R & D NOTES

Viscosity of Continuous Mixtures Using Nonequilibrium Molecular Dynamics

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The accurate estimation of viscosity of fluid mixtures is an important scientific and engineering problem. In many processes, e.g., in the petroleum and biochemical industries, mixtures have a large number of components, sometimes referred to as polydisperse or continuous mixtures (Olien, 1987). At present, the methods commonly used for such mixtures consist of characterizing them as mixtures of a finite number of components. The viscosity of such a hypothetical mixtures can then be calculated using an appropriate correlation (Reid et al., 1987). Static equilibrium properties of such polydisperse systems have been the subject of great interest recently (See for example, Briano and Glandt, 1984; Gualteri et al., 1982). However, little has been done on transport properties.

In this paper we examine the viscosity of many-component mixtures using the method of nonequilibrium molecular dynamics (NEMD)(Ciccotti and Hoover, 1986). We have chosen NEMD to investigate such systems, because it is an essentially exact statistical mechanical tool, and can therefore be used to evaluate techniques for characterizing polydisperse mixtures as mixtures with finite components (N-fluid theories).

Theory and Method

In our work we have used the time varying oblique boundary conditions method with homogeneous shear (Ciccotti and Hoover, 1986). The simulation is based on the conventional microcanonical algorithm, but instead of the usual orthogonal periodic boundary conditions, time varying boundary conditions are used (for details the reader is referred to the recent review by Evans and Morris, 1984). At low strain rates, such an algorithm leads to couette flow, where the profile is linear, and is defined by the strain rate γ (Bird et al., 1960)

$$\frac{\partial U_x}{\partial y} = \gamma. \tag{1}$$

The shear viscosity of such a system can be obtained by calculating the shear stress, P, defined by Evans and Morris (1984) as:

$$P_{xy} = \frac{1}{V}\left[\sum_i \frac{L_x L_y}{M_i} - \frac{1}{2}\sum_{ij} r_{ij}\frac{\partial \phi}{\partial r_{ij}} \cdot \frac{x_{ij} y_{ij}}{r_{ij}^2}\right] \tag{2}$$

and the viscosity can then be obtained from the expression

$$\eta = -\frac{P_{xy}}{\gamma} \tag{3}$$

In Eq. 2, L is the momentum, M the molecular weight, V the volume of the simulation cube, x and y components of r, the intermolecular distance, and ϕ the intermolecular potential. The intermolecular potential we have used here is the simple Lennard-Jones potential. For mixtures we have used the usual Lorentz-Berthelot rules (Reed and Gubbins, 1973) for cross interactions. We would like to add here that transport properties such as viscosity are known not to be very sensitive to the intermolecular potential function used and the results obtained here should be realistic for a wide range of compounds.

In our previous work on viscosity of equimolar binary mixtures modelled as hypothetical pure fluids (one fluid approximation) (Murad, 1986), we found that the simpler Kay's mixing rule worked as well as other more complicated rules such as van der Waals/Enskog mixing rules for dense fluids (Mo and Gubbins, 1976). In addition, we also found that although for large size ratios none of the mixing rules did particularly well, they all appear to be satisfactory for ϵ, and for M ratios that are large. In this study we have, therefore, used Kay's mixing rule only and have paid more attention to mixtures with varying molecular sizes. Our primary objective has been to determine the optimal number of components a many-component mixtures should be characterized with to obtain accurate viscosity values.

The mixtures we have examined have a uniform distribution as shown in Figure 1, with molecular sizes between σ_2 and σ_1, molecular weights between M_2 and M_1, and energy parameters between ϵ_2 and ϵ_1. For contrast we have also shown a nonlinear distribution. The uniform distribution is probably a more strin-

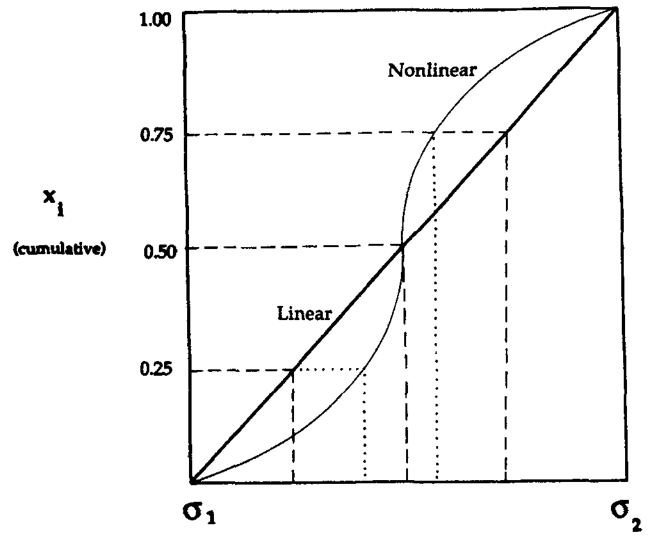

Figure 1. Characterization of a continuous mixture with a finite number of components.
A 4-component characterization is shown here.

gent test of the characterization techniques we wish to examine here. We have characterized these mixtures as 1-, 2-, 4-, 16-, 64- and 256-component equimolar mixtures, as explained in Figure 1 for a four-component characterization. Kay's mixing rule was used to characterize all components within $x_i \leq 0.25$ as one component and so on. The method of nonequilibrium molecular dynamics was then used to obtain the viscosity.

Results

In our work we have examined mixtures with ϵ, σ, M ranges that would roughly correspond to those in the $C_1//C_{16}$ hydrocarbon range. We have carried out studies in which only one of the three parameters vary at a time, and others in which all three vary simultaneously. A range of state conditions have also been examined to determine any state dependence.

The viscosity of a 256-component mixture was calculated first (see Figure 1). We have approximated this as our limiting value for polydispersity, and refer to this as a reference value η_o. The viscosities of the 1-, 2-, 4-, 16-, 64-component mixtures, characterized using Kay's rule were then calculated. Results obtained for $\rho^* = \rho\sigma_1^3 = 1.0$ and $T^* = kT/\epsilon_1 = 1.0$, (when only σ varies) are shown in Figure 2A. We estimate the accuracy of these results to be within four percent. They show that the single-component characterization gives errors of up to 20 percent and more. The two-component characterization gives essentially the same results as the 256-component mixture. In addition, going to a higher order characterization does not improve results any further, as illustrated in Figure 2B. The one- and two-component characterization used here is similar in spirit to the so-called one- and two-fluid theories (Prausnitz et al 1986), although for our two-fluid simulation we have not used any other approximations (such as the ideal mixing approximation sometimes used in thermodynamic theories). Results for $\rho^* = 2.0$, and $T^* = 2.0$ show essentially the same features.

For mixtures in which only ϵ, and M vary, the results appear to be quite insensitive to the characterization, and even the single-component characterization, works quite well. This is shown quite clearly in Table 1, for a range of state conditions. In Table 2 we have shown results when all three parameters ϵ, σ, and M vary simultaneously, corresponding roughly to the $C_1//C_{16}$ hydrocarbon range. Also shown are results when only σ varied, and the other two parameters were equal. The results seem to indicate that the mixing rules do better when all three parameters vary simultaneously, thus showing some possible cancellation of errors in more realistic mixtures, where all parameters do indeed vary simultaneously. Results also show that as density decreases, the accuracy improves somewhat.

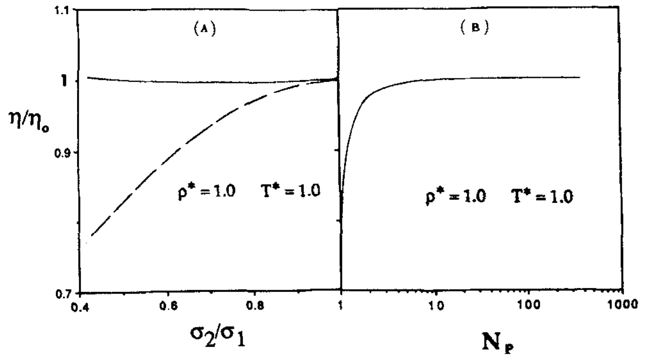

Figure 2. A. Results for 1- and 2-fluid approximations as a function of molecular size ratios.
B. Effect of number of components used in characterizing polydisperse mixtures on viscosities obtained via NEMD.
— 2-fluid; ----- 1-fluid

Conclusions

We have calculated the viscosity of many-component mixtures using nonequilibrium molecular dynamics. Our results show that for such mixtures, two-fluid type theories do considerably better than one-fluid type approximations. In addition, the two-fluid results are essentially identical to those obtained for polydisperse mixtures. This is most probably explained by the fact that in the two-fluid approximation local composition variations are accounted for which are not accounted for in one-fluid theories. Our results are in contrast to those obtained for thermodynamic properties where both one- and two-fluid approximations are known to give essentially similar results (Prausnitz et al., 1986). Our results also show that if a good approximate method can be developed for two-component mixtures, it should work well for many-component mixtures as well. We are currently working on developing such a theory.

Finally, our results show that in more realistic mixtures in which all three parameters, ϵ, σ, and M vary, some cancellation

Table 1. Effect of Variations in Molecular Weight and Energy Parameter Ratios on Viscosity

T^*	ρ^*	ϵ_2/ϵ_1	M_2/M_1	σ_2/σ_1	η_1/η_0
1.0	1.0	0.264	1.0	1.0	1.03
1.0	1.0	1.0	0.071	1.0	1.07
1.0	0.7	0.264	1.0	1.0	1.03
1.0	0.7	1.0	0.071	1.0	1.02

Table 2. Results for Mixtures with $\epsilon_2/\epsilon_1 = 0.264$, $\sigma_2/\sigma_1 = 0.474$, and $M_2/M_1 = 0.071$

T^*	ρ^*	η_1/η_0	η_2/η_0
1.0	1.0	0.86 (0.78)**	0.98 (1.02)
1.5	1.0	0.90 (0.84)	1.00 (1.02)
1.0	0.7	0.97 (0.81)	0.99 (1.03)

**are results for $\epsilon_2/\epsilon_1 = 1.000$, $\sigma_2/\sigma_1 = 0.474$, and $M_2/M_1 = 1.000$.

of errors probably takes place compared to those in which only σ, the most significant parameter, varies.

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Notation

R = Boltzmann constant
$L\alpha$ = a component of the momentum vector
M_i, M_j = molecular weight component i and j
$P_{\alpha\beta}$ = $\alpha\beta$ component of pressure tensor
r_{ij} = vector joining centers of masses of molecules i and j
T = temperature
T^* = kT/ϵ_1
$U\alpha$ = α component of translational velocity vector
V = volume of molecular dynamics system
x, y = components of position vector

Greek letters

γ = strain rate in couette flow
ϵ_i, ϵ_j = energy parameter for Lennard-Jones potential for components i and j
ρ = number density
ρ^* = $\rho\sigma_1^3$
η_o = viscosity of continuous mixture
η_i = viscosity of mixture (i component)
σ_i, σ_j = size parameter for Lennard-Jones potential for components i and j
ϕ = intermolecular potential

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