International Journal of Thermophysics, Vol. 21, No. 1, 2000

The Effect of Model Internal Flexibility Upon NEMD Simulations of Viscosity

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Received June 10, 1999

The influence of model flexibility upon simulated viscosity was investigated. Nonequilibrium molecular dynamics (NEMD) simulations of viscosity were performed on seven pure fluids using three models for each: one with rigid bonds and angles, one with flexible angles and rigid bonds, and one with flexible bonds and angles. Three nonpolar fluids (propane, *n*-butane, and isobutane), two moderately polar fluids (propyl chloride and acetone), and two strongly polar fluids (methanol and water) were studied. Internal flexibility had little effect upon the simulated viscosity of nonpolar fluids. While model flexibility did affect the simulated viscosity of the polar fluids, it did so principally by allowing a density-dependent change in the dipole moment of the fluid. By using a rigid model with the same geometry and dipole moment as the average flexible molecule at the same density, it was shown that the direct effect of flexibility is small even in polar fluids. It was concluded that internal model flexibility does not enhance the accuracy of viscosities obtained from NEMD simulations as long as the appropriate model geometry is used in the rigid model for the desired simulation density.

KEY WORDS: viscosity; NEMD simulation; flexible models; rigid bond lengths.

1. INTRODUCTION

Nonequilibrium molecular dynamics (NEMD) simulations have been used extensively in the past few years to study the viscosity of fluids represented

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0195-928X/00/0100-0045$18.00/0

by models of varying complexity. Many of the early models used in conjunction with NEMD determinations of viscosity used rigid bond and angle constraints [1–3], so that atoms within the molecules remained fixed at their equilibrium positions regardless of shear rate. Many recent simulations have included harmonic intramolecular potentials [4–6] between sites to model vibrational and bending motions. Internal flexibility is assumed to improve the potential model and therefore the accuracy of simulated viscosities. This seems logical, because internal flexibility can absorb energy from the applied shear. Tironi et al. [7], however, concluded that "the introduction of flexibility creates more problems than it solves, and does not improve the accuracy of rigid point charge models." This statement, made primarily with regard to thermodynamic and structural properties of point-charge models, has not been extensively tested to our knowledge, though studies on nonpolar fluids have shown that rotations around bonds can affect the simulated viscosity [8]. Specifically, Tironi et al. argue that treating flexibility by classical mechanics does not bring the simulation closer to reality. This view is congruent with earlier discussions on the applicability of classical treatments for internal flexibility [9] and the view held by some that fixed bond lengths are to be preferred over a classical treatment of vibrations. The two approaches can lead to different properties. For example, the dihedral distribution has been shown to be different when bonds are held rigid by constraints in the equations of motion than when a classical vibrational treatment is applied with essentially an infinite spring constant [10].

Inclusion of internal flexibility in the potential model is not only an accuracy issue, but a question of efficiency. Because vibrational frequencies must be modeled with a much finer time scale than translational and rotational motion, short time steps must be used if flexibility is included. While there are methods that reduce the computational penalty for including flexibility, the CPU costs can still be significant, especially since long simulations must be run to minimize the noise at lower shear rates to obtain accurately the value at zero shear. Simulation CPU times when using flexible models can range from 20% more to several times those incurred when using rigid models, so it is important to weigh any improved accuracy in the final result against those costs.

We report here the results of NEMD simulations in which we have selectively frozen various internal modes of motion to determine their effect upon the viscosity. We want to see the individual effects of these modes upon the simulated viscosities and their significance to the accuracy of those values. By understanding the relative contributions of various model assumptions on the predicted viscosity, CPU costs can be proportioned wisely to improve those model simplifications that have the largest impact.

2. MOLECULAR MODELS

Seven model fluids were simulated. Models representing methanol, propyl chloride, acetone, water, butane, isobutane, and propane were chosen to include significant structural and charge variations.

Pairwise additive interactions consisting of Lennard–Jones (LJ) dispersion potentials and point-charge potentials (where appropriate) were used. The intermolecular pair potential u_{ij} between site i and site j (on different molecules), separated by distance r_{ij} was taken to be

$$u_{ij}=4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12}-\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right]+\frac{q_i q_j}{r_{ij}} \tag{1}$$

where ε_{ij} and σ_{ij} are the standard LJ parameters and q_i and q_j are the partial charges located on the corresponding sites. For simplicity, the united-atom (UA) approximation was used to treat $-\mathrm{CH}_x$ groups as single interacting sites centered at the carbon nucleus; all other atoms were represented by a unique site. The molecular structures for the methanol [11], water [12], and *n*-butane [13] models were obtained from the literature. The other equilibrium structures were obtained from geometry optimization calculations using HF/STO-3G *ab initio* calculations in SPARTAN. Values for the equilibrium bond lengths and angles used for all rigid and flexible models are given in Table I; LJ site parameters and charges are listed in Table II.

The potential energy for internal flexibility was modeled as a sum of simple harmonic functions between sites within the molecule,

$$u_{\text{intra}}=\sum_{\text{bonds}}\tfrac{1}{2}k_r(r-r_0)^2+\sum_{\text{angles}}\tfrac{1}{2}k_\theta(\theta-\theta_0)^2 \tag{2}$$

The harmonic spring constant parameters used in the flexible models were obtained from the molecular mechanics libraries contained in Hyperchem, except for water. The harmonic potential parameters for the SPC-based water model are the same as those used in other studies [7, 12, 14]. In all cases, harmonic potentials were grafted onto the rigid models without adjusting any parameters. This was done in order to isolate unambiguously individual effects of model flexibility on the simulated viscosity values.

A torsional potential was also included for propyl chloride and *n*-butane in both the flexible and the rigid models. The torsional potential energy u_{tor} was modeled in terms of the torsional angle, ϕ, using

$$\frac{u_{\text{tor}}(\varphi)}{k}=\sum_{i=0}^{5}a_i\cos^i\varphi \tag{3}$$

Table I. Intramolecular Model Parameters for Eq. (2)

Fluid	Bond	r_0 (nm)	k_r (10^{26} J · m^{-2})	Angle	Θ_0 (deg)	k_θ (J · deg^{-2})
Methanol	CH_3—O	0.1425	3.228	CH_3—O—H	108.5	64.20
	O—H	0.0945	2.770			
Acetone	CH_3—C	0.1518	2.690	CH_3—C=O	121.7	84.38
	C=O	0.1212	6.504	CH_3—C—CH_3	116.6	73.38
Propyl chloride	CH_3—CH_2	0.1550	2.650	CH_3—CH_2—CH_2	111.3	82.55
	CH_2—CH_2	0.1550	2.650	CH_2—CH_2—Cl	110.1	102.73
	CH_2—Cl	0.1771	1.945			
Water	O—H	0.1000	4.637	H—O—H	109.5	116.67
Propane	CH_3—CH_2	0.1523	2.650	CH_3—CH_2—CH_3	112.4	82.55
n-Butane	CH_3—CH_2	0.1541	2.650	CH_3—CH_2—CH_2	112.5	82.55
	CH_2—CH_2	0.1545	2.650			
Isobutane	CH_3—CH	0.1537	2.650	CH_3—CH—CH_3	110.7	82.55

Table II. Intermolecular Potential Parameters for Eq. (1)

Fluid	Site	(ε/k) (K)	σ (nm)	q (esu)
Methanol [12]	CH_3	105.20	0.3740	0.265
	O	86.50	0.3030	−0.700
	H	0.0	0.0	0.435
Acetone [16]	CH_3	72.00	0.3920	−0.032
	C	50.00	0.3000	0.566
	O	58.40	0.2800	−0.502
Propyl chloride [17]	CH_3	91.22	0.3861	0.0
	CH_2 (—CCH_2)	57.52	0.3983	0.0
	CH_2 (—CCl)	57.52	0.3983	0.25
	Cl	162.11	0.3555	−0.25
Water [12]	O	78.20	0.3166	−0.82
	H	0.0	0.0	0.41
Propane [13]	CH_3	72.00	0.3923	0.0
	CH_2	72.00	0.3923	0.0
n-Butane [13]	CH_3	88.07	0.3905	0.0
	CH_2	59.38	0.3905	0.0
Isobutane [13]	CH_3	80.52	0.3910	0.0
	CH	40.26	0.3850	0.0

where k is Boltzmann's constant and values for the constants are given in Table III. The torsional potential for *n*-butane was developed by Ryckaert and Bellemans [15]. For propyl chloride, Hyperchem was used to calculate the potential as a function of torsional angle, and the resultant values were used to regress the constants in Eq. (3).

Three models, varying in degree of internal flexibility, were used for each fluid. All three models included a torsional potential for propyl chloride and *n*-butane. In the rigid (R) model, no additional intramolecular potential was included, as bond lengths and bond angles were maintained at fixed values. The rigid-bond (RB), flexible-angle model used the harmonic potential for angle bending, but maintained fixed bond lengths. And the flexible (F) model used Eq. (2) for both angle bending and bond vibrations.

Table III. Torsional Potential Parameters for Eq. (3)

Fluid	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
n-Butane	1116.0	1462.0	−1578.0	−368.0	3156.0	−3788.0

3. SIMULATIONS

All simulations were performed for constant number of molecules, volume, and thermal kinetic energy using a computer program similar to that used by us in studies of alkanes [3, 8, 18] and polar fluids [19, 20]. A molecular version of the isothermal SLLOD equations of motion was used in conjunction with the Gaussian mechanics equations [1, 21] that include constraints to maintain temperature and shear rate for Couette flow as constants of motion. For the R and RB models, Gaussian mechanics were also used to maintain the rigid constraints. A fourth-order-correct predictor-corrector integration scheme was employed. An r-RESPA algorithm, based on that developed by Cummings and co-workers [4] and Mundy et al. [22], was used for the F-model simulations.

The LJ potential was spherically truncated at 1.0 nm, and standard long-range cutoff corrections were included. Coulombic interactions were handled with an Ewald sum method that has been developed for the Lees–Edwards boundary conditions [19] commonly used in NEMD simulations.

All simulations were initiated by placing 216 molecules in a simple cubic lattice and then equilibrated by performing the NEMD simulations until the energy was constant. Time steps were 1.2 fs in length. Each simulation was run an additional 100 to 200 ps beyond equilbration during which time the pressure tensor was obtained from block averages. The shear viscosity, η, at each shear rate, $\dot{\gamma}$, was computed from 5 to 15 block averages of 10,000 to 30,000 time steps each. The shear-thinning regime was used to extrapolate values of simulated viscosity to $\dot{\gamma}=0$ using an assumed linear relationship between $\eta(\dot{\gamma})$ and $\dot{\gamma}^{1/2}$ [1–3, 8, 18–20]. Weights calculated from the variance of the block averages at each shear rate were used with a weighted least-squares fit of the data to obtain the value at zero shear.

4. RESULTS AND DISCUSSION

The viscosity results obtained at zero shear and their variances are summarized in Table IV. Also shown are experimental values. The densities shown in Table IV correspond to the reported experimental density [23] in the case of methanol and the density corresponding to 0.1 MPa for the other fluids as obtained from the DIPPR database [24].

The results can perhaps best be examined in terms of molecule type. Results for the three nonpolar molecules studied, propane, *n*-butane, and isobutane, were essentially independent of model type. Model flexibility

Table IV. Simulation Results

Fluid	T (K)	ρ (mmol · cm^{-3})	η_{exp} (mPa · s)	η_{R} (mPa · s)	η_{RB} (mPa · s)	η_{F} (mPa · s)
Methanol	248.15	26.78	1.280	1.37 ± 0.05	1.53 ± 0.04	1.64 ± 0.04
	337.85	23.44	0.326	0.34 ± 0.01	0.36 ± 0.01	0.44 ± 0.01
	453.20	18.66	0.0883	0.088 ± 0.004	0.098 ± 0.003	0.102 ± 0.004
Acetone	253.15	14.40	0.5123	0.49 ± 0.02	0.45 ± 0.02	0.48 ± 0.02
	273.15	13.61	0.3987	0.38 ± 0.01	0.29 ± 0.01	0.29 ± 0.01
	333.15	12.82	0.2286	0.224 ± 0.003	0.207 ± 0.004	0.207 ± 0.003
Propyl chloride	200.0	12.68	1.374	1.44 ± 0.01	1.35 ± 0.02	1.32 ± 0.02
	250.0	11.99	0.588	0.66 ± 0.01	0.67 ± 0.02	0.63 ± 0.01
	300.0	11.24	0.332	0.388 ± 0.005	0.361 ± 0.006	0.347 ± 0.003
Water	300.0	55.74	0.877	0.49 ± 0.01	0.54 ± 0.01	0.68 ± 0.01
	400.0	51.80	0.215	0.178 ± 0.008	0.186 ± 0.006	0.222 ± 0.005
	500.0	46.38	0.119	0.112 ± 0.005	0.116 ± 0.005	0.125 ± 0.003
Propane	150.0	15.20	0.660	0.62 ± 0.01	0.58 ± 0.01	0.58 ± 0.01
	225.0	13.37	0.212	0.219 ± 0.003	0.208 ± 0.002	0.211 ± 0.003
	300.0	11.07	0.0947	0.096 ± 0.003	0.094 ± 0.002	0.093 ± 0.001
n-Butane	200.0	11.63	0.491	0.46 ± 0.01	0.44 ± 0.01	0.45 ± 0.01
	275.0	10.32	0.195	0.185 ± 0.004	0.188 ± 0.002	0.191 ± 0.002
	350.0	8.67	0.0996	0.091 ± 0.002	0.091 ± 0.001	0.092 ± 0.001
Isobutane	150.0	12.25	1.9811	0.58 ± 0.01	0.057 ± 0.01	0.55 ± 0.01
	200.0	11.53	0.6436	0.34 ± 0.01	0.34 ± 0.01	0.35 ± 0.01
	300.0	9.44	0.1471	0.119 ± 0.002	0.109 ± 0.002	0.116 ± 0.002

had no significant effect upon the zero-shear viscosity at any of the densities studied. For propane, the rigid model viscosities were slightly higher than those for the flexible model, but the magnitude of the effect is barely larger than the statistical uncertainty in the values.

For the polar molecules that do not hydrogen bond, propyl chloride and acetone, the viscosity for the RB and F models were essentially the same, within the accuracy of the simulations. However, the viscosity for the R model is larger than the other two models by about 5 to 10%. This suggests that internal flexibility has a small but noticeable effect on the viscosity of polar fluids. This effect is primarily due to the angle bending modes, not bond stretching, since the RB and F models produce essentially identical results. This was also suggested by van Gunsteren [25].

Interestingly, the results for the strongly polar models that hydrogen bond, methanol and water, exhibit a significant *increase* in viscosity with increasing flexibility. The increase in viscosity between the R and the F models for these two fluids is of the order of 25 to 30%. Flexible angles still make more of a difference than flexible bonds, but even the latter provides a noticeable increase in viscosity.

This increase in viscosity with increased flexibility seems counterintuitive to the idea that flexibility provides a way to relieve the drag from one molecule to the next. We suggest that there are at least two ways in which model flexibility affects the simulated viscosity. We refer to the reduction of drag by dissipation of energy to the internal modes as the primary effect. Parts of the molecule can flex and twist to relieve shear via this mechanism. A secondary effect also occurs as a function of the fluid density. The r_o values given in Table I and used as fixed bond lengths in the R model were determined for isolated molecules. However, the average bond lengths for the flexible model depend upon the density of the fluid. At the densities of our simulations, the O$-$H bond for the flexible model was found to be extended relative to the r_o value, and all other bond lengths were found to be shorter than the corresponding r_o value. Similarly, the angles in the F model were, on the average, slightly different at the simulation densities than the equilibrium values given in Table I. The angles for methanol, water, and acetone decreased slightly, while all others increased at the simulation densities. The fluid density changes the geometry of the molecule for flexible models. While these changes are rather inconsequential for nonpolar fluids, all of the above-mentioned geometry changes increase the dipole moment relative to the R model, and because the coulombic interactions have a different spatial dependence than the LJ portion of the potential, the result is an increase in viscosity. We refer to the effect that this geometry compression has upon the viscosity when using flexible models as a secondary effect.

Table V. Comparison of R, R2, and F Models for Methanol and Water

Fluid	T (K)	η_{exp} (mPa·s)	η_{R} (mPa·s)	η_{R2} (mPa·s)	η_{F} (mPa·s)
Methanol	248.15	1.280	1.37 ± 0.05	1.62 ± 0.05	1.64 ± 0.04
	337.85	0.326	0.34 ± 0.01	0.42 ± 0.01	0.44 ± 0.01
	453.20	0.0883	0.088 ± 0.004	0.097 ± 0.002	0.102 ± 0.004
Water	300.0	0.877	0.49 ± 0.01	0.62 ± 0.01	0.68 ± 0.01
	400.0	0.215	0.178 ± 0.008	0.205 ± 0.004	0.222 ± 0.005
	500.0	0.119	0.112 ± 0.005	0.124 ± 0.004	0.125 ± 0.003

To test the significance of the secondary effect, simulations using a fourth model for methanol and water were conducted. This fourth model, R2, used rigid bonds and angles but with the geometry constrained to that observed for the average F-model molecule at the same density. In this way, the results compare directly the primary influence of model flexibility upon the viscosity, eliminating effects due to a difference in geometry at the given conditions [26]. Table V shows a comparison of the results using the R2 model with the R and F models for methanol and water. In most cases, the R2 model results are very similar to those obtained from the F model, suggesting that the primary effects of vibration and angle-bending have only a very small direct influence upon the viscosity and that the larger dipole moment in the actual bulk fluid accounts for most of the dependence

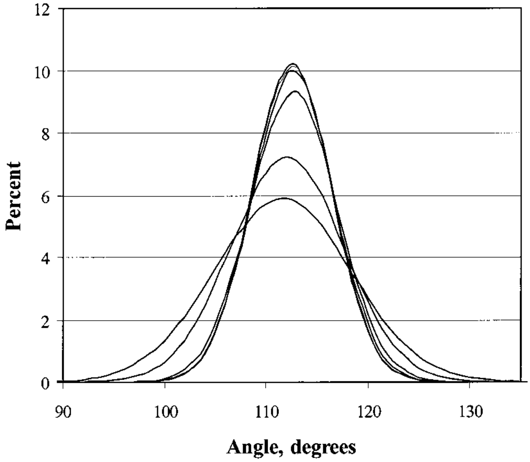

Fig. 1. Effect of shear on angle distribution of propane at 150 K. The displayed lines are in order from the highest peak to the lowest for shear rates 25, 81, 196, 400, 900, 2000, and 3000 ns^{-1}, respectively.

of the simulated viscosity on model flexibility. This important result indicates that rigid models can be effectively used in NEMD simulations even in the case of quite polar fluids, if the appropriate geometry for the desired density is used. The density-dependent geometry can be obtained from a single, short, equilibrium simulation on a flexible model, thereby saving considerable CPU time.

The effects of shear rate on F-model geometries were also examined. The effect of shear rate on bond angle for propane is shown in Fig. 1. There is relatively little change in angle with shear, but there is an increase in the breadth of the angle distribution at the higher shear rates. Similar results were found for bond lengths. In this study, only shear rates below about $400\,\mathrm{ns}^{-1}$ were used, where the effects of shear rate on the flexible model appear to be small. Nevertheless, because the viscosity at zero shear is desired, a rigid model with bonds and angles fixed at their zero-shear values may even be preferable to a flexible model in order to avoid changes in geometry with shear at some of the higher shear rates.

5. CONCLUSIONS

Our results indicate that internal flexible modes do not directly affect the simulated viscosity significantly for nonpolar molecules and that inclusion of potential models for these modes is not the most efficient use of CPU time. For slightly polar molecules, bond vibrations have little effect upon the simulated viscosity, but angle bending can have a noticeable effect that may be important if the rest of the model is very accurate. However, our studies with strongly polar molecules suggests that the main effect of internal flexibility upon polar fluid viscosity comes not as a direct result of the internal flexibility, but due to the density changes in the geometry and dipole moment that flexibility permits. Use of bond lengths and angles appropriate for the fluid density in rigid models is an easy way to eliminate these secondary effects and obtain reliable viscosity values without including costly model flexibility. Rigid model bond lengths and angles can, for example, be determined from a flexible model in a very short equilibrium simulations. These values can then be used with a computationally cheap rigid model to perform the several long NEMD simulations usually used to determine the viscosity at zero shear.

ACKNOWLEDGMENT

Support of this project by Neste Oil Company, Espoo, Finland, is gratefully acknowledged.

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