475g Rheological and Structural Studies of Liquid Decane, Hexadecane, and Tetracosane under Planar Elongational Flow Using Nonequilibrium Molecular Dynamics Simulations

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1. Introduction

There exist two important standard flows in rheology[1]: shear flow [*e.g.*, planar Couette flow and Hagen-Poiseuille flow] and elongational flow [*e.g.*, uniaxial elongational flow (UEF), biaxial elongational flow (BEF), and planar elongational flow (PEF)]. In contrast to shear flow, it is extremely difficult to perform real experiments in elongational flow, and thus only a few experimental data are available for this flow field.[1] Research is still in progress toward developing improved experimental apparati and methodologies for measuring elongational viscosities.[1] In this regard, without a doubt, the computational feasibility of simulating elongational flows would be tremendously helpful. With the help of Kraynik and Reinelt's[2] discovery of the temporal and spatial periodicity of lattice vectors in PEF, it has been possible, in principle, to perform nonequilibrium molecular dynamics (NEMD) simulations of PEF without any limit of simulation time. Recently, however, Todd and Daivis[3] have reported an aphysical phase transition after a certain time interval in NEMD simulations of PEF when using the so-called SLLOD algorithm, which has been extensively used in NEMD simulations over three decades, especially for shear flow. As shown by the present authors[4] very recently, the instability comes from the SLLOD algorithm itself due to its inconsistency of the fundamental principle, i.e., Newtonian dynamics. All these problems have been completely resolved by the present authors[4] using the so-called proper-SLLOD (or p-SLLOD) algorithm.

2. Technical approach

In our previous work[4] using the p-SLLOD algorithm, we demonstrated its fundamental correctness by applying it for a simple WCA fluid. In the present work, we extend our simulation methodology for NEMD simulations of PEF from simple fluids to relatively short complex fluids. We explore three alkanes, $C_{10}H_{22}$ (decane), $C_{16}H_{34}$ (hexadecane) and $C_{24}H_{50}$ (tetracosane), which previously have been studied under shear flow.[5-7] Thus, an advantage of choosing the three alkanes is to compare NEMD simulation results of PEF and those of shear flow, *i.e.*, compare zero-elongation-rate viscosity and zero-shear-rate viscosities. An NEMD simulation for these alkanes under shear flow was previously carried out by Cui *et al*.;[6] therefore, it appears to be most appropriate to choose the same state points as those used by Cui *et al*.,[6] for comparison: the temperature, T=298 K, and the density, r=0.7247 g/cm^3, for decane, T=323 K and r=0.7530 g/cm^3 for hexadecane, and T=333 K and r=0.7728 g/cm^3 for tetracosane. Exploring these states by NEMD simulations, we employed 200 molecules for decane, 162 molecules for hexadecane, and 100 molecules for tetracosane. The potential model employed for our systems is essentially the same as that used by Cui *et al*.[6] for shear flow. The model was proposed by Siepmann *et al*.,[8] and is known as the SKS united-atom model, with the exception that the rigid bond is replaced by a flexible one with harmonic potential **3. Results and Discussion**

Two elongational viscosities, h_1 and h_2, were separately calculated with appropriate rheological definitions. For all three alkanes, h_1 and h_2 showed tension-thinning behavior as elongation rate increased. It was observed that h_1 and h_2 are, in general, not identical to each other, indicating that two independent viscometric functions actually exist. Consistent with the theoretical prediction, h_1 and h_2 appeared to converge to each other at low elongation rate, *i.e.*, in the Newtonian regime. For the three

alkanes, the zero-elongation-rate viscosities calculated in this work agreed well with the zero-shear-rate viscosities reported by Cui *et al.*[6] Another interesting similarity between shear[6,7] and planar elongational flow was found in that for both flows there exists a minimum in the hydrostatic pressure at constant density *vs.* strain rate for these alkanes. The mean square end-to-end distance of chains $<R_{ete}^2>$ and the mean square radius of gyration of chains $<R_g^2>$ showed different trends from those in shear flow. After reaching a plateau value, $<R_{ete}^2>$ and $<R_g^2>$ were shown to increase further as elongation rate increases. This phenomenon has been interpreted by conjecturing that chains are fully stretched at high elongational rates. This conjecture was well supported by examination of the intramolecular LJ energy. The effect of elongation flow on three bonded intramolecular interactions (*i.e.,* bond-stretching, bond-bending, and torsion) was investigated in detail with further help of the distribution functions. The bond-bending and torsional energy showed a similar trend to each other, but a different behavior was observed in the bond-stretching energy. An important observation common in these three interactions was that all three modes were suppressed to small values at high elongation rates. We conjecture that a liquid-crystal-like, nematic structure, characterized by a strong chain alignment with a fully stretched conformation, exists in systems at high elongation rates. **4. References**

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