A molecular dynamics study of a short-chain polyethylene melt.  
I. Steady-state shear

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Abstract

Utilizing a united atom potential model and reversible reference system propagator algorithm (rRESPA) multistep dynamics, we have performed equilibrium and nonequilibrium molecular dynamics simulations of a monodisperse C\(_{100}\)H\(_{202}\) polyethylene melt at 448 K and 0.75 g/cm\(^3\). We report a variety of properties calculated at equilibrium including rotational relaxation time and self-diffusion coefficient as well as shear-enhanced diffusion and rheological properties calculated under steady-state shearing conditions. Shear thinning is observed in the viscosity and normal stress coefficients over the range of strain rates studied. A minimum in the hydrostatic pressure is observed at an intermediate strain rate that is associated with a minimum in the intermolecular Lennard–Jones potential energy as well as transitions in the strain-rate-dependent behavior of several other viscous and structural properties of the system. The shear field also imposes significant alignment of the chains with the flow direction, approaching a limiting angle of approximately 3\(^\circ\) at high strain rate. In addition, the self-diffusion coefficients (calculated in terms of the unconnected positions according to the Cummings–Wang formalism) are markedly enhanced under shear compared to the equilibrium state (up to two orders of magnitude at the highest shear rate studied).

Keywords: Polyethylene; Nonequilibrium molecular dynamics; Shear-enhanced diffusion

1. Introduction

Molecular simulation has benefited enormously from the continued growth in speed of computer processors as well as their integration into massively parallel supercomputers. As the effective speeds of

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processors have increased, the size and complexity of the computational problems they can be used to solve have increased dramatically. During the past two decades, the liquid alkanes of small to intermediate molecular size have been studied extensively by molecular simulation using potential models of increasing complexity and realism. Use of the nonequilibrium molecular dynamics (NEMD) simulation technique [1,2] has allowed investigation of the strain-rate dependent rheology of these alkane systems. At the high shear strain rates accessible to simulation, the liquid alkanes have shown certain rheological behaviors characteristic of polymer systems, including shear thinning (e.g. [3]) and non-zero normal stress differences (e.g. [4,5]). Though thermal noise in small simulation systems (typically ≤100 molecules) has limited the studies to high strain rates (γ ≥10^8 s⁻¹), such conditions are commonly experienced by lubricants in engines and other machinery (γ >10^7 s⁻¹ [6]) and are beyond the range of strain rates that can be studied experimentally. In addition, the transition from Newtonian to non-Newtonian behavior is observable by simulation for these liquid alkanes within the range of strain rates accessible in these computational studies.

Polymeric systems have also frequently been studied by molecular simulation. Due in part to the extreme computational expense involved in simulating molecules of polymeric length, these studies have usually been limited to very small system sizes, short time-scales, simplified polymer models, and/or coarse-grained simulation techniques. Recently, attention has been focused on performing equilibrium molecular dynamics (EMD) simulations of relatively long chain alkanes (e.g. C_{100}H_{202}) using the same types of realistic united atom [7–9] and explicit atom [10] potential models that have been used extensively to study short-chain liquid alkanes. In the first case, united atom models, each carbon and its bonded hydrogens are collapsed into a single interaction site. In the second case, each atom is modeled explicitly. Harmandaris et al. [9] performed EMD of polydisperse linear polyethylene melts of mean molecular lengths C_{78} and C_{156}. Paul et al. [11] found quantitative agreement between simulation and experiment for the dynamic structure factor of C_{100} after correcting for a 20% difference in the self-diffusion coefficient. At a single strain rate expected to fall within the Newtonian regime, Mondello and coworkers [12] used NEMD to calculate the viscosity of C_{66}H_{134} and found excellent agreement with predictions of the Newtonian viscosity based on a combination of equilibrium properties and the Rouse model. Prior to the present work, the calculation of Mondello et al. represented the longest alkane chain to which NEMD had been applied using a realistic united atom model. Our interest is in gaining a molecular-level understanding of the rheology of alkane liquids and polymers using molecular models that preserve as much as possible of the details of the intermolecular interactions and intramolecular architecture. The feasibility of EMD calculations on C_{100}H_{202} led us to perform NEMD simulations of a C_{100}H_{202} melt.

2. Background

2.1. Molecular model

The potential model used for polyethylene is essentially the same as the united atom model for alkanes proposed by Siepmann et al. [7] (SKS), with the modification that the fixed bond length is replaced by a stiff harmonic bond-stretching potential. In this model, the methyl and methylene groups are treated as spherical interaction sites with interaction centers located at the centers of the carbon atoms. The interaction between sites on different molecules and between sites separated by more than three bonds
on the same molecule is described by the well-known Lennard–Jones (LJ) potential

\[ u_{ij}(r) = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r} \right)^{12} - \left( \frac{\sigma_{ij}}{r} \right)^{6} \right]. \]  

(1)

A cut-off distance of 2.5\(\sigma_{\text{CH}_2}\) (9.825 Å), where \(\sigma_{\text{CH}_2}\) is the LJ size parameter of the CH\(_2\) united atom, was used. The Lorenz–Berthelot combining rules \([\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}, \sigma_{ij} = (\sigma_i + \sigma_j)/2]\) were used for the unlike interactions. Siepmann and coworkers fit the value of \(\epsilon_{\text{CH}_2}\) to yield the correct increase in critical temperature for \(n\)-alkanes containing 8–16 carbons and then adjusted \(\epsilon_{\text{CH}_3}\) to achieve the best absolute values of the critical temperatures of the same alkanes [13]. The intramolecular interactions include a bond-stretching term, a bond-bending term, and a torsional term characterizing the preferred orientation and rotational barriers around all non-terminal bonds. The bond stretching is described by a harmonic potential of the form

\[ V_s(r) = -\frac{k_s}{2} (r - r_{eq})^2, \]  

(2)

with an equilibrium bond length of \(r_{eq} = 1.54\) Å and a force constant \(k_s/k_B = 452,900\) K/Å\(^2\) [14] where \(k_B\) is Boltzmann’s constant. The bond-angle bending is governed by a harmonic potential of the form

\[ V_b(\theta) = -\frac{k_b}{2} (\theta - \theta_b)^2, \]  

(3)

with the force constant \(k_b/k_B = 62,500\) K/rad\(^2\) and equilibrium bond angle \(\theta_b = 114^\circ\) [15]. The torsional potential is of the form

\[ V_t(\phi) = \sum a_i [\cos(\phi)]^i \]  

(4)

and was developed by Jorgensen [16]. The potential parameters are summarized in Table 1.

<table>
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<th>Potential Model Parameters</th>
<th>Value</th>
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2.2. Simulation methodology

The equations of motion used to generate a homogeneous boundary driven planar Couette flow are the SLLOD equations [1] (incorporating a Nosé thermostat),

\[ \dot{r}_{ia} = \frac{\tilde{p}_{ia}}{m_{ia}} + \gamma y_{ia} \hat{x}, \]

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

\[ \dot{\xi} = \frac{p_{\xi}}{Q}, \]

\[ \dot{p}_{\xi} = F_{\xi}, \]

where \( r_{ia}, \tilde{F}_{ia}, \) and \( \tilde{p}_{ia} \) are the coordinates of, force on, and momentum of atom \( a \) in molecule \( i \), \( y_{ia} \) and \( p_{y,ia} \) are its \( y \)-components, and \( m_{ia} \) is the mass. The strain rate of the imposed shear field is denoted \( \gamma \), \( \hat{x} \) is a unit vector in the \( x \)-direction, \( \xi, p_{\xi}, \) and \( Q \) are the variables related to the Nosé thermostat:

\[ F_{\xi} = \sum_{i,a} \frac{\tilde{p}_{ia}^2}{m_{ia}} - 3Nk_B T, \]

\[ Q = 3Nk_B T \tau^2, \]

where \( \tau \) is the Nosé thermostat time constant, \( T \) is the absolute temperature, and \( N \) is the total number of atoms in the system. The equations of motion for the EMD case are obtained by setting \( \gamma = 0 \) in the equations above. The equations of motion were integrated using the reversible reference system propagator algorithm (rRESPA) multiple time step technique, the details of which can be found in the works of Tuckerman et al. [17] and Cui et al. [18]. All of the intramolecular interactions were treated as fast motions (smaller time step of 0.47 fs) and the intermolecular interaction as the slow motion (larger time step of 2.35 fs).

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

\[ \eta = -\frac{\langle \sigma_{xy} \rangle}{\dot{\gamma}}, \]

where \( \langle \sigma_{xy} \rangle \) is the average of the \( xy \)-component of the pressure tensor \( P \) and \( \dot{\gamma} \) is the strain rate characterizing the shear field. We have chosen the \( x \)-direction to be the flow direction and the \( y \)-direction to be the flow gradient direction, so \( \dot{\gamma} = \partial u_x / \partial y \) where \( u_x \) is the streaming velocity in the \( x \)-direction. The first and second normal stress coefficients are calculated according to the equations

\[ \Psi_1 = -\frac{\langle \sigma_{xx} \rangle - \langle \sigma_{yy} \rangle}{\dot{\gamma}^2}, \]

\[ \Psi_2 = -\frac{\langle \sigma_{yy} \rangle - \langle \sigma_{zz} \rangle}{\dot{\gamma}^2}. \]
Since the streaming velocity is applied to the atomic sites in our NEMD simulation, we calculate the pressure tensor \( P \) according to the atomic formalism (expressions for and discussions of the atomic and molecular formalisms can be found in [19], for example).

2.3. Self-diffusion in a Couette strain field

Molecular simulation calculations of self-diffusion coefficients under equilibrium conditions are usually performed either in terms of mean squared displacements and the Einstein relation or velocity autocorrelation functions and the Green–Kubo relation. When the former method is employed for chain systems, the self-diffusion coefficient is calculated in terms of the limiting slope of the mean squared displacement (MSD) of the chain centers of mass as a function of time based on the Einstein relation

\[
2t \, D = \frac{1}{2} \langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle,
\]

where \( D \) is the self-diffusion coefficient and \( \vec{r}_i \) is the position of the center of mass of molecule \( i \). The notation \( \langle \cdots \rangle \) is indicative of the fact that the MSD is averaged over all the molecules in the system as well as many different time origins and corresponding initial positions \( \vec{r}_i(0) \). For the case of diffusion in a flow field, this approach is inadequate since both diffusion and convection will affect the MSD. Previously, Cummings et al. [20] derived Einstein and Green-kubo relations for self-diffusion in a Couette strain field. They introduced the quantity \( \vec{q}_i(t) \) defined by

\[
\frac{d\vec{q}_i}{dt} = \frac{\vec{p}_i}{m}, \quad \vec{q}_i(0) = \vec{r}_i(0),
\]

where, physically, the vector \( \vec{q}_i \) describes the unconvected position of molecule \( i \). The \( y \) and \( z \) components of \( \vec{q}_i \) are the same as the \( y \) and \( z \) components of \( \vec{r}_i \), but the \( x \) components differ by the integrated streaming velocity. Cummings et al. derived the following Einstein relations:

\[
\langle \Delta q_x^2(t) \rangle = 2D_{xx}t,
\]

\[
\langle \Delta y^2(t) \rangle = 2D_{yy}t,
\]

\[
\langle \Delta z^2(t) \rangle = 2D_{zz}t,
\]

\[
\langle \Delta q_x(t) \Delta y(t) \rangle = (D_{xy} + D_{yx})t.
\]

Cummings and coworkers studied the LJ fluid at its triple point and observed substantial shear-enhanced diffusion in all three directions [20]. Several additional simulation studies of self-diffusion in atomic fluids under flow have been performed [21–23]. Malandro and Lacks [24] observed that shear strains cause the disappearance of local minima of the potential energy surface of the LJ fluid at its triple point, leading to mechanical instabilities and associated atomic displacements which gave rise to shear-enhanced self-diffusion. They observed the enhancement to decrease with increasing temperature and strain rate.

Implementing the formalism developed by Cummings and coworkers, in our case for chain molecules, we considered two options: (1) integrate Eq. (15) for each atom individually and determine the center-of-mass positions and MSDs of each chain from the individual values of \( q_x, y, \) and \( z \) of its constituent atoms and (2) integrate Eq. (15) only for the center-of-mass of each chain, not each individual atom. Although in retrospect Method 2 seems preferable, our initial calculations were performed using Method 1. Later, we performed tests at a couple representative states to confirm that the results obtained were independent
of the choice of Method 1 or 2 within statistical error. In practical terms, calculation of the self-diffusion coefficients in a Couette strain field via the Einstein relations only adds one additional equation of motion (for $q_x$) which must be integrated. We chose to employ a fourth order predictor–corrector to integrate the equation for $q_x$, effectively using the multiple timestep algorithm used to integrate the SLLOD equations as a ‘black box’ to provide the peculiar momenta necessary in Eq. (15).

3. Results and discussion

The simulations involved either 200 (EMD) or 400 (NEMD) C$_{100}$H$_{202}$ molecules (i.e. 20 000 or 40 000 united atoms) at a temperature of 448 K and $\rho=0.75$ g/cm$^3$, estimated from the data in Pearson et al. [25]. The 200-molecule simulations involved a cubic simulation box with a box-length of 85.3 Å. This is approximately twice the average equilibrium chain end-to-end distance but is less than the distance spanned by a fully extended chain ($\sim$129 Å). Since the high rates of shear applied in this study induce significant chain alignment and extended chain configurations in the flow direction, the 400-molecule system used for NEMD involved a box 85.3 Å in the $y$- and $z$-directions but 170.6 Å in the $x$-direction (i.e. the flow direction). Average system properties such as hydrostatic pressure and potential energies per molecule were in agreement for the two system sizes. The initial 200-molecule configuration was generated by placing the chains in the simulation cell and assigning LJ size parameters that were only approximately 20% of their normal values. The size parameters were gradually increased to full size (i.e. excluded volume was gradually turned on) during the course of a 70 ps simulation in order to provide more rapid equilibration. The system was then equilibrated for 7 ns. Subsequent to equilibration, we accumulated the equilibrium properties of the system over a period of 5.6 ns as well as the nonequilibrium properties at shear rates ranging from $\dot{\gamma}=1.5 \times 10^8$ to $4.3 \times 10^{11}$ s$^{-1}$ (reduced shear rates $\dot{\gamma}^*=\gamma^*(\sigma^2/\epsilon)^{1/2}$ of 0.00036–1.0). At these shear rates, we do not expect the results to depend significantly on the details of the thermostat [26,27]. The initial 400-molecule configuration was generated by simply replicating the equilibrated 200-molecule configuration in the $x$-direction prior to performing additional equilibration.

3.1. Equilibrium properties

Though our primary interests lie in the area of rheology, several equilibrium properties are of interest as well, including the average chain dimension, the self-diffusion coefficient, and rotational relaxation time. The average chain dimension and diffusion coefficient are important because they help us gauge the agreement or lack thereof between properties predicted by the potential model and corresponding properties measured by experiment. The rotational relaxation time is important because it aids in analyzing viscosity versus strain rate data. Finally, all three of the properties can be used in conjunction with results from the Rouse model of unentangled polymer melts to predict the zero-shear viscosity [12].

For a linear Gaussian chain, its squared radius of gyration ($R_g^2$) is related to its squared end-to-end distance ($R_{ee}^2$) by the relation $R_g^2 = R_{ee}^2/6$. Based on averages accumulated during the course of the EMD run whose average pressure (no long-range corrections) was 23.7 MPa, we measured for our C$_{100}$H$_{202}$ system $R_g^2=300.5\pm0.2$ Å$^2$ and $R_{ee}^2=1776\pm2$ Å$^2$ which corresponds to $R_g^2 = R_{ee}^2/5.9$. This is closer to Gaussian-chain behavior than has been observed previously for a C$_{100}$ melt [28] as well as melts of shorter alkanes [8,12,29].
Using the MSD of the chain centers of mass, we estimated the self-diffusion coefficient of the C\textsubscript{100}H\textsubscript{202} chains under equilibrium conditions to be \(1.85 \times 10^{-6}\) cm\(^2\)/s, approximately twice the experimental value as estimated from the correlation \(D=1.65/M_w^{1.98}\) cm\(^2\)/s based on experimental measurements [25]. If we were to take the C\textsubscript{90} experimental data [25] and use the Rouse model to correct for molecular weight difference, as did Paul et al. [28] and Harmandaris et al. [9], the estimated experimental value for C\textsubscript{100} at 448 K would be \(1.26 \times 10^{-6}\) cm\(^2\)/s. This is somewhat closer to the \(D\) determined by EMD. However, the EMD result still represents an overprediction by nearly 50%, consistent with the model’s performance for shorter molecules (e.g. C\textsubscript{24}, C\textsubscript{30} and C\textsubscript{44} [12]).

We have also attempted to analyze the global rotational motion of the molecules as characterized by the orientational relaxation of the longest principal axis of each molecule’s ellipsoid of inertia. Ignoring the short-time behavior, the first-order angular correlation function exhibits exponential decay with a characteristic relaxation time of \(\tau=3.3\) ns. The time allowed for equilibration (7 ns) is approximately twice the rotational relaxation time (\(\tau\)), indicating that the equilibration time was probably sufficient but at the lower end of the range of times that would be considered acceptable. Interestingly, \(\tau\) for C\textsubscript{100} is 100 times larger than the value calculated for C\textsubscript{10} at the same temperature but somewhat higher density (\(\rho=0.766\) g/cm\(^3\)) [12], consistent with \(\tau\) scaling at least approximately as the square of the number of carbons as predicted by the Rouse model [30].

Mondello and coworkers [12,31] have compared the various estimates of the zero-shear viscosity based on the Rouse model and properties from EMD simulations to the viscosity calculated by NEMD at a strain rate less than \(\tau^{-1}\) (the expected transition from Newtonian to shear thinning behavior [3,4]) for alkanes ranging from C\textsubscript{10} to C\textsubscript{66}. They found that that the zero-shear viscosity predicted from the Rouse model and \(\tau\) was in good agreement with the NEMD results (within 20%) for all of the systems studied. Making this same calculation for our C\textsubscript{100} system, the predicted zero-shear viscosity is 5.4 cP. This value will be referred to as \(\eta_1\) in the next section. The correlation due to Pearson et al. [25] \(\eta=2.1 \times 10^{-5} M_w^{1.8}\) cP (\(M<5000\)) yields a zero-shear viscosity for C\textsubscript{100} of \(\eta=9.7\) cP, approximately twice the value predicted by simulation. In most cases, our experience has been that the SKS model yields viscosity predictions [32,33] that underestimate the experimental values [34] by 30–50%. One notable exception is the branched C\textsubscript{30} molecule squalane for which viscosities predicted at two temperatures (using the SKS model as extended to branched alkanes by Mondello and Grest [29]) were in quantitative agreement with experiment [35]. Even a 50% underestimate of the viscosity is a fairly remarkable prediction since the model was fit to completely different physical properties (vapor–liquid equilibria of much shorter chains). Also, the model seems to do a good job of characterizing the variation of viscosity with temperature [33,35]. Our results suggest that the model’s performance is equally good for C\textsubscript{100}, a molecule an order of magnitude larger than the molecules that were used to parameterize the potential.

### 3.2. Viscometric properties

In Fig. 1 shear viscosity is plotted versus strain rate for C\textsubscript{100}H\textsubscript{202}. The viscosities are averaged over simulation runs with durations (neglecting the time required to reach steady state) ranging from 0.25 ns at the highest strain rate to 2.8 ns at the lowest strain rate. The horizontal dashed line is the predicted zero-shear viscosity (\(\eta_1\), mentioned previously, based on the EMD results and the Rouse model. The vertical dot-dashed line is the inverse of the rotational relaxation time. Shear thinning is observed over the entire range of strain rates with average power law exponents of \(-0.61\) at the lower strain rates and \(-0.35\) at the higher. The weaker shear thinning at higher strain rate may be the precursor of a
Fig. 1. Viscosity vs. strain rate for C\textsubscript{100}H\textsubscript{202} at 448 K and 0.75 g/cm\textsuperscript{3}. The horizontal dashed line is the predicted zero-shear viscosity based on EMD and the Rouse model, and the vertical dot-dashed line is the inverse of the rotational relaxation time. Two power-law regions are observed with a transition between the two occurring at $\dot{\gamma} \approx 1.7 \times 10^{10}$ s\textsuperscript{-1}.

second Newtonian regime. However, we chose not to attempt any simulations at higher strain rates because of concerns about possible artifacts due to the thermostat at higher strain rates (e.g. $\dot{\gamma}^* \geq 4$) [26,27]. For polymeric liquids, power law exponents are generally reported in the range $-0.4$ to $-0.9$ [36].

No judgment can yet be made regarding the observation (or lack thereof) of the Newtonian plateau for C\textsubscript{100}H\textsubscript{202} at strain rates less than the inverse of the rotational relaxation time. The 2.8 ns run at the lowest strain rate, though quite lengthy in terms of the required computational resources, is of insufficient length to draw any conclusions. Our experience for shorter alkane chains [33] is that runs of up to an order of magnitude longer are required to achieve good estimates of the viscosity at such low strain rates. The error bar, estimated from the scatter in the block averages during the course of the simulation, is likely to be an underestimate of the true uncertainty in the simulation for such a relatively short run at such a low strain rate. At this time, we have chosen not to devote the large computational resources necessary to continue this low strain rate run to a more satisfactory duration. In summary, we are confident of our results for all but the smallest strain rate and view our result at that strain rate as preliminary.

The first and second normal stress coefficients are plotted versus shear rate in Fig. 2, and their ratio is plotted in Fig. 3. Both coefficients exhibit shear thinning with a power law exponent of approximately $-1.4$. The Doi–Edwards (DE) model for entangled polymers predicts $\Psi_1(\dot{\gamma}) \propto \dot{\gamma}^{-2}$ and $\Psi_2(\dot{\gamma}) \propto \dot{\gamma}^{-2.5}$ as $\dot{\gamma} \to \infty$ [37]. At the highest strain rate ($\dot{\gamma} = 4.3 \times 10^{11}$ s\textsuperscript{-1}), $-\Psi_2/\Psi_1 = 2/7$, the value predicted by the DE model (with ‘independent alignment,’ an approximation made for mathematical convenience) in the limit of low strain rates [37]. As strain rate decreases from $\dot{\gamma} = 4.3 \times 10^{11}$ s\textsuperscript{-1}, $-\Psi_2/\Psi_1$ also decreases before reaching a value of approximately 0.19, apparently independent of strain rate from $3.83 \times 10^{10}$ to $4.3 \times 10^{8}$ s\textsuperscript{-1}. The value of $-\Psi_2/\Psi_1$ is much higher at the lowest strain rate, but that simulation run is too
short to influence any conclusions. The first normal stress difference \((\sigma_{xx} - \sigma_{yy})\) is plotted versus shear stress in Fig. 4. Two regimes are evident: \(\sigma_{xx} - \sigma_{yy} \propto \sigma_{xy}^{1.6}\) for \(\dot{\gamma} \leq 4.3 \times 10^{9} \text{ s}^{-1}\) and \(\sigma_{xx} - \sigma_{yy} \propto \sigma_{xy}^{0.89}\) for \(\dot{\gamma} \leq 1.7 \times 10^{10} \text{ s}^{-1}\). The value of 1.6 is consistent with the experimental measurements made on various multigrade oils by Williamson et al. [38].

Fig. 2. First and second normal stress coefficients vs. shear rate for C_{100}H_{202} at 448 K and 0.75 g/cm³.

Fig. 3. Ratio of second to first normal stress differences vs. shear rate for C_{100}H_{202} at 448 K and 0.75 g/cm³.
3.3. Average chain dimensions and shear-induced alignment

Molecular configurations and alignment for C_{100}H_{202} show significant dependence on strain-rate at the shear rates covered in this study. The average squared radius of gyration is plotted versus strain rate in Fig. 5. At the lowest strain rates, $R_g^2$ approaches its equilibrium value. As strain rate increases, the shear field deforms the chain configurations and elongates the chain molecules. At the highest strain rates, $R_g^2$ becomes independent of strain rate and takes on a value approximately 1.67 times larger than the equilibrium one.

One measure of the structural order in the system is the order tensor, which is defined as [39,40]

$$S = \frac{3}{2} \left( \frac{1}{N} \sum_{i=1}^{N} (e_i e_i - \frac{1}{3} I) \right),$$

where $e_i$ is the unit vector along the end-to-end direction of the molecule $i$, $I$ is a second-rank tensor with a value of 0 for the off-diagonal elements and a value of 1 for the diagonal elements, and the summation is over all $N$ molecules in the system. The angle braces indicate an ensemble average. The eigenvector corresponding to the largest eigenvalue (the order parameter) of the order tensor gives the preferential orientation of the molecules relative to the flow field. Though the linear-regime value of the alignment angle is 45°, Fig. 6 reveals significant shear-induced alignment even at the lowest strain rate. Based on NEMD studies of shorter alkane chains, Cui et al. [3] associated the sharp decrease from 45° of the alignment angle with the transition from Newtonian to shear-thinning behavior. The departure from 45° even at the lowest strain rate suggests that the system may not have reached steady state or that it may be beyond the Newtonian regime even at this strain rate. At high rates of strain, the alignment
angle approaches a limiting value of approximately 3°, almost complete alignment with the flow field. Simulations of \( n-C_{30}H_{62} \) at 372 K revealed a limiting value of 6.8° [33]. Indeed, the high shear rate limit of the alignment angle tends to decrease with increasing chain backbone length for linear and branched alkanes [3,33].
3.4. Hydrostatic pressure and potential energy

In Fig. 7 the hydrostatic pressure (no long-range corrections) is plotted versus strain rate. At low strain rates, the pressure approaches the equilibrium value. At high strain rates, shear dilatancy is observed with $P \propto \dot{\gamma}^{0.9}$. In the range $1.7 \times 10^{10} \text{s}^{-1} < \dot{\gamma} < 3.8 \times 10^{10} \text{s}^{-1}$, a minimum in hydrostatic pressure is observed. This pressure minimum has also been observed in simulations of $n$-C$_{28}$H$_{58}$ [5] and $n$-C$_{30}$H$_{62}$ [33], but not for branched alkanes. The intermolecular LJ potential energy also exhibits a minimum at $\dot{\gamma} \approx 3.8 \times 10^{10} \text{s}^{-1}$ (see Fig. 8), as does the torsional potential energy. These observations can be understood in terms of two competing phenomena: the ordering induced by the shear field (tending to lower the energy) and the effect of the high rates of shear that causes more frequent and stronger collisions and keeps chains out of the minimum energy states. The former effect dominates at lower strain rates and the latter at higher strain rates, leading to the occurrence of minima in the pressure and energy as a function of strain rate. In fact, Figs. 1, 3-8 all show transitional behavior occurring in the range $1.7 \times 10^{10} \text{s}^{-1} < \dot{\gamma} < 3.8 \times 10^{10} \text{s}^{-1}$. This is where the viscosity’s power law exponent changes from $-0.61$ to $-0.35$ (Fig. 1), where the ratio $-\Psi_2/\Psi_1$ becomes $\dot{\gamma}$-dependent with increasing $\dot{\gamma}$ (Fig. 3), where the power law exponent for the dependence on the shear stress of the first normal stress difference changes from 1.6 to 0.89 (Fig. 4), where $R^2$ and the alignment angle reach their high-$\dot{\gamma}$ limits (Figs. 5 and 6), and where the pressure and intermolecular LJ potential energy exhibit minima (Figs. 7 and 8). The range of strain rates at which these transitions occur may simply be related to the attainment of the maximum shear-induced alignment. Alternatively, it may be associated with the shear rate exceeding the timescale of local chain dynamics (such as the rates of torsional transitions, correlated torsional transitions, or bond vector autocorrelation) which would be expected to occur roughly in the range $10^{-9}$ to $10^{-11} \text{s}^{-1}$ [10,28,41,42].

Fig. 7. Hydrostatic pressure vs. shear rate for C$_{100}$H$_{202}$ at 448 K and 0.75 g/cm$^3$. 
3.5. Shear-enhanced self-diffusion

Using the Cummings–Wang formalism, the basic details of which were described in the section on simulation methodology, we have calculated the diagonal elements of the self-diffusion tensor for \( n-C_{100}H_{202} \) in the Couette shear field. In Fig. 9, the MSDs at \( \dot{\gamma} = 1.53 \times 10^{11} \text{ s}^{-1} \) are plotted. Averages were taken over
Table 2
Diffusion coefficients of C\textsubscript{100}H\textsubscript{202} under planar Couette flow at 448 K and 0.75 g/cm\textsuperscript{3}

<table>
<thead>
<tr>
<th>Strain rate (s\textsuperscript{-1})</th>
<th>Reduced strain rate\textsuperscript{a}</th>
<th>Number of time origins</th>
<th>$D_{xx}$\textsuperscript{b}</th>
<th>$D_{yy}$\textsuperscript{b}</th>
<th>$D_{zz}$\textsuperscript{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.06×10\textsuperscript{9}</td>
<td>0.0025</td>
<td>100</td>
<td>4.94</td>
<td>–</td>
<td>–</td>
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<tr>
<td>2.13×10\textsuperscript{9}</td>
<td>0.005</td>
<td>163</td>
<td>5.27</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>4.25×10\textsuperscript{9}</td>
<td>0.01</td>
<td>95</td>
<td>9.28</td>
<td>1.48</td>
<td>1.44</td>
</tr>
<tr>
<td>3.83×10\textsuperscript{10}</td>
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<td>185</td>
<td>47.0</td>
<td>2.39</td>
<td>7.18</td>
</tr>
<tr>
<td>1.53×10\textsuperscript{11}</td>
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<td>151</td>
<td>5.47</td>
<td>13.8</td>
</tr>
<tr>
<td>2.27×10\textsuperscript{11}</td>
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<td>75</td>
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<td>6.35</td>
<td>30.6</td>
</tr>
</tbody>
</table>

\textsuperscript{a} $\dot{\gamma}(m\sigma^2/\rho)^{1/2}$.
\textsuperscript{b} 10\textsuperscript{-6} cm\textsuperscript{2}/s.

The 400 molecules in the simulation and multiple time origins, each separated from the next by 2.35 ps. From the long-time limit of these curves, the diffusion coefficients are calculated using the Einstein relations. The behavior seen in Fig. 9 is typical of that observed for $\dot{\gamma}>4.25×10^9$ s\textsuperscript{-1}: $D_{xx} \gg D_{zz} > D_{yy}$. Over this range of $\dot{\gamma}$, $D_{xx} \propto \dot{\gamma}$. At $\dot{\gamma}=4.25×10^9$ s\textsuperscript{-1}, $D_{zz} \approx D_{yy} \approx D$ (where $D$ is the equilibrium self-diffusion coefficient). For smaller strain rates, the simulations were not run long enough to generate MSDs in the $y$ and $z$ directions of sufficient magnitude to have confidence in the calculated values and $D_{yy}$ and $D_{zz}$ (though $D_{yy}=1.77$ and $D_{zz}=1.70$ calculated at $\dot{\gamma}=1.06×10^9$ are certainly in agreement with the equilibrium value $D=1.8$). The calculated diffusion coefficients are compiled in Table 2 and plotted in Fig. 10. At the highest strain rate, $D_{xx}$ is an order of magnitude larger than $D_{zz}$ and two orders of magnitude larger.

Fig. 10. Diffusion coefficients vs. shear rate for C\textsubscript{100}H\textsubscript{202} at 448 K and 0.75 g/cm\textsuperscript{3}. Methods 1 and 2, which are defined in the text, refer to the details of the application of the Cummings–Wang formalism.
than $D_{yy}$ and $D$. This shear-enhancement of diffusion for C$_{100}$H$_{202}$ is much larger than the factor of 2 enhancement observed previously for the LJ fluid at its triple point [20]. In addition, for the LJ system, the observed trend was $D_{xx} > D_{yy} > D_{zz}$ with all three of similar magnitude. At the lowest strain rate at which diffusion was studied for C$_{100}$H$_{202}$, $D_{xx}$ was still approximately 2.5 times larger than $D$. The values of $D_{xx}$ in Table 2 were calculated using Method 1 (as described in the section on simulation methodology). Also plotted in Fig. 10 are calculations at two representative strain rates which were performed using Method 2, confirming our expectation the resulting diffusion coefficients would be insensitive to the choice of Method 1 versus Method 2.

4. Conclusions

We have described results for a variety of properties calculated by molecular dynamics simulation at equilibrium and under steady-state shear for C$_{100}$H$_{202}$ using a united atom model for alkanes. Shear thinning is observed in the viscosity and normal stress coefficients over the range of strain rates studied. A minimum in the hydrostatic pressure is observed at an intermediate strain rate that is associated with a minimum in the intermolecular LJ potential energy as well as transitions in the strain-rate-dependent behavior of several other viscous and structural properties of the system. In addition, the self-diffusion coefficients are markedly enhanced under shear compared to the equilibrium state (up to two orders of magnitude at the highest shear rate studied).

Though the extremely large magnitude of the shear-enhancement of self-diffusion was somewhat surprising to the authors, in retrospect, significant enhancement in $x$-direction should not have been unexpected. Since at high $\dot{\gamma}$ the chains are almost completely aligned with the flow direction ($x$-direction), the chains move more easily along their own backbones (essentially in the $x$-direction) than in either the velocity-gradient or neutral directions (though the enhancement in the neutral direction relative to the velocity-gradient direction is not as easily rationalized). Snakelike diffusive motion along the contour of a chain’s backbone in an entangled polymer melt is called ‘reptation’ [43] and is the basis of the DE model of entangled polymers [30]. As will be discussed in the second paper in this series, the C$_{100}$H$_{202}$ melt (though too short to be entangled) exhibits transient behavior upon onset of shear that is strikingly similar to predictions from the DE model. In addition, the diffusion results presented here may have important implications for the current effort in the rheological community to improve the state of the art in the theoretical treatment of polymer melts undergoing fast flows.

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