419a Test of Viscoelastic Models for Predicting the Rheological Properties of Short-Chain Liquid Alkanes under Shear and Planar Elongational Flow Using Nonequilibrium Molecular Dynamics Simulations

Chunggi Baig, Bangwu Jiang, Brian J. Edwards, David J. Keffer, and Hank D. Cochran

1. Introduction

There have been tremendous efforts in developing a "good" viscoelastic model in a practical sense, i.e., predicting well real experimental data, and in a physical sense, i.e., being founded on sound physical bases.[1,2] Although numerous viscoelastic models (either empirical or physical with a firm microscopic basis) have been proposed, none of them is good enough to fit to various kinds of complicated experimental data. To date, our understanding is still far from a "perfect" viscoelastic model of complex systems. However, since it is extremely important to have a good model both practically and theoretically, our efforts on seeking a better model continue by expanding our knowledge base of polymeric systems through trial-and-error. To this aim, it would be very beneficial to recognize and identify the characteristic merits of the existing viscoelastic models. In the present work, we test several viscoelastic models, each of which has its own sound physical basis, by fitting them to rheological data obtained from nonequilibrium molecular dynamics (NEMD) simulations of short-chain alkanes under both shear and planar elongational flow (PEF). While the NEMD method under shear has been already developed and well known, the NEMD methodology for PEF has been developed only very recently by the present authors.[3] To date, rheological data from shear flow (either from experiments or simulations) have been exclusively used in fitting viscoelastic models, due to the difficulty in obtaining experimental data under elongational flow. Because the recent development of the NEMD methodology by the present authors[3] allows for the straight-forward generation of rheological data from elongational flows, we can now fit viscoelastic models to both shear and elongational data. It is also important for readers to realize directly from the present study that a viscoelastic model which was good for fitting shear data may be bad for fitting elongational data.

2. Technical approach

In this work, we study three alkanes, $C_{10}H_{22}$ (decane), $C_{16}H_{34}$ (hexadecane) and $C_{24}H_{50}$ (tetracosane). The potential model and state points employed for our systems are essentially the same as that used by Cui *et al*.[4] for shear flow. The potential model was proposed by Siepmann *et al*.,[5] 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. The state point for each system is that 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 elongation rates used in this study are in the range of 0.0005≤ ≤ 1.0. In this study, by fitting simulation data of both shear and PEF flow, we investigate five well-known viscoelastic models: the upper-convected Maxwell (UCM) model, the Rouse model, the Finitely-Extensible Nonlinear Elastic model with the Peterlin approximation (FENE-p model), the Extended White/Metzner (EWM) model, and the Giesekus model.[6] In this work, we use only a single mode for each viscoelastic model. In order to obtain model parameters in each model, we fit the conformation tensor, which is considered the most important physical quantity in theory from both thermodynamical and rheological viewpoints[6]. Fitting to the conformation tensor, while theoretically advantageous is not the conventional method of fitting rheological properties, which relies on stress data, because of the difficulty in measuring the conformation tensor experimentally. This is a real advantage of simulations over experiment. From a statistical viewpoint, conformation tensor is also a better quantity than stress tensor because the former is a quantity averaged over individual chains whereas the latter is a collective property of the entire system. **3. Results and Discussion**

According to the symmetric property dictated by the kinematics of shear and PEF, only three components of the conformation tensor (, ,) are considered in PEF and four components (, , ,) in shear flow: all the other components for each flow are identically zero. As a linear model, the UCM model can only predict the linear behavior, i.e., Newtonian viscosity. Therefore, in getting two parameters (relaxation time *l* and modal concentration *n*) involved in the model, we selected only several most reliable linear data for each alkane. The relaxation time *l* was obtained by fitting the conformation tensor, and the modal concentration *n* by fitting viscosity data (in fact, the modal concentration *n* for every model was obtained by fitting viscosity data since it is a most reliable material function). As expected, the nonlinear behavior of fluids, i.e., shear thinning or tension-thinning phenomenon, could not be predicted at all by the UCM model. This incapability in predicting nonlinear behavior was also true in the Rouse model as the more complex, but still linear model due to the intrinsic linear characteristics of the model. Nonlinear behaviors were predicted by the other three nonlinear viscoelastic models: the FENE-p, EWM, and Giesekus model. These models contain one more parameter, compared with the above linear models. The additional parameter is crucial in fitting the nonlinear data, i.e., the UCM model is recovered from each model removing the additional fitting parameter. It turned out that each nonlinear model did a good job for one type of flow, but not both at the same time in general. This could be judged by comparing the parameters obtained between shear flow and PEF. **4. References**

[1] R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids*, *Vol. 1. Fluid Mechanics*, 2nd ed. (Wiley-Interscience, New York, 1987).

[2] R. B. Bird, R. C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids*, *Vol. 2. Kinetic theory*, 2nd ed. (Wiley-Interscience, New York, 1987).

[3] C. Baig, B. J. Edwards, D. J. Keffer, and H. D. Cochran, J. Chem. Phys. **122**, 114103 (2005).

[4] S. T. Cui, S. A. Gupta, P. T. Cummings, and H. D. Cochran, J. Chem. Phys. **105**, 1214 (1996).

[5] J. I. Siepmann, S. Karaborni, and B. Smit, Nature **365**, 330 (1993).

[6] A. N. Beris and B. J. Edwards, *Thermodynamics of Flowing Systems*, (Oxford University Press, New York, 1994).