AUA model NEMD and EMD simulations of the shear viscosity of alkane and alcohol systems

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Received 26 June 2003

Abstract

The viscosities of alkanes (propane, isobutane, nonane), alcohols (ethanol, propanol, isopropanol, 2-butanol) and isopropanol + nonane mixtures were calculated using non-equilibrium and equilibrium molecular dynamics (NEMD and EMD) simulation methods. The nonane, isopropanol and nonane + isopropanol mixture simulations were performed in response to the First Industrial Simulation Challenge. Intermolecular interactions were modeled using an anisotropic united-atom Buckingham exponential-6 potential. The force field parameters were optimized using pure component viscosity data. The resulting viscosities are compared with literature values, with the result that the anisotropic united-atom model together with the exponential-6 model can give good predictions of the viscosity of n-alkane and alcohol systems.
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Keywords: Molecular dynamics simulations; n-Nonane; Propane; Isobutane; Isopropanol; Ethanol; Propanol; 2-Butanol; AUA model; UA model; Exponential-6 potential; Ewald sum method; Partial charge; Viscosity; NPT; NVT

1. Introduction

Computer simulations offer a link between models of intermolecular interactions and observed macroscopic properties. It is fair to say that after decades of efforts, scientists have developed and employed theories and simulation techniques that enable us to simulate any property imaginable [1,2]. Results of these simulations are not only of scientific interest, but also of engineering and industrial interest. This later interest has arisen because it is becoming increasingly possible for one to select materials for a process based only on a knowledge of their molecular structure and resulting interactions with other materials. A major impediment to wide-spread industrial acceptance of computer simulation today is in fact our incomplete knowledge of the simulation force field and the lack of transferability of a force field from the properties upon which it was based to the simulation of other properties. A good example is the fact that the OPLS force field [3] gives reasonable dense liquid equilibrium properties but generally will yield liquid viscosity simulations that are 30% low as compared to experimental data.

In this study, we have simulated the shear viscosity of a series of normal hydrocarbons and alcohols and mixtures of isopropanol + n-nonane. The motivation for the later set of simulations was one of the problems posed in the First Industrial Challenge for the Simulation of Material properties, Problem Set #3, [4] although our more general goal is to develop a force field which is transferable between properties and members of a homologous series.

2. Force field

2.1. Background

Most molecular modeling is based on the assumption that the intermolecular potential between a pair of structured molecules can be modeled as a sum of interactions between every intermolecular pair of atoms or group of atoms, and that these interactions depend only on the separation of the atoms (groups). All these models have an implicit orientation dependence, which recognizes that the relative positions of the atoms (groups) within the molecule is the major factor in defining the molecular shape [5].

Three kinds of models, all atom (AA), united atom (UA) and anisotropic united atom (AUA) models, are in common use. The AA and UA models have been widely used to pre-

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dict equilibrium and transport properties of pure fluids and some mixtures. There are indications that AA models better represent experimental data but they are computationally extremely expensive for large systems or molecules because one must consider interactions between every atom in a molecule with every atom in every other molecule in its implementation. Thus, the computational burden is heavy compared to the UA model where atoms are grouped together into simpler and fewer interaction sites [5].

In this study, a new version of the anisotropic united atom model (AUA) [6–9] that incorporates the exponential-6 intermolecular potential along with fixed bond lengths and bond angles, was used in calculating the intermolecular interactions. The AUA model was originally proposed by Toxvaerd [6] (referred to as AUA1 in this manuscript) which incorporated the Lennard–Jones 12–6 intermolecular potential. The advantage of the AUA approach is that it can include some of the positive features of the AA model without the computational expense. The AUA1 model was based on the observation that the pressure in fluids of propane, pentane, and decane scaled incorrectly with respect to temperature and density when calculated with traditional united-atom models. The AUA model is a simple extension of the united-atom model, in that it maintains the carbon centers as the moving centers, but lets the intermolecular potential originate from the geometrical center of the site. As such, the site-site interactions depend on the instantaneous chain configuration. Toxvaerd and Padilla proposed an AUA2 model [7] optimized using PVT and self-diffusion coefficients. In 1997, the AUA3 [10] model was proposed by Toxvaerd based on a study of the pentane and decane systems over a wide range of pressures ($\sim$350 MPa) and temperatures (298–673 K).

Dysthe et al. [11,12] used the AUA2 and AUA3 models and the Green-Kubo method to simulate the transport properties of liquid n-butane, n-decane, *n*-hexadecane, and alkane mixtures. Generally good results were observed in the simulations, though at high density and low temperature, the viscosity was underestimated.

Ungerer et al. [8,9] optimized the anisotropic united atom potential for linear alkanes on the basis of selected equilibrium properties of ethane, *n*-pentane, and *n*-dodecane. The optimized parameters for the CH_2, CH_3 and CH groups form a regular sequence with those of methane and the force centers are found between the carbon and hydrogen atoms, as expected. The resulting potential, called AUA4, has been compared with Toxvaerd's potential (AUA3). An investigation performed at temperatures ranging from 140 to 700 K and with various chain lengths up to 20 carbons atoms has shown AUA4 provides systematic improvements of vapor pressures, vaporization enthalpies, and liquid densities for pure *n*-alkanes. Significant improvements have been also noticed for the critical temperatures of n-alkanes, estimated from coexistence density curves, and for the equilibrium properties of $CO_2 + n$-alkane binary mixtures. Ungerer et al. also report self-diffusion coefficients of *n*-hexane that are slightly improved by the new potential, but still exceed those

Table 1
LJ based AUA model potential parameters

Model	Group	σ (Å)	ε (K)	d_{aua} (Å)
AUA1	CH			
	CH_2	3.527	80	0.32
	CH_3	3.527	120	0.32
AUA2	CH			
	CH_2	3.527	80	0.37
	CH_3	3.527	120	0.275
AUA3	CH			
	CH_2	3.516	79.87	0.4
	CH_3	3.516	119.8	0.18
AUA4	CH	3.3625	50.98	0.64599
	CH_2	3.4612	86.29	0.38405
	CH_3	3.6072	120.15	0.21584

obtained experimentally low temperatures. Simulations [9] have also been performed to extend the AUA4 potential to branched and long chain alkanes (C_{20}, C_{25} and C_{30}) and for binary and ternary mixtures [13]. Based on these results, the AUA potential shows an interesting degree of transferability. Table 1 summarizes site parameters for the various AUA models.

As described above, the AUA model has been utilized successfully in equilibrium simulations, but has seldom been explored in non-equilibrium simulations, especially for polar fluids. A goal of this work was to predict the viscosity of nonane and isopropanol and their mixtures at specified state points as well as to simulate the viscosity of other alkanes (propane, isobutane) and alcohols (ethanol, propanol, 2-butanol) using the nonequilibrium molecular dynamics (NEMD) method. The compositions of the mixtures studied specified in the simulation challenge problem and were 50/50 and 25/75 mol% *n*-nonane/isopropanol. One of our goals is to develop a force field that is transferable between different properties, thus we chose to investigate an AUA model that has a more repulsive core.

2.2. Force field details

Schematics of some of the molecular models are shown in Fig. 1. In the *n*-alkane model, CH_3 and CH_2 groups are taken as molecular sites with the same masses, while the interaction centers are located at the points a little bit away from the carbon atom centers, the displacement being denoted as d_{aua}. The net effect of this is to consider the influence of hydrogen atoms without explicitly increasing the number of sites. In the alcohol model, CH_3, CH_2, CH groups and O and H atoms are taken as molecular sites. In the isopropanol model, partial charges were assigned to all of the AUA interaction sites. Bond lengths and angles were constrained using the Gaussian constraint method [14–16] however, the torsional angles are free in the models.

The intermolecular potential function was assumed to be composed of two independent parts. The intermolecu-
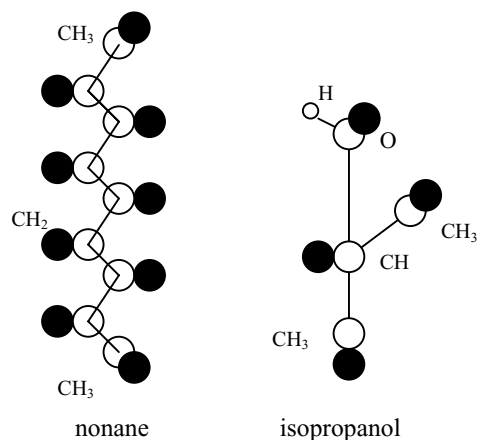
Fig. 1. Schematic sketch of AUA model. Centers of carbon atoms (used by UA model) are represented by circles, and the interaction centers by solid circles (AUA model).

lar site–site potential was modeled using pair-wise additive Buckingham exponential-6 potentials [17,18].

$$u(r) = \begin{cases} \dfrac{6\varepsilon}{s_0 - 6} \left\{ \exp\left[s_0 \left(1 - \dfrac{r}{r_0} \right) \right] - \dfrac{s_0}{6} \left(\dfrac{r}{r_0} \right)^{-6} \right\} & r \geq r_{max} \\ \infty & r < r_{max} \end{cases} \tag{1}$$

where r_{max} is the smallest positive intermolecular separation for which $u'(r) < 0$. The potential parameters are ε, r_0, s_0 where $u(r_0) = -\varepsilon$ and $u(\sigma) = 0$. The parameter s_0 is the repulsive steepness parameter and the relation between σ, s_0 and r_0 can also be obtained by numerically solving Eq. (1). A coulombic potential was added to this potential when partial charges were included in the alcohol simulations.

The Lorenz–Berthelot combining rules were used for the exponential-6 parameters for cross interactions between heterogeneous sites.

$$\varepsilon_{12} = \sqrt{\varepsilon_{11} \varepsilon_{22}} \tag{2}$$

$$\sigma_{12} = \frac{\sigma_{11} + \sigma_{22}}{2} \tag{3}$$

$$s_{12} = \sqrt{s_{11} s_{22}} \tag{4}$$

The intramolecular potential parameters are essentially identical to those from the OPLS model [3,19]. Thus non-bonded intramolecular interactions for sites more than three bonds apart were modeled using a Lennard–Jones [6,12] potential, Eq. (5). The LJ parameters in alkanes were those for a nonane CH_2 group and the LJ parameters for 2-butanol were from reference [19].

$$u_{LJ}(r) = 4\varepsilon_a \left[\left(\frac{\sigma_a}{r} \right)^{12} - \left(\frac{\sigma_a}{r} \right)^6 \right] \tag{5}$$

where the a denotes an intramolecular parameter. Rotations about internal single bonds were permitted in accordance with the model torsional potential.

$$u(\phi) = \sum_i c_i \cos^i \phi \tag{6}$$

where $u(\phi)$ is the torsional potential energy and ϕ is torsional angle. Parameters used are from the Ryckaert–Bellemans potential [20] for nonane and from the OPLS potential [19] for isopropanol.

The parameters used in this work were developed based on the AUA4 for ε, σ and d_{aua}, and the values for repulsive steepness parameter, s_0, were taken from the literature [18,21]. The partial charge parameters used in this work were based on those used by Rowley et al. [22–25] and Jorgensen

Table 2
Force field parameters used in this work[a]

Parameter	CH$_3$	CH$_2$	CH	O	H
ε (K)	140	93.34	59.4	94.0	0.0002[b]
σ (Å)	3.72	3.57	3.5	3.13	1.856
S_0	16	22	24	28	12
d_{aua} (Å)	0.18	0.24	0.5	0	0
Partial charge	0.002e	0.29e	0.001e	−0.82e	0.53e
Bond lengths (Å)	CH$_3$–CH$_2$: 1.531				
	CH$_2$–CH$_2$: 1.535				
	CH$_3$–CH: 1.524				
	CH–O: 1.408				
	O–H: 0.944				
Bond angles (°)	∠CH$_3$–CH–O:110.92				
	∠CH–O–H: 109.51				
	∠CH$_3$–CH–CH$_3$: 112.56				
	∠CH$_3$–CH$_2$–CH$_3$: 114				
	∠CH$_2$–CH$_2$–CH$_3$: 112.43				
	∠CH$_3$–CH$_2$–CH$_2$: 112.41				

[a] All interactions were truncated at 12 Å.
[b] From reference [23].

et al. [19] in their simulations of polar molecular systems. The force field parameters are listed in Table 2 and were optimized for the pure fluids using a trial-and error method based on pure fluid viscosity for fluids not included in the simulation challenge. Details of the optimization procedure are given in reference [26].

3. Simulations

In all of the simulations performed, conventional reduced units, periodic boundary conditions, spherical cut-offs and Verlet neighbor list have been used [27,28]. The NEMD simulations were performed using a fifth-order Gear predictor-corrector numerical integration scheme [28]. A molecular version of the isothermal shear algorithm [29], SLLOD, was applied in conjunction with Gaussian thermo-stat [14,30].

The equations of motion for NPT ensemble were developed by Daivis and Evans [31]

$$
\begin{aligned}
\dot{\boldsymbol{r}}_{i\alpha} &= \frac{\boldsymbol{p}_{i\alpha}}{m_\alpha} + \boldsymbol{n}_x \gamma y_i + \dot{\varepsilon}\boldsymbol{r}_i \\
\dot{\boldsymbol{p}}_{i\alpha} &= \boldsymbol{F}_{i\alpha}^N + \boldsymbol{F}_{i\alpha}^C - \frac{m_\alpha}{M_i}\boldsymbol{n}_x \gamma \boldsymbol{p}_{yi} - \frac{m_\alpha}{M_i}\xi\boldsymbol{p}_i - \frac{m_\alpha}{M_i}\dot{\varepsilon}\boldsymbol{p}_i \\
\dot{V} &= 3\dot{\varepsilon}V \\
\ddot{\varepsilon} &= \frac{(p - p_0)V}{QNkT} \\
\xi &= \frac{\sum_{i=1}^N (1/M_i)\left\{F_i \cdot p_i - \gamma p_{xi}p_{yi}\right\}}{\sum_{i=1}^N (1/M_i)p_i^2} - \dot{\varepsilon}
\end{aligned}
\tag{7}
$$

where $r_{i\alpha}$ is the position of site α on molecule i, $p_{i\alpha}$ the momentum of site α on molecule i while p_i the momentum of the whole molecule, y_i the y direction coordinate of r_i, the center of molecule i. F^N represents the force due to potential interactions and F^C the intramolecular constraint forces. In these equations, m_α is the mass of a site, M_i is the mass of the molecule, n_x is a unit vector in the x direction, γ is the shear rate, ξ is the thremostatting multiplier, p_{yi} is the y component of the momentum of molecule i, $\dot{\varepsilon}$ is the dilation rate. V is the volume of the system and p is the hydrostatic pressure, calculated through $(1/3)\text{Tr}(P)$, where P is the pressure tensor. p_0 is the target pressure and N is the number of molecules. T is the molecular temperature of the system held constant by a Gaussian thermostat and Q

Table 3
Simulated viscosities under different shear rates for methanol in reduced units[a]

γ^*	η^*, This work (N = 125)	η^*, This work (N = 216)	η^*, Wheeler and Rowley
0.9087	3.82 ± 0.33	3.791 ± 0.33	3.646
0.445	4.392 ± 0.66	4.383 ± 0.67	4.265
0.0568	–	5.644 ± 5.08	5.4062

[a] $\gamma^* = \gamma\sigma(m/\varepsilon)^{1/2}$, $\eta^* = \eta\sigma^2/(m\varepsilon)^{1/2}$.

Table 4
Simulated shear dependent viscosity of n-nonane

$\gamma \times 10^{-9}\,\text{s}^{-1}$	$\eta \times 10^4\,\text{Pa s}$
3.0621	4.78 ± 14.83
4.5931	5.11 ± 9.86
7.655	4.41 ± 5.8
11.48	4.23 ± 3.94
15.31	4.15 ± 2.92
26.79	3.98 ± 1.67
38.27	3.74 ± 1.17
47.85	3.46 ± 0.93
68.89	3.25 ± 0.65
122.48	2.63 ± 0.37

is a damping factor chosen by trial and error to control the pressure fluctuations.

The molecular pressure tensor is given by

$$
\boldsymbol{p} = \frac{1}{V}\left\{\sum_i \frac{\boldsymbol{p}_i\boldsymbol{p}_i}{M_i} + \sum_{i<j}^N \boldsymbol{R}_{ij}\boldsymbol{F}_{ij}\right\}
\tag{8}
$$

where R_{ij} and F_{ij} are the distance between the center of mass of the molecules and total force on molecule i from molecule j. The shear dependent viscosity, η, is obtained from the constitutive relation:

$$
\eta(\gamma) = -\frac{1}{2\gamma}(\langle P_{xy}\rangle) + (\langle P_{yx}\rangle)
\tag{9}
$$

and the zero shear vicosity is extrapolated from the linear response theory [16] expression:

$$
\eta = \eta_0 + A\gamma^{12}
\tag{10}
$$

More sophisticated models exist for the non-Newtonian viscosity. For example the Carreau–Yasuda model [32] incorporates five parameters to model the shear dependence of the viscosity and is capable of representing the shear thinning and Newtonian plateau regions for polymers

$$
\frac{\eta - \eta_o}{\eta - \eta_\infty} = [1 + (\lambda\gamma)^a]^{n-1/a}
\tag{11}
$$

Unfortunately application of this equation requires a clear definition of the Newtonian plateau (e.g., low shear rates)

Table 5
Shear dependence of the viscosity of isopropanol and its mixtures with n-nonane

$\gamma\ (\times 10^{-9}\,\text{s}^{-1})$	$\eta\ (\times 10^4\,\text{Pa s})$		
	$x_{C_3H_8O} = 1$	$x_{C_3H_8O} = 0.75$	$x_{C_3H_8O} = 0.5$
3.728	17.49 ± 25.42	9.8 ± 14.34	7.371 ± 11.6
5.592	–	9.07 ± 9.43	–
7.455	–	8.9 ± 7.15	7.473 ± 5.91
14.91	–	7.31 ± 3.69	6.59 ± 2.99
23.3	14.37 ± 4.15	7.18 ± 2.37	5.487 ± 1.85
33.55	11.55 ± 2.88	6.39 ± 1.59	4.95 ± 1.33
59.64	7.5 ± 1.55	4.86 ± 0.91	4.0 ± 0.75
93.19	6.55 ± 1.01	4.09 ± 0.57	3.45 ± 0.47
134.2	5.27 ± 0.7	3.37 ± 0.39	2.97 ± 0.33

Table 6
Summary of simulated pure fluid and mixture viscosities[a]

Substance	Method	T (K)	ρ (g/cm^3)	η ($\times 10^4$ Pa s)		
				Sim.	Exp[b]	%
Propane	NEMD–NVT	180	0.63772	3.973	3.873	2.58
	NEMD–NVT	250	0.57117	1.778	1.781	−0.17
Isobutane	NEMD–NVT	250	0.61758	2.789	2.947	−5.37
n-Nonane	NEMD–NPT	300		5.211	6.50	−19.8
	EMD–NPT	300		4.051	6.50	−38.68
Ethanol	NEMD–NVT	298	0.7870	19.35	19.42	−0.36
Isopropanol	NEMD–NPT	300		19.82	19.86	−0.21
	EMD–NPT	300		18.63	19.86	−6.20
Propanol	NEMD–NVT	298	0.7996	20.70	19.68	5.18
2-Butanol	NEMD–NVT	298	0.8108	43.79	44.44	−1.47
	NEMD–NVT	298	0.8024	35.47	30.0	18.23
75% isopropanol	NEMD–NPT	300		10.49	10.40	0.87
25% n-nonane	EMD–NPT	300		11.21	10.40	7.79
50% isopropanol	NEMD–NPT	300		8.320	7.56	10.05
50% n-nonane	EMD–NPT	300		7.366	7.56	−2.57

[a] NPT simulations were performed at 0.1 MPa.
[b] n-Nonane and n-nonane + isopropanol experimental data were obtained by NIST as part of the simulation challenge.

and with the system sizes used in this study, we could not determine them with any statistical accuracy. Thus we have used the simpler and perhaps less accurate linear response model.

The equilibrium molecular dynamics Green–Kubo method was also utilized to simulate the viscosity [31,33].

$$\eta_0 = \frac{V}{10 k_B T} \lim_{\tau \to \infty} \int_0^\tau dt \langle \boldsymbol{P}^{0s}(t) \cdot \boldsymbol{P}^{0s}(0) \rangle \qquad (12)$$
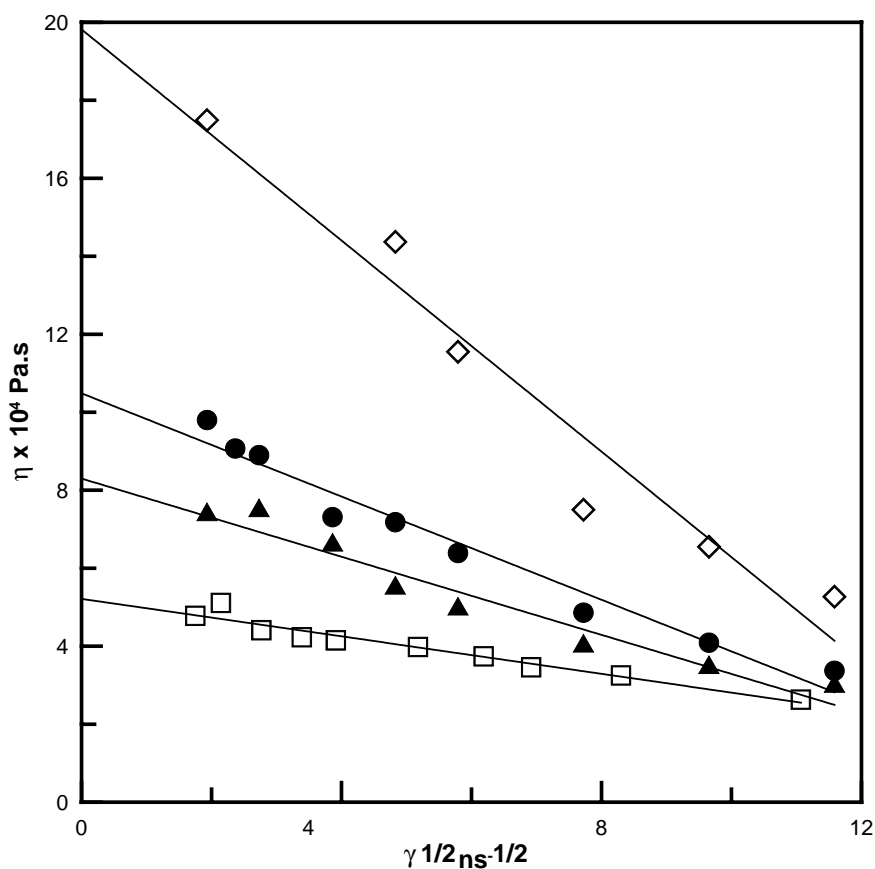

Fig. 2. Simulated shear dependent viscosities for nonane ($\diamond$), isopropanol ($\square$), 75% isopropanol ($\bullet$) and 50% isopropanol ($\blacktriangle$) vs. $\gamma^{1/2}$.

where $\boldsymbol{P}^{0s}(t)$ denotes the symmetric traceless part of the pressure tensor. In this expression, all elements of the stress tensor are used in the calculation of viscosity. In the limit $\gamma \to 0$, Eq. (9) should give the same viscosity result as that obtained from Eq. (11).

Simulations were started by placing 125 molecules for pure systems and 216 molecules for mixture systems on a cubic lattice. Each system was equilibrated for 500,000 time steps keeping N, V and T constant. The systems were then equilibrated in the NPT ensemble for 200,000 time steps for n-nonane and the mixture systems and 300,000 for isopropanol. The time steps used were 1 fs for alkane systems, and 0.672 fs for systems containing an alcohol. In the production stage, each simulation was run for 600,000–1,700,000 time steps at different shear rates during which the pressure tensor, P, was calculated, and the shear viscosity at each shear rate was computed and averaged. For 2-butanol systems, the time steps is 0.745 fs, and the simulations were run 900,000 steps for lower shear rates and 500,000 for higher shear rates. Data in the shear-thinning regime were used to extrapolate values of simulated viscosity to obtain a zero shear value. For EMD simulations, after 400,000 time steps equilibration, 2,800,000 time steps were run for nonane, and 1,300,000 time steps for isopropanol and their mixtures in NPT ensemble.

In the nonane simulations, a multi-time step (MTS) method [34] was utilized with a 6.7 Å primary neighbor radius and the secondary forces were explicitly reevaluated every seven steps. In the equilibration stage, it was found that the appropriate value of the dilation damping factor QNkT for the alkane systems is 80.0, 10.0 for the mixture systems and 1.0 for the alcohol systems. In the production stage, the QNkT values were increased to 160.0, 80.0, 40.0, respectively.

For the alcohols, the coloumbic potential was calculated using the NEMD–Ewald method developed by Wheeler and Rowley [22]. In their work the Ewald sum method was used in conjunction with the Lees–Edwards sliding boundary conditions to simulate the viscosity of polar molecules with NEMD. The method is applicable to a molecular fluid confined in an arbitrary parallelepiped simulation unit cell. The unit cell potential is partitioned into real-space and reciprocal-space portions, which are added together to count the coloumbic potential energy of the cell in an infinite lattice of cell images. The real-space portion is calculated in the same manner as the eponential-6 potential over short-range interactions within the cutoff distance. In order to test our implementation of the NEMD–Ewald method, we first repeated their methanol simulation at one state point ($T = 337.85$ K, $\rho = 23.44$ kmol/m^3) under three shear rates. The
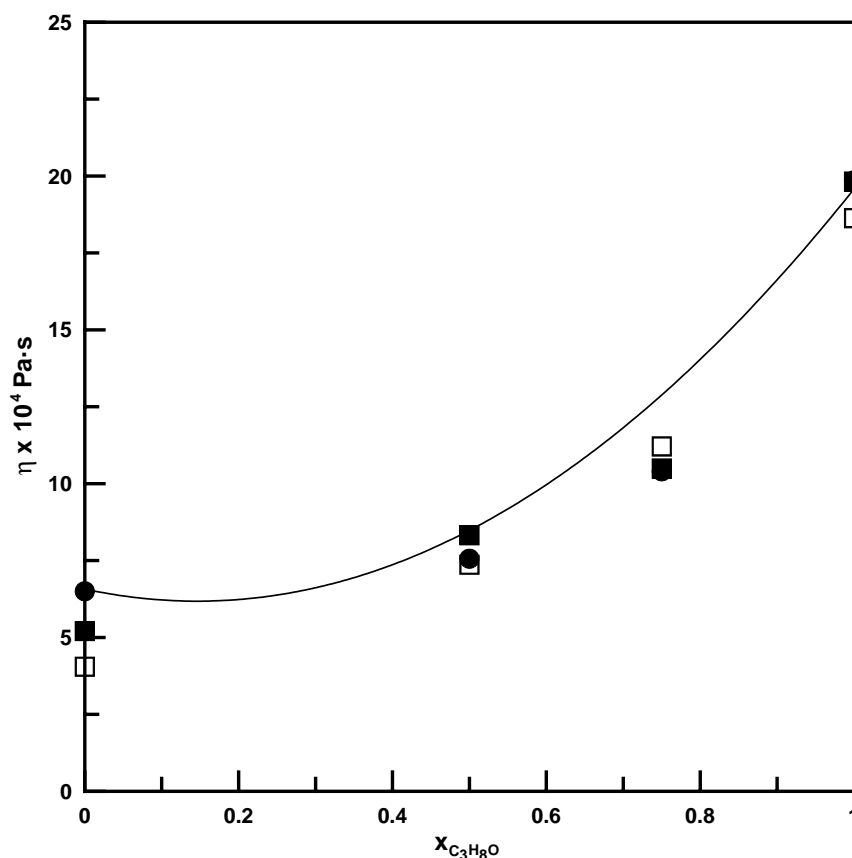

Fig. 3. Comparison of simulated viscositiy values from NEMD (■) and from EMD (□) with those calculated from the method of Grunberg and Nissan [35] (solid line) and experimental values (●).

comparison is given in Table 3 and the results agree to within the combined uncertainties of the simulations. For the Ewald sum parameters, the convergence parameter was chosen to be 0.5 with a 12 Å cutoff distance.

4. Results

The results of the simulations are summarized in Tables 4–6. Tables 4 and 5 give the dependence of the viscosity on the shear rate for the Simulation Challenge systems. Table 6 compares the zero shear viscosity results obtained by fitting Eq. (10) to the simulation data with experimental measurements. Examples of this procedure are illustrated in Fig. 2 for the Simulation Challenge systems. Also included in Table 6 are the EMD simulation results for the Simulation Challenge systems. These latter results are generally lower than those obtained from the NEMD method. One would generally expect this since the NEMD extrapolation method tends to over estimate the location of the Newtonian plateau. Both methods substantially underestimate the viscosity of pure nonane. This may indicate a problem with the CH_2 parameters developed in this work, especially the value of σ where a small change can produce a large effect in the excluded volume of the system, which in turn has a large effect on the viscosity. The simulations for shorter pure alkanes and alcohols agree well ($<10\%$) with the experimental results.

The simulated mixture viscosities typically agree with the experimental results to within 10%. The mixture viscosity values also were estimated from the method of Grunberg and Nissan [35], with the results being illustrated in Fig. 3. Although the trend of the prediction generally agrees with the simulation results, the agreement is not quantitative and may indicate that a binary interaction parameter is needed in the model.

5. Summary and conclusions

In this study we have explored the application of a new force field model to the simulation of the viscosity of pure alkanes, alcohols and their mixtures. Since the force field model is new, some of the intermolecular parameters had to be determined by trial and error adjustment based on agreement experimental viscosity data for small molecular systems. Given these parameters, we simulated the systems required in the First Industrial Simulation Challenge and found good agreement with the experimental data apart from n-nonane. We speculate that the lack of agreement with nonane comes from a problem with the CH_2 group parameters and we are currently performing a more systematic determination of that and other group parameters for our proposed model. We conclude from this study that the AUA-exponential-6 potential model coupled with the NEMD simulation method can predict the viscosity of alkanes, alcohols and their mixtures with acceptable accuracy, although further adjustments in the force field parameters are needed.

References

[1] B.R. Brooks, E.C. T III, Theor. Chem. Acc. 99 (1998) 279–288.
[2] M. Mondello, G.S. Grest, J. Chem. Phys. 103 (1995) 7156–7165.
[3] W.L. Jorgensen, J.D. Madura, C.J. Swenson, J. Am. Chem. Soc. 106 (1984) 6638–6646.
[4] R. G. Mountain, First Industrial Simulation Challenge (2002), http://www.cstl.nist.gov/FluidSimulationChallenge/.
[5] S.L. Price, Curr. Top. Mol. Simul. 1 (1996) 85–106.
[6] S. Toxvaerd, J. Chem. Phys. 93 (1990) 4290–4295.
[7] P. Padilla, S. Toxvaerd, J. Chem. Phys. 94 (1991) 5650–5654.
[8] P. Ungerer, C. Beauvais, J. Delhommelle, A. Boutin, B. Rousseau, A.H. Fuchs, J. Chem. Phys. 112 (2000) 5499–5510.
[9] E. Bourasseau, P. Ungerer, A. Boutin, A.H. Fuchs, Mol. Sim. 28 (2002) 317–336.
[10] S. Toxvaerd, J. Chem. Phys. 107 (1997) 5197–5204.
[11] D.K. Dysthe, A.H. Fuchs, B. Rousseau, J. Chem. Phys. 110 (1999) 4047–4059.
[12] D.K. Dysthe, A.H. Fuchs, B. Rousseau, J. Chem. Phys. 112 (2000) 7581–7590.
[13] P. Ungerer, A. Boutin, A.H. Fuchs, Mol. Phys. 99 (2001) 1423–1434.
[14] R. Edberg, D.J. Evans, G.P. Morris, J. Chem. Phys. 84 (1986) 6933–6939.
[15] G.P. Morriss, D.J. Evans, Comput. Phys. Commun. 62 (1991) 267–278.
[16] D.J. Evans, G.P. Morriss, Statistical Mechanics of Nonequilibrium Liquids, Academic Press, New York, 1990.
[17] J.R. Errington, A.Z. Panagiotopoulos, J. Chem. Phys. 111 (1999) 9731–9738.
[18] T.M. Reed, K.E. Gubbins, Aplied Statistical Mechanics, McGraw-Hill, New York, 1973.
[19] W.J. Jorgensen, J. Phys. Chem. 90 (1986) 1276–1284.
[20] J.P. Ryckaert, A. Bellemans, Discuss. Faraday Soc. 66 (1978) 95.
[21] J.R. Errington, A.Z. Panagiotopoulos, J. Phys. Chem. B 103 (1999) 6314–6322.
[22] D.R. Wheeler, N.G. Fuller, R.L. Rowley, Mol. Phys. 92 (1997) 55–62.
[23] D.R. Wheeler, R.L. Rowley, Mol. Phys. 94 (1998) 555–564.
[24] R.L. Rowley, Y. Yang, T.A. Pakkanen, Int. J. Thermophys. 21 (2000) 703–717.
[25] N.G. Fuller, R.L. Rowley, Int. J. Thermophys. 19 (1998) 1039–1048.
[26] H. Zhang, Development of a Molecular Simulation Force Field for Transport Properties, Ph.D. Thesis, Colorado School of Mines, Golden, CO, 2003.
[27] J.M. Haile, Molecular Dynamics Simulation, Elementary Methods, Wiley, New York, 1997.
[28] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Oxford University Press, New York, 1987.

[29] D.J. Evans, G.P. Morriss, Comput. Phys. Repts. 1 (1984) 297–343.

[30] R.L. Rowley, J.F. Ely, Mol. Sim. 7 (1991) 303–323.

[31] P.J. Daivis, D.J. Evans, J. Chem. Phys. 100 (1994) 541–547.

[32] R.B. Bird, R.C. Armstrong, O. Hassager, Dynamics of Polymeric Liquids: Fluid Mechanics, Wiley, New York, 1987.

[33] S.T. Cui, P.T. Cummings, H.D. Cochran, Mol. Phys. 93 (1998) 117–121.

[34] W.B. Street, D.J. Tiledesley, G. Saville, Mol. Phys. 35 (1978) 639–648.

[35] R.C. Reid, J.M. Prausnitz, B.E. Poling, The Properties of Gases and Liquids, fourth ed., McGraw-Hill, New York, 1987.