Monte Carlo Simulation of Liquid p-Xylene

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Propriedades termodinâmicas do líquido p-xileno foram calculadas no ensemble isotérmico e isobárico à temperatura de 298K e pressão de 1.0 atm através do método de Monte Carlo. As moléculas do líquido foram representadas por um modelo rígido de 3 sítios; funções de Lennard-Jones, com parâmetros obtidos através de cálculos *ab initio* e dados experimentais, foram utilizadas para representar a superfície de potencial. Duas simulações independentes, com 80 e 200 moléculas do líquido na célula de referência, foram efetuadas. Os resultados obtidos concordam muito bem com dados experimentais da literatura.

Monte Carlo statistical mechanics calculations of liquid p-xylene in the NPT (isothermal-isobaric) ensemble at 298K and 1.0 atm have been performed. Standard Metropolis importance sampling and cubic box boundary conditions were used. The p-xylene monomers were represented by a rigid three-site united atom model and the intermolecular interaction energy was approximated by a combination of Lennard-Jones type potentials. Parameters for the intermolecular potential were derived from *ab initio* molecular orbital calculations and experimental data. Two independent simulations, with 80 and 200 molecules in the reference box, were carried out. The results obtained are in fine agreement with the experimental data.

Key words: *Monte Carlo simulation, p-xylene, isothermal-isobaric ensemble.*

Introduction

The correlation between molecular structure and the macroscopic behavior of molecular liquids has been enlightened by statistical mechanics studies of many classical model Hamiltonian[1]. Nevertheless, despite the efforts put into the development of mathematical methods, the solution of the appropriate statistical mechanics equations for most complex systems is hardly obtainable without the aid of numerical methods. Particularly for amorphous system, the complexity of the intermolecular potential function and the lack of spatial symmetry impose extra difficulties to direct mathematical calculation. Therefore numerical computation is the natural alternative to obtain averaged values from the statistical mechanics formulae. Starting with the pioneer work of Metropolis *et al.*[2] and Alder and Wainwright[3] the Monte Carlo and Molecular Dynamics computer simulation methods have been widely used in the numerical determination of thermodynamic properties of molecular systems[4,5]. Furthermore, with the rapid advance in computer technology, the capabilities of these simulation methods are being continuously extended to provide a deeper insight into the relationship between molecular structure and thermodynamic properties[6,7].

Methodology

Monte Carlo simulation of liquid p-xylene in the isothermal and isobaric ensemble at 298K and 1.0 atm was performed by using standard Metropolis importance sampling, cubic box boundary conditions and minimum image criterion[5]. The Monte Carlo computer code used was written by one of us and conveniently tested against results already published in the literature[8].

As indicated in Fig. 1 the p-xylene molecule was represented by a rigid three-site united atom model. The ME to CM distance was obtained by geometry optimization of the p-xylene molecule at the Hartree-Fock level with the 3-21G basis set using the Hondo molecular orbital package[9]. The

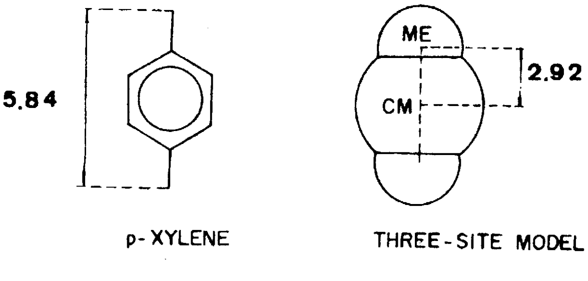


FIG. 1

Figure 1. *p-xylene molecule and the three-site united atom model.*

Table 1. *Lennard-Jones potential functions parameters for p-xylene.*

Site	σ/Å	ε/kJ mol^{-1}
CM	4.96	5.016
ME	3.91	0.669

interaction energy E_{ab} between molecules a and b was represented by potentials centered on the sites already indicated in Fig. 1, that is

$$E_{ab} = \sum_{i}^{\text{on a}} \sum_{j}^{\text{on b}} A_{ij}/(r_{ij})^{12} - B_{ij}/(r_{ij})^{6}$$

were r_{ij} is the distance between site **i** and **a** and site **j** in **b** and the sums are over the three sites in both molecules. Parameters A_{ij} and B_{ij} were obtained by the combining rules $A_{ij}= (A_{ii}A_{jj})^{1/2}$ and $B_{ij}= (B_{ii}B_{jj})^{1/2}$. For each site **k**, parameters A_{kk} and B_{kk} were expressed as[12] $A_{kk} = 4\varepsilon_{kk}\sigma_{k}$ and[6] $B_{kk} = 4\varepsilon_{kk}\sigma_{k}$, where σ_k and ε_k are the Lennard-Jones parameters of site **k**. The set of Lennard-Jones parameters used in the present calculation are presented in Table 1. For the methyl group the Lennard-Jones parameters previously published by Jorgensen *et al.*[10] were used. Parameters for the CM site were them obtained by fitting the pair energy E_{ab} given by Eq. 1 to energy values calculated with the empirical single-center potential function of Wilhelm and Batino[11]. Two independent Monte Carlo simulations with 80 and 200 molecules in the reference box were carried out; in both cases the initial box volume was calculated by using the experimental density of the liquid. Starting from an arbitrary initial monomer distribution in the reference box, new configurations were then generated by randomly translating and rotating the molecules along randomly chosen cartesian directions. The maximum ranges for monomer translation ($\Delta r=\pm$ 0.15Å) and rotation ($\Delta\ \theta= \pm$ 15.0 degree) were adjusted to provide an acceptance/trial ratio of about 0.45 for the new configurations. A volume move was attempted every 600 new configurations; the maximum ranges for volume moves (± 250Å^3 for the box with 80 molecules and ± 700Å^3 for the one with 200 molecules) were adjusted to provide the same acceptance/trial ratio as above. The intermolecular interaction was truncated at a cut-off radius $\mathbf{r}_c$=8Å in the 80-molecule box and $\mathbf{r}_c$=15Å in the one with 200 molecules. The CM to CM site-site distance was used as reference for cut-off range estimates. The contribution from molecular interactions beyond $\mathbf{r}_c$ was estimated by using long-range corrections as discussed by Al-len and Tildesley[5]. In the equilibration segment of the calculation 800k new configurations (1k=1000) were generated. All the results obtained in this segment were discarded. Averaging for the thermodynamic properties was then performed by generating 1600k new configurations for the 80-molecule box and 2400k for the one with 200 molecules.

Results and discussions

In a Monte Carlo Calculation of statistical mechanics averages the convergence is faster for those properties which are obtained directly as a configurational average and slower for those which are obtained from fluctuations[5]. The intermolecular energy and the density of liquids are among the former while the heat capacity C_p, the isothermal compressibility κ and the coefficient of thermal expansion α are examples of slowly convergent properties. After these observations, the present Monte Carlo averages are compared to experimental data in Table 2. One observes that the agreement between theoretical and experimental values for the p-xylene density and heat of vaporization is very good. ΔH_{vap} was calculated from standard thermodynamic formulae by adding RT to the negative value of the averaged internal energy E_i. The intermolecular heat capacity C_p^i reported in Table 2 has been corrected by adding 5/2R (20.78 J K^{-1} mol^{-1}), to include the contribution from the kinetic energy of translation of the p-xylene molecules. To further investigate the heat capacity of this liquid the contribution from intramolecular degrees of freedom must be estimated. The MOPAC-AM1 semiempirical molecular orbital package[12] was used to calculate the contribution of from vibrational degrees of freedom to the heat capacity. This contribution was found to be 91.96 J K^{-1} mol^{-1} at 298K. After this necessary correction one observes that the result obtained for the heat capacity of liquid p-xylene is in fine agreement with the experimental data. The values obtained for the isothermal compressibility and the coefficient of thermal expansion are also close to the experimental data. Nevertheless, as the convergence for these two averaged quantities is usually slow, this close numerical agreement should be taken with some caution.

As a partial conclusion the thermodynamic results obtained with the three-site model for the p-xylene molecule are in fair agreement with the experimental data. The density is the only variable that shows an appreciable size dependence.

Compared to the periodic organization of crystalline solids the structure of a liquid is more difficult to be comprehended. A deeper understanding of the liquid structure, that is,

Table 2. *Calculated and experimental properties of liquid p-xylene at 25°C and 1 atm.*

	this work		expt.[b]
	80	200	
d/(kg/m^3)	840	856	860
-E_i/(J/mol)	39.74	40.52	
ΔH_{VAP}/(kJ/mol)	42.22	43.0	42.40
C_p^i/(J/K mol)	56.0	56.8	
C_p/(J/Kmol)	128	129	133.7
κ/(atm^{-1})x10^4	0.90	0.69	0.74
α/(deg^{-1})x10^3	0.84	0.63	1.02

a- results obtained with 80 and 200 molecules in the reference box
b- experimental results from ref. 19

Table 3. *Site-site distances calculated at the minimum energy position*

Distance	Configuration		
d/(Å)	A	B	C
CM-CM	5.2	5.6	7.6
ME-CM	5.95	4.8	4.68

its degree of order determined from the thermal movement and the molecular cohesiveness is provided by the analysis of radial distribution functions. In Monte Carlo and Molecular Dynamics simulation of liquids this important information is straightforwardly obtained by the analysis of the configuration chain generated during calculation[5]. Radial distribution functions obtained in the present calculation form the 200-molecule simulation box are presented in Fig. 2. One observes that the ME-CM pair correlation curve exhibit a well defined peak centered at 4.7Å. The CM-CM pair correlation exhibit a high peak centered at 5.5Å and a smaller one near 7.3Å. To investigate the origin of these features in the radial distribution functions we present in Fig. 3 the behavior of the pair energy E_{ab} as a function of the CM-CM site-site distance for some preferential molecular orientations. Site-site distance calculated at the minimum energy position are presented in Table 3. The position and shape of the first peak in the ME-CM pair distribution can be attributed to the spread from 4.7 to 5.9Å found on the ME-CM distances shown on Table 3. A correlation between the first peak in the CM-CM pair distribution function near 5.5Å and the minimum energy position found for configurations A and B is also deducible; the shoulder observed near 7.3Å might be explained by combinations of T-shaped configurations as indicated in Fig. 3C. A similar behavior was reported by Narten and Habenschuss[13] on the experimental carbon-carbon distribution function for liquid ethylene. Therefore, the structure of liquid p-xylene ascertained by the three-site potential model discussed above corroborates the existence of dimerous like structures in liquid phase aromatic compounds as already discussed in theliterature[14,15] . Moreover, the contribution of the first peak in the CM-CM radial distribution function indicates a predominance of stacked structures over T-shaped ones. To further investigate the configuration of the p-xylene dimer, a molecular mechanics calculation using simulated annealing was performed[16]. We found that the configuration of lowest energy (-10.41 kJ/mol) is very similar to the ones presented in Fig. 3B. It is interesting to note that Jorgensen and Severance[15] using an all-atom model for the benzene molecule

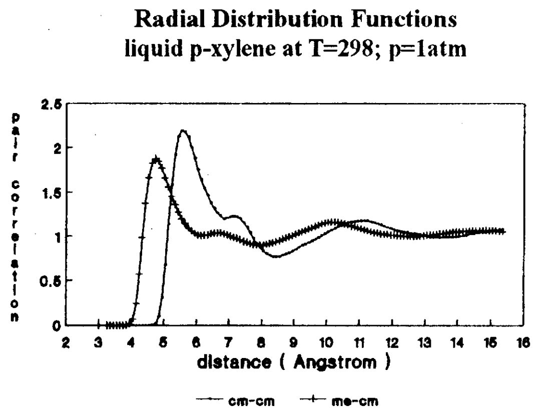


Figure 2. *CM-CM and ME-CM radial distribution functions.*

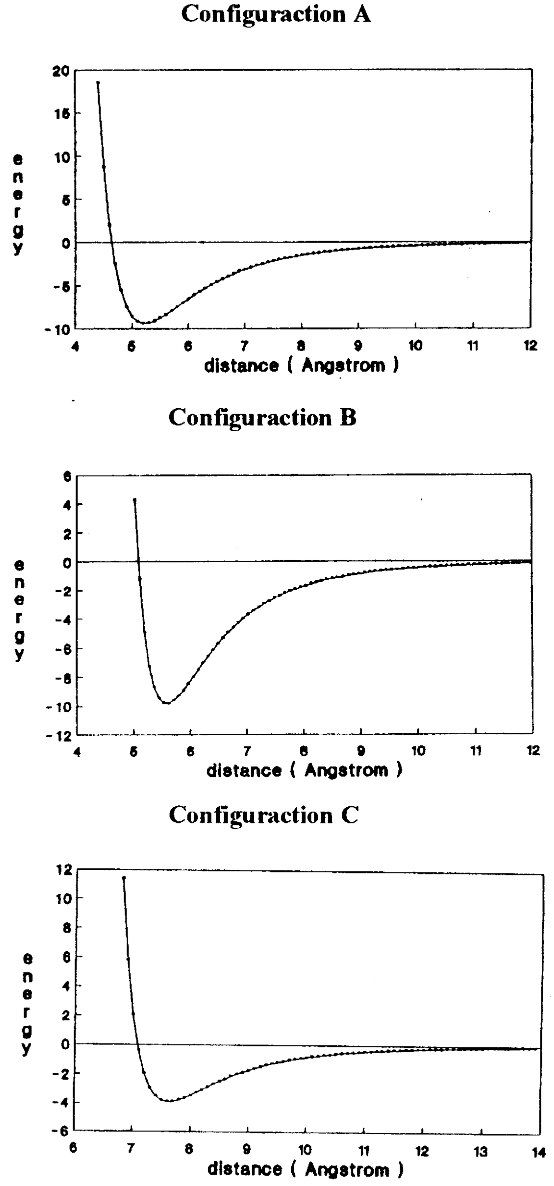
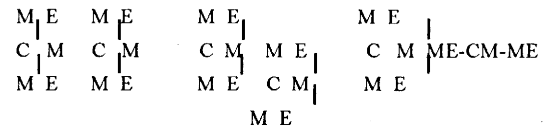


Figure 3. *Interaction of coplanar p-xylene monomers as a function of the d(CM-CM)distance; the configurations (energy in kJ/mol) are schematically shown bellow*
Configuration A Configuration B Configuration C



found a large predominance of T-shaped dimer configurations over face-to-face stacked ones in liquid benzene. The present molecular mechanics result is comparable to the one reported by Jorgensen and Severance[15] in the sense that both preferential configurations shows a complex formation through an enhancement of the interaction between rings and hydrogen atoms. It is important to note that in the p-xylene molecule the hydrogen atoms of the methyl group are out of the ring plane. Therefore, in the face-to-face stacked form of the p-xylene dimer show in Fig. 3B the interaction between ring and hydrogen atoms is favorable, whereas in the benzene dimer the ring-hydrogen at-oms interaction is enhanced by the T-shaped configuration.

The broad structure in the CM-CM and ME-CM radial distributions above 8Å indicates that the organization of the p-xylene molecules is short ranged. Compared to the pair distribution functions found for water[17] at this same tem-perature and pressure, the broadness of these peaks also indicates a lower degree of ordering. This finding corroborates the general observation that the standard entropy of most aprotic organic liquids is comparatively higher than that of water[18]. The present calculation was carried out in a 33 MHz Quantum workstation running Unix V.

Conclusions

The thermodynamic properties of liquid p-xylene have been calculated with the Monte Carlo method in the isothermal-isobaric ensemble at 298K and 1 atm. A good agreement with the experimental data was found, indicating the usefulness of the rigid three-site potential model used to represent the p-xylene molecule. A substantial contribution from intramolecular degrees of freedom to the heat capacity was observed. The size dependence of the calculation was examined by comparing results from independent simulations with 80 and 200 molecules in the reference box; for all properties but the density, a negligible size dependence was found. The features observed in the radial distribution functions are consistent with short range pair correlation and the existence of dimerous like structures in liquid.

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