Shear behavior of squalane and tetracosane under extreme confinement. II. Confined film structure

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This paper focuses on the structural characteristics of confined squalane and tetracosane under shear flow conditions. Nonequilibrium molecular dynamics simulation is used to explore the rheology of these model lubricants. A preceding paper describes the molecular model and the simulation method, and examines interfacial slip. The lubricants are confined between model walls that have short chains tethered to them, thus screening the wall details. In this paper we examine the density profiles and chain conformations of the alkanes under shear flow conditions. Our results indicate a profound influence of the walls on the fluid structure. In particular, when the wall spacing is close to an integral multiple of the molecular diameter, tetracosane shows the formation of distinct layers with the molecules being in a fully extended state. This behavior is not observed for squalane. Under shear flow conditions the molecules tend to orient parallel to the walls, as would be expected, with a greater degree of orientation (a) close to the walls, (b) at the positions of local density maxima, and (c) at higher strain rates. © 1997 American Institute of Physics.
reduced with $\sigma_{\text{CH}_2} = 3.93 \, \text{Å}$, energy with $E_{\text{CH}_2}/k = 47 \, \text{K}$ and the mass with $m_{\text{CH}_2} = 14 \, \text{amu}$) unless otherwise stated. In the following discussion, temperature of the wall ($T_{\text{wall}}$) is taken to mean the temperature at which the first two atoms of the tethered chains are thermostatted, which is 300 K unless otherwise stated. The temperature of the fluid is referred to as $T_{\text{fluid}}$, and is found to be nearly constant across the width as shown in the third paper of this series. 11

**A. Density profiles**

An important structural characteristic of confined fluids is a wall-induced layering parallel to the walls. This layering is induced by the monomer pair correlation function $g(r)$ and the sharp cutoff in fluid density at the wall. We begin our analysis by examining the density profiles for squalane, which are normalized by the average site density in the center. When the walls are placed far apart, the influence of the walls on the degree of order in the center is expected to be minimal. Figure 1 depicts the site density profiles for two systems that differ in the wall spacing. As expected, the molecules tend to organize in strata parallel to the wall, with the degree of order diminishing with distance from the wall (as can be seen in Figure 16 to be presented later). For the wider wall spacing ($w = 15.06$) there is a semblance of a bulk-like homogeneous fluid region in the center of the film. As the wall spacing is decreased, the central peak in the density profile becomes well-defined and the bulk-like region no longer exists. This latter behavior is depicted in Figure 1 for a wall spacing $w = 9.25$ and the same wall velocity as for the wider wall spacing; note that five distinct layers of the fluid are observed. In each case, close to the boundaries, the liquid density is vanishingly low because molecules are excluded from this region by repulsion between the tethered chains and the fluid molecules, but the local density is correspondingly large at a distance of about one diameter removed. To obtain more information on the location of particular sites, we examine the respective site density profiles. Figure 2 compares the densities of the middle (atom numbers 15 and 16) and end groups (atom numbers 1 and 24) for $w = 9.25$. As is the case for other state points, there is no evidence to suggest a tendency for either group to dominate in a particular region.

We also find that at a given wall spacing the density profiles for the range of wall velocities examined are not very different from one another (see Figure 3). This observation has been previously reported12,13 where the authors note that the density profiles under shear and at equilibrium are identical. This observation indicates that in spite of the large velocities, the wall has a strong effect on the resulting fluid structure. Evidence of this striking wall effect is further provided in Figure 4, which compares the density profiles for squalane at three wall spacings that differ by $<1.0 \sigma$ (the

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**FIG. 1.** The site density profiles for squalane; solid line: $w = 15.06$, $v_{\text{wall}} = 0.5$, $T_{\text{fluid}} = 491 \, \text{K}$, $P_{\text{yy}} = 210$; dashed line: $w = 9.25$, $v_{\text{wall}} = 0.5$, $T_{\text{fluid}} = 506 \, \text{K}$, $P_{\text{yy}} = 220$.

**FIG. 2.** The site density profiles of the middle (15 and 16) and end (1 and 24) groups for squalane; $w = 9.25$, $v_{\text{wall}} = 0.5$, $T_{\text{fluid}} = 506 \, \text{K}$, $P_{\text{yy}} = 220$.

**FIG. 3.** The site density profile for squalane at the indicated wall velocities; $w = 9.25$. 10328 Gupta, Cochran, and Cummings: Shear under extreme confinement. II. J. Chem. Phys., Vol. 107, No. 23, 15 December 1997

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calculated values of \( P_{yy} \) are nearly the same for the three wall spacings. The figure indicates that for these narrow spacings there appears to be some critical spacing for which the middle layer becomes well-defined. This observation is also noted at other wall velocities. Clearly the wall spacing can have a profound influence on the molecular interaction and structure.

The density profiles for tetracosane are qualitatively similar to those for squalane except at low velocities for certain wall spacings. Figure 5 compares the density profiles for squalane and tetracosane for \( v = 9.25 \). The velocity is relatively high, and the calculated pressures \( P_{yy} \) for the two systems are identical. Note that the peaks for tetracosane are more well defined, which could lead to speculation that the lack of side branches is the cause of this difference. Also shown in Figure 5 is the density profile of sites along the 24-carbon backbone of squalane. This profile is very similar to the overall profile for squalane, suggesting that the difference between the profiles for the two types of molecules may originate from the tetracosane being in an extended state as compared to squalane. Such a conformation might allow for a better discretization into layers.

As compared to squalane, tetracosane is able to assume interesting configurations at certain wall spacings. Figure 6, which is adapted from the preceding paper of this series,\(^5\) shows a snapshot from a simulation of tetracosane \((v = 9.25)\) at a relatively low velocity and temperature. When the velocity is reduced and the spacing between the walls is close to an integral multiple of the molecular diameter, then the fluid adopts a very well-defined layered structure with virtually all the molecules in a fully extended (FE) state. Visualization of the molecules during the simulations do not indicate solidification, rather the molecules are in a state similar to a liquid crystalline one. It should be noted this FE layering exists in spite of the absolute wall velocities that range between 1 and 10 m/s. The corresponding density profile for this system shows five peaks of equal height corresponding to the five distinct layers and is similar to the profile shown in Figure 7 which indicates four layers. For a fixed wall velocity this FE layering disappears as the wall temperature is raised. To test how sensitive this FE layering is to the wall spacing, we have performed simulations at different wall spacings. We observe four FE layers at \( v = 8.03 \) and \( 8.19 \) while there is no FE layering at \( v = 8.60 \); at \( v = 9.25 \), a fifth layer appears. Figure 7 which compares the density profiles for \( v = 8.19 \) and \( 8.60 \), illustrates the differences in the fluid structure. In light of this observed FE layering at certain wall spacings, it seems reasonable to speculate that for a simulation where the top wall is allowed to move vertically under a constant normal pressure, the wall spacing might adjust to give rise to a configuration similar to that in Figure 6 where the molecules are in a fully extended state. Such a configuration would be energetically favorable. We also note that examination of the flow behavior of squalane for a range of wall spacings has revealed no evidence of the kind of FE layering that we observe for tetracosane, indicating that even very short branches along the chain backbone, which can disrupt regular packing, can significantly change the confined flow behavior of a fluid.

**B. Chain conformations**

Having described the basic structural features of the confined fluid, we now examine the chain conformations. One of the measures of chain dimensions is the mean squared chain end-to-end distance defined via

\[
\langle R_{ee}^2 \rangle = \langle (r_{Na} - r_{1a})^2 \rangle,
\]

where \( r_{ja} \) is the \( \alpha \)-th \((\alpha = x, y, z)\) component of the position of site \( j \). Figure 8 shows, for squalane as a function of position, \( \langle R_{ee}^2 \rangle \) calculated as a fraction of \( \langle R_{ee}^2 \rangle \) for a fully extended chain. The wall spacing is \( w = 9.75 \), and results are depicted for both equilibrium and non-equilibrium conditions. Compared to the equilibrium case, \( \langle R_{ee}^2 \rangle \) under shear
flow is similar at all positions. This observation is somewhat surprising since one might expect the chains to be elongated under shear. It is instructive to inspect the individual components of the mean squared chain end-to-end distance, i.e., along the three directions — flow (x), shear gradient (y) and the neutral direction (z). Figure 9 shows these individual components under shear flow. As expected, the chains are mainly extended along the shear direction. However, the chains at all locations are far from being fully extended. We also observe that for these relatively wider wall spacings, the dimensions in the z direction are larger than in the y direction near the walls, while there is little difference in the center.

For the same wall spacing and wall velocity, tetracosane shows a somewhat higher degree of elongation than squalane, with the difference being larger at lower velocities, as is depicted in Figure 10. This figure compares $\langle R_{ee}^2 \rangle$ for the two molecules. Note that for a given wall velocity, the calculated normal pressures are similar. Since the two molecules have the same backbone length, the data in Figure 10 suggest that the side branches in squalane hinder the molecules from assuming elongated configurations.

A more detailed understanding of the conformations adopted by the chains can be obtained by investigating the shape characteristics of the molecules. We investigate the shape of these molecules by representing each molecule in terms of an equivalent spheroid having the same moment of inertia. The moment of inertia tensor of molecule $i$ is given by:

$$I_{i\alpha\beta} = \sum_j (r_j^2 \delta_{\alpha\beta} - r_j \delta_{\alpha j} r_j),$$

where $\alpha, \beta = x, y$ and $z$ coordinates, $\delta_{\alpha\beta}$ is the Kronecker delta, and $r_j$ is the distance in the $\alpha$ direction of site $j$ from the center of mass. The sum is over all sites $j$ of molecule $i$. Information about the shape of the molecule can then be obtained by diagonalizing the moment of inertia ten-

![Image of a molecule](image1)

**FIG. 6.** Snapshot from a simulation of tetracosane; $w=9.25$, $v_{wall}=0.05$, $T_{fluid}=313$ K. Black atoms: end groups.

![Image of site density profile](image2)

**FIG. 7.** The site density profile for tetracosane at two different wall spacings; $v_{wall}=0.01$. 

**FIG. 10.** Comparison of $\langle R_{ee}^2 \rangle$ for tetracosane and squalane at two different wall velocities.
sor to obtain the eigenvectors $a$, $b$ and $c$, and the principal moments $I_{aa}$, $I_{bb}$, and $I_{cc}$. The lengths of the semiaxis vectors are given by

$$a = \frac{\sqrt{5(I_{bb} + I_{cc} - I_{aa})}}{2N}, \quad b = \sqrt{\frac{5(I_{aa} + I_{cc} - I_{bb})}{2N}}, \quad c = \sqrt{\frac{5(I_{aa} + I_{bb} - I_{cc})}{2N}}.$$ 

The eigenvector $a$ corresponds to the smallest eigenvalue and is the molecular axis vector. Figure 11 shows $a$, $b$, and $c$ as a function of center of mass position at $v_{wall}=0.5$. Similar values of $a$, $b$, and $c$ to those shown in Figure 11 are calculated at lower velocities. The semi-axis length $c$ is close to zero near the wall indicating, not unexpectedly, a two-dimensional shape of the molecules. In addition to this flattening near the wall, the non-zero values of $a$ and $b$ suggest the molecules being in a somewhat coiled state. This interpretation is supported by the calculated values of the square of the radius of gyration ($R_g^2 \approx 50 \, \text{Å}^2$); note that $R_g^2 = 82.9 \, \text{Å}^2$ for a fully extended chain. As the distance from the walls increases, the molecules are able to readjust to add a third dimension. The coiling or folding of the molecules near the walls is even more pronounced at higher densities as can be seen in Figure 12. However, in the next layer, semiaxis $a$ (largest dimension) increases significantly, before settling to a value of about 1.2 nm as one moves towards the center. For tetracosane, the variations of the semiaxis lengths are qualitatively similar to those for squalane, except in cases where the molecules form FE layers.

The chain orientation as a function of position can be more directly determined by examining the orientational cor-
The molecular axis orientational correlation function, \( S_{2M} \), is defined by

\[
S_{2M}(y) = \frac{3(\cos^2 \theta) - 1}{2},
\]

where \( y \) is the position of the chain center of mass, and \( \theta \) is the angle between the molecular axis vector \( \mathbf{a} \) and the \( y \) axis. If molecules (on average) are aligned parallel to the walls, \( S_{2M}(y) = -0.5 \), if they are at right angles to the walls, \( S_{2M}(y) = 1.0 \), and \( S_{2M}(y) = 0 \) for isotropic orientation of the chains. Figure 13 shows \( S_{2M}(y) \) for two different velocities. In both cases, close to the walls the chains are parallel to the walls, which is consistent with semiaxis \( c \rightarrow 0 \). Away from the walls, the chains still exhibit a certain degree of alignment with the wall, more so for the higher velocity which is as expected. Figure 14 shows \( S_{2M} \) for tetracosane for the same wall spacing and wall velocities as for squalane, which indicates that in the center, tetracosane exhibits a higher degree of alignment than does squalane. Results at higher densities (note the solid line in Figure 14) indicate that the degree of alignment in the center increases with the density.

In analogy with a liquid crystal, we have also calculated the shear alignment using the order tensor defined by the second rank tensor,

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

where \( \mathbf{e}_i \) is the unit vector along the end-to-end direction of the molecule \( i \), \( \mathbf{1} \) is a unit second rank tensor and the summation is over all \( N \) molecules in the system. The largest eigenvalue of the order tensor \( S \) is 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. Figure 15
comparatively small, these oscillations seen in the tendency towards isotropic orientation. We also note that the vectors have a tendency to orient parallel to the walls. Away from the walls there is a tendency towards anisotropic orientation. We also note that the oscillations seen in $S_{2B}$ correlate with the oscillations in the density profiles, with the greater parallel orientation at the points of highest density.

III. SUMMARY

These simulations have given us some insight into the conformations that these medium-sized alkanes adopt in such narrow confinements at relatively high densities as might be expected in actual lubrication applications. In particular, we have noticed an interesting behavior relating to tetracosane which is an alkane with no side branches. The lack of side branches for this linear alkane allows the molecule to form very well-defined layers with the molecules being in a fully extended state (Figure 6). This behavior is observed when the wall spacing is close to an integral multiple of the molecular diameter. For the various state points that we have examined, we do not find this phenomenon to occur for squalane. Previous experiments have also noted that branched alkanes show the greatest tendency to remain in a "liquid-like" state. Note that this layering for tetracosane occurs in spite of wall velocities being of the order of 10 m/s. One might expect that at these high velocities, the fluid would not be able to sustain such a high degree of order. Furthermore, this layering occurs only at high overall densities of the fluid, akin to the conditions in a surface force apparatus, where the fluid is forced into such conformations, the number of atomic sites in a given volume ends up being very high. Another aspect revealed by these simulations is that one does not need to have a crystalline solid surface to induce the kind of well-defined layers that have been observed. As Figure 4 of the previous paper in this series indicates, the tethered chain ends are in constant motion along the directions parallel to the wall and do not provide for a well-defined surface.

From our observations it appears reasonable to speculate that in simulations of linear alkanes at a constant normal pressure (where the top wall is free to move), the wall spacing would automatically adjust so as to accommodate an integral number of layers of fully extended chains. Under such conditions, one could very well have a situation similar to that in Figure 17 for simple fluids, at least at relatively low velocities, where the molecules are in a "solid-like" state. Furthermore, if the fluid atoms are able to pack close to the solid surface as in Figure 17, then such a structure could offer a very large resistance to any relative motion of the walls.

In spite of the layering observed for the linear alkane, our results do not suggest a glass transition, rather the molecules appear to be in a state similar to a liquid crystalline one. In general, for these medium-sized alkanes, we observe that under shear flow conditions the molecules tend to orient parallel to the walls, as would be expected, with a greater degree of orientation (a) close to the walls, (b) at the positions of local density maxima, and (c) at higher strain rates.

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