Shear-Induced Order and Rotation in Pipe Flow of Short-Chain Molecules.

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(received 14 September 1993; accepted in final form 11 April 1994)

PACS. 02.70 – Computational techniques.
PACS. 61.25E – Molecular liquids.
PACS. 47.50 – Non-Newtonian dynamics.

Abstract. – In a series of molecular-dynamics simulations, oligomer fluids undergoing Poiseuille (pipe) flow are shown to experience rotational motion and mean orientation that is dependent on the local shear rate. Local molecular alignment is found to reflect the competition between the Maxwell forty-five degree prediction and a preferred orientation parallel to the flow close to the boundary. The molecules, each consisting of four linked hard spheres, and both fully flexible and semi-rigid chains are studied; the flow is driven by a uniform field, with the pipe walls serving both as non-slip boundaries and thermal sinks for the shear-generated heat.

Introduction. – Molecular-dynamics (MD) simulation provides the most direct means of investigating classical many-particle systems [1]. Because of the wealth of detail incorporated in the simulations, the method is capable of revealing the atomistic mechanism underlying macroscopic collective behaviour. MD simulations addressing such phenomena include the generation of structured flow patterns that develop, for example, in fluid flow past an obstacle and in thermal convection [2]. The corresponding continuum problems have been well studied using conventional hydrodynamics, and provide quantitative tests of the applicability of MD methods to relatively complex flow problems.

Continuum fluid dynamics theory is most thoroughly developed for Newtonian fluids, but where more complex behaviour must be explained the basis for the continuum method is less firmly grounded, as the macroscopic equations fail to even acknowledge the atomic nature of matter. Prominent in this category are liquid polymers that exhibit a range of exotic rheological properties [3] not encompassed by «conventional» fluid dynamics. Understanding the detailed mechanisms underlying these phenomena is a long-term task for MD, assuming the requisite length and time scales can be achieved.

This paper addresses a more limited problem: the molecular behaviour in a fluid of chain molecules undergoing pipe flow. In the case of Newtonian fluids this is a simple analytically soluble problem, but for structured molecules with internal degrees of freedom the problem has no continuum description, so that MD becomes the method of necessity.

The earliest discussion of the effect of shear on molecular orientation in fluids dates back
to Maxwell [4]; a readily observable consequence of such ordering is the phenomenon of optical birefringence. Previous MD studies of sheared molecular fluids have dealt with the uniformly sheared Couette flow of short alkane chains [5-7]. Use of non-equilibrium MD and sliding periodic boundaries (with in some instances, a constant shear rate) facilitated the study of homogeneous systems without explicit boundaries, a particularly important benefit in view of the very small systems considered (up to 64 molecules). Dimers have also been studied [8].

Methodology. – The model used here abstracts the principal characteristics of short-chain molecules, namely the excluded volume of the monomers, a limited variation of the bond length between adjacent monomers, and a controlled degree of chain flexibility. There are of course numerous ways to enrich the model in order to represent real chains (such as alkanes) more closely, but the issue here is one of devising the simplest models that retain the essential ingredients. The monomers of the chains are represented by hard spheres [9]; adjacent spheres are linked by placing them in an infinite potential well whose width limits the range of bond lengths. Chain flexibility can be controlled by introducing a repulsive core that restricts the approach of second neighbours. The evolution of a hard-sphere system of this type proceeds by means of impulsive collisions [10]: collisions between monomers (both the excluded-volume type and collisions used to restrict bond lengths and angles) are discrete events, and between successive collisions the monomers move freely.

To emulate pipe flow, longitudinal motion must be suppressed in a thin layer of fluid adjacent to each wall. This is achieved [2] by dividing the wall into strips perpendicular to the flow, and enforcing the rule that wall collisions in successive strips alternate between energy-conserving specular collisions and velocity reversals. This produces the effect of a rough wall, while at the same time retaining the computational simplicity of a boundary that is geometrically flat. Hard walls bound the system only along one of its dimensions, and periodic boundaries apply in the other directions. A uniform field drives the flow.

Fluids modelled by MD are inherently viscous, and the shear resulting from the driving force and non-slip walls produces viscous heating; this must be removed to maintain a steady temperature distribution. In the case of Couette flow, heat can be removed through the walls (if the flow is driven by wall motion), by incorporating a thermostat into the dynamical equations, or by simply rescaling particle velocities. For pipe flow, on the other hand, the only available mechanism involves heat extraction through the walls; rescaling velocities to match some theoretical temperature profile is not possible for lack of theory. Thus, whenever particles collide with the walls, in addition to being subjected to the non-slip mechanism, the velocity magnitudes are scaled to match the ambient wall temperature.

In order to analyse the behaviour, the simulation region is divided into a series of layers parallel to the flow. When associating properties with the layers, those that are based on monomers are attributed to the layer in which the monomer itself resides, whereas for molecular properties the layer is determined by the position of the centre of mass. Flow velocity is in the former category, angular momentum, orientation and end-to-end distance are in the latter.

Results. – In this report chains of length four are discussed. Relatively large systems were used—14,700 four-sphere chains—to minimize finite-size effects. The spheres have unit diameter (all distances are expressed in terms of this length), and the bonds linking adjacent monomers can stretch freely by up to 10%. To investigate the effect of chain stiffness, both fully flexible and partially rigid (hereinafter referred to as «stiff») chains were considered. For the latter, flexibility is restricted by limiting the distance of closest approach of second neighbours to 2.125, equivalent to a change of bond direction of up to 30°. The computational
cost associated with this method of restricting bond bending increases rapidly if the angle is reduced much further, namely an increase in the number of collisions that regulate the flexibility; the value chosen represents a reasonable compromise. The size of the system is 79 × 79 in the shear plane, and 13.5 in the perpendicular direction, corresponding to a monomer density of 0.7.

Computation time is determined by the number of collisions processed, with stiff chains requiring nearly three times as many collisions to evolve over a given period with respect to flexible chains. Run lengths were typically 1800 time units, corresponding to $4 \times 10^9$ collisions in the case of stiff chains, sufficient for the molecules in midstream to circulate through the system approximately 60 times. Data was accumulated over intervals of 50 time units. The simulations were begun with all chains arranged on a lattice, with the monomers having random thermal velocities but no bulk flow. For the runs reported here the initial chain orientation was perpendicular to the plane of shear (in order to establish whether the chains might retain this alignment—no such tendency was noted).

Several of the key results are summarized in the plots that follow. Error bars reflect the measured sample spread, although in most cases the smoothness of the results is an indication of the precision achieved. The coordinates are chosen so that flow is in the $y$-direction; the (normalized) $x$-coordinate spans the distance between the pipe walls, and the $z$-axis is perpendicular to the shear plane.

Figure 1 shows the flow velocity profiles for the flexible and stiff chains based on a subdivision into 20 layers. Under identical conditions, the flexible molecules flow faster. The results of fitting the profiles to quadratic functions, motivated by the analytic result for the Newtonian case [11], are also given; such fits are especially good in view of the complex nature of the flow—as will become apparent subsequently. The non-slip boundary mechanism is seen to be highly effective, even after allowing for averaging across each layer. Temperature profiles (not shown) are similarly well approximated by quartics, again resembling the Newtonian result.

Cross-stream plots of molecular angular momentum appear in fig. 2. Only the angular-momentum component normal to the shear plane is considered; for symmetry reasons the remaining components should average to zero. The behaviour is consistent with the $x$-dependence of the shear, namely faster rotation as shear increases, with the exception

Fig. 1.

Fig. 1. – Cross-stream flow velocity profiles for flexible (---) and stiff (——) chains; the curves show the quadratic fits.

Fig. 2.

Fig. 2. – Cross-stream angular-momentum profiles for flexible (---) and stiff (——) chains.
of the reduction as the walls are approached—obviously walls hinder the rotation. The stiff chains show a slight reduction in the maximum values (beyond that due to the different flow speeds); since this reduction is strongest close to the walls where rotation is inhibited anyway, this result is understandable.

Figure 3 shows cross-stream profiles of the parallel-order parameter, defined as \( (\Delta y^2 - \Delta x^2)/(\Delta x^2 + \Delta y^2 + \Delta z^2) \), with distances measured between the thermal monomers of each chain, and no weight being given to details of internal organization. This definition reflects the average molecular alignment parallel to the flow in the shear plane; the choice suffers from a certain arbitrariness, but does have the advantage of simplicity, and gives a clear indication of the preferred alignment (at least for relatively short chains)—a value of unity corresponds to complete alignment parallel to the flow. There is no order at midstream—not unexpected since shear is absent. The shape of the curves near the walls still retains some size-dependence (not shown), more so for stiff chains, even for these comparatively large systems. The perpendicular order parameter \( (\Delta z^2)/(\Delta x^2 + \Delta y^2 + \Delta z^2) - 1/3 \) measures the tendency to orient out of the shear plane; the results (not shown) indicate values close to zero for the flexible chains, whereas the stiff chains yield zero at midstream and values which drop to about \(-0.1\) near the walls—clearly the chains avoid aligning along this direction.

The \( x \)-dependence of the distribution of molecular orientational angle (\( \theta \)) in the shear plane, again based on the relative displacement of the terminal monomers, is shown in fig. 4 for flexible chains. The 5 layers of equal thickness cover the flow from the wall to midstream; symmetry is used to combine results from the two halves of the flow, and to halve the angular range due to the equivalence of the chain ends. The deviation from a uniform distribution is strongest in the layer closest to the wall, reflecting a tendency to align parallel to the flow; in the interior the distributions peak near (but below) \( 45^\circ \)—the Maxwell result. The peak in the layer closest to the wall is even more pronounced for stiff chains (not shown). Because of the varying shear rate across the pipe, the results effectively cover a range of shear rates studied for the Couette problem [7]. The latter also revealed a \( 45^\circ \) orientational preference at low shear rate, corresponding to the originally observed extinction angle (the angle of

**Fig. 3.** - Parallel-order parameter profiles (defined in the text) for flexible (---) and stiff (-----) chains.

**Fig. 4.** - Distribution of molecular orientational angle (\( \theta \)) for flexible chains, measured over a series of layers parallel to the flow; the plots are ordered—the solid line shows the wall layers, the shortest dashes the midstream layer.
Fig. 5. – Mean-square end-to-end distance as a function of orientation angle for flexible chains (plot order as in fig. 4).

polarization at which birefringence vanishes) [4], with the peak shifting to smaller angles as the shear rate increased, a situation analogous to pipe flow as the wall is approached.

Figure 5 shows the orientation angle dependence of the mean-square end-to-end distance for flexible chains. Molecules in the layer adjacent to the wall exhibit maximal extension when parallel to the flow and minimal extension at −45° orientation, while those in inner layers show a tendency to stretch when near the 45° orientation. The values cover a relatively broad range, although there is no indication that chains are excessively stretched or compacted—separation can range from 1 to 3.3. In contrast, stiff chains (not shown) experience only very limited length variation since the smallest separation is 2.2.

Discussion. – The present work has demonstrated the feasibility of using detailed MD simulation for studying the microscopic features of the non-uniformly sheared flow of structured molecules. The results reveal the coupling that occurs between shear and rotation, as well as the influence of shear rate on molecular orientation and conformation. Although the approach adopted here differs in many respects from earlier work [7], the results are mutually consistent; the present work has the advantage of larger system size, a benefit slightly reduced by the non-uniform nature of the flow.

The study of polymer rheology will require longer chains (and hence larger systems) in order to enhance the degree of interaction between chains—including more severe steric hindrance and entanglement than can occur with the very short chains considered here. The intrinsic time scales of such effects are determined in part by the rates at which molecules undergo major conformational change, and these may well be beyond the limits of present-day MD. But, as ever-increasing computer power is brought to bear on problems of this type, one can expect to see increased understanding of the molecular mechanisms responsible for some of the more fascinating properties of non-Newtonian liquids.

REFERENCES