Nonequilibrium Molecular Dynamics Simulation of Shear Viscosity of Polar Liquids[1]

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ABSTRACT

Nonequilibrium molecular dynamics (NEMD) simulations were performed on model polar fluids representing acetone, propyl chloride, and dimethyl formamide. The purposes of the study were (1) to further test a recently developed method for applying the Ewald sum treatment of long-range forces to NEMD simulations with Lees-Edwards boundary conditions, (2) to study the effect of different constituent groups and their partial charges upon fluid viscosity, and (3) to examine the relative magnitudes of the van der Waals and coulombic contributions to fluid viscosity. The new Ewald sum method worked well producing simulated viscosities for all three fluids that were in excellent agreement with correlated experimental data. Generally, viscosities predicted without the partial charges were too low and exhibited the wrong density dependence. While methyl chloride's viscosity is primarily due to the dispersion interactions, coulombic interactions contribute up to 30% of the viscosity for the other two fluids.

KEY WORDS: shear viscosity; molecular simulations; nonequilibrium molecular dynamics; Ewald sum; polar fluids

1. INTRODUCTION

Nonequilibrium molecular dynamics (NEMD) simulations have been used extensively in the past few years to study the viscosity of fluids represented by models of varying complexity. While earlier studies focused on simulations of *n*-alkane models to test simulation methodology and the applicability of the models [1-11], more recent studies have focused heavily on simulations of branched alkanes [12-15]. These studies indicated that the viscosity was very sensitive to the intermolecular potential model used. The variety of fluids studied thus far has been quite limited, and relatively simple models have been used. For example, straight-chain alkanes have been modeled generally with equivalent or homogeneous united-atom (UA) models. In these models, the basic structure is defined by bonded sites located at carbon centers, and van der Waals forces are computed from interactions between sites on different molecules. More recent efforts to model branched alkanes have used nonequivalent or heterogeneous UA sites to account for the difference between primary, secondary, and tertiary carbons [15]. With increasing computational speed, more sophisticated models are being used, such as all-atom models with interaction sites at every atomic center.

Equilibrium MD (EMD) simulations of thermodynamic properties have for several years used more complex potentials in which non-parafinic chemical groups are present that create a partial charge separation or a dipole moment. Models for polar fluids therefore generally include coulombic interactions between partial charges at various sites in the molecule in addition to standard site-site dispersion interactions. As coulombic interactions are of much longer range than van der Waals interactions, special techniques, such as the Ewald sum method, are commonly employed. Because NEMD viscosity simulations are commonly done

with Lees-Edwards or "sliding brick" boundary conditions [16,17], for which the Ewald sum method was not previously applicable, very little modeling of polar fluid viscosity has been attempted. Recently, Wheeler et al. [18] extended the Ewald sum method to NEMD simulations with Lees-Edwards boundary conditions, and tested the method using a model for methanol. Simulated methanol viscosities agreed very well with experimental data.

In this work, we apply this newly developed NEMD Ewald sum method to models of three polar molecules. The objectives of the study were (1) to investigate the effectiveness of the new Ewald method on different chemical constituents beyond those in the methanol model, (2) to study the effect of different constituent groups and their partial charges upon fluid viscosity, and (3) to examine the relative magnitudes of the van der Waals and coulombic contributions to fluid viscosity.

2. MOLECULAR MODELS

To study the effect of different constituent groups upon fluid viscosity, we chose to perform viscosity simulations on models for acetone, propyl chloride, and dimethyl formamide (DMF). In conjunction with the results previously obtained for a model of methanol [18], this study provides a a comparison of molecules of roughly the same structure and size with differing chemical groups and polar interactions.

A site-site UA molecular model with fixed bond lengths and bond angles was used for all of the simulations performed in this study. The intermolecular potential function was assumed to be comprised of two independent parts. The site-site dispersion potential was modeled using pair-wise additive Lennard-Jones (LJ) potentials while the coulombic potential was modeled

by assignment of partial charges to these same sites. All CH_x sites were modeled as UA sites located at carbon centers; all other sites were atomic, located at atomic centers.

The LJ parameters and site partial charges (δq) are reported in Table I. These values were obtained from previously reported simulations [19-21] of thermodynamic properties for similar fluids. Lorentz-Berthelot combining rules were used for all heterogeneous interactions.

Equilibrium bond lengths and angles were determined from molecular mechanics calculations. The values obtained from Hyperchem (MM2 model), as shown in Table II, were constrained to be constants of motion throughout the simulation by solving the appropriate Gaussian mechanics equations. Rotation about internal single bonds was permitted in accordance with the model torsional potential,

$$U = \sum_{i=1}^{6} A_i \cos^{i-1}\phi \qquad \textbf{(1)}$$

where U is potential energy and ϕ is torsional angle. Hyperchem was again used to calculate the potential as a function of torsional angle, and the resultant values were used to regress the parameters A_1 through A_6 in Eq. (1). The values obtained for these parameters are given in Table III.

We have found that use of rigid bond constraints causes the feed-back mechanism used in conjunction with the method of Gaussian mechanics [12] to become unstable whenever there is a planar portion of the molecule. Both acetone and DMF have planar portions, and so it was necessary to introduce a slight (less than 2.5°) out-of-plane angle into each of these molecules. This small "kink" in the molecule produced little change in the equilibrium bond lengths and angles.

3. SIMULATIONS

NEMD simulations were performed using a NVT (canonical) ensemble with a fourth-order predictor-corrector numerical integration scheme. The code is similar to that previously used in studies of *n*-alkanes [1,2], branched alkanes [15], and methanol [18]. A molecular version of the isothermal shear algorithm known as SLLOD [17] was used in conjunction with the Gaussian mechanics equations [3,4] that include constraints to maintain bond lengths, bond angles, temperature, and shear rate for Couette flow as constants of motion. The LJ potential was spherically truncated at 1.02 nm, and the long range cut-off correction was included. Coulombic interactions were handled with the recently reported Ewald sum method as applied to Lees-Edwards boundary conditions [18]. The Ewald sum method requires that the cell potential be partitioned into real-space and reciprocal-space portions. The real-space portion is a sum over short-range interactions and is accomplished in the same manner as for the dispersion interactions. To sum the interactions in reciprocal space, one deforms the cubic cell consistent with the shear shift of the molecules at each time step. Particles in the cubic cells are mapped to a monoclinic lattice system in which the angle between the *y*-*z* and *x*-*z* planes at each time step is related to $\gamma\Delta t$, where γ is the shear rate defined by dv_x/dy, v_x is the *x* component of velocity, and Δt is elapsed time. The reciprocal-space sum is then performed for the infinite lattice of monoclinic cells instead of the cubic cells. Further details of the method are given in [18].

Simulations were initiated by placing 216 molecules in a simple cubic lattice. Equilibration from the lattice structure was accomplished with 150,000 time steps, each of 1.2 fs duration. Each simulation was then run for an additional 110,000 time steps during which

the pressure tensor was calculated. The shear viscosity at each shear rate, γ, was computed from eleven block averages of 10,000 time steps each. In accordance with previous procedures [2,3,15,18], the shear-thinning regime was used to extrapolate values of simulated viscosity to zero shear. Extrapolation was performed using a weighted (in accordance with the standard deviation of the block averages) linear least squares fit of η (viscosity) vs $\gamma^{1/2}$.

4. RESULTS AND CONCLUSIONS

The viscosity results extrapolated to zero shear are summarized in Table IV. Simulations were performed at selected temperatures and at the density corresponding to 1.0 bar for the given temperature. This was done to facilitate comparison of simulated results with values available in the literature. Densities were calculated from liquid correlations given in the DIPPR database [22]. Figures 1-3 illustrate the results at individual shear rates for each of the three fluids and the weighted, linear, least squares fit of the data. Standard deviations, σ, are omitted from the figures for clarity, but the average values of σ were 0.09, 0.04, 0.03, 0.01, 0.007, 0.004 cP for $\gamma^{1/2}$ values of 5, 7, 9, 14, 20 and 30 $ns^{-1/2}$, respectively. Also shown in Table IV are smoothed experimental values obtained from the DIPPR recommended correlations for viscosity at 1.0 bar (i.e., at the calculated density).

Simulated values of the viscosity for all three fluids were observed to be in quite good agreement with the smoothed experimental values. Generally, agreement was within 10%. These models appear to predict viscosities well with the same potential parameters previously used for simulation of thermodynamic properties. The results also show that different chemical constituents produce differing contributions to the viscosity, but these contributions are handled

reasonably well with the partial charge models used in this work.

To examine the relative magnitudes of the van der Waals and coulombic contributions to the fluid viscosity, we repeated the simulations with all partial charges turned off (set to zero). The results of these simulations are also shown in Figures 1-3 and the zero-shear values obtained from a linear regression of those data are reported in Table IV. It is evident from the results that the van der Waals interactions dominate methyl chloride's viscosity, but that coulombic interactions contribute up to 30% or more of the viscosity for acetone and DMF at the higher densities. Additionally, there is a density dependence to the coulombic contribution; i.e., the nonpolar model significantly underpredicts viscosity at higher densities while the polar

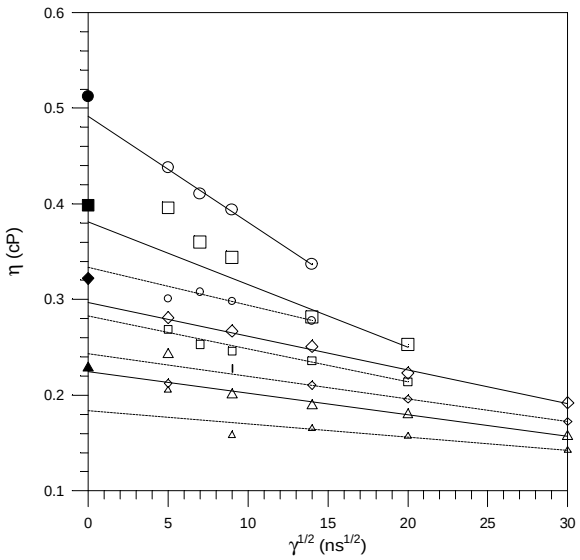


Figure 1. Viscosity results for acetone as a function of $\gamma^{1/2}$. Simulated points are shown with open symbols (larger for polar model, smaller for nonpolar), experimental data with filled symbols, and the linear fit with lines (solid for polar model, dashed for nonpolar). Isotherms shown are 253.15 K (○,●); 273.15 K (□,■); 293.15 K (◇,♦); and 333.15 K (Δ,▲).

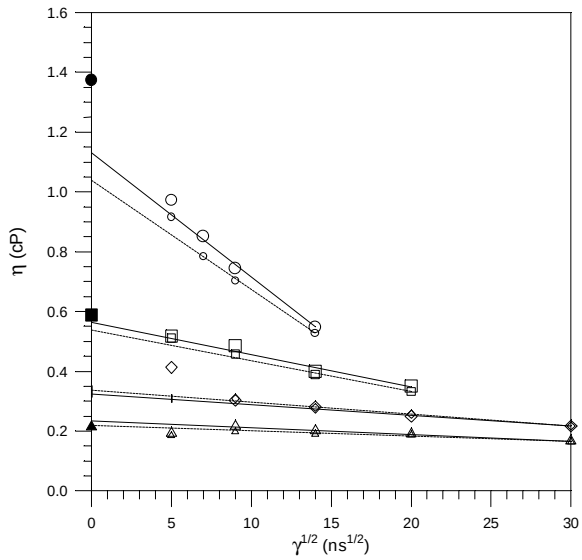
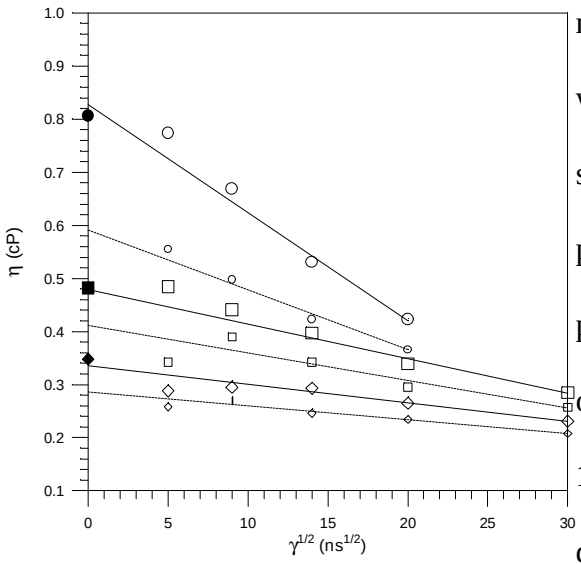


Figure 2. Viscosity results for propyl chloride as a function of $\gamma^{1/2}$. See Fig. 1 caption for meaning of symbols and lines. Isotherms shown are 200.15 K (○,●); 250.15 K (□,■); 300.15 K (◇,♦); and 350.15 K (Δ,▲).



model represents the real fluid viscosity quite well over the range of viscosities studied. A similar density-dependent deviation between the polar and nonpolar predictions was observed previously for methanol [18], but the magnitude of the deviation was even larger, ranging from -1% at low density to -71% at the highest density.

Figure 3. Viscosity results for DMF as a function of $\gamma^{1/2}$. See Fig. 1 caption for meaning of symbols and lines. Isotherms shown are 300.15 K (○,●); 350.15 K (□,■); and 400.15 K (◊,♦).

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Table I. Parameters Used in the Molecular Models

Molecule	Site	ε/k (K)	σ (nm)	δq (esu)
Acetone [19]	CH_3	72.0	0.392	-0.032
	C	50.0	0.300	0.566
	O	58.4	0.280	-0.502
Propyl chloride [20]	CH_3	91.22	0.3861	0.0
	CH_2 (-CH_2)	57.52	0.3983	0.0
	CH_2 (-Cl)	57.52	0.3983	0.25
	Cl	162.11	0.3555	-0.25
DMF [21]	CH	57.91	0.380	0.5
	O	105.75	0.296	-0.5
	N	85.61	0.325	-0.57
	CH_3	85.61	0.380	0.285

Table II. Bond Distances and Angles

molecule	bond	distance (nm)	angle	angle (degrees)
Acetone	C—CH_3	0.1518	CH_3—C—CH_3	116.62
	C═O	0.1212	CH_3—C═O	121.69
Propyl chloride	CH_x—CH_x	0.1550	CH_3—CH_2—CH_2	111.28
	CH_2—Cl	0.1771	CH_2—CH_2—Cl	110.13
DMF	CH═O	0.1207	O═CH—N	125.87
	CH—N	0.1384	CH—N—CH_3 (O side)	117.35
	N—CH_3	0.1455	CH—N—CH_3 (H-side)	118.65
			CH_3—N—CH_3	124.00

Table III. Torsional Angle Parameters for Eq. (1)

Molecule	A_1	A_2	A_3	A_4	A_5	A_6
Propyl chloride	896.766	3062.954	1258.272	-5871.73	96.615	566.745
DMF	9677.4	-11.0082	-9773.9	-87.8231	432.1192	-236.5926

Table IV. Simulation Results for η at Zero Shear

molecule	T (K)	ρ (kmol/m^3)	η_{exp} (cP)	$\eta_{sim\ (polar)}$ (cP)	$\eta_{sim\ (nonpolar)}$ (cP)
Acetone	253.15	14.395	0.512	0.49 ± 0.05	0.33 ± 0.04
	273.15	13.985	0.399	0.38 ± 0.03	0.28 ± 0.03
	293.15	13.611	0.322	0.30 ± 0.02	0.24 ± 0.01
	333.15	12.820	0.229	0.22 ± 0.01	0.18 ± 0.01
Propyl chloride	200.15	12.683	1.374	1.13 ± 0.20	1.11 ± 0.20
	250.15	11.989	0.588	0.56 ± 0.03	0.54 ± 0.04
	300.15	11.235	0.332	0.32 ± 0.02	0.34 ± 0.01
	350.15	10.395	0.213	0.23 ± 0.01	0.22 ± 0.01
DMF	300.15	12.901	0.806	0.83 ± 0.04	0.59 ± 0.04
	350.15	12.247	0.482	0.48 ± 0.02	0.41 ± 0.02
	400.15	11.547	0.348	0.34 ± 0.02	0.29 ± 0.01