Viscosity of Mixtures of Diatomic Fluids Using Nonequilibrium Molecular Dynamics

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In the design and operation of industrial processes, there is frequently a need for estimating the viscosity of dense fluid mixtures. Many empirical and semiempirical approaches have been developed in the past few decades (Reid et al., 1987). Such approaches are known to fail in several cases. There is, therefore, a need to replace such approaches with those that are more fundamental in nature. With recent advances in experimental techniques, molecular theory, and computer simulation methods, this is now becoming possible (Gubbins, 1989).

In previous studies (Murad, 1986, 1989), we examined the viscosity of mixtures of simple spherical molecules, using the method of nonequilibrium molecular dynamics (NEMD). In this paper, we have extended our work to mixtures of homonuclear diatomic compounds. Computer simulations, with the method of NEMD, have been used to evaluate and develop molecular-based mixing rules that could subsequently be generalized to a corresponding states formalism. Such a direct comparison between a theory and simulation can be extremely useful, since one has much more control over the variables in a simulation, as compared to an actual experiment. In addition, since both the theory and simulation can use the same model(s), one can then test the various approximations in a theory more directly. When a theory is directly tested against experimental results, both the model(s) used and the approximations in the theory (e.g., retaining only the leading term of an expansion and other mathematical or intuitive approximations) are tested simultaneously. As can be expected, good results can sometimes be obtained because of a fortuitous cancellation of errors, and erroneous conclusions about the accuracy of a theory can be drawn.

Theory and Method

In our work we have modeled all homonuclear diatomics with a site-site Lennard-Jones potential (Rigby et al., 1986). The sites are placed, as is usual, on the nuclei of the two atoms. The total pair potential thus consists of four Lennard-Jones interactions

$$\phi(R\omega_1\omega_2) = \sum_{\alpha=1,2} \sum_{\beta=1,2} 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{\alpha\beta}}\right)^{6}\right] \qquad (1)$$

where R is the vector joining the centers of mass of the two molecules, ω_i the orientation of the molecules, $r_{\alpha\beta}$ the scalar distance between site α of the first molecule and site β of the second, and $\epsilon_{\alpha\beta}$ and $\sigma_{\alpha\beta}$ are the Lennard-Jones parameters for these interactions. We have used the Lorentz-Berthelot rules (Reed and Gubbins, 1973) to characterize them as

$$\sigma_{\alpha\beta} = (\sigma_\alpha + \sigma_\beta)/2$$
$$\epsilon_{\alpha\beta} = (\epsilon_\alpha \epsilon_\beta)^{1/2} \qquad (2)$$

In subsequent sections we have referred to σ_α, ϵ_α as molecular size and energy parameters, because we are dealing with homonuclear molecules and each molecule has only one independent set of these parameters. In addition, to completely characterize these molecules, the bond length also needs to be specified; as in Eq. 1, $r_{\alpha\beta}$ will obviously depend upon it.

To calculate the viscosity we have applied the time-varying oblique boundary conditions by using the NEMD 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 detailed information refer to 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 (Bird et al., 1960)

$$\frac{\partial u_x}{\partial y} = \gamma \qquad (3)$$

The shear viscosity of such a system can be obtained by calculating the shear stress P, and the viscosity from

$$\eta = -\tfrac{1}{2}(P_{xy} + P_{yx})/\gamma \qquad (4)$$

It is noted that in the case of diatomics the shear stress tensor at a particular instant may not necessarily be symmetric, since the potential model used here is anisotropic (see Eq. 1). This leads to the form of Eq. 4 used.

We used the above procedure to calculate viscosity of both pure diatomic fluids and their mixtures. The results have then been used to develop a corresponding states approach that would allow the viscosity of an arbitrary mixture of diatomics to be characterized by a hypothetical pure diatomic. In addition, we also examined the effect of bond length on the viscosity of such fluids.

The use of NEMD made it possible to look at the individual effect of the molecular parameters as well as several effects simultaneously. This enables theories to be tested more rigorously than against experimental data, where all variables change simultaneously and therefore cancellation of errors is possible. This, combined with the exact nature of these molecular dynamics techniques, makes it ideal to test many current engineering methods and to develop new ones.

Results

This work examines homonuclear diatomic molecules (e.g., N_2, Cl_2, and Br_2) and their mixtures. Homonuclear diatomics with reduced bond lengths ($\ell/2\sigma$) of between 0.2 and 0.6 were investigated. Diatomics such as N_2, F_2, Cl_2, Br_2, as well as long linear molecules such as CS_2 modeled as linear diatomics would fall roughly within this range (Gray and Gubbins, 1984). For mixtures, size ratio σ_2/σ_1 of 0.67 and 1.50 was studied. This would also cover the range of almost all real mixtures. Therefore, the results presented here represent mixtures of both practical and theoretical interest. Most of the studies were carried out at liquid-like reduced densities, $\rho^* \equiv \rho\sigma_o^3 = 0.4$, and $T^* \equiv kT/\epsilon_o = 2.0$, where σ_o and ϵ_o are the parameters used in representing pure fluids in our investigations. Some studies done at different densities or temperatures examine the effect of these state variables, which are needed in evaluating mixing rules.

Table 1 shows results obtained for pure fluids and mixtures, in which the molecular size and energy parameters are kept fixed (these have been referred to previously as σ_o and ϵ_o), and only the bond length is allowed to vary. These results are accurate to about 5%, or 0.1, in reduced units. It can be seen from the results on pure fluids that the viscosity varies approximately linearly with bond length, according to the following relation

$$\eta^* = 0.87 + 3.6\,(\ell^* - 0.3) \qquad (5)$$

Table 1. Effect of Bond Length Variation on Viscosity of Pure Fluids and Mixtures ($\rho^* = 0.4$, $T^* = 2.00$)

χ_1	χ_2	l_1^*	l_2^*	η^*(NEMD)	η^*(CALC)
1.0	0	0.2	—	0.65 ± 0.1	0.51
1.0	0	0.3	—	0.9 ± 0.1	0.87
1.0	0	0.4	—	1.2 ± 0.1	1.23
1.0	0	0.5	—	1.6 ± 0.1	1.59
1.0	0	0.6	—	2.0 ± 0.1	1.95
0.5	0.5	0.2	0.4	0.9 ± 0.1	0.87
0.5	0.5	0.3	0.6	1.4 ± 0.1	1.41
0.25	0.75	0.3	0.6	1.6 ± 0.1	1.68
0.75	0.25	0.3	0.6	1.2 ± 0.1	1.14
0.125	0.875	0.3	0.6	1.8 ± 0.1	1.82
0.875	0.125	0.3	0.6	1.0 ± 0.1	1.00

Viscosity values obtained using Eq. 5 are shown as η^* (CALC) in Table 1. These values agree satisfactorily with the NEMD results although it would not be the case at smaller bond length values. Clearly the linear equation cannot be extrapolated to $\ell^* = 0$. This significant result should be useful in developing corresponding states-type theories for polyatomic fluids. It means that knowing the viscosity at two bond lengths is sufficient for predicting it at other bond lengths. As mentioned previously, the bond lengths we have studied cover the range of most such homonuclear diatomic compounds.

From the results for mixtures in Table 1, another significant conclusion can be drawn about the mixing rule for bond length: i.e., simple mole averaging is sufficient.

$$\ell_x^* = \Sigma\, x_i\, \ell_i^* \qquad (6)$$

Thus, all the data in Table 1 can be compactly represented by Eqs. 5 and 6. This can be a powerful predictive technique for such mixtures. Comparison of results using Eqs. 5 and 6 to those of NEMD in Table 1 show good agreement.

In Table 2, we have shown results for mixtures in which both bond length and molecular size vary simultaneously. The mixture parameters were chosen such that all these mixtures become equivalent to our hypothetical pure fluid at $\ell^* = 0.45$ if simple mole averaging rules were valid for both σ and ℓ. Its viscosity calculated from Eqs. 5 and 6 is 1.40, as shown as η_1^* (CALC) in Table 2. It is clear from the results that simple mole averaging cannot adequately represent our results. A close examination of these results, however, shows that simple mole averaging for ℓ must be adequate, since the results for cases when both components have ℓ^* of 0.45 and when one has an ℓ^* of 0.3, and the other an ℓ^* of 0.6 are essentially identical in all cases. We also tested the so-called van der Waals mixing rules (although they probably are not designed for use with atomic diameters in polyatomics) for σ,

$$\sigma_x^3 = \Sigma\, x_i\, x_j\, \sigma_{ij}^3 \qquad (7)$$

Results obtained using Eqs. 6 and 7 are shown as η_2^* (CALC) in Table 2. (For this purpose, we performed additional pure fluid calculations at different densities.) With these mixing rules, the results of mixtures seem to be well represented.

Two other parameters that affect viscosity of mixtures would be the molecular weight and energy parameter (related to critical temperature). However, our previous studies (Murad, 1986, 1989a, 1989b) and those of others (Huber and Ely, 1989) have shown that these parameters do not play a key role in any mixing rules for such mixtures.

Table 2. Effect of Bond Length and Molecular Size Variations on Viscosity of Equimolar Binary Mixtures ($\rho^* = 0.4$, $T^* = 2.0$)

l_1^*	l_2^*	σ_1^*	σ_2^*	η^*(NEMD)	η_1^*(CALC)	η_2^*(CALC)
0.45	0.45	0.8	1.2	1.7 ± 0.1	1.4	1.7
0.45	0.45	0.9	1.1	1.5 ± 0.1	1.4	1.5
0.3	0.6	0.8	1.2	1.7 ± 0.1	1.4	1.7
0.3	0.6	0.9	1.1	1.5 ± 0.1	1.4	1.5
0.3	0.6	1.2	0.8	1.7 ± 0.2	1.4	1.7
0.3	0.6	1.1	0.9	1.4 ± 0.1	1.4	1.5

Acknowledgment

This research was supported by a grant from the Division of Chemical Sciences, the Office of Basic Energy Research, Department of Energy, through Grant No. DE-FG02-87ER13769. The author also acknowledges many useful discussions with P. V. Ravi.

Notation

R = vector joining center of masses of two molecules
r = scalar distance between two sites
ℓ = bond length
u = translational velocity
y = component of position vector
P = pressure tensor
x_i = mole fraction of i
T^* = reduced temperature, kT/ϵ_o
M = molecular weight

Greek letters

ω_i = orientation of molecule i
$\epsilon_\alpha, \sigma_\alpha$ = Lennard-Jones energy parameter and size parameter of atomic site α
γ = strain rate
ρ^* = reduced density, $\rho\sigma_o^3$
η^* = reduced viscosity, $\eta\sigma_o^2/(\epsilon_o M)^{1/2}$
ℓ^* = reduced bond length, $\ell/2\sigma_o$
σ^* = reduced size parameter, σ/σ_o

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Manuscript received Jan. 25, 1990.