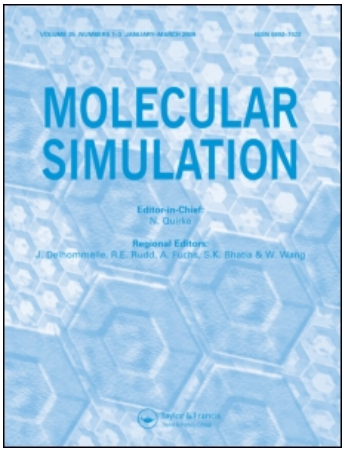

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THE RHEOLOGY OF *n*-DECANE AND 4-PROPYL HEPTANE BY NON-EQUILIBRIUM MOLECULAR DYNAMICS SIMULATIONS

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In a recent paper [*Mol. Sim.*, **16**, 229 (1996)], we reported non-equilibrium molecular dynamics (NEMD) simulation of planar Couette flow for normal (*n*-butane) and isomeric butane (*i*-butane) molecules using two collapsed atom models and an atomistically detailed model. It was found that the collapsed atom models predict the viscosity of the *n*-butane quite well, but the viscosity of *i*-butane by those models is underpredicted. It was also found that the atomistically detailed model does not yield quantitative agreement with the viscosity of either the *n*-butane or *i*-butane, but it does have the one positive feature that the calculated viscosity of *i*-butane is higher than that of *n*-butane (branching increases viscosity) as observed experimentally. In the present paper, we present results of NEMD simulations of planar Couette flow for normal decane and 4-propyl heptane molecules using the same models. The results show exactly the same branching effect on the viscosity as for the case of *n*- and *i*-butanes. We find that the viscosity of *n*-decane predicted by the collapsed models is in excellent agreement with the experimental value and the calculated viscosity of 4-propyl heptane by those models is smaller than that of *n*-decane. For the atomistically detailed model, the quantitative agreement with the experiments is poor for the viscosity of either the *n*-decane or 4-propyl heptane, but the calculated viscosity of 4-propyl heptane is higher than that of *n*-decane (branching increases viscosity). In this case, since the experimental value for the viscosity is not known, we cannot conclude that the role of interactions including H atoms plays in the right way. However, the significant difference on the branching effect on the viscosity in the collapsed models and the atomistically detailed model is once more observed following in the case of *n*- and *i*-butane.

Keywords: Non-equilibrium molecular dynamics; *n*-decane; 4-propyl heptane; viscosity

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1. INTRODUCTION

In recent years, the non-equilibrium molecular dynamics (NEMD) simulations have emerged as a powerful tool for the study of thermal transport coefficients-self-diffusion coefficient, shear and bulk viscosities, and thermal conductivity of both simple and molecular fluids. Recent development include the SLLOD algorithm for shear viscosity [2, 3], the color current technique for self-diffusion coefficient [4], the Evans algorithm for thermal conductivity [5, 6], and the use of Gauss's principle [4–7] of least constraint for isokinetic and/or isobaric ensemble simulations.

Evans and his coworkers have used NEMD to study the rheological behavior of liquid alkanes such as butane, decane, eicosane, tridecane, and 5-butyl nonane under homogeneous shear in NVT and NpT ensembles [8–11]. Initially, the alkane model used by them was the Ryckaert-Bellemans (RB) collapsed atom model [12–15] in which methyl and methylene groups are represented by spheres interacting via Lennard-Jones (LJ) potentials. The main benefit of this model is to reduce a considerable amount of computing time by reducing the number of interaction sites. In their later works [9–11], they replaced the LJ potentials by LJ potentials truncated at its minimum $r = 2^{1/6}\sigma$, and shifted so that the potential is zero at the point of truncation. This potential is often referred to as the Weeks-Chandler-Andersen (WCA) prescription [16, 17].

Chynoweth and his coworkers have adopted and expanded the RB model by accounting for intramolecular interactions between the RB blobs [18]. For this, bond stretching and bond angle bending potentials have been added to the original torsional potential of the RB model. They used this model for the rheological properties of liquid *n*-butane [19] and liquid *n*-hexadecane [20] by NEMD simulation method. They reported a behavior [19] of strain rate dependent viscosity of *n*-butane, i.e., the linear dependence of viscosity on $\gamma^{1/2}$, which is different from Evans and his coworkers' result, i.e., an intermediate Newtonian region around 10^{11} s^{-1} and a second shear-thinning region at higher shear rates [6]. They also reported a NEMD study of liquid *n*-hexadecane [20]. In their study, although low-shear-rate simulations are restricted by long computational times, for the given model the onset of the non-Newtonian region is estimated to be around 10^{10} s^{-1} and the liquid's first Newtonian regime is clearly seen.

The branching effect on the dynamic properties of liquid alkanes such as the self diffusion coefficient, viscosity, and thermal conductivity is of considerable interest. For liquid butane, the experimentally observed viscosity [21] is found to increase with branching. However, for liquid

pentane, hexane, and heptane, branching decreases the viscosity – 0.240 cP and 0.223 for *n*-pentane and *i*-pentane, 0.326 and 0.306 for *n*-hexane and *i*-hexane, and 0.409 and 0.384 for *n*-heptane and *i*-heptane [22], respectively.

To investigate the molecular cause of the structural branching effect upon viscosity, NEMD simulations of LJ site-site models representing *n*-butane and *i*-butane were performed over much of the density range for which experimental data are available, by Rowley and Ely [23]. Simulated viscosities at zero shear agreed very well with experimental data over the entire density range. Site-size, non-equilibrium molecular alignment and molecular geometry were the primary factors causing both the similarities and differences between isomers' viscosity and rheology.

More recently, Lee and Cummings [1] have reported an NEMD simulations of planar Couette flow of *n*-butane and *i*-butane molecules using the three different models [24–26]. They found that the collapsed atomic models predict the viscosity of *n*-butane quite well in general agreement with previous workers [18, 23, 27] but if these models are applied to the isomer, the viscosity is underpredicted. They also found that their atomistically detailed model did not yield quantitative agreement with the viscosity of either the *n*-butane or its isomer. However this model have the one positive feature that the calculated viscosity of *i*-butane is higher than that of *n*-butane (branching increases the viscosity) as observed experimentally. The results suggest that the inclusion of H atoms may be important in correctly predicting the effect of molecular structure on physical properties of liquid alkanes.

In this paper, we examine the Newtonian and strain rate dependent rheological properties of several models for *n*-decane and 4-propyl heptane. Our models are three different ones, i.e., the original RB collapsed atom model [12–15], the expanded second collapsed atom model [18, 19], and finally an atomistically detailed model.

The paper is organized as follows: Section 2 contains a brief description of molecular models and MD simulations methods followed by Section 3 which presents the results of our simulations and Section 4 where our conclusions are summarized.

2. MOLECULAR DYNAMICS SIMULATIONS AND MOLECULAR MODELS

In the present study, we have carried out MD simulations using the three different models for liquid *n*-decane and 4-propyl heptane at 481 K. Each

simulation was carried out in the NVT ensemble; the density and hence the length of cubic simulation box were fixed (0.630 g/cc and 2.163 nm) [13]. The usual periodic boundary condition in the x-, y- and z-directions and minimum image convention for pair potential were applied. A spherical cut-off of radius $R_c = 2.5\sigma$, where σ is the LJ parameter, was employed for all the pair interactions. A Gaussian thermostat [4–7] was used to keep the temperature of the system constant.

A. The Original RB Collapsed Atomic Model (Model I)

Monomeric units are treated as single spheres with masses given in Table I. They interact through an LJ potential between the spheres in different molecules and between the spheres more than three apart on the same molecule. The C—C—C—C torsional rotational potential is given by the original Ryckaert-Bellemans form [12]:

$$V(\phi) = c_0 + c_1 \cos\phi + c_2 \cos^2\phi + c_3 \cos^3\phi + c_4 \cos^4\phi + c_5 \cos^5\phi \quad (1)$$

where ϕ is the C—C—C—C dihedral angle. The LJ parameters and c_i's are listed in Table I.

The MD simulations were performed using the Verlet algorithm [28] for the time integration of the equations of motion with a time step of 0.001 ps and the RATTLE algorithm [29] for the bond length and bond angle constraints. MD runs of at least 2,000,000 time steps each were needed for the liquid alkane system to reach equilibrium. The equilibrium properties were then averaged over 10 blocks of 100,000 times steps (100 ps) for a total of 1,000,000 time steps (1,000 ps).

B. The Expanded Collapsed Atomic Model (Model II)

This model includes the C—C bond stretching and C—C—C bond angle bending potentials in addition to the LJ and torsional potentials of model I:

$$V_b(r_{ij}) = K_0(r_{ij} - r_e)^2 \quad (2)$$

$$V_a(\theta) = K_1(\theta - \theta_e)^2 - K_2(\theta - \theta_e)^3 \quad (3)$$

The equilibrium bond length (r_e) and bond angle (θ_e), and the force constants (K_0, K_1 and K_2) are used by Chynoweth *et al.* [18, 19] which are

TABLE I Potential parameters for three different models of liquid alkanes

Model I	LJ parameters	σ (nm)	ε (kJ/mol)				
	C — C	0.3923	0.5986				
	torsional [1]	c_0 (kJ/mol)	c_1	c_2	c_3	c_4	c_5
	C — C — C — C	9.279	12.136	−13.120	−3.060	26.240	−31.495
Model II	bond stretching	r_e (nm)	K_0 (kJ/mol nm^2)				
	C — C	0.153	132600				
	bond angle bending	θ_e (deg)	K_1 (kJ/mol deg^2)			K_2 (kJ/mol deg^3)	
	C — C — C	109.47	0.05021			0.000482	
Model III	LJ parameters		σ (nm) [2]		ε (kJ/mol) [2]		
	C — C	0.33665	(0.33665)	[0.3207]	0.40561	(0.40561)	[0.3519]
	C — H	0.27983	(0.30561)	[0.2763]	0.17219	(0.17219)	[0.3345]
	H — H	0.22300	(0.27457)	[0.2318]	0.07310	(0.07310)	[0.3180]
	bond stretching	r_e (nm)	K_0 (kJ/mol nm^2)				
	C — C	0.153	210000				
	C — H	0.110	147000				
	bond angle bending	θ_e (deg)	K_1 (kJ/mol deg^2)				
	C — C — C	111.0	0.07346				
	C — C — H	109.5	0.05588				
	H — C — H	107.9	0.04667				
	torsional	K_3 (kJ/mol)					
	C — C — C — H	11.72					

[1] The same tortional parameters are used for models II and III.
[2] $(\cdots)$ are used in Ref. [1] and $[\cdots]$ are Muller-Plathe *et al.*'s [32].

originally provided by the work of White and Boville [30], and are given in Table I.

For the integration over time, we adopted Gear's fifth-order predictor-corrector algorithm [31] with a time step of 0.0005 ps for all the *n*-alkanes. A total of 1,000,000 or 1,500,000 time steps was simulated each for the average and the configurations of molecules were stored every 10 time steps for further analysis.

C. The Atomistically Detailed Model (Model III)

The explicit presence of H atoms in the alkane molecule increases the number of interactions in inter and intra LJ potentials between H and H between C and H atoms, as well as introducing C—H bond stretching, C—C—H and H—C—H bond angle bending, and also terminal C—C—C—H potentials. The bond stretching potential is of the same form as Eq. (2) but the bond angle bending potential has the form of Eq. (2) rather than Eq. (3). The terminal C—C—C—H torsional potential has a different form

$$V(\phi) = K_3(1 + 4\cos^3\phi - 3\cos\phi) \tag{4}$$

from the C—C—C—C Eq. (1). Here ϕ is the C—C—C—H dihedral angle and the potential parameters are listed in Table I.

The Gear's fifth-order predictor-corrector algorithm [32] was also used with a time step of 0.00033333 ps. The equilibrium properties were then averaged for a total of 1,500,000 time steps (500 ps).

In an NEMD simulation study of the isomeric effect on the viscosity of butanes using model III, Lee *et al.* [1] initially used the potential parameters developed by Muller-Plathe *et al.* for polyisobutylene [32] (shown in Tab. I) except for the C—C—C—C torsional potential parameters. The NEMD results for *n*-butane and *i*-butane with these potential parameters deviated strongly from experiment. The calculated pressure was approximately −1000 atm in the absence of shear at a density of 0.583 g/cc and temperature of 291.0 K and under a homogeneous shear, the calculated density profiles showed a density inhomogeneity as shown in Figure 1 of Ref. [1]. In NpT ensemble simulation at a pressure of 1 atm and temperature of 291.0 K, the density in the absence of shear was found to be 0.722 g/cc, much higher than the expected value of 0.583 g/cc.

In the MD simulation study of *n*-alkane tricosane by Ryckaert *et al.* [33], a flexible-chain model was used in which the hydrogen atoms are incorporated explicitly, and the C—C and C—H bond lengths, and the

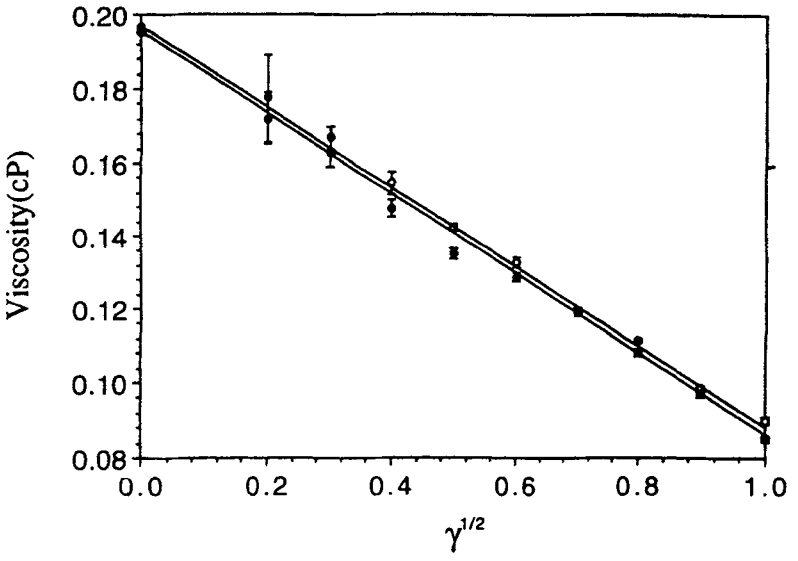

FIGURE 1 Strain rate dependent viscosities of models I and II of *n*-decane. Open circles: model I and filled circles: model II.

H—H distances are constrained as constants. The intermolecular potential between atoms consists of "exp-6" interactions Lee *et al.* [1] inferred LJ parameters from the exp-6 parameters by keeping the position of the potential minimum unchanged. The resulting potentials are in good agreement with the original exp-6 potentials, but the set of LJ parameters, which do not follow the Lorentz-Berthelot mixing rule since the σ for H atoms is slightly too large, was further modified by changing the LJ parameters for H atom to comply with the mixing rule. The final LJ parameters used for their work [1] are given in Table I. However, the calculated pressures of *n*-butane and *i*-butane using these parameters were very high (about 1000 atm), similar to those of model I.

We have further modified the LJ parameter σ for the H atom to obtain a reasonable pressure of *n*-butane for model III by comparing the MD calculated pressures for various sets of σ for H atom. The final LJ parameters are listed in Table I.

3. RESULTS AND DISCUSSION

The strain rate dependent viscosity and pressure of our NEMD simulations are shown in Tables II, III and IV. The viscosity at zero strain rate was

TABLE II The viscosity and pressure for models I and II of *n*-decane at various strain rates obtained from our NEMD simulations at 481 K and 0.630 g/cc (numbers in the parentheses represent the statistical uncertainty in the least significant digits)

Run length (ps)	$\gamma (ps^{-1})$	*model I*		*model II*	
		$\eta (cP)$	*P (bar)*	$\eta (cP)$	*P (bar)*
	0.0	0.198		0.197	
1,500	0.04	0.172(7)	1692(38)	0.177(8)	297(18)
1,200	0.09	0.167(5)	1649(55)	0.163(6)	285(13)
1,200	0.16	0.155(4)	1681(49)	0.147(4)	299(14)
1,000	0.25	0.142(3)	1667(63)	0.135(3)	298(12)
1,000	0.36	0.133(3)	1652(60)	0.129(3)	335(13)
1,000	0.49	0.119(2)	1655(46)	0.119(2)	326(17)
600	0.64	0.108(2)	1668(64)	0.111(2)	348(12)
600	0.81	0.0987(15)	1780(66)	0.0971(12)	362(12)
600	1.00	0.0900(11)	2068(97)	0.0851(9)	468(14)

TABLE III The viscosity and pressure for models I and II of 4-propyl heptane at various strain rates obtained from our NEMD simulations at 481 K and 0.630 g/cc cc (numbers in the parentheses represent the statistical uncertainty in the least significant digits)

Run length (ps)	$\gamma (ps^{-1})$	*model I*		*model II*	
		$\eta (cP)$	*P (bar)*	$\eta (cP)$	*P (bar)*
	0.0	0.160		0.166	
1,500	0.04	0.153(8)	1661(53)	0.157(9)	239(14)
1,200	0.09	0.147(7)	1643(44)	0.149(7)	240(13)
1,200	0.16	0.145(5)	1628(33)	0.139(6)	218(13)
1,000	0.25	0.140(3)	1661(43)	0.134(4)	239(15)
1,000	0.36	0.137(3)	1637(50)	0.130(3)	258(12)
1,000	0.49	0.132(2)	1658(75)	0.125(2)	245(13)
600	0.64	0.127(2)	1690(36)	0.118(2)	292(23)
600	0.81	0.126(1)	1965(77)	0.114(2)	272(29)
600	1.00	0.120(1)	2256(90)	0.106(1)	538(28)

TABLE IV The viscosity and pressure for model III of *n*-decane and 4-propyl heptane at various strain rates obtained from our NEMD simulations at 481 K and 0.630 g/cc (numbers in the parentheses represent the statistical uncertainty in the least significant digits)

Run length (ps)	$\gamma (ps^{-1})$	*n-decane*		*4-propyl heptane*	
		$\eta (cP)$	*P (bar)*	$\eta (cP)$	*P (bar)*
	0.0	0.333		0.404	
1,500	0.04	0.293(38)	1050(75)	0.363(52)	1113(76)
1,200	0.09	0.280(26)	997(80)	0.333(32)	960(71)
1,200	0.16	0.246(19)	982(73)	0.295(29)	1078(81)
1,000	0.25	0.213(19)	1111(71)	0.260(20)	1060(72)
1,000	0.36	0.194(15)	1058(76)	0.228(16)	1057(65)
1,000	0.49	0.167(11)	944(66)	0.207(12)	1053(63)
600	0.64	0.154(8)	924(65)	0.188(10)	939(66)
600	0.81	0.141(4)	1109(64)	0.170(4)	1286(65)
600	1.00	0.125(4)	1186(68)	0.153(4)	1429(72)

obtained from a linear squares fit of the NEMD simulated viscosity values using the equation $\eta(g) = \eta(0) - A\gamma^{1/2}$. In Figure 1, we have plotted the strain rate dependent viscosity of *n*-decane at 481 K and 0.630 g/cc which is a slightly different state point (480 K and 0.6136 g/cc) studied by Mundy *et al.* [34] and Cui *et al.* [35]. The other simulated state point for liquid *n*-decane is at 298 K and 0.7247 g/cc [36]. The experimental viscosity of *n*-decane in the range of pressures 100 – 140 bar is 0.196 ± 0.006 cP [37]. Mundy *et al.* obtained 0.190 ± 0.015 cP by equilibrium molecular dynamics (EMD) simulation using the Green-Kubo formula of the molecular stress-stress autocorrelation function and Cui *et al.* obtained 0.191 ± 0.012 cP by EMD and 0.197 ± 0.003 cP by NEMD. Those values are in good agreement with the experimental value. Our results for the viscosity of *n*-decane using two collapsed model at a slightly different state point are within the same category. Earlier NEMD study by Edberg *et al.* [27] reported 0.153 ± 0.009 cP ($N = 27$, number of molecules) and 0.165 ± 0.015 cP ($N = 54$) for the viscosity on *n*-decane which are also in good agreement with the experimental value 0.163 cP at $T = 481$ K and $P \approx 0$ [37].

The strain rate dependent viscosity of 4-propyl heptane at 481 K and 0.630 g/cc is plotted in Figure 2. The calculated viscosity of 4-propyl heptane from a linear squares fit of the NEMD simulated viscosity values

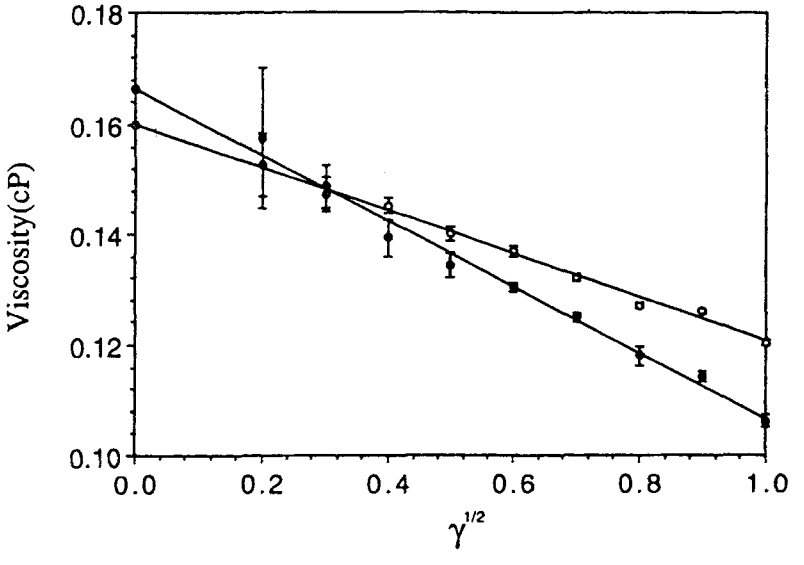

FIGURE 2 Strain rate dependent viscosities of models I and II of 4-propyl heptane. Open circles: model I and filled circles: model II.

are 0.160 cP for model I and 0.166 cP for model II. According to our NEMD simulation results of *n*-decane and 4-propyl heptane, branching decreases the viscosity. The effect of branching on the viscosity of *n*-butane and *i*-butane was previously studied by Rowley *et al.* [23] and by Lee and Cummings [1]. For models I and II of liquid butane, branching decreases the viscosity but for model III, the calculated viscosity of *i*-butane is higher than that of *n*-butane as observed experimentally [1].

Daivis *et al.* [10] reported the NEMD study for viscosity for *n*-tridecane and 5-butyl nonane at 273 K and 1 atm using WCA potential [16, 17]. They found that the general trend of decreasing viscosity at low strain rates followed by an increase in the viscosity at higher strain rates was observed and the viscosity for the linear alkane was always less than that of the branched alkane. For example, they obtained 0.865 cP for the branched alkane and 0.761 cP for the linear alkane. Both NEMD results differ substantially from the experimental values – 2.768 cP for 5-butyl nonane and 2.948 cP for *n*-tridecane [38].

We now turn our attention to the atomistically detailed model, model III, for *n*-decane and 4-propyl heptane. The strain rate dependent viscosity and pressure are listed in Table III. The calculated pressures are very high, almost around 1000 bar; the over-prediction of the pressure and the over-prediction of the viscosity may be related since both quantities are derived from elements of the pressure tensor. The strain rate dependent viscosity is plotted in Figure 3. Although the value of the viscosity is too high compared to experiment, it can be seen that the NEMD simulations using model III show that branching increases viscosity. This result is exactly opposite to those of models I and II (collapsed models) of *n*-decane and 4-propyl heptane. This suggests that the inclusion of H atoms (and accordingly the consideration of H — H and C — H LJ potential, and C — H and H — H bond stretching, and C — C — H and H — C — H bond angle bending interactions) in intermolecular and intramolecular potential models may be important in correctly predicting the effect of molecular structure on alkane rheology.

In equilibrium molecular dynamics (EMD) simulations of liquid alkanes [24–26], the calculated viscosities of *n*-decane and 4-propyl heptane for models I and II through the Green-Kubo formula at 298.15 K result in the opposite directions as branching occurs (0.313 → 0.386 cP for model I and 0.342 → 0.273 for model II). For model III, branching increases viscosity (0.288 → 0.300 cP). In contrast of the large difference of the calculated viscosities for those alkanes between the collapsed models and the atomistically detailed model by the NEMD, almost the same magnitude

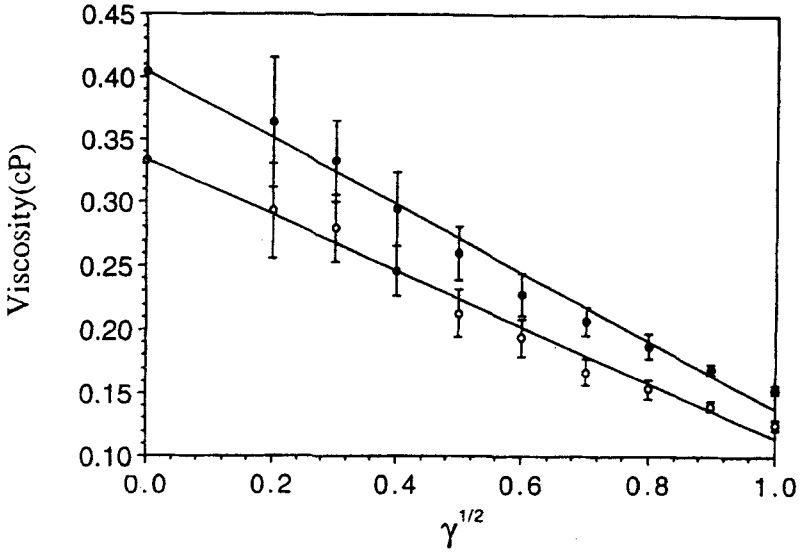

FIGURE 3 Strain rate dependent viscosities of model III of *n*-decane and 4-propyl heptane. Open circles: *n*-decane and filled circles: 4-propyl heptane.

of the calculated viscosities in the EMD are probably related to the pressures in the EMD ranged over 0 to −300 atm (about 1000 bar for model III in the NEMD).

4. CONCLUSION

In this paper, we presented results of NEMD simulations of planar Couette flow for normal decane and 4-propyl heptane molecules using three different models. The results showed exactly the same branching effect on the viscosity as for the case of normal and isomeric butanes. We found that the viscosity of *n*-decane predicted by the collapsed models is in excellent agreement with the experimental value, while the viscosity of 4-propyl heptane predicted by those models is smaller than that of *n*-decane. For the atomistically detailed model, the quantitative agreement with the experiments is poor for the viscosity of either the *n*-decane or 4-propyl heptane, but the calculated viscosity of 4-propyl heptane is higher than that of *n*-decane, consistent with other theoretical studies which find that branching increases viscosity. The significant difference on the branching effect on the viscosity in the collapsed models and the atomistically detailed model is

similar to that found in the case of normal and isomeric butane. The branching effect on the viscosity of C_{17} systems (6-pentyl duodecane and 5-dibutyl nonane) will be presented in a future publication [39].

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