molecule is shown in figure 1.

Molecular dynamic simulations were performed using the GROMACS 4.5.3 package [8], [9] with the following conditions: The simulations were carried out in the NPT ensemble. Velocities were generated according to a Boltzmann distribution at $T_{env} = 300K$, the V-rescale thermostat [10] was used to drive the temperature to $T = 480K$ and the Berendsen pressure coupling [11] kept $P = 1 \text{ atm}$. The initial configuration was obtained by randomly disposing 128, 256 and 512 molecules in a cubic box with dimensions that set the initial density to 1000 $\text{kg m}^{-3}$. Standard periodic boundary conditions and the minimum image convention were applied. A cut off distance of 1.2 $\text{nm}$ was used and corrections for Coulomb interactions beyond cut off were performed using the Particle Mesh Ewald [12], [13]. The switch method was used to bring from 0.6 to 0.7 $\text{nm}$ the LJ potential to zero. After equilibration with the
steepest descent method to converge the maximum force to 100 kJ mol⁻¹ nm⁻¹; a trajectory of 0.5 ns was generated with a time step Δt = 2 fs.

Fig. 1: Geometric view of the Hexachloroethane molecule. Carbons are gray and Chloride are green.

III. STATIC AND STRUCTURAL PROPERTIES

A. Liquid Phase

The results obtained in the liquid phase were compared between the different size system, yielding the same energies, slight differences in the density and equal radial distribution functions (rdf's) up to the half-box distance, it is for this reason that from now on we will only refer to the system of 512 molecules.

![Potential Energy](image)

Fig. 2: Potential Energy as a function of the simulation time: (red line). The inset shows the density: (blue line)

Figure 2 shows the potential energy of the simulation, it finds an stable value after 200 ps and around the same time the simulation box fluctuates less than 1% and the density (as is shown in the inset of figure 2) stabilizes also. From now on we will take the last 200 ps to compute different equilibrium properties of the system, unless other is said. The average density of the simulated liquid phase is 1180 kg m⁻³.

The structure factor of the liquid phase of C₂Cl₆ can be characterized in terms of the atomic radial distribution functions \( g_{\alpha\beta}(r) \), which gives the probabilities of finding atoms of type \( \beta \) at a distance \( r \) away from a center atom type \( \alpha \). In order to compare the simulation results with neutron scattering experiment, we construct the total radial distribution function [14]:

\[
g_{total}(r) = g_{intra}(r) + g_{inter}(r)
\]

Taking separately the intra and inter molecular contributions:

\[
g_{intra}(r) = \frac{b_{bc}b_{ge}c(r) + 12b_{bc}b_{ge}c_{ci}(r) + 15b_{bc}b_{ge}c_{ci}(r)}{W_{intra}}
\]

\[
g_{inter}(r) = \frac{4b_{bc}b_{ge}c(r) + 24b_{bc}b_{ge}c_{ci}(r) + 36b_{bc}b_{ge}c_{ci}(r)}{W_{inter}}
\]

where the numerical factors account for the number of possible pairs of two species and \( b_{bc} = 0.646, b_{Cl} = 0.9577 \) are the neutron scattering lengths of the two atom types of our molecule. The weights are used to normalize the distributions:

\[
W_{intra}(r) = b_{C}b_{C} + 12b_{C}b_{Cl} + 15b_{Cl}b_{Cl}
\]

\[
W_{inter}(r) = 4b_{C}b_{C} + 24b_{C}b_{Cl} + 36b_{Cl}b_{Cl}
\]

In figure 3 the computed C-C, C-Cl, Cl-Cl and total radial distribution functions are showed. The intra-molecular contributions are not presented here, as they are huge well defined peaks corresponding to the bond distances defined in the molecule model. The molecular coordination number \( n_c \) was computed for the first and second solvation shells, defined as the positions of the first and second minima of the total radial distribution function. In this case they are at \( r_1 = 10.5 \) Å and \( r_2 = 16.5 \) Å respectively:

\[
n_{c1} = 4\pi\rho \int_{0}^{r_1} r^2 g_{total}(r)dr
\]

### Table I. Force field parameters.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>( b_0 ) nm</th>
<th>( K_b ) kJ mol⁻¹ nm⁻⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bonds</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-C</td>
<td>0.15730</td>
<td>2.7457 x 10⁶</td>
</tr>
<tr>
<td>C-Cl</td>
<td>0.17600</td>
<td>8.1000 x 10⁶</td>
</tr>
<tr>
<td>Angles</td>
<td>( \theta_0 ) nm</td>
<td>( K_{\theta} ) kJ mol⁻¹</td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>109.1</td>
<td>1440.0</td>
</tr>
<tr>
<td>Cl-C</td>
<td>109.5</td>
<td>618.0</td>
</tr>
<tr>
<td>Dihedral</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl-C-Cl</td>
<td>3.77</td>
<td>3</td>
</tr>
<tr>
<td>NB LJ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-C</td>
<td>2.3970816 x 10⁻³</td>
<td>2.053489 x 10⁻⁴</td>
</tr>
<tr>
<td>C-Cl</td>
<td>4.5836352 x 10⁻³</td>
<td>5.604463 x 10⁻⁵</td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>8.7647044 x 10⁻³</td>
<td>1.5205921 x 10⁻⁵</td>
</tr>
<tr>
<td>1-4 LJ</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl-Cl</td>
<td>8.7647044 x 10⁻³</td>
<td>1.5205921 x 10⁻⁵</td>
</tr>
</tbody>
</table>

\( b_{c6} \) kJ mol⁻¹ nm⁶ and \( C_{12} \) kJ mol⁻¹ nm⁻¹².
\[ n_{c_2} = 4\pi \rho \int_{r_1}^{r_2} r^2 g_{total}(r) dr \]  
(13)

For the first solvation shell it was found \( n_{c_1} = 12.7 \) molecules and \( n_{c_2} = 39.43 \) molecules for the second one.

The neutron scattering structure factor was computed taking the Fourier transform of the total radial distribution function (see eq. 7):

\[ S(q) - 1 = 4\pi \rho \int_0^{r_e} (g_{total}(r) - 1) \frac{\sin qr}{qr} dr \]  
(14)

We took the number density \( \rho = 1 \) and let it as a scaling factor to compare later with the experimental results. The cut off of the integration was taken as one of the last points of the radial distribution function intercepted by the 0 axis to avoid termination effects. Figure 4 shows the results of the neutron scattering experiment compared to the structure factor computed with eq. 14 for the simulation at the same conditions: \( T = 480 \text{K} \) and \( P = 1 \text{ atm} \). Good agreement with the experiment is seen. The intermolecular structure contributes in the low q region, while the intramolecular contributions are mostly important at large q values. Three well defined peaks appear at 1.0, 2.7 and 4.7 Å\(^{-1}\).

**B. Solid Phase and Simulated Annealing**

After having obtained good agreement between the structure of the liquid phase between the simulation and the experimental results we study the evolution of the \( \text{C}_2\text{Cl}_6 \) starting from a solid phase at 300K and heating the system again up to 480K. Some changes in the simulation details presented in section II were made: The initial configuration was not constructed from random disposition since the system never reached the solid state, instead an initial BCC configuration was taken with molecules in the corners and center of a unit cell, disposing in total 504 molecules. After initial equilibration with the steepest descent method velocities were generated at 150K and then we let the system evolve for 10 ps. After this a trajectory of 500 ps were generated. Starting from the final configuration at 300K we implemented a simulated annealing methodology to increase the temperature in 30K during 10 ps, and then equilibration of 100 ps for each temperature were allowed before heating again the system. By this way we obtained results at 7 different temperatures: 300, 330, 360, 390, 420, 450 and 480K. Densities are registered in Table II.

**Table II.** Densities as a function of the temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Average density kgm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>300K</td>
<td>1680.0</td>
</tr>
<tr>
<td>330K</td>
<td>1656.5</td>
</tr>
<tr>
<td>360K</td>
<td>1610.7</td>
</tr>
<tr>
<td>390K</td>
<td>1581.3</td>
</tr>
<tr>
<td>420K</td>
<td>1530.9</td>
</tr>
<tr>
<td>450K</td>
<td>1371.1</td>
</tr>
</tbody>
</table>

Figure 5 shows the partial and total radial distribution functions at \( T=300\text{K} \), the last one computed from eq. 7. We can see that important differences arise compared to the rdf’s at 480K, strong oscillations with an slow decaying show the positional order of the system, as is expected for the solid phase temperatures registered for \( \text{C}_2\text{Cl}_6 \), between 4 and 344K [5].

The molecular coordination number was computed from eq. 12 and 13, defining the first and second solvation shells at 7.8Å, with \( n_{c_1} = 8.2 \) molecules, and 10.5Å, with \( n_{c_2} = 4.22 \) molecules respectively. Although the first solvation shell is not clearly defined as a minima in the total radial distribution...
function, a change in the slope is observed besides the
definition of the minima in the partial distributions. From
here is clear a high ordered phase, consistent with the BCC
initial structure.

Fig. 5: Simulated partial and total radial distribution functions
for \( T = 300 \) K and \( P = 1 \) atm. The graphics are vertically
displaced for clarity (0.5, 1.0 and 2.0 units), the horizontal
lines show the corresponding value for 1.

Finally figure 6 show the temperature dependent evolution
of the partial C-Cl radial distribution function, since it
contains good qualitative structure arrangement of \( C_2Cl_6 \)
and marked differences arise. The \( g_{ccl}(r) \) is presented
from bottom to top, with increasing temperature, displaced
vertically and graphics at 330K and 390K are omitted for the
sake of clarity, as they are intermediate to those presented.
Three important features are present. The marked oscillations
are damped from 450K. The first peak that is related to
the distance at which the next neighbours start to locate
changes in three stages, at 300K is well defined and from
360K it becomes wider beginning to decrease its high in
comparison to the second peak to end being smaller at 480K.
Finally the position of the second minima in \( g_{ccl}(r) \), related
to the first solvation shell, is displaced to the right as the
temperature increases, which shows an expansion, as is given
by the decrease of the density, and a possible change in the
arrangement of first neighbours. It is interesting to see how at
420K occurs a change in the first two peaks, being a frontier
where at lower temperatures the first peak is higher and
the opposite happens when the temperature is above this point.

Figure 7 shows a molecule density map for the simulation
box viewed from the z-axis for 300, 420, 450 and 480K,
this density mapping is the average during 100 ps for each
temperature. Red color indicates a higher density and therefore
a higher localization of molecules. It is interesting to confirm
the change that we observed mathematically in the radial
distribution functions (figure 6) seeing a high ordering in
figures 7a and 7b, lower molecule localization (premelting
effects) in figure 7c and a no localized state in figure 7d,
corresponding to the liquid phase.

IV. MEAN SQUARE DISPLACEMENT

Analysis of the mean square displacement MSD as
a function of the simulation time and for the different
temperatures in the present work was made. The mean
square displacement was computed for the equilibration
time for each temperature (100 ps). The results are shown
in figure 8. The MSD is presented from bottom to top in
order of increasing temperature, MSD’s at 330 and 390K
are omitted as they are only intermediate between 300-360K
and 360-420K respectively. The long time curve has a
low slope, almost constant, up to 420K, this is a typical
behaviour in a system with low diffusivity, the atoms are
nearly in the same position. The behaviour changes at
450 and 480K, where the slope of the long time curve
increases considerably, it is in this temperature region that
the change to a liquid phase is expected (\( T_m = 458 \) K). This
results are in concordance with the change observed in the
radial distribution functions at the same values of temperature.

The self diffusion coefficient was taken as the slope of
the MSD between 5 ps and 50 ps according to the Einstein
relation:

\[
D = \frac{1}{6t} \lim_{t \to \infty} \langle [r(t_0 + t) - r(t_0)]^2 \rangle
\]  \hspace{1cm} (15)

Figure 9 shows the results of the self diffusion coefficients
for different temperatures, as it was expected from the mean
square displacement, the diffusivity is very low and almost
constant up to 420K. At 450K the system starts to present
the diffusion process; as is expected for a liquid phase,
and the diffusion coefficient is higher at 480K. Again this
Fig. 7: Density map of molecules viewed from the Z-axis for the simulation box. Color scale indicates growing density mapping from blue to red.

Fig. 8: Mean square displacement (for different system temperatures. From bottom to top: 300, 360, 420, 450 and 480 K.

result agrees with the mean square displacement and radial distribution function changes.

V. CONCLUDING REMARKS AND FUTURE WORK

Using classical molecular dynamics simulation we have studied structural properties for a liquid phase (480K) and
a solid region (300-450K) of C$_2$Cl$_6$. We have obtained good agreement between experimental neutron scattering and simulation structure factors in the liquid phase. The evolution of the partial radial distribution functions ($g_{ccl}$ see figure 6) along the temperature showed the transition from solid (high ordered phase) to liquid phase, this transition occurred around 450K temperature, which is in agreement with the melting temperature of C$_2$Cl$_6$ T$_m$ = 458K considering that the simulation fluctuations were around 10K, this proved us the validity of the force field and the parameters taken to describe the C$_2$Cl$_6$. Results of mean square displacements and self diffusion coefficients are in agreement with static properties, the C$_2$Cl$_6$ went from a low diffusivity region to a high diffusivity one beginning at 450K.

Further analysis should be carried out in the region of (300-450K) in order to study the orientational structure and dynamics, to identify the reported plastic phase [3], [4]. At the time we are studying the spatial distribution functions [15] defining vectorial and planar products to define the disposition and orientation of the molecules at different solvation shells to learn about the orientational changes, for this we use the results of the radial distribution functions and coordination numbers in order to analyze separately each solvation shell. Figure 10 shows some bivariate analysis; related to the spatial distributions, at room temperature and at the liquid phase at 480K. Analysis in the region (344-458K) will be conducted to gain knowledge of this system and about the orientational transition between plastic and liquid phases.

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