Molecular dynamics simulation of liquid trimethylphosphine
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Structural and dynamical properties of liquid trimethylphosphine (TMP), (CH3)3P, as a function of temperature is investigated by molecular dynamics (MD) simulations. The force field used in the MD simulations, which has been proposed from molecular mechanics and quantum chemistry calculations, is able to reproduce the experimental density of liquid TMP at room temperature. Equilibrium structure is investigated by the usual radial distribution function, g(r), and also in the reciprocal space by the static structure factor, S(k). On the basis of center of mass distances, liquid TMP behaves like a simple liquid of almost spherical particles, but orientational correlation due to dipole–dipole interactions is revealed at short-range distances. Single particle and collective dynamics are investigated by several time correlation functions. At high temperatures, diffusion and reorientation occur at the same time range as relaxation of the liquid structure. Decoupling of these dynamic properties starts below ca. 220 K, when rattling dynamics of a given TMP molecules due to the cage effect of neighbouring molecules becomes important. © 2011 American Institute of Physics. [doi:10.1063/1.3624408]

I. INTRODUCTION

Trimethylphosphine (TMP), (CH3)3P, and trimethylphosphine oxide (TMPO), (CH3)3PO, are used in NMR spectroscopy as probe molecules of acidic sites.1–5 The first of such investigations was reported by Lunsford et al.,1 who described the role of Brönsted and Lewis acidity in governing catalytic activity in zeolites and catalytic surfaces, and proposed a method to evaluate the nature, strength, and number of acidic sites in a catalyst. According to Lunsford et al.,1 the 31P nucleus is a more attractive candidate for surface characterization than 13C and 15N because 31P possesses a large chemical-shift range and is more easily detected by NMR spectroscopy. Since then, several works have been concerned on the use of TMP or TMPO as probe molecules of acidic sites.3–5 For instance, Kao et al.2 indicated the advantage of TMP over other NMR probes, such as pyridine or methylamine, proper to high sensitivity of the31P nucleus advantage of TMP over other NMR probes, such as pyridine or methylamine, proper to high sensitivity of the31P nucleus due to its high magnetogyric ratio and natural abundance. They also performed ab initio calculations in order to investigate the structure of the TMP – Brönsted acid site complex in zeolite.5 They defined the protonated form of zeolite as HY and two kind of complex, hydrogen-bonded neutral complex (TMP-HY) and ion pair complex (TMPH+Y-). These calculations provided the optimized structure of both species indicating that the former is more stable.

Few works have been dedicated to structural and dynamical properties of pure liquids derived from alkyl phosphine, even though properties of the neat liquid play an important role to understand how it will behave in a binary mixture or in a complex fluid. Density of liquid TMP is 0.735 g cm−3 at room temperature.6 The gas phase structure has been investigated by electron diffraction7 and microwave spectroscopy.8 The C–P bond length obtained from microwave tends to be shorter than obtained from electron diffraction measurement, respectively, 1.841 Å and 1.846 Å, while the C-P-C angle is similar 98.6(3)°. Magnuson9 obtained 1.843 Å and 99.1° by ab initio calculations, and Liang and Fox10 obtained 1.8456 Å and 98.6° by MM3 force-field calculations. The structure of TMP has been also studied by x-ray measurements of the solid phase,11 in which the C–P distance and the C-P-C angle is within the range 1.827(3)–1.841(5)Å and 99.1(1)–99.4(1)°, respectively. In a recent work,12 we have performed ab initio calculations of monomers and dimers of trialkylphosphine oxides in order to obtain structural information. In this work, we use molecular dynamics (MD) simulations to investigate structure and dynamics of liquid TMP, and as a far reaching aim, TMP might be a prototype molecule for phosphonium ions, which are typical cations used in room temperature molten salts, the so-called ionic liquids.13

II. COMPUTATIONAL DETAILS

A. The potential energy function model

Liquid TMP was simulated with a potential energy function including intermolecular Lennard-Jones and Coulomb interactions:

\[
U(r_{iαβ}) = \sum_{i=1}^{N} \sum_{α=1}^{4} \sum_{j=1}^{N} \sum_{β=1}^{4} \left\{ 4ε_{αβ} \left( \frac{σ_{αβ}}{r_{iαβ}} \right)^{12} - \left( \frac{σ_{αβ}}{r_{iαβ}} \right)^6 + \frac{q_{iα} q_{jβ}}{r_{iαβ}} \right\},
\]

where

\[
ε_{αβ} = \frac{ε_1 + ε_2}{2}, \quad σ_{αβ} = \frac{σ_1 + σ_2}{2},
\]

and \(r_{iαβ}\) is the distance between the atoms i and j in the molecule αβ. The parameter values are taken from Ref. 12.
where \( r_{i\alpha\beta} \) is the distance between atom \( \alpha \) of molecule \( i \) and atom \( \beta \) of molecule \( j \), and \( q_\alpha \) and \( q_\beta \) are the corresponding partial charges. A united atom model has been used, i.e., hydrogen atoms are not explicitly considered, so that \( \text{CH}_3 \) is a single site, and each TMP molecule has four interaction sites. The TMP molecule was considered as a rigid body, with the same geometry obtained by electron diffraction measurements, i.e., C–P bond length 1.846 Å, and C–P–C angle 98.6°. Table I provides the parameters of Eq. (1) used in this work. The Lennard-Jones parameters \( \varepsilon \) and \( \sigma \) used in this work were proposed in the MM3 force field. The partial charges obtained by the restrained electrostatic potential and dipole moment obtained by quantum chemistry calculations using density functional theory DFT (B3LYP) with the 6-311+G(3df,2p) basis set. This same basis set has been used in a previous work on structural and thermodynamic stability of monomer and dimers of trialkylphosphine oxides. The partial charges were derived from the best fit to electrostatic potential and dipole moment obtained by quantum chemistry calculations using density functional theory DFT (B3LYP) with the 6-311+G(3df,2p) basis set. This same basis set has been used in a previous work on structural and thermodynamic stability of monomer and dimers of trialkylphosphine oxides. The partial charges were obtained by the restrained electrostatic potential method in GAUSSIAN03 program gave a dipole moment of 1.18 D for the TMP molecule, which is in good agreement with experiment (1.19 D).

### B. The MD simulations

We used the PACKMOL package to generate a starting configuration containing 1000 molecules of TMP in a cubic box. The MD simulations of TMP were carried out in different temperatures within the 162–323 K range. It should be noted that the melting temperature of TMP is 187 K, so that we aim to establish eventual differences between solid- and liquid-like dynamics. We performed the MD simulations with the GROMACS package. Pressure and temperature were controlled with the method of Berendsen et al. of small coupling to an external bath. Average density \( \rho \) of liquid TMP at 1 bar and different temperatures was obtained by MD simulation performed in \( NpT \) ensemble. After obtaining \( \rho \) at given temperature, MD simulations were performed in \( NVT \) ensemble with fixed box size according to the equilibrium density. Equilibration periods were typically 1.0 ns long, and productions runs were 4.0 ns long at each thermodynamic state. (Liquid TMP was first simulated at the highest temperature, and then cooled to other temperatures). Equations of motions were integrated with the leap-frog algorithm with time step of 2.0 fs. Bond lengths and angles were constrained with the LINCS algorithm. Long-range Coulombic interactions were handled with the particle-mesh Ewald sum method.

### III. RESULTS AND DISCUSSION

#### A. Structure

The model used in the MD simulations of liquid TMP gives average density at room temperature (0.740 g cm\(^{-3}\)) in good agreement with experiment (0.735 g cm\(^{-3}\)). Figure 1 shows the temperature dependence of \( \rho \) obtained by the MD simulations of TMP. There is not a sharp increase of \( \rho \) that would indicate crystallization upon cooling, instead the bent \( \rho(T) \) curve suggests that the simulated system is going to a supercooled liquid state because of very fast cooling rate achieved in the simulations.

Equilibrium structure of TMP in the solid phase was investigated by electron diffraction and x-ray spectroscopy, but these studies focused on molecular geometry, paying no attention to intermolecular distances. Thus, there is a lack of experimental data concerning the equilibrium structure of liquid TMP that could be compared with MD results of static structure factor, \( S(k) \), and radial distribution function, \( g(r) \). The total \( S(k) \) is the combination of partials \( S_{\alpha\beta}(k) \) given by:

\[
S_{\alpha\beta}(k) = \sum_{i=1}^{N} \sum_{j=1}^{N} e^{ik \cdot (r_i - r_j)},
\]

where \( \alpha \) and \( \beta \) stand for each atom of molecules \( i \) and \( j \). In a neutron scattering measurement, each \( S_{\alpha\beta}(k) \) is weighted by the molar fraction of the species, \( x_\alpha \) and \( x_\beta \), and by the corresponding neutron scattering length, \( b_\alpha \) and \( b_\beta \). Figure 2 shows \( S(k) \) calculated by MD simulations without the weight factors of neutron scattering lengths because there is no experimental \( S(k) \) available for liquid TMP to compare with calculated \( S(k) \), and the treatment given is similar to \( g(r) \) for center of mass. It is clear from Fig. 2 that the main peak of \( S(k) \) shifts to higher wavevectors and becomes sharper as the system is cooled. The \( S(k) \) is useful to reveal any intermediate-range order (IRO) eventually present in the system, but the absence of a pre-peak at \( k \) smaller than the main peak gives no indication of IRO in liquid TMP. Since the main peak is related to nearest neighbour distances, the high \( k \) shift is due to increase density and the sharpening is due to a more ordered local structure upon cooling.
Short-range local structure is more easily viewed by the usual radial distribution function, $g(r)$. The more ordered structure of TMP at low temperature is evident by $g(r)$ for the center of mass of TMP showed in Figure 3. At least four coordination shells can be seen in the oscillations of $g(r)$ for TMP at 162 K, while the oscillations almost disappear after the second shell for TMP at 298 K. The coordination number in liquid TMP increases when the system is cooled. This is clear from the histograms of Figure 4, which shows the distribution of the number of nearest neighbours around a given TMP molecule, i.e., a pair of molecules closer than 0.75 nm. There is a significant increase of the average coordination number when the system is cooled from 298 to 162 K. The high coordination number indicates that the equilibrium structure in liquid TMP is mainly determined by packing effects of spheres, although orientational ordering at short-range should play a role because of the significant dipole moment of a TMP molecule.

Further details on local structure are revealed by partial radial distribution functions, $g_{\alpha\beta}(r)$, between pairs of atoms $\alpha$ and $\beta$ of different molecules. Figure 5 shows the three partial $g_{\alpha\beta}(r)$ calculated by MD simulation of liquid TMP at 298 K. The shoulder at distance shorter than 0.5 nm observed in $g_{CP}(r)$ and $g_{CC}(r)$ indicates oriented local structure. It should be noted the weak and broad first peak in $g_{CP}(r)$ and $g_{CC}(r)$, indicating that although orientational correlation between $C_3$ axes of neighbouring TMP molecules might occur, there are many different relative orientations from spinning around the $C_3$ axis. In order to reveal the role of local orientational correlation between TMP molecules, we calculated histograms of occurrence of angles between $C_3$ axes of a given pair of molecules as long as the center of mass of these molecules are closer than 0.5 nm or further apart than 0.75 nm. The resulting histograms for liquid TMP at 298 K shown in Figure 6 indicate no orientational correlation between molecules that are far apart each other, but significant orientational correlation due to dipole-dipole correlation occurs between molecules that are close together.

**B. Dynamics**

Figure 7 shows velocity time correlation functions, $C_v(t) = \langle v_i(t) \cdot v_i(0) \rangle$, and the corresponding density of states, DoS, i.e., the Fourier transform of $C_v(t)$, calculated by MD simulations of TMP at different temperatures. The $C_v(t)$

![FIG. 2. Static structure factor, $S(k)$, calculated by MD simulations of TMP at 162 and 298 K.](image1)

![FIG. 3. Radial distribution function, $g(r)$, at high and low temperatures of liquid TMP.](image2)

![FIG. 4. Histograms of number of neighbouring molecules around a given TMP molecule calculated by MD simulations at 162 (black line) and 298 K (red line).](image3)

![FIG. 5. Partial radial distribution functions, $g_{\alpha\beta}(r)$, calculated by MD simulation of liquid TMP at 298 K. Bold line corresponds to P-P pair, thin line to C-C pair, and dashed line to C-P pairs.](image4)
decays monotonically at high temperatures, and starts to display oscillations at lower temperatures because of the cage effect of neighbouring molecules around a given TMP molecule. Correspondingly, the zero frequency limit of DoS decreases at low temperature because it is related to the diffusion coefficient, and the DoS display a distinct maximum at non-zero frequency. In other words, a more solid-like characteristic is observed in liquid TMP simulated at low temperatures. The diffusion coefficient, $D$, can be obtained either by the integral of $C_v(t)$ or by the linear regime at long time of the mean squared displacement (MSD):

\[
\frac{1}{6t} \langle |r(t) - r(0)|^2 \rangle.
\] (3)

Figure 8 shows the temperature dependence of MSD calculated by MD simulations of liquid TMP. The cage regime between short-time ballistic and the long-time diffusive regimes is only barely seen as a not well developed plateau at intermediate times in the MSD at the lowest temperature, for which the linear diffusive regime starts at ca. 10.0 ps.

Figure 9 shows the reorientational autocorrelation functions, $C_r(t)$, calculated for a unitary vector on the $C_3$ axis for liquid TMP at different temperatures. The data were fit with a stretched exponential function as described previously (see Figs. 6 and 9 in Ref. 24). The inset graph in Figure 9 shows the best fit at 298 K, in which the stretching exponent $\beta$ was higher (0.89) than in lower (0.75) temperature. The slight reduction of $\beta$ at low $T$ reveals the stretched behaviour of $C_r(t)$ with decreasing temperature. Characteristic times for reorientation, diffusion, and structural relaxation will be compared in the following. Structural relaxation is obtained by
space-time pair correlation functions, i.e., the van Hove function, $G(r, t)$. Figure 10 shows the self part $G_s(r, t)$, which gives the spatial correlation of a given molecule at different times:

$$G_s(r, t) = \frac{1}{N} \sum_{i=1}^{N} \delta [r + r_i(0) - r_i(t)]. \hspace{1cm} (4)$$

Figure 11 shows the distinct part $G_d(r, t)$, which gives the correlation of two different molecules in a time interval between 0 and $t$:

$$G_d(r, t) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \delta [r + r_j(0) - r_j(t)]. \hspace{1cm} (5)$$

The data in Figs. 10 and 11 correspond to TMP simulated at room temperature, for which the structure is almost completely lost after ca. 10.0 ps (see Fig. 11). In order to extract the structural relaxation time, we calculated the spatial Fourier transform of $G_d(r, t)$, the so-called intermediate scattering function, $F(k, t)$:

$$F(k, t) = \frac{1}{N} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \exp \left\{ -i k [r_i(t) - r_j(0)] \right\}. \hspace{1cm} (6)$$

Figure 12 shows $F(k, t)$ at the wave-vector corresponding to the main peak of $S(k)$ (see Fig. 2) calculated for TMP at different temperatures. The structural relaxation time, $\tau_\alpha$, is obtained from a stretched exponential fit to $F(k, t)$.

A simultaneous plot as a function of temperature gives a perspective view of different characteristic times of liquid TMP. The data collected in Figure 13 show that $D^{-1}, \tau_r$, and $\tau_\alpha$ display the same activation energy at high temperatures, and then they decouple at low temperatures. Thus, single particle diffusion and reorientational dynamics at high temperatures take place within the same time window as structural relaxation. When temperature decreases, decoupling of single particle and collective dynamics occurs because rattling and librational dynamics become more important as a given TMP molecule is trapped in a temporary cage made of neighbouring molecules.

**C. Dielectric properties**

Dielectric properties of liquid TMP were investigated by the calculation of the time correlation function of the total dipole moment, $C_M(t) = \langle M(t) \cdot M(0) \rangle$, where $M(t)$ is the sum of the dipole moment of all of the molecules, $M(t) = \sum_{j=1}^{N} \mu_j(t)$. The Fourier transform of $C_M(t)$, $\Phi_M(\omega)$, gives a frequency dependent dielectric constant, $\varepsilon(\omega)$, when the conducting boundary condition is used for the
TABLE II. Static dielectric constant and Kirkwood factor for SPC/E water model and liquid TMP at room temperature.

<table>
<thead>
<tr>
<th>System</th>
<th>$G_k$</th>
<th>$\varepsilon$</th>
<th>$\varepsilon_\infty$</th>
<th>$\varepsilon - \varepsilon_\infty$</th>
<th>$g_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water (SPC/E model)</td>
<td>3.6</td>
<td>68.4</td>
<td>1</td>
<td>67.4</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>3.8(2)$^a$</td>
<td>71(3)$^a$</td>
<td>70$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid TMP</td>
<td>3.39</td>
<td>22.3</td>
<td>1</td>
<td>21</td>
<td>2.31</td>
</tr>
<tr>
<td></td>
<td>(0.03)$^b$</td>
<td>(0.2)$^b$</td>
<td>(0.02)$^b$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Reference 27.
$^b$Error from two blocks averaging (Refs. 26 and 28).

The static dielectric constant is given by

$$\varepsilon(\omega) - \varepsilon_\infty = \frac{\langle |M(0)|^2 \rangle}{3Vk_BT\varepsilon_0} [1 + i\sigma \Phi_M(\sigma)].$$  \hspace{1cm} (7)

The static dielectric constant is given by

$$\varepsilon = \varepsilon_\infty + \frac{\rho \mu^2}{3k_BT\varepsilon_0} G_k,$$ \hspace{1cm} (8)

where $\rho$ is the number density, $\mu$ is the dipole moment of a single molecule, $\varepsilon_\infty$ is the infinite frequency dielectric constant, and $\varepsilon_0$ is the vacuum dielectric permittivity. The finite system Kirkwood factor $G_k$ is related to the average of cross correlations of the dipole moment of molecules $i$ and $j$:

$$G_k = \frac{\langle |M(0)|^2 \rangle}{N\mu^2} = 1 + \frac{N-1}{\mu^2} \langle \mu_i \mu_j \rangle.$$ \hspace{1cm} (9)

The Kirkwood factor $g_k$ describing orientational correlations in an infinite sample is

$$g_k = \frac{2\varepsilon - \varepsilon_\infty}{3\varepsilon} G_k.$$ \hspace{1cm} (10)

Table II compares dielectric constants and Kirkwood factors of liquid TMP with the well-known SPC/E model for water, for which a good agreement has been found with previous work.\(^{27}\) Two simulations with 4 ns of trajectory were performed, in which statistical errors were computed from the block averaging procedure described in the literature.\(^{26,28}\) Figure 14 shows $C_M(t)$ calculated for the SPC/E water model and liquid TMP. The $C_M(t)$ of water calculated in this work agrees with the result shown in Fig. 1 of Ref. 29. The $C_M(t)$ of TMP decays faster than water proper to strong dipole orientation from hydrogen bonding in liquid water, as also stressed in a detailed MD simulation investigation of dielectric properties of dimethyl sulphoxide.\(^{30}\) The dipole-dipole correlation can be expressed as a radial distribution function of neighbouring dipoles, $D_\Delta(r)$, as described recently by Nymand and Linse\(^{27}\) and Takahashi et al.\(^{31}\) for liquid water study. The function $D_\Delta(r)$ for liquid TMP at two different temperatures are shown in Figure 15, in which it is clear that dipole-dipole correlation is enhanced at low temperature, remaining for longer range, than at room temperature. In fact, $G_k$ calculated from MD simulation of liquid TMP at room temperature is greater than 1, also indicating the alignment of the dipole moment between neighbouring molecules. In the authors’ knowledge, experimental data of $\varepsilon$ are not available for liquid TMP. Nevertheless, the resulting value $\varepsilon \sim 22$ calculated in this work for TMP is reasonable in light of other systems, for instance, triethylphosphate (13.2), trimethylphosphate (20.6), and ammonia (23.0).\(^{32}\)

IV. CONCLUSIONS

In this work, we carried out MD simulations of liquid trimethylphosphine, which is a typical probe molecule of acidic sites in NMR measurement. The model used in the MD simulations of liquid TMP gives average density very close to the experimental value at room temperature. We found no indication of an intermediate range order in the simulated system proper to the absence of a pre-peak in $S(k)$. The effect of decreasing temperature on $S(k)$ is a high $\Delta k$ shift and sharpening of the main peak due to increase density and more ordered local structure. Overall, the equilibrium structure of liquid TMP is the result of packing of almost spherical particles, although orientational correlation is observed at short distances because of dipole interactions. Single particle translational and reorientational dynamics are strongly coupled to structural relaxation at high temperatures. Decoupling between single particle and collective dynamics is observed upon decreasing temperature, when the simulated system goes into a supercooled liquid state, rather than crystalline state, proper to the high rate of cooling achieved in MD simulations. The
model used in the MD simulations of TMP can be a prototype model for phosphonium ions, which are typical cations used in ionic liquids.

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