Molecular dynamics simulations of the rheology of normal decane, hexadecane, and tetracosane

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Extensive nonequilibrium molecular dynamics simulations have been carried out for liquid decane, hexadecane, and tetracosane at densities corresponding to atmospheric pressure and near ambient temperatures. The strain-rate-dependent viscosity has been obtained for strain rates ranging over several orders of magnitude. At high strain rate, the viscosities for all alkanes studied here have similar values and exhibit similar power-law shear-thinning behavior with a slope between about −0.40 and −0.33. Accompanying this shear thinning is the onset of orientational order and the alignment of the alkane molecules with the flow direction. The alignment angle tends to 45° at very low strain rate and is significantly smaller at high strain rate. This suggests that the chains substantially align in the flow direction and that the dominant motion at high strain rate is the sliding of the chains parallel to the flow. At low strain rate, the shear viscosity shows a transition to Newtonian behavior. The Newtonian viscosity can be obtained from the plateau value of the shear viscosity at the lowest strain rates calculated from the nonequilibrium molecular dynamics simulation (NEMD). This is demonstrated by comparing the viscosity of decane obtained by extrapolating the NEMD simulation with an independent calculation using the standard Green–Kubo method. The transition from the non-Newtonian regime to the Newtonian regime is also correlated with the disappearance of orientational order and with the longest relaxation time of the liquid alkanes simulated. © 1996 American Institute of Physics.

INTRODUCTION

The rheological properties of liquid alkanes of intermediate molecular sizes (C_{20}–C_{40}) are among the most important properties in lubricant performance. However, a thorough, realistic study of these systems by molecular simulations has previously been limited by the high computational cost. With the advent of the massively parallel supercomputers, it is now possible to carry out systematic studies of these systems with the objective of identifying the most important factors affecting the rheology. This can provide significant insight and guidance to the design of synthetic lubricants with desired properties.

Computer simulation has contributed considerably to our current understanding of the structural and rheological properties of liquid alkanes. Nonequilibrium molecular dynamics simulations (NEMD), in particular, have played a major role in characterizing the properties of the alkane chains under the conditions of planar Couette shear flow. These simulations have so far been limited to relatively short chains. NEMD simulations have been carried out for eicosane (C_{20}H_{42}), however, to minimize computation time, that study used a Weeks–Chandler–Anderson (WCA) potential for the intermolecular site–site interaction, so that only qualitative conclusions could be made. A more realistic simulation was carried out for hexadecane at relatively high temperature and density in which the Ryckaert–Bellemans mode was used. The calculated Newtonian viscosity was almost three times lower than the experimental value.

A recent model proposed by the group at Shell Research predicted accurately the phase envelope of the linear alkanes from C_6 to C_{48}. The model was subsequently used by Mundy et al. and Cui et al. to predict quantitatively the viscosity of normal decane at a liquid state condition similar to those in the phase envelope calculation (high temperature, moderately high density). The model was assessed by Mondello and Grest for a number of equilibrium properties at near ambient temperature conditions. The diffusion coefficient was found to be in reasonable agreement with experimental results for decane but less so for tetracosane. The same model was also used by Stevens et al. in their boundary layer lubrication study. It is, thus, of interest from both a practical and fundamental point of view to extend the rheological studies for decane to the ambient temperature conditions and to longer chains.

We have recently implemented a multiple time step algorithm to perform molecular simulations for chain molecules under Couette flow on massively parallel supercomputers, particularly the Intel Paragon. This allows us to systematically study the rheological properties of liquid alkanes with molecular size of industrial interest. In the following, we report the results of such a NEMD study.
EQUATIONS OF MOTION AND THEORY

The equations of motion used for liquid alkanes under planar Couette flow are the slod equations with Nosé dynamics,\textsuperscript{7}

\[ \dot{r}_{ia} = \frac{\mathbf{p}_{ia}}{m_{ia}} + \gamma \mathbf{y}_{ia} \hat{x} \]

\[ \dot{p}_{ia} = \mathbf{F}_{ia} - \gamma p_{y,ia} \hat{x} - \dot{\zeta} \mathbf{p}_{ia} \]

\[ \dot{\zeta} = \frac{\zeta}{Q} \]

\[ \dot{p}_{\zeta} = F_{\zeta} \]

where \( r_{ia}, \mathbf{F}_{ia} \) and \( \mathbf{p}_{ia} \) are the coordinates of, force on, and momentum of atom \( a \) in molecule \( i \), \( p_{y,ia} \) are its \( y \) components, \( m_{ia} \) is the mass, and \( \hat{x} \) is a unit vector in \( x \) direction. The quantities \( \zeta, p_{\zeta}, \) and \( Q \) are the variables related to the Nosé thermostat,

\[ F_{\zeta} = \sum_{ia} \frac{p_{ia}}{m_{ia}} - 3Nk_B T \]

\[ Q = 3Nk_B T \tau \] \( \tau \) is the Nosé thermostat time constant, \( k_B \) is Boltzmann’s constant, \( T \) is the absolute temperature, and \( N \) is the total number of atoms in the system.

In a NEMD calculation, the strain-rate dependent viscosity \( \eta \) is determined from the constitutive relation

\[ \eta = \frac{-\langle P_{xy} \rangle + \langle P_{yx} \rangle}{2 \gamma} \]

where \( \langle P_{xy} \rangle \) and \( \langle P_{yx} \rangle \) are the averages of the \( xy \) and \( yx \) components of the pressure tensor \( \mathbf{P} \) and \( \gamma \) is the strain rate characterizing the shear field. We have chosen the \( x \) direction to be the flow direction and \( y \) direction to be the flow gradient direction, so that \( \gamma = \partial u_x / \partial y \) where \( u_x \) is the streaming velocity in the \( x \) direction.

Note that distinction should be made whether the atomic or molecular tensor is used in Eq. (2). A number of publications have discussed the subject of the atomic and molecular pressure tensor formalisms in molecular simulation. For a system at equilibrium in the absence of an external force, the equivalence between the two in calculating the transport coefficients has been analytically proven,\textsuperscript{10,11} and numerically verified.\textsuperscript{10,12} For a system in planar Couette flow, the equivalence between the two has been discussed by Edberg et al.\textsuperscript{13}

In our NEMD simulation, as the streaming velocity is applied to the atomic site, the corresponding pressure tensor \( \mathbf{P} \) is calculated using the atomic formalism.

\[ PV = \sum_{i,a} m_{ia} \mathbf{v}_{ia} \mathbf{v}_{ia} + \frac{1}{2} \sum_{i,a} \sum_{j,b} (r_{ia} - r_{jb}) \mathbf{f}_{ia,jb} \]

\[ + \sum_{i,a} \delta r_{ia}^{(\text{int})} \]

where the indices \( i \) and \( j \) refer to molecules \( i \) and \( j \), indices \( a \) and \( b \) refer to interactions sites \( a \) and \( b \) in molecules \( i \) and \( j \), respectively, \( \mathbf{f}_{ia,jb} \) is the interaction force between site \( a \) on molecule \( i \) and site \( b \) on molecule \( j \). \( \delta r_{ia}^{(\text{int})} \) is the position vector of site \( a \) on molecule \( i \) relative to the center of mass of molecule \( i \), \( f_{ia}^{(\text{int})} \) is the total intramolecular force on site \( a \) on molecule \( i \), and \( m_{ia}, r_{ia}, \) and \( \mathbf{v}_{ia} \) are the mass, position, and velocity, respectively, of site \( a \) on molecule \( i \). Note that since the total intramolecular force sums to zero for a given molecule, the last term in Eq. 2(a) does not depend on the choice of origin in the determination of \( \delta r_{ia} \), so this can be conveniently chosen to be the center of mass of the molecule.

In our equilibrium molecular dynamics simulation, the pressure tensor is calculated using the molecular formalism,

\[ \mathbf{P}^\text{m}V = \sum_{i} m_i \mathbf{v}_i \mathbf{v}_i + \frac{1}{2} \sum_{i,j} \sum_{\sigma \neq j} (r_i - r_j) \mathbf{F}_{ij} \]

\[ \eta = \frac{V}{k_B T} \int_0^\infty dt \langle P_{xy}^m(t) P_{xy}^m(0) \rangle \]

In this equation, \( \langle P_{xy}^m(t) P_{xy}^m(0) \rangle \) is the correlation function of the \( xy \) component of symmetric part of the molecular pressure tensor.

In the absence of an external field, the system is isotropic so that \( xy, yz, \) and \( xz \) components are equivalent and use of all the three off-diagonal elements improves the statistics. In a recent publication, Daisvis and Evans\textsuperscript{14} showed that the tensorial property of the viscosity coefficient allows the use of all elements of the pressure tensor in the calculation of the viscosity, so that

\[ \eta = \frac{V}{10k_B T} \int_0^\infty dt \langle \mathbf{P}^{\text{sym}}(t) \cdot \mathbf{P}^{\text{sym}}(0) \rangle \]

where \( \mathbf{P}^{\text{sym}}(t) \) denotes the symmetric traceless part of the pressure tensor (the molecular tensor in this calculation) and the operator \( \cdot \) implies the double contraction of two second rank tensors. An expression for the correlation function equivalent to the one in Eq. (6) was derived by Fixman in an earlier paper.\textsuperscript{15}

THE MODEL AND SIMULATION METHODS

The model used for this simulation is the same as the model used for the simulation of decane in a previous publication.\textsuperscript{7} For completeness, we briefly describe the model and simulation technique. The interested reader is referred to the original publications for details.\textsuperscript{5–7}

The alkanes are modeled by a united atom model, the same as that used in.\textsuperscript{5} This model is essentially the same as that used by Siepmann et al.\textsuperscript{5} in calculating the phase envelope of alkanes, with the modification that the fixed bond length is replaced by a stiff harmonic bond stretching potential. The intermolecular interaction and the interaction between atoms separated by three or more atoms in the same molecule is described by a Lennard-Jones (LJ) potential. A
TABLE I. State points simulated for the liquid alkanes.

<table>
<thead>
<tr>
<th>Alkane type</th>
<th>T (K)</th>
<th>( \rho ) (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n )-decane</td>
<td>298</td>
<td>0.7247(^a)</td>
</tr>
<tr>
<td>( n )-hexadecane (A)</td>
<td>300</td>
<td>0.770(^b)</td>
</tr>
<tr>
<td>(B)</td>
<td>323</td>
<td>0.753(^b)</td>
</tr>
<tr>
<td>( n )-tetracosane</td>
<td>333</td>
<td>0.773(^b)</td>
</tr>
</tbody>
</table>

\(^a\)Reference 17.
\(^b\)Reference 18.

cutoff distance of 9.825 (Å) for the LJ interaction was used in this study. The intramolecular interactions consist of bond angle bending and torsional potentials. The bond angle bending potential is a harmonic potential, and the torsional potential is that by Jorgenson \textit{et al.}\(^{16}\) The state points studied correspond to the density of the alkane at atmospheric pressure and at the respective temperatures.\(^{17,18}\) These are listed in Table I.

The equations of motion were integrated using a multiple time step technique with Nose constant temperature dynamics. Details can be found in the works of Tuckerman \textit{et al.}\(^{13}\) and Cui \textit{et al.}\(^{7}\) In our implementation for this calculation, two time step sizes were used. All the internal interactions were treated as fast motions and the intermolecular interaction as the slow motion. The large time step was 2.35 fs, and the small time step was 0.235 fs. The initial configurations were prepared by starting the chains in the all-trans conformation and the center of mass of chains at cubic lattice points. The chains were initially all aligned in the \( x \) direction. When the chain length exceeded half of the simulation box length, the chains were shifted by half of a lattice constant in the \( y \) and \( z \) directions to avoid overlapping. The atoms were grown to their full size from nearly zero diameter in 47 ps during which velocity scaling was used to efficiently remove the heat produced by the process. The system was then further equilibrated for at least another 2 ns before starting the NEMD simulation. The strain rate dependent properties of the systems were calculated based on the simulation runs after the systems had reached steady state under the influence of the shear flow. This is roughly estimated to be the time for the particle at the top of the simulation cell to traverse the entire box length, about 25 ps at strain rate \( \gamma = 1 \) at density \( \gamma = 0.7728 \) g/cm\(^3\) for tetracosane and smaller for other alkanes in this study. The configuration of a neighboring higher strain rate was used as the starting configuration for the next smaller strain rate as this allows the system to reach steady state more quickly than starting from an equilibrium configuration. We have actually used a relatively large time for the system to reach the steady state at each strain rate, ranging between 100 ps for the high strain rate to 470 ps for the low strain rate.

THE SIMULATION RESULTS

A. The shear thinning and structural order

The viscosity is plotted in Fig. 1 for decane, hexadecane, and tetracosane at respective state points as a function of strain rate. These state points correspond to the experimental equilibrium density at atmospheric pressure at the respective temperatures. The figure is plotted on a log–log scale and the strain rate covers several orders of magnitude. As can be seen from the figure, the viscosity shows shear thinning behavior as a function of strain rate, typically observed in chain molecule fluid systems. At larger shear, the shear thinning follows a power law. The slope of the log–log plot varies from \(-0.33\) to \(-0.41\) for the three state points. This can be compared with the experimentally observed slopes of \(-0.4\) to \(-0.9\) for polymeric fluids. This suggests that even though the alkane chains studied here are very short in comparison to polymer systems, they nevertheless exhibit some of the generality of the long-chain systems. Another interesting aspect is that the shear viscosities for decane, hexadecane, and tetracosane at high strain rate nearly overlap each other. Intuitively, this behavior should be related to the fact that at high strain rate, these fairly short and stiff alkane chains are well aligned with each other so they can slide past each other easily. In addition, the longer chain systems align with a smaller angle in the flow direction (see below), resulting in a similar viscosity even though the chain lengths are different.

Accompanying the shear thinning behavior is the alignment of chains with the flow direction. In analogy with a liquid crystal, we have calculated the shear alignment using the order tensor defined by the second rank tensor,\(^{20}\)

\[
S = \frac{3}{2} \left( \frac{1}{N} \sum_{i=1}^{N} \left( \mathbf{e}_i \mathbf{e}_i - \frac{1}{3} \mathbf{I} \right) \right)
\]  

where \( \mathbf{e}_i \) is the unit vector along the end-to-end direction of the molecule \( i \), \( \mathbf{I} \) is a unit second rank tensor and the summation is over all \( N \) molecules in the system. The brackets indicate an ensemble average. An alternative for the definition of \( S \) is

\[
S = \left( \frac{1}{N} \sum_{i=1}^{N} \mathbf{r}_i \mathbf{r}_i \right)
\]
where $r_i$ is the end-to-end distance of molecule $i$. It is easy to see that as each term in the sums in Eqs. (7) and (8) can be averaged independently, they all give identical contribution. Thus, apart from a diagonal term in Eq. (7) and a proportionality constant, the two definitions are equivalent. In particular, both definitions should give the same eigenvectors within statistical uncertainty. The advantage of Eq. (7) is that the largest eigenvalue is precisely the liquid crystal order parameter. We have calculated the alignment angle which is defined as the angle between the flow direction and the eigenvector corresponding to the largest eigenvalue of the order tensor defined by Eq. (7). Figure 2 shows the alignment angle of decane, hexadecane (state B), and tetracosane with the flow direction. The general feature is that at low strain rate the alignment angles decreases sharply with increasing strain rate and appears to approach a low alignment angle asymptotically at high strain rate. As the length of the molecules increases, the alignment angle at the same strain rate decreases. This is consistent with the aforementioned insensitivity of the viscosity with the variation of chain length at high strain rate. The longer chain molecules slide past each other with the same viscosity as the shorter chain molecules by aligning themselves better. At the lowest strain rate studied in this work, the alignment angle reaches $45^\circ$, in agreement with the prediction of the birefringence for the extrapolation to zero strain rate to obtain the Newtonian viscosity.\textsuperscript{3} For small molecules, a square root extrapolation has often been used since the viscosity vs strain rate is well described by a functional form $\eta = \eta_0 - \eta_1 \gamma^{1/2}$, in accordance with mode-coupling theory. For fluids composed of chain molecules such as alkanes, the power law behavior of the viscosity vs strain rate indicates a qualitative difference between the dynamical behaviors of the chain molecules and simple atomic fluids, particularly at high density. The experimental evidence for polymeric liquids suggests that the viscosity vs strain rate is Newtonian at low strain rate and follows a power law shear thinning at high strain rate. Although the liquid alkanes studied in this work are much shorter than polymers, the viscosity vs strain behavior is evidently similar to that of polymeric liquids. In addition, as will be shown in the following, studies of other properties of the system, such as the order tensor, individual molecule size, and the relaxation time, all suggest that at the lowest strain rate studied in this work, the system has reached the Newtonian regime. It is therefore more appropriate to use the plateau value of the viscosity at very low strain rate for the Newtonian viscosity. Considerably larger simulation times are required to go beyond the lowest strain rate studied in this work.

To further verify the reliability of the extrapolated viscosity from the low strain rate nonequilibrium calculation, we carried out equilibrium simulation for decane at the same temperature and density as the nonequilibrium simulation. The viscosity is calculated by integrating the time correlation function of the pressure tensor using the Green–Kubo formula Eqs. (5) and (6). Figure 3 shows the result from a production run of 3161 ps. The plateau values of the viscosity from all elements and from off-diagonal elements are $0.64 \pm 0.05$ (cP) and $0.72 \pm 0.07$ (cP), respectively. We note here that the result from all the elements of the traceless symmetric pressure tensor using Eq. (6) is likely to be more accurate as it uses the six nonzero elements of the tensor, while there are only three independent off-diagonal elements. This is also seen from the better plateau behavior for the former in Fig. 3. These values are in very good agree-

**FIG. 2.** Alignment angle vs strain rate for decane, hexadecane at state B, and tetracosane. The equilibrium limit of $45^\circ$ is reached approximately at the lowest strain rate studied in this work.

**FIG. 3.** Viscosity from integration of the time correlation function of the pressure tensor using all elements and off-diagonal elements only (see text).
ment with the result from the NEMD simulation which gives a viscosity value of 0.61±0.08 (cP).

C. Rotational relaxation of an alkane molecule

It is suggested in the literature\(^3\) that the transitional strain rate between the Newtonian viscosity and non-Newtonian viscosity is roughly the inverse of the longest relaxation time of the system. Intuitively, this results from the formation of shear induced ordering in the liquid. When the shearing field exceeds the inverse of the relaxation time, the system cannot respond fast enough to the external force due to the flow field so that some degree of ordering starts to appear, resulting in reduced viscosity, i.e., shear thinning. In a previous study,\(^3\) the Rouse model was used to estimate the relaxation time. To obtain a more accurate value for the relaxation time, we have calculated the rotational relaxation time for hexadecane by studying the rotational relaxation of the end-to-end directional vector. From the rate of the exponential decay of the vector we can determine the relaxation time. Figure 4 shows this decay for hexadecane at the two state points A and B. The relaxation times thus determined for hexadecane at state points A and B are \(\tau_A = 296\) ps and \(\tau_B = 188\) ps, respectively.

The inverse of the relaxation times give 0.0034 (ps\(^{-1}\)) and 0.0053 (ps\(^{-1}\)), which are equivalent to reduced strain rates of 0.0079 and 0.0125, respectively. For decane and tetracosane, Mondello and Grest\(^8\) found the rotational relaxation time to be 58 ps and 531 ps; the inverse is thus 0.017 (ps\(^{-1}\)) and 0.0019 (ps\(^{-1}\)), respectively, corresponding to reduced strain rates of 0.041 and 0.0044. These values are significantly larger than the lowest strain rate simulated in this work for each corresponding state point. The essentially constant viscosity at low strain rate in Fig. 1 and a simple inspection of Table II and Fig. 1 suggests that the longest relaxation time (in this case, the rotational relaxation time) gives a reasonably accurate estimate for the transitional strain rate between the Newtonian and non-Newtonian viscosity.

D. The behavior of individual molecules

In Figs. 5(a)−(c), we exhibit the squared radius of gyration vs strain rate for decane, hexadecane, and tetracosane at the respective conditions. As can be seen from the figures, beginning at small strain rate, the radius of gyration first increases and then decreases with strain rate at large strain rate. We also see that for decane, the variation with strain rate is very small, reflecting the fact that the chain is very stiff for such short molecules. For hexadecane, there is a small range in strain rate when the radius of gyration reaches a maximum and stays essentially constant. Berker et al.\(^3\) saw similar behavior in their simulation of hexadecane. For tetracosane, however, this behavior of the radius of gyration has changed. These behaviors of the radius of gyration may be attributed to shear induced stretching and deformation of the chain molecules under the influence of the flow field. The analysis of Morris et al.\(^3\) provided a more detailed picture by studying the distribution of the end-to-end distance. For decane at strain rate less that 1.0, their data showed very little dependence of the end-to-end distance distribution function on the strain rate, which is consistent with our result for decane. For eicosane at strain rate less than 0.49, their data showed an increase of the maximum as well as a shift in the position of the maximum to higher strain rate. This suggests that, on the average, chains are stretched in the corre-

![Graph of rotational relaxation of end-to-end unit vector for states A and B of hexadecane.](Image)

**FIG. 4.** Rotational relaxation of the end-to-end unit vector for states A and B of hexadecane. The dashed lines are fit to the simulation results with exponentials. The characteristic times of the functions give the relaxation times \(\tau_A\) and \(\tau_B\).

<table>
<thead>
<tr>
<th>Strain rate (\gamma) (m/s(^2))</th>
<th>Viscosity (\eta) (cP)</th>
<th>Run length (ns)</th>
<th>Viscosity (\eta) (cP)</th>
<th>Run length (ns)</th>
<th>Viscosity (\eta) (cP)</th>
<th>Run length (ns)</th>
<th>Viscosity (\eta) (cP)</th>
<th>Run length (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0005</td>
<td>n-C(<em>{10})H(</em>{22})</td>
<td>1.63 (28)</td>
<td>8.15</td>
<td>1.24 (12)</td>
<td>6.58</td>
<td>2.13 (11)</td>
<td>6.60</td>
<td></td>
</tr>
<tr>
<td>0.0005</td>
<td>n-C(<em>{16})H(</em>{34})</td>
<td>1.52 (15)</td>
<td>1.92</td>
<td>1.29 (8)</td>
<td>3.57</td>
<td>1.87 (8)</td>
<td>4.25</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>n-C(<em>{10})H(</em>{22})</td>
<td>1.34 (8)</td>
<td>1.41</td>
<td>1.05 (4)</td>
<td>3.27</td>
<td>1.41 (4)</td>
<td>3.24</td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>n-C(<em>{16})H(</em>{34})</td>
<td>0.813(31)</td>
<td>0.517</td>
<td>0.751(15)</td>
<td>1.88</td>
<td>0.803(13)</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>0.09</td>
<td>n-C(<em>{24})H(</em>{60})</td>
<td>0.586(10)</td>
<td>0.635</td>
<td>0.552 (8)</td>
<td>1.88</td>
<td>0.581 (6)</td>
<td>1.79</td>
<td></td>
</tr>
<tr>
<td>0.16</td>
<td>n-C(<em>{30})H(</em>{62})</td>
<td>0.461 (7)</td>
<td>0.611</td>
<td>0.413 (5)</td>
<td>1.06</td>
<td>0.445 (6)</td>
<td>1.60</td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>n-C(<em>{40})H(</em>{82})</td>
<td>0.385 (8)</td>
<td>0.540</td>
<td>0.356 (4)</td>
<td>0.846</td>
<td>0.363 (3)</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>0.36</td>
<td>n-C(<em>{48})H(</em>{84})</td>
<td>0.334 (3)</td>
<td>0.423</td>
<td>0.311 (3)</td>
<td>0.822</td>
<td>0.313 (2)</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>0.64</td>
<td>n-C(<em>{60})H(</em>{122})</td>
<td>0.266 (4)</td>
<td>0.350</td>
<td>0.253 (2)</td>
<td>1.25</td>
<td>0.252 (2)</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>1.00</td>
<td>n-C(<em>{80})H(</em>{162})</td>
<td>0.225 (2)</td>
<td>0.400</td>
<td>0.216 (2)</td>
<td>0.681</td>
<td>0.220 (2)</td>
<td>0.75</td>
<td></td>
</tr>
</tbody>
</table>

sponding strain rate range. At higher strain rate, the reverse trend was found. Although the exact strain rate at which this reversion occurs probably depends on the chain length and even the state point, the qualitative trend is consistent with the behavior of the radius of gyration of the alkanes seen in this simulation. At low strain rate, the radius of gyration tends to the equilibrium value. For decane, the equilibrium value of $R_g^2$ is $11.27\pm0.05$ ($\text{Å}^2$), in comparison to the extrapolated value from low strain rate, $11.26$ ($\text{Å}^2$). Mondello and Grest obtained $R_g^2=11.49\pm0.02$ ($\text{Å}^2$) at equilibrium for decane. This slight difference is likely due to the slightly greater flexibility for our decane model in which a bond vibration potential is introduced. For hexadecane, the squared radii of gyration are $25.77\pm0.07$ ($\text{Å}^2$) and $25.0\pm0.08$ ($\text{Å}^2$) for the state points A and B at equilibrium, compared with the low strain rate extrapolation of $25.72$ ($\text{Å}^2$) and $25.15$ ($\text{Å}^2$). For tetracosane, the extrapolated value from low strain rate $R_g^2$ is $48.5$ ($\text{Å}^2$), which agrees within statistical uncertainty with the equilibrium value of $48.8\pm0.3$ ($\text{Å}^2$), and also with the value of $48.9\pm0.4$ ($\text{Å}$) obtained by Mondello and Grest.

E. The hydrostatic pressure

Figure 5 shows the hydrostatic pressure of decane, hexadecane, and tetracosane vs strain rate. It is seen that at low strain rate, the pressure is equal to the equilibrium pressure at zero strain rate within statistical uncertainty. At relatively high strain rate, the pressure increases nearly linearly with the strain rate. This behavior is consistent with the simulation result of Berker et al. for hexadecane but different from the results for simple atomic liquids, for which both mode coupling theory and simulations suggest that the shear dilatancy follows a 3/2 power. Because of the complexity of the chain molecules, there is no reason to expect the theory for simple atomic systems to be applicable to these systems. Recent computer simulations have produced a variety of behavior for shear dilatancy of hydrocarbon chain liquids. Clarke and Brown obtained a temperature dependent slope for hexane, Morris et al. saw a quadratic dependence for decane and eicosane fluids interacting with WCA potential. Our simulations on decane at high temperature and moderate density showed a 3/2 power law shear dilatancy behavior. For the decane, hexadecane, and tetracosane liquids studied in this work, the shear dilatancy does not show significant dependence on chain length.

At low strain rate, the hydrostatic pressure tends to the equilibrium value. This is seen by the nearly constant values of the pressure for reduced strain rate less than about 0.01 for all three alkanes studied here. For decane, the equilibrium...
pressure is 46.3±0.9 (MPa) as compared to the low strain rate asymptotic value of 47.6±0.5 (MPa). For hexadecane at state points A and B, the equilibrium pressures are 42.9±0.7 (MPa) and 39.6±0.7 (MPa), compared to the low strain rate values of 43.8±0.6 (MPa) and 40.6±0.5 (MPa). For tetradecane, the low strain rate pressure gives a value of 34.6±0.7 (MPa). The equilibrium pressures, when corrected with the long range contribution, become −3.0±0.9, −9.2±0.7 and −10.4±0.7, and −15.9±0.7 (MPa) for decane, hexadecane at state points A and B, and tetracosane, respectively. Mondello and Grest8 obtained slightly higher pressure values of −1.3±0.2 and −10.8±0.6 (MPa) for decane and tetradecane (the reason for this difference may be due to the use of a spring potential in our model in place of their rigid bond for neighboring CH groups). The effect of different pressure tensor formalisms on the viscosity is negligible as is demonstrated from our equilibrium and nonequilibrium calculation. We also note that the pressure tends to the plateau value at a fairly large strain rate, while the viscosity tends to the plateau value at a lower strain rate, and the alignment angle tends to the limiting value of 45° only at very low strain rates. This can be understood from the fact that the pressure is a time average of the pressure tensor components itself while the viscosity is obtained from the constitutive relation Eq. (2), which is thus magnified by many orders of magnitude at small strain rate. Since by definition, the alignment angle is the eigenvector corresponding to the largest eigenvalue of the order tensor, it is directly related to the structural order in the system. Consequently, the most stringent criteria for linearity is the order parameter or the alignment angle. Our results show that the linear regime has been reached for the lowest strain rate studied. We also point out that, at very low strain rate near the transition between the Newtonian and non-Newtonian behavior the viscosity is not sensitive to the variation of the strain rate.

**SUMMARY**

In conclusion, we have reported the rheological properties of decane, hexadecane, and tetracosane under planar Couette flow at dense liquid conditions. We established that the Newtonian viscosity can be reliably obtained from an extrapolation of the plateau value of the strain rate dependent viscosity at low strain rate. The transition from Newtonian to non-Newtonian viscous behavior is correlated with a number of properties of the liquid, such as the order tensor, the rotational relaxation time, and to a lesser extent the hydrostatic pressure. At high strain rate, in addition to the usual power law shear thinning behavior observed for the liquid alkanes, we also see that the viscosity is insensitive to the hydrocarbon chain lengths studied in this work.

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