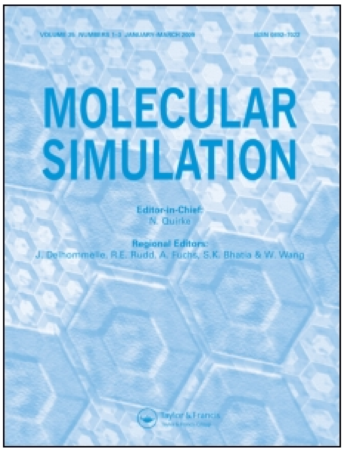

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ESTIMATION OF SOLVENT DIFFUSION COEFFICIENTS USING MOLECULAR DYNAMICS SIMULATIONS

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Molecular dynamics simulations have been used to investigate diffusion in two commonly used industrial solvents, toluene and tetrahydrofuran. Several different models for the solvents are compared (flexible vs. rigid, all-atom vs. united atom), and it is found that united atom and all-atom models of the solvents produce very different diffusion coefficients at the experimental density. This disagreement can be explained by the pressure dependence of the diffusion coefficient, which is found to vary in accord with the Chapman-Enskog result for hard spheres. It is recommended that force fields be parametrized carefully to produce reasonable pressures at the experimental densities, or that simulations be carried out at constant pressure, if they are to be used for the purposes of calculating transport coefficients.

KEY WORDS: Diffusion coefficients, solvents, Chapman-Enskog, molecular dynamics

INTRODUCTION

Many processes in the chemical and manufacturing industries rely on the use of solvents. Mathematical models of such processes often require diffusion coefficients of the solvent or solute as input [1]. Further, the conditions under which the particles diffuse often change with time, as in a polymerization reaction or the drying of a coating. As the experimental measurement of solvent or solute diffusion coefficients under a wide variety of conditions represents a formidable task, an alternative method of obtaining estimates of diffusion coefficients is desirable. This paper deals with the application of molecular dynamics (MD) computer simulations to obtain estimates of diffusion coefficients for the solvents toluene and tetrahydrofuran (THF).

Accurate values of diffusion coefficients, D, for simple liquids can be calculated from MD trajectories using the Einstein relation

$$D = \lim_{t \to \infty} \langle [\mathbf{r}(t) - \mathbf{r}(0)]^2 \rangle / 6t \tag{1}$$

where $\mathbf{r}(s)$ denotes the position of a particle at time s and the angle brackets denote an average over particles and time origins [2]. A recent study indicates that it is also possible to obtain accurate values of D for penetrant diffusion in amorphous polymers using MD simulations, although a strong dependence on the force field was observed [3]. As diffusion in pure solutions and penetrant diffusion in glassy polymers represent two extreme limits of the processes described in the previous paragraph, it seems likely that MD methods will yield reasonable results in intermediate regimes as well.

The present work seeks to establish which features of a solvent model influence the diffusion process in pure and mixed solvents, as a precursor to examining diffusion in the more complex conditions described above. In particular, comparison is made between solvent models in which the intramolecular degrees of freedom are allowed (flexible) and models in which they are frozen (rigid). Also compared are solvent models in which all atoms are explicitly included in the interaction potential ("all-atom") and models in which CH, CH_2 and CH_3 groups are represented by a single interaction site with an effective pair potential ("united atom").

SIMULATION DETAILS

MD simulations were carried out for pure toluene, pure THF and mixed toluene/THF systems using the DREIDING force field [4]. The DREIDING force field employs van der Waals interaction parameters which are based on fits of crystal structure and heat of sublimation data. Specification of the atom types and bonding (i.e. which atoms are connected) uniquely determines all of the relevant interactions. The molecular structures and DREIDING atom types employed in this work are shown in Figure 1. These may be used in conjunction with Reference [4] to determine the values of all the force field parameters required for the present work.

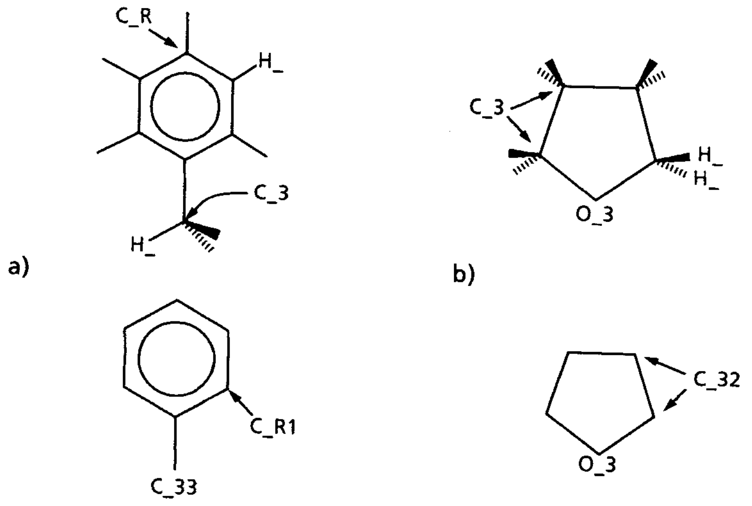

Figure 1 Diagrams indicating the chemical structures and DREIDING atom types used in the simulations for toluene (a) and THF (b). The upper and lower structures correspond to the all-atom models and the united atom models, repectively. All bonds are shown explicitly. Equilibrium bond lengths and angles are uniquely defined by the atom types and connectivity (see Reference [4].)

The pure solvent systems were prepared by placing randomly oriented molecules of the appropriate type on lattice sites within a sphere of radius R centered on a molecule at the origin (typically, $R \sim 15$ Å). The sphere of solvent molecules was then superimposed on a cubic box, whose dimensions were determined by requiring the volume to be that occupied by a specified number of molecules, N, at the experimental room temperature density. Molecules where either eliminated or translated into the box, until a system consisting of exactly N molecules in a cubic box was obtained. In this way, generation of the initial configuration can be carried out from within the graphical user interface of the MD program (Appendix A), and it is possible to generate mixed systems of arbitrary composition in a straightforward manner. Once the initial configuration was obtained, periodic boundary conditions were applied, and the system was relaxed using conjugate gradient minimization of the energy to eliminate overlapping atoms. Subsequently, an equilibration MD run of at least 10 ps was carried out before collecting statistics.

For the mixed toluene/THF system, the initial configuration was generated in the same manner, except that spherical shells of the different solvent molecules were alternately placed in layers about the central molecule, and a longer equilibration period was allowed. The density of the mixed solvent system was determined from that of the two pure components by assuming there is no volume change on mixing. In order to reduce the amount of computer time required, the total number of interaction sites was held to about 500 for the pure solvent runs which employed the all-atom model. The actual values of the density and N are reported with the simulation results below.

After equilibrating the starting configurations, production runs were initiated by reassigning random velocities, sampled from a Boltzmann distribution at 300 K, to all of the atoms in the equilibrated starting configuration. Run lengths were typically greater than 100 ps, and are reported with the simulation results. D was calculated for each run using Equation (1) and the center of mass coordinates of the molecules. Values of D reported below are estimated to have an accuracy of ±30%, based on the analysis of eight 100 ps segments of an 800 ps all-atom, rigid THF run. The large error bound is probably due to the small system size (39 molecules), and is likely much smaller for the united atom runs. Details of the implementation of the MD method are outlined in Appendix A.

RESULTS AND DISCUSSION

Results of THF simulations employing the flexible all-atom, rigid all-atom and rigid united atom solvent models are presented in Table 1. Within the stated accuracy, values of D for flexible and rigid all-atom models are in agreement. However, the value of D calculated for the rigid, united atom model of THF is an order of magnitude larger at the same density! Table 1 suggests two possible explanations for this discrepancy. The number of molecules in the united atom runs is four times that in the all atom runs. One might imagine a scenario in which the distance between a THF molecule and its periodic images is so small that a structuring of the surrounding liquid is introduced which inhibits diffusion. However, since the MD box length is ~17 Å and the maximum diameter of a THF molecule is ~7 Å, this does not seem likely. A second explanation is suggested by the average pressures, P, reported in Table 1. The pressures calculated for the all-atom runs are quite high,

Table 1 Results of MD simulations with various models of THF.

Run	*Model*	*N*	*Density* *(g/cm^3)*	*time* *(ps)*	*⟨T⟩ (K)*	*⟨P⟩ (GPa)*	*D* *(10^{-9} m^2/s)*
1	flexible, all-atom	39	0.8810	100	299	0.0725	0.36
2	rigid, all-atom	39	0.8810	800	292	0.0592	0.41
3	rigid, united atom	156	0.8810	200	300	−0.0126	4.33

~0.06 GPa, while the corresponding value for the united atom simulation is actually negative.

To investigate the effects of system pressure on diffusion, a series of united atom runs was carried out, in which the volume of the MD box had been reduced by 5, 10, 15 or 20 percent. (Reducing the volume of the MD box is roughly equivalent to *increasing* the van der Waals radii of the united atoms - in either case the free volume fraction is reduced.) Each compression of the MD cell was followed by a minimization, in order to eliminate hard core overlaps. The results of the subsequent MD runs, reported in Table 2, show that D depends very strongly on density, ρ, and, consequently, on P. Further, comparison of data for Run 7 in Table 2 with the all-atom runs in Table 1 indicates that D is essentially the same for all the models at comparable values of P.

The results presented thus far indicate diffusion depends strongly on the force field, in agreement with Reference [3]. However, it is *not* possible to conclude that either the united atom or all-atom is better *per se*. Experimental values of D for toluene and cyclohexane at infinite dilution in benzene at 298 K are 1.85 and $2.09 \times 10^{-9}\,\mathrm{m^2/s}$, respectively, so one would expect to find $D \sim 2 \times 10^{-9}\,\mathrm{m^2/s}$ for THF self-diffusion. At the experimental density, the all-atom force field yields P too high and D too low, while the united atom force field yields P too low and a value of D which is probably too high. On the other hand, Run 5 in Table 2 shows that for $P \sim 0$, the united atom force field provides reasonable results for D. It appears that potential parameters must be optimized to produce correct $P(\rho, T)$ values, in order to produce reasonable diffusion behavior. Alternatively, the simulations should be carried out at constant P, in which case ρ would no longer correspond exactly to the experimental density. The pressure dependence of D is an aspect which was not discussed in Reference [3].

It is interesting to consider the results of Table 2 in greater detail. According to

Table 2 Results of MD simulations with the rigid, united atom THF model as a function of density.

Run	*N*	*Density* *(g/cm^3)*	*time* *(ps)*	*⟨T⟩ (K)*	*⟨P⟩ (GPa)*	*D* *(10^{-9} m^2/s)*
3	156	0.8810	200	300	−0.013	4.33
4	156	0.9268	40	297	−0.011	2.97
5	156	0.9789	40	301	−0.003	2.27
6	156	1.0369	40	300	0.014	1.20
7	156	1.1016	150	300	0.042	0.38

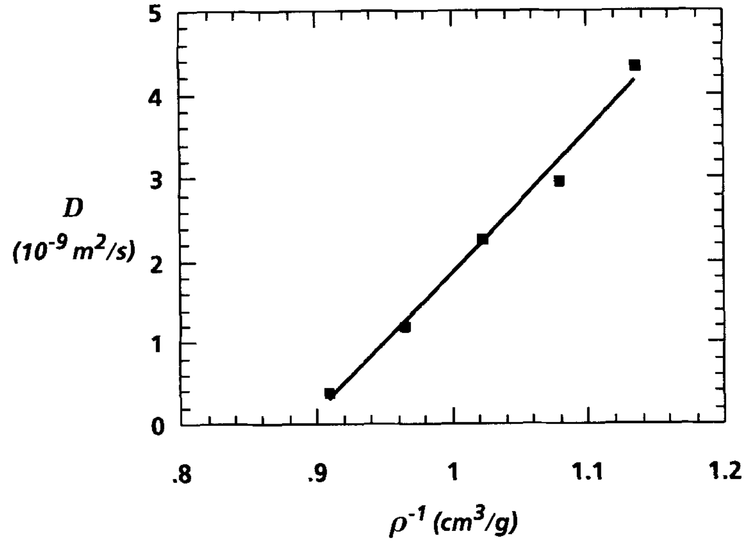

Figure 2 THF diffusion coefficient versus density from the MD results in Table 2. Data points are indicated by the squares. The straight line is merely a guide to the eye.

the Chapman-Enskog solution of the Boltzmann equation for dilute hard-sphere gases, [8] D should vary as $1/\rho$. Figure 2 shows a plot of D versus $1/\rho$ taken from the data in Table 2. The relationship is indeed linear, indicating that the relatively dense fluids studied here exhibit Chapman-Enskog-like diffusive behavior. This is somewhat surprising, as the Boltzmann equation is derived by assuming that the transport process is dominated by binary collisions of particles with zero size.

Finally, Table 3 presents results for MD runs with rigid, all-atom models of pure toluene and a 50% by weight toluene/THF mixture. To facilitate comparison with pure THF, the results of Run 2 from Table 1 are reproduced as well. Both P and D for the mixed solvent system are found to be roughly equal to the average of the corresponding values observed for the pure solvents. The observation that P for the mixed system is the average of the two pure fluid values can be attributed to the assumption of no volume change on mixing, used to determine the density. Recent MD studies of diffusion in equimolar, binary "soft-hard-sphere" fluids suggest that the slight differences observed between D_{tol} and D_{THF} for the mixed system may be real, [9] however, the accuracy of the present calculations does not

Table 3 Results of MD simulations with rigid, all-atom models for pure and mixed solvent solutions. The toluene/THF mixture is approximately 50% by weight.

Run	*Model*	*N*	*Density (g/cm^3)*	*time (ps)*	$\langle T \rangle$ *(K)*	$\langle P \rangle$ *(GPa)*	*D* $(10^{-9} m^2/s)$
8	toluene	35	0.8622	200	295	0.0274	0.77
9	toluene/ THF	$N_{\mathrm{tol}} = 22$ $N_{\mathrm{THF}} = 28$	0.8706	200	297	0.0424	$D_{\mathrm{tol}} = 0.55$ $D_{\mathrm{THF}} = 0.59$
2	THF	39	0.8810	800	292	0.0592	0.41

permit such a claim. In light of the strong dependence of D on P discussed above, it is not clear that the $P = 0$ values of D for the two pure solvent systems reported in Table 3 would differ significantly from each other or from the corresponding values in the mixed solution.

CONCLUSIONS

Molecular dynamics simulations using the DREIDING force field [4] have been carried out at constant volume and temperature for liquids composed of model toluene and THF solvent molecules. Comparisons were made between rigid and flexible solvent models and between all-atom and united atom models on the basis of thermodynamic and diffusive data. Diffusion coefficients calculated for pure THF solutions at the experimental density differed greatly between all-atom and united atom models, but were very similar for flexible and rigid all-atom models. Neither the all-atom nor the united atom model gave reasonable results for the diffusion coefficient at the experimental density. The discrepancy between diffusion coefficients for all-atom and united atom models was shown to be largely attributable to differences in the average pressure for the two models. At the same time, it was noted that the diffusion coefficient calculated for the model THF system varied inversely with density, as predicted by the Chapman-Enskog result for dilute hard spheres.

It appears necessary to parametrize force fields to give a reasonable pressure at the experimental density in order to obtain proper diffusive behavior. Alternatively, simulations should be carried out at constant pressure in order to minimize problems related to parametrization.

APPENDIX A

The MD simulations were carried out using either version 3.0 or 3.1 of the POLYGRAF software from Molecular Simulations, Inc., with the default DREIDING force field [4]. In the DREIDING force field, the total potential energy, U_{tot}, is written as a sum of valence (U_{val}) and non-bonded (U_{nb}) terms. The valence energy is given by

$$U_{\text{val}} = U_{\text{bond}} + U_{\text{angle}} + U_{\text{tors}} + U_{\text{inv}}, \tag{A.1}$$

where U_{bond} is a bond stretching term, U_{angle} is a bond angle bending term, U_{tors} is a dihedral angle torsion term and U_{inv} is a four-body inversion term. The non-bonded energy arises from a sum of van der Waals (U_{vdw}), electrostatic (U_Q) and explicit hydrogen bond (U_{hb}) terms

$$U_{\text{nb}} = U_{\text{vdw}} + U_Q + U_{\text{hb}}. \tag{A.2}$$

Details of the exact form of these interaction terms can be found in Reference [4]. For toluene and THF, the inversion and hydrogen bond terms do not contribute to the potential energy, and, for the purposes of this study, the electrostatic contribution has been neglected. For simulations carried out with rigid molecules, the valence energy is zero, leaving only the non-bonded van der Waals term in the potential energy.

Since there are no long range (electrostatic) forces present in the systems being modeled, a neighbor list with a cutoff distance of 9.0 Å was employed for the nonbonded interactions. Atom-atom interactions were multiplied by the switching function

$$S(x, x_{\text{on}}, x_{\text{off}}) = \begin{cases} 1, & x \leq x_{\text{on}} \\ (x_{\text{off}} - x)^2(x_{\text{off}} + 2x - 3x_{\text{on}})/(x_{\text{off}} - x_{\text{on}})^3, & x_{\text{on}} < x < x_{\text{off}} \\ 0, & x \geq x_{\text{off}}. \end{cases} \tag{A.3}$$

In Equation (3), the x's denote the squares of distances between two atoms; the calculations reported here were carried out with $x_{\text{on}} = (8.0\ \text{Å})^2$ and $x_{\text{off}} = (8.5\ \text{Å})^2$.

Simulations were carried out with periodic boundary conditions in the canonical (NVT) ensemble, using the leap-frog or summed Verlet algorithm [5] to integrate the equations of motion. Rigid molecule dynamics were carried out using quaternions [6]. Canonical ensemble trajectories were generated using the Nosé-Hoover [7] thermostat method. Specifically, the Nosé-Hoover method yields the equations of motion

$$dq_i/dt = p_i/m_i \tag{A.4}$$

$$dp_i/dt = -\partial U/\partial q_i - \zeta p_i \tag{A.5}$$

$$Q\, d\zeta/dt = \sum_i p_i^2/m_i - gkT_0 \tag{A.6}$$

where, for flexible systems, the q_i, p_i and m_i are the atomic coordinates, momenta and masses, respectively, g is the number of degrees of freedom, T_0 is the temperature of the heat bath, Q is an adjustable inertial parameter controlling the coupling of the molecules to the bath and ζ is the friction force. In POLYGRAF, the value of the inertial parameter Q is chosen by the relation

$$Q = gkT_0\tau^2/2\pi^2, \tag{A.7}$$

where τ is a relaxation time for the particular system. Typically, τ should be about the same as the shortest vibrational period. The simulations reported here were carried out with POLYGRAF's default values for τ, namely $\tau = 0.1$ ps and $\tau = 10.$ ps for systems with flexible and rigid molecules, respectively.

Within the canonical ensemble, the magnitude of the kinetic energy fluctuations are bounded by the relation

$$\langle K^2 \rangle - \langle K \rangle^2 = 3N(k_B T)^2/2, \tag{A.8}$$

where K is the kinetic energy, N is the number of particles, T is the absolute temperature of the system and k_B is Boltzmann's constant [7]. Equation (A.8) was used to ensure that proper canonical trajectories were generated. Using the values of τ cited above with integration timesteps of 0.2 fs for flexible molecule systems and 5.0 fs for rigid molecule systems produced satisfactory results, and these time steps were used for all runs reported here. It is worth noting that trial runs made with flexible, all-atom THF molecules, τ values of 0.5, 0.1 and 0.02 ps and the POLYGRAF default integration timestep of 1.0 fs failed to satisfy Equation (A.8).

Finally, the molecular geometries used for rigid molecule runs were generated by minimizing the atomic positions in an isolated molecule subject to the valence and non-bonded terms of the DREIDING force field and the constraint that all of the carbon atoms lie in a plane. The resulting structures were then used to generate starting configurations for the solvents as outlined in the main body of this report.

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