International Journal of Thermophysics, Vol. 19, No. 4, 1998

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

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Nonequilibrium molecular dynamics (NEMD) simulations were performed on model polar fluids representing acetone, propyl chloride, formamide, and dimethyl formamide. The purposes of the study were (1) to test further 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 four fluids that were in good agreement with correlated experimental data. Generally, viscosities predicted without the partial charges were significantly low and exhibited an incorrect density dependence. While methyl chloride's viscosity is due primarily to the dispersion interactions, coulombic interactions contribute substantially to the viscosity of the other three fluids, particularly at higher densities.

KEY WORDS: acetone; dimethyl formamide; Ewald sum; formamide; molecular simulations; nonequilibrium molecular dynamics; polar fluids; propyl chloride; shear viscosity.

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

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[1] Paper presented at the Thirteenth Symposium on Thermophysical Properties, June 22–27, 1997, Boulder, Colorado, U.S.A.

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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 differences 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 nonparaffinic 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 must be employed to include the long-range nature of the interactions. The simplest technique commonly used is a spherical truncation of the long-range potential. However, it has recently been shown [16, 17] that a spherical truncation of coulombic forces can sometimes lead to significant errors in simulated viscosities, even if the truncation distance is quite large. A better technique for handling long-range potentials is the Ewald sum method which includes interaction information, essentially to infinite distance. However, until recently this method was not applicable to the "sliding brick" or Lees–Edwards boundary conditions (LEBC) [18, 19] used in nonequilibrium viscosity simulations. Wheeler et al. [16] extended the Ewald sum method to NEMD simulations with LEBC 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 four 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, formamide, and dimethyl formamide (DMF). In conjunction with the results previously obtained for a model of methanol [16], this study provides 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 pairwise 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 [20–22] of thermodynamic properties for similar fluids in which the coulombic potential was truncated at a specified distance. 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

Table I. Parameters Used in the Molecular Models

Molecule	Site	ε/k (K)	σ (nm)	δq (esu)
Acetone [20]	CH_3	72.0	0.392	−0.032
	C	50.0	0.300	0.566
	O	58.4	0.280	−0.502
Propyl chloride [21]	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
Formamide [22]	CH	57.91	0.380	0.5
	O	105.75	0.296	−0.5
	N	85.61	0.325	−0.85
	H(−N)	0	0	0.425
DMF [24]	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 Lengths and Angles

Molecule	Bond	Length (nm)	Angle	Angle (deg)
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
Formamide	$CH=O$	0.1205	$O=CH-N$	124.58
	$CH-N$	0.1369	$CH-N-H$ (O-side)	117.71
	$N-H$	0.1021	$CH-N-H$ (H-side)	120.00
			$H-N-H$	122.29
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

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,

$$U=\sum_{i=1}^{6} A_i \cos^{i-1}\phi \tag{1}$$

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.

The normal Gaussian bond constraint method [12] fails when there is a planar portion of the molecule due to a singularity in the matrix equation. This occurs for acetone, formamide, and DMF. The problem was resolved by introducing a slight (less than 2.5°) out-of-plane angle into

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	3,062.954	1,258.272	5,871.73	96.615	566.745
Formamide	10,377.82	11.0403	−10,352.0	−117.725	216.2796	−111.49
DMF	9677.4	−11.0082	−9773.9	−87.8231	432.1192	−236.5926

each of these molecules. Subsequently we implemented the method of constraining rigid systems due to Ciccotti et al. [23] that eliminates this planar constraint problem. Acetone simulations were repeated with the new method, and no noticeable difference could be observed between the results obtained for the perfectly planar model and those obtained for the slightly "kinked" model molecules.

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 [16]. A molecular version of the isothermal shear algorithm known as SLLOD [19] was used in conjunction with the Gaussian mechanics equations [3, 4] that include constraints to maintain bond lengths, bond angles, temperature (i.e., translational kinetic energy), and shear rate for Couette flow as constants of motion. The LJ potential was spherically truncated at 1.02 nm, and the long-range cutoff correction was included. Coulombic interactions were handled with the recently reported Ewald sum method as applied to LEBC [16]. The

Table IV. Simulation Results for η at Zero Shear

				Polar model		Nonpolar model	
Molecule	T (K)	ρ (kmol · m^{-3})	η_{exp} (mPa · s)	η_{sim} (mPa · s)	Dev. (%)	η_{sim} (mPa · s)	Dev. (%)
Acetone	253.15	14.395	0.512	0.49 ± 0.05	−4	0.33 ± 0.04	−36
	273.15	13.985	0.399	0.38 ± 0.03	−5	0.28 ± 0.03	−30
	293.15	13.611	0.322	0.30 ± 0.02	−7	0.24 ± 0.01	−25
	333.15	12.820	0.229	0.22 ± 0.01	−4	0.18 ± 0.01	−21
Propyl chloride	200.15	12.683	1.374	1.51 ± 0.06	10	1.35 ± 0.05	−2
	250.15	11.989	0.588	0.67 ± 0.04	13	0.64 ± 0.02	9
	300.15	11.235	0.332	0.37 ± 0.01	12	0.35 ± 0.01	7
	350.15	10.395	0.213	0.24 ± 0.01	15	0.24 ± 0.01	11
Formamide	300.15	25.034	3.218	3.66 ± 0.10	12	0.81 ± 0.09	−75
	350.15	24.072	1.166	1.61 ± 0.05	38	0.63 ± 0.05	−46
	400.15	23.063	0.620	0.80 ± 0.03	29	0.41 ± 0.02	−34
	450.15	21.995	0.421	0.57 ± 0.03	36	0.33 ± 0.03	−22
DMF	300.15	12.901	0.806	1.01 ± 0.03	25	0.63 ± 0.06	−22
	350.15	12.247	0.482	0.55 ± 0.01	12	0.41 ± 0.02	−15
	400.15	11.547	0.348	0.37 ± 0.02	7	0.30 ± 0.02	−15

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 the 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 the 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 Ref. 16.

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 200,000 time steps during which the pressure tensor was calculated. The shear viscosity at each shear rate, γ, was computed from 20

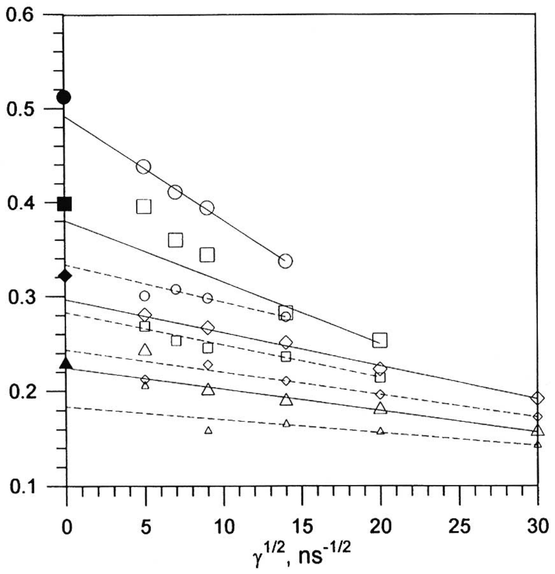

Fig. 1. Viscosity results for acetone as a function of $\gamma^{1/2}$. Simulated points are shown with open symbols (larger for polar model, smaller for nonpolar), experimental data with filled symbols, and the linear fit with lines (solid for polar model, dashed for nonpolar). Isotherms shown are 253.15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

block averages of 10,000 time steps each. In accordance with previous procedures [2, 3, 15, 16], 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 0.1 MPa 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 [24]. Figures 1–4 illustrate the results at individual shear rates for each of the four 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, and 0.004 mPa·s 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 0.1 MPa (i.e., at the calculated density).

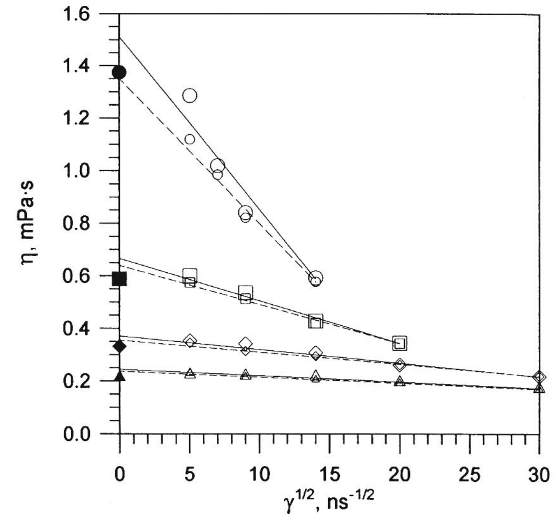

Fig. 2. Viscosity results for propyl chloride as a function of $\gamma^{1/2}$. See the legend to Fig. 1 for the meaning of symbols and lines. Isotherms shown are 200.15 K (○, ●), 250.15 K (□, ■), 300.15 K (◇, ◆), and 350.15 K (△, ▲).

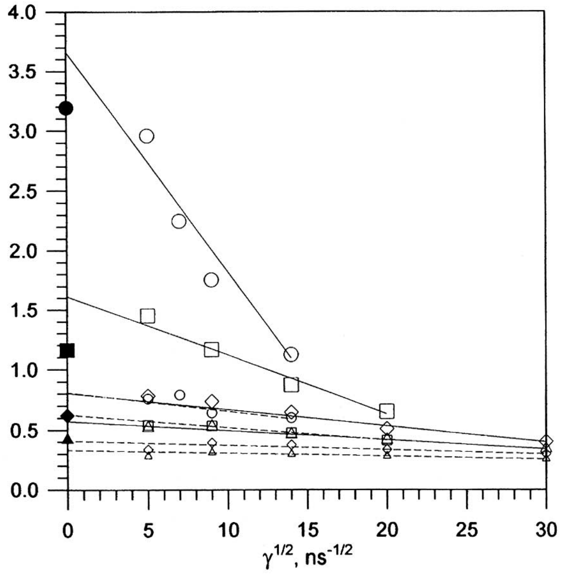

Fig. 3. Viscosity results for formamide as a function of $\gamma^{1/2}$. See the legend to Fig. 1 for the meaning of symbols and lines. Isotherms shown are 300.15 K (○, ●), 350.15 K (□, ■), 400.15 K (◇, ◆), and 450.15 K (△, ▲).

The agreement between the simulated viscosity values and those obtained from experiment varied for each of the four fluids. It ranged from 4% for acetone to 38% for formamide. The large deviations that are apparent in formamide may be due to inadequate modeling of hydrogen bonding. The relatively good agreement with experiment for three of the four fluids is encouraging in light of the fact that simple potential models were used with no adjustable parameters.

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 Figs. 1–4 and Table IV. It is evident from this table that the coulombic interactions contribute significantly to the viscosity. While van der Waals forces dominate the viscosity for methyl chloride, coulombic interactions contribute up to 30% or more of the viscosity for acetone, DMF, and formamide at higher densities. The relative effect of polar interactions on viscosity is clearly a function of density. Predicted viscosities using the nonpolar model are strongly density dependent, but the density dependence is not present when the fluid model includes the partial charges on the sites. This indicates that the polar model better represents the drag

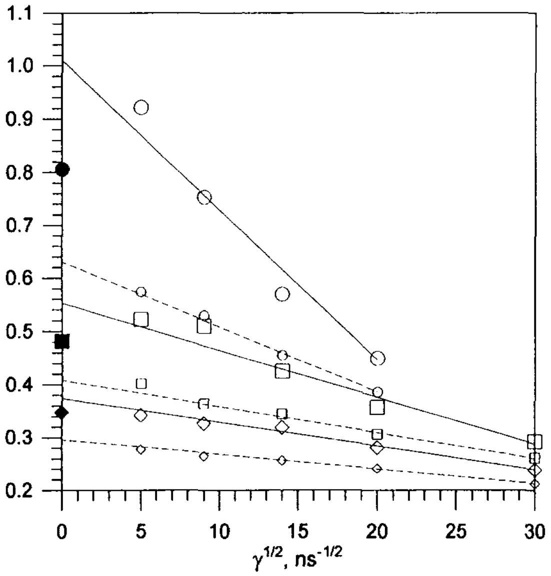

Fig. 4. Viscosity results for DMF as a function of $\gamma^{1/2}$. See the legend to Fig. 1 for the meaning of symbols and lines. Isotherms shown are 300.15 K (○, ●), 350.15 K (□, ■), and 400.15 K (◇, ◆).

forces occurring under shear for these fluids and that the Ewald sum method (or an equivalent method) should be used to simulate effectively the viscosity of polar fluids.

ACKNOWLEDGMENTS

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the ACS, for partial support of this research. We also wish to thank Dean R. Wheeler for the use of his NEMD Ewald code.

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