

An ASEP/MD study of liquid chloroform

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Abstract

ASEP/MD, a QM/MM method that makes use of the mean field approximation, was applied to liquid chloroform. The method has previously been successfully applied to other polar and hydrogen-bonded liquids; this study of chloroform can be considered as a verification of the performance of the method for nonpolar liquids, whose molecules have a small dipolar moment and where the electrostatic interaction is only of secondary importance. Two different quantum levels were used for the description of the solute, and two different sets of Lennard-Jones parameters were employed; calculations with and without geometry optimization were made. The calculated electronic structure of the CHCl_3 molecule in the liquid state and its vaporization energy agree with data from other studies and experiment. The obtained radial distribution functions and neutron scattering cross-section are also found to be in satisfactory agreement with those obtained with other models.

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1. Introduction

Liquid chloroform is one of the most widely used organic solvents in chemical physics, and it has been the subject of numerous theoretical and experimental investigations. It is a good reference medium for studies on the distribution of organic molecules between aqueous and nonpolar solvents [1], and its small, nearly spherical molecules make it a good target for theoretical modelling and simulations. Different attempts have been made to model chloroform molecules in the liquid state: Hsu and Chandler [2] proposed a five site hard spheres model, Jorgensen et al. developed a four site model [1], several other authors have used different five site models [3–7], and Chang et al. employed a polarizable five site model [8].

Most of these models give adequate descriptions of the structural and thermodynamical properties of the liquid, although some discrepancies have been found with five site models [6]. In general, the parameters used to represent the chloroform molecules in the force field are empir-

ical, obtained directly from experiment (like the geometry) or by fitting their values (atomic charges and Lennard-Jones parameters) to reproduce a set of experimental properties.

In our group, we have developed a new method combining quantum mechanics and molecular mechanics, called ASEP/MD (Average Solvent Electrostatic Potential from Molecular Dynamics), which is able to provide optimized geometries and wave functions for molecules in the liquid state or in solution. This method has already been applied to a variety of pure liquids, like water [9], alcohols [10] or hydrogen fluoride [11,12], giving in all cases, with a minimum of empirical parameters, reasonable results for molecular geometries, atomic charges, interaction energies, and solvent structures.

In this work, we apply the ASEP/MD method to liquid chloroform in order to study its thermodynamical and structural properties and to assess the performance of the method when applied to systems where the electrostatic interaction is not the most important one. As a side result, a new set of parameters for the CHCl_3 molecule is obtained from quantum calculations, instead of empirical considerations or fitting procedures.

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The rest of this paper is structured in the following way. Section 2 presents a short description of the ASEP/MD method. More details about the specific computations performed are given in Section 3. The results obtained and their discussion are exposed in Section 4. Finally, Section 5 contains our main conclusions.

2. Method

The calculations in this work were performed with the ASEP/MD method, a QM/MM method that makes use of the mean field approximation. The method has been described in previous papers [13–16]. Here, we shall present just a brief outline. For more details and schemes, the reader is referred to said papers.

As mentioned above, ASEP/MD is a method combining QM and MM techniques, with the particularity that full QM and MD calculations are alternated and not simultaneous. During the MD simulations, the intramolecular geometry and charge distribution of all molecules is considered as fixed. From the resulting data, the average electrostatic potential generated by the solvent on the solute is obtained. This potential is introduced as a perturbation into the solute's quantum mechanical Hamiltonian, and by solving the associated Schrödinger equation, one gets a new charge distribution for the solute, which is used in the next MD simulation. This iterative process is repeated until the electron distribution of the solute and the solvent structure around it are mutually equilibrated.

Also, in previous work [17,18] it was shown how the geometry of the solute molecule can be optimized in the ASEP/MD framework. At each step of the ASEP/MD procedure, the gradient and Hessian on the system's free-energy surface can be obtained, and so they can be used to search for stationary points on this surface by some optimization method. After each MD simulation, the solute geometry is optimized within the fixed "average" solvent structure by using the free-energy derivatives. In the next MD simulation, the new solute geometry and charge distribution are used. This approach allows the optimization of the solute geometry simultaneously to the solvent distribution.

In the case of pure liquids, like the present work, it is possible to apply the "completely coupled" version of ASEP/MD, meaning that after each iteration of the process the geometry and atomic charges obtained for the quantum solute molecule are transferred to each one of the solvent molecules for the next MD simulation. In this way, all the molecules in the system benefit from the quantum description of the solute and their equivalence is maintained throughout the MD simulations.

Due to the equivalence of solute and solvent when a pure liquid is studied, the vaporization enthalpy can be calculated with the formula [10]:

$$\Delta H_{\text{vap}} = -\frac{1}{2}(E_{\text{elect}} + E_{\text{vdw}} + E_{\text{Stark}}) - E_{\text{dist}} + RT, \quad (1)$$

where E_{elect} is the electrostatic interaction between the quantum electron distribution and the average solvent electrostatic potential, E_{vdw} is the average van der Waals interaction between solute and solvent (as calculated during the MD simulation), E_{dist} is the solute distortion energy, i.e., the energy spent in polarizing the CHCl_3 molecule from its *in vacuo* nuclear and electronic structure to the in solution state. This last energy is calculated as the difference:

$$E_{\text{dist}} = \langle \Psi | \hat{H}^0 | \Psi \rangle - \langle \Psi^0 | \hat{H}^0 | \Psi^0 \rangle, \quad (2)$$

where Ψ and Ψ^0 are the wave functions in solution and *in vacuo*, respectively, \hat{H}^0 is the *in vacuo* Hamiltonian for the solute, and $\hat{H}^{0'}$ is the *in vacuo* Hamiltonian but with the solute geometry found in solution, i.e., the solvent potential is not included. E_{Stark} in Eq. (1) is the Stark component of the interaction energy, due to the correlation between the motion of the solvent nuclei and the response of the solute electron distribution, which is ignored in mean field methods, like ASEP/MD. In a previous work [15], we proposed an approximate expression that provides an estimate of the Stark component, being proportional to the solute polarizability and to the fluctuations in the electric field generated by the solvent at the position occupied by the solute. In that work, it was also found that this approximate expression can usually recover around 50% of the error. Given this last result, E_{Stark} was estimated as twice the value returned by the approximate expression.

3. Computational details

Quantum calculations in the ASEP/MD framework were performed with the Gaussian 98 [19] suite of programs. Two different calculation levels were chosen: Hartree-Fock (HF) and density functional theory (DFT) with the B3LYP functional [20,21]. In both cases, the basis set was Dunning's augmented correlation consistent polarized double- ζ , aug-cc-pVDZ [22].

Molecular dynamics simulations were carried out with the open source program Moldy [23]. In these simulations, CHCl_3 molecules are represented with rigid geometries, so that no intramolecular force terms are needed. Intermolecular forces are represented through a combination of electrostatic and Lennard-Jones terms. The electrostatic interaction is given by point charges located at the nuclei, with values obtained from the quantum calculations with the CHELP procedure [24]. Lennard-Jones potentials are calculated in the usual manner:

$$V_{\text{LJ}} = 4\varepsilon_{ij} \left[\frac{\sigma_{ij}^{12}}{r_{ij}^{12}} - \frac{\sigma_{ij}^6}{r_{ij}^6} \right], \quad (3)$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}, \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2},$$

where r_{ij} is the distance between sites i and j . Two different sets of Lennard-Jones parameters (ε_i and σ_i) were used: the parameters given by Jorgensen, Briggs and Contreras [1] (hereafter called JBC) and those given by Dietz and

Table 1
Lennard-Jones parameters for the chloroform molecule

Site	JBC[1]		DH[25]	
	σ_i (Å)	ε_i (kcal/mol)	σ_i (Å)	ε_i (kcal/mol)
C	3.80	0.080	3.40	0.102
Cl	3.47	0.300	3.44	0.300
H	0.00	0.000	2.20	0.020

Heinzinger [25] (DH), both are shown in Table 1. JBC parameters assume a geometrical mean for σ , but the difference in this case is not significant.

A total number of 256 CHCl_3 molecules were simulated in a cubic box of 32.48 Å side (matching the experimental [26] density of 1479.9 kg/m³). Periodic boundary conditions were applied, and spherical cutoffs were used to truncate the molecular interactions at 14.2 Å. The electrostatic interaction was calculated with the Ewald method [27]. The temperature was fixed at 298 K by using a Nosé–Hoover thermostat [28,29]. A time step of 0.5 fs was used, each MD simulation was run for 150 000 time steps (25 ps of equilibration, 50 ps of production).

The completely coupled version of ASEP/MD was applied. HF calculations were performed with and without geometry optimization (these calculations will be called, respectively, “HF” and “HF-opt”), using the JBC Lennard-Jones parameters. DFT calculations were carried out with geometry optimization and with both JBC and DH parameter sets. Since the completely coupled version was used, the geometry of the solvent molecules as well as that of the solute was changed in every ASEP/MD cycle; the RFO method [30–32] was used for this, employing a convergence criterium of $10^{-5} E_h/a_0$ for the norm of the gradient at each cycle of the process.

Final results are calculated as the average of the last few cycles of the ASEP/MD process, where most properties are converged, and the standard deviation provides some measure of the uncertainties. In this work, the ASEP/MD calculations were run for up to 10 to 20 cycles and the averages are taken over the last 5 to 10 cycles, depending on the case.

4. Results and discussion

The geometry of the CHCl_3 molecule was optimized in vacuo at both HF and DFT levels. The results obtained are shown in Table 2. Compared to the experimental values, it is clear that both methods give a too short C–H bond and too long C–Cl bonds, while DFT gives longer bonds in all cases; the H–C–Cl angle is correctly reproduced. Table 2 also shows the dipole moment and atomic charges obtained with the CHELP procedure. In general, it can be said that the B3LYP calculations give results closer to experiment, except for the C–Cl bond lengths.

The results obtained in solution are given in Table 3. For the HF calculation there was no geometry optimization in solution, so the geometrical parameters shown are

Table 2
In vacuo geometry, dipole moment, and atomic charges of the chloroform molecule^a

	HF	DFT	Experimental [35]
C–H	1.078	1.090	1.100
C–Cl	1.769	1.789	1.758
H–C–Cl	107.9	107.8	107.6
μ	1.215	1.111	1.04 [36]
q_C	0.569	0.508	
q_H	–0.038	–0.036	
q_{Cl}	–0.177	–0.157	

^a Distances in Å, angles in deg., charges in e , and dipole moments in D.

Table 3

In solution optimized geometry, dipole moment, and atomic charges of the chloroform molecule^a (in parenthesis, the standard deviation of the last few digits)

	HF ^b	HF-opt	DFT-JBC	DFT-DH
C–H	1.078	1.078(0)	1.090(0)	1.089(0)
C–Cl	1.769	1.767(0)	1.787(0)	1.786(0)
H–C–Cl	107.9	108.0(0)	107.8(0)	107.8(0)
μ	1.314(28)	1.334(23)	1.213(34)	1.173(35)
q_C	0.578(3)	0.536(28)	0.485(34)	0.478(26)
q_H	–0.031(3)	–0.012(12)	–0.009(17)	–0.015(12)
q_{Cl}	–0.183(1)	–0.176(6)	–0.159(6)	–0.155(5)

^a Distances in Å, angles in deg., charges in e , and dipole moments in D.

^b In vacuo geometry.

those obtained *in vacuo*. The dipole moment increases by about 8%, the change in atomic charges is also small and to greater absolute values. When geometry is allowed to relax (HF-opt calculation) a slightly larger increase is found in the dipole moment (10%), and the C–Cl distance is shortened by 0.002 Å, while the C–H bond length does not vary from the *in vacuo* value. DFT results differ from HF-opt but show a similar trend with respect to the *in vacuo* values: a small shortening of the C–Cl bonds is almost the only change in geometry, the dipole moment increases between 5% and 9%. In all calculations with geometry optimization the charges on C and H tend to decrease in absolute value, which reduces the dipole moment due to the C–H bond more than that of the C–Cl bonds, accounting for the increase in total dipole moment.

In short, when the CHCl_3 molecule is put in the solution, it suffers only small changes. Its geometry does not vary appreciably from the gas phase state and its dipole moment is only slightly enhanced, as expected for a mostly nonpolar liquid. The two different Lennard-Jones parameter sets give very similar results. The change in the dipole moment is consistent with the value obtained with a polarizable model (0.13 D, 13%) [8].

The vaporization energy of chloroform in liquid state was calculated as shown in Eq. (1). The results, as well as the values of the different components are displayed in Table 4. As can be seen, all four methods give very similar results. In all cases the interaction energy is dominated by the Lennard-Jones (van der Waals) interaction, while the electrostatic one is even smaller than thermal fluctuations

Table 4
Vaporization enthalpy and its components (see Eq. (1)) for liquid chloroform, in kcal/mol, at 298 K (in parenthesis, the standard deviation of the last few digits)

	HF	HF-opt	DFT-JBC	DFT-DH	Experimental [33]
E_{elect}	-0.48(12)	-0.54(9)	-0.35(8)	-0.23(9)	
E_{vdw}	-13.22(23)	-13.22(17)	-12.94(22)	-13.15(26)	
E_{Stark}	-0.19(2)	-0.21(3)	-0.19(3)	-0.18(2)	
E_{dist}	0.02(1)	0.01(1)	0.01(1)	0.00(1)	
ΔH_{vap}	7.51	7.58	7.32	7.37	7.44

(which are around 0.6 kcal/mol at 298 K), this is consistent with the nonpolar nature of the liquid. Also, as expected from the small changes experienced by the CHCl_3 molecule when going from gas phase into the liquid, the distortion energy can be considered negligible. The estimated Stark component, being a correction to the electrostatic interaction, is very small as well; nonetheless, with respect to E_{elect} , it is more important than for other systems previously studied [15], this is due to the relatively high polarizability of chloroform ($\sim 55 e^2 a_0^3 / E_h$, as calculated at B3LYP level). The experimental vaporization energy of 7.44 kcal/mol [33] is reproduced very closely by all four methods, with errors smaller than 2% in all cases.

When the results obtained with other CHCl_3 models are examined, one may find a closer agreement with the experimental vaporization energy: Jorgensen et al. [1] obtain 7.48 kcal/mol, Barlette et al. [6] give 7.46 kcal/mol, and Chang et al. [8] 7.43 kcal/mol. However, all these models have been designed to reproduce experimental properties of liquid chloroform, including the enthalpy of vaporization, so that a close agreement with experiment is expected. In this work, atomic charges and molecular geometry are obtained from quantum calculations and the only empirical quantities introduced are the Lennard-Jones parameters. The empirical nature of CHCl_3 models also explains the fact that the two Lennard-Jones parameter sets employed do not produce significantly different results, even though the van der Waals interaction energy is by far the most important component. In relation to this, the differences in atomic charges defined for different models can be explained by the small magnitude of the electrostatic component, which allows a higher flexibility in the charges.

The different atomic radial distribution functions (rdfs, $g(r)$) are shown in Fig. 1, only the rdfs corresponding to the DFT-JBC calculation are displayed, the other results being quite similar. In general, the rdfs show well defined peaks, which indicates the existence of some structural order in liquid chloroform. The $g_{\text{CC}}(r)$ function exhibits a high peak at 5.35 Å, integration of this peak up to the minimum at 7.65 Å yields a coordination number of 13.4 which is consistent with a liquid resembling a close packing of almost spherical molecules (a perfect close packing would have a coordination number of 12). The $g_{\text{CH}}(r)$ function shows a peak at 6.05 Å with a shoulder at around 4.7 Å, this broad peak integrates to coordination number of

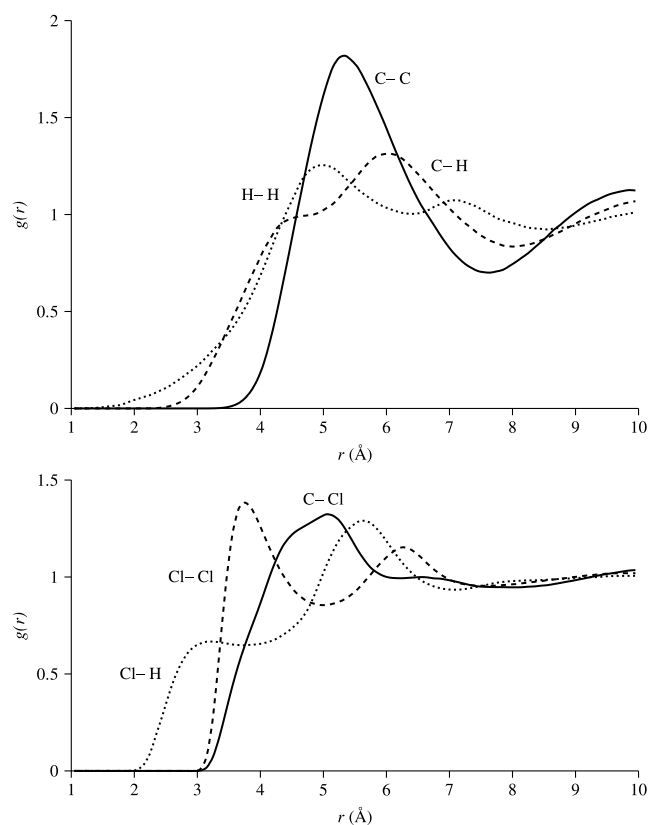


Fig. 1. Atomic radial distribution functions for liquid chloroform, from the DFT-JBC calculation.

15.5. The $g_{\text{HH}}(r)$ function has a first peak at 4.95 Å and a secondary one at 7.05 Å, integration of the first peak up to the minimum at 6.45 Å gives a coordination number of 7.5. The $g_{\text{CCl}}(r)$ function displays a shouldered peak at 5.05 Å, which by integration yields a coordination number of 6.9. The $g_{\text{ClCl}}(r)$ function shows a very steep peak at 3.75 Å (coordination number of 2.8) and a secondary one at 6.25 Å, with a total coordination number of 12.6. Finally, the $g_{\text{ClH}}(r)$ exhibits a first shallow peak at 3.15 Å, which integrates to a coordination number of 0.8, and a second one at 5.65 Å, giving a total coordination number of 10.6.

All these rdfs are very similar to those reported by Barlette et al. [6], only some differences in the height of the peaks are worth mentioning. This variation is due to the different charge distribution employed by said authors and in this work, the latter having atomic charges with larger absolute value, which leads to a somewhat more

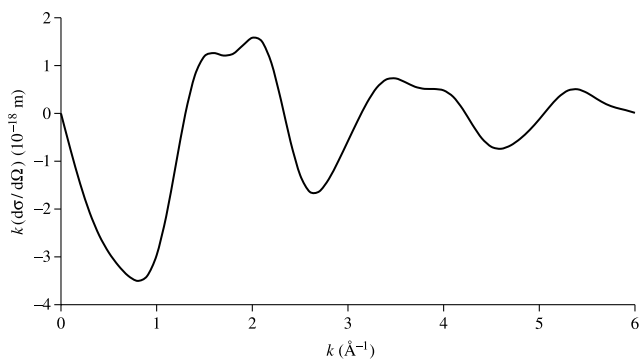


Fig. 2. Calculated cross-section for liquid chloroform, from the DFT-JBC calculation.

structured liquid. There are, however, more important differences with the rdfs given by Chang et al. [8], although they are not critical, but in that work the authors used a polarizable force field for the CHCl_3 molecule, which is significantly different from the simple, non polarizable, force field used here.

In order to establish a comparison with experiment, the neutron scattering cross-section was calculated from the rdfs, as a weighted sum of partial structure factors [8]:

$$S'_{ab} = S_{ab}(k) - 1 = \frac{4\pi\rho}{k} \int_0^\infty |g_{ab}(r) - 1| \sin(kr)rdr, \quad (4)$$

$$\begin{aligned} (d\sigma/d\Omega)(k) = & 0.33089S'_{\text{CC}}(k) + 2.86013S'_{\text{CCl}}(k) \\ & + 6.18045S'_{\text{ClCl}}(k) + 0.10468S'_{\text{HH}}(k) \\ & - 1.60855S'_{\text{CH}}(k) - 0.37129S'_{\text{CH}}(k), \end{aligned} \quad (5)$$

where k is the scattering wave vector, ρ is the liquid density, $S_{ab}(k)$ is the partial structure factor due to the $g_{ab}(r)$ rdf, and $(d\sigma/d\Omega)(k)$ is the scattering cross-section. The representation of the cross-section (times k) obtained from the simulations is shown in Fig. 2. This curve features a series of maxima and minima which are located at the same values of k found experimentally by Bertagnolli and Chieux [34]. However, the depth of the first minimum and the height of the first peak are underestimated in the present work, and there is a shoulder structure in the first peak that is not present in the experimental data, although this same result is obtained with a polarizable model by Chang et al. [8]. Nonetheless, the shape of the second peak (around 4 \AA^{-1}) is better reproduced in this work than with the polarizable model.

5. Conclusions

A mean field QM/MM method, ASEP/MD, has been applied to liquid chloroform. This has led to the obtention of an optimized molecular structure and charge distribution for the CHCl_3 molecule in solution. The changes with respect to the gas phase structure are small: C–Cl bond lengths decrease slightly and the dipole moment increases in around 10%, which agrees with previous calculations.

The calculated vaporization energy also agrees with the experimental value, and the Lennard-Jones component is

found to be the most important contribution. Different sets of Lennard-Jones parameters give equivalent results, in spite of the relative weight of their contribution.

The structure of liquid chloroform, analyzed in terms of the radial distribution functions and the neutron scattering cross-section, is consistent with other studies and with the experiment.

In sum, the ASEP/MD method is shown to work satisfactorily for liquid chloroform and, by extension, for non-polar liquids where the electrostatic contribution to the interaction energy is not the main one. Due to the use of the “completely coupled” variant, all molecules in the system are optimized simultaneously with a minimum number of empirical parameters.

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