The Viscosity of Dense Fluid Mixtures: Mixing Rules Reexamined Using Nonequilibrium Molecular Dynamics

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Introduction

The accurate prediction of the viscosity of liquid and dense gas mixtures is an important problem in engineering. The most common techniques are based on using mixing rules that enable one to model the mixture as a hypothetical pure fluid. Several such mixing rules have been developed in the past few decades (Reid et al., 1976). In this note we examine the accuracy of these mixing rules in a very precise way, by comparing them directly with exact computer simulation results using the method of nonequilibrium molecular dynamics (NEMD; Evans and Morris, 1984). 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.

Method

All fluids studied in this note were modeled using a Lennard-Jones potential, which is of the form

$$\phi = 4\epsilon \, [(\sigma/r)^{12} - (\sigma/r)^{6}] \tag{1}$$

where ϕ is the molecular interaction energy when two molecules are at a distance r. σ and ϵ are the Lennard-Jones parameters. For simple fluids σ and ϵ are related to the critical volume and temperature, respectively. Most of the currently used engineering correlations are either based on, or extrapolated from, fluids that can be adequately described using a Lennard-Jones potential. The conclusion we will draw in our study will therefore be quite general.

The computer simulations were carried out using the nonequilibrium molecular dynamics method. In a molecular dynamics simulation one usually starts with a system of N molecules (N usually between 100 and 1,000) which are assigned some arbitrary initial positions in a cube (e.g., face-centered cube) whose size is determined by the desired density of the system. A Gaussian velocity distribution can then be given to the individual molecules such that the resulting molecular kinetic energy corresponds to the temperature of interest. To model an infinite system it is usual to use periodic boundary conditions (Streett and Gubbins, 1977). Newton's equations of motion can then be solved for each molecule in the system to study its time evolution. In a nonequilibrium molecular dynamics simulation, in addition to the above the system is usually also given a hydrodynamic velocity profile. The simplest profile to study is the couette flow, where the profile is linear, and is defined by the strain rate γ (Bird et al., 1960)

$$\frac{\partial u_x}{\partial y} = \gamma \tag{2}$$

To maintain such a profile during the simulation one can use time varying oblique boundary conditions (Evans and Morris, 1984). The shear viscosity of the system can then be obtained by calculating the shear stress, P, defined as (Evans and Streett, 1978)

$$P_{xy} = \frac{1}{V}\left[\sum_i \frac{L_x L_y}{M_i} - \frac{1}{2}\sum_{ij} r_{ij}\frac{\partial\phi}{\phi r_{ij}} \cdot \frac{x_{ij}\, y_{ij}}{r_{ij}^2}\right] \tag{3}$$

and using the equation

$$\eta = -\frac{P_{xy}}{\gamma} \tag{4}$$

In Eq. 3 L is the momentum, V the volume, and x, y the components of r. The NEMD algorithm outlined above was first used to study a pure system with Lennard-Jones parameters ϵ_1 and σ_1, and molecular weight M_1. The actual values of these parameters is unimportant, since they themselves are used to make all other variables dimensionless; we however chose these parameters to correspond to methane. The viscosity of this system was studied at a temperature equal to ϵ_1/k, where k is the Boltzmann factor, and a number density of $0.7/\sigma_1^3$. This simulation was then used as the standard with which all subsequent mixture simulations were compared. It also served as a test of our algorithm since this state condition has also been simulated by others (Heyes, 1983). This viscosity is referred to as η_o.

Equimolar mixtures were then simulated, keeping the temperature and number density of the system constant and equal to that of the pure system studied. The first component of the binary system was identical to the pure fluid described earlier. The second component had parameters of ϵ_2, σ_2, and M_2. The cross-interactions were modeled using the usual Lorentz-Berthelot rules (Reed and Gubbins, 1973).

$$\left.\begin{aligned}\sigma_{12} &= \frac{\sigma_1+\sigma_2}{2}\\ \epsilon_{12} &= (\epsilon_1\,\epsilon_2)^{1/2}\end{aligned}\right\} \tag{5}$$

We carried out three sets of simulations for the mixtures. In the first set two of the three ratios (ϵ_2/ϵ_1, σ_2/σ_1, and M_2/M_1) were set equal to unity, and one was varied between 1.0 and 0.2 (Since the equations are symmetric, this is equivalent to varying the ratios between 1.0 and 5.0 also). In the second set only one of the ratios was set to unity, and the other two ratios were varied. Finally, in the third set all three ratios were varied simultaneously. The mixture viscosity is referred to as η_x.

The mixing rules for viscosity were then examined. The two representative sets we picked for a detailed examination were the simpler Kays rule defined by the equations (Smith and Van Ness, 1975)

$$\left.\begin{aligned}\sigma_x &= \sum_\alpha x_\alpha\sigma_\alpha\\ \epsilon_x &= \sum_\alpha x_\alpha\epsilon_\alpha\\ M_x &= \sum_\alpha x_\alpha M_\alpha\end{aligned}\right\} \tag{6}$$

and the more recent rules developed by Mo and Gubbins (1976), which use the Van der Waals mixing rules for σ_x and ϵ_x, and Enskog dense gas theory for M_x,

$$\left.\begin{aligned}\sigma_x^3 &= \sum_{\alpha\beta} x_\alpha x_\alpha\sigma_{\alpha\beta}^3\\ \epsilon_x\sigma_x^3 &= \sum_{\alpha\beta} x_\alpha x_\beta\epsilon_{\alpha\beta}\sigma_{\alpha\beta}^3\\ (\epsilon_x M_x)^{1/2}\,\sigma_x^{-2} &= \sum_{\alpha\beta} x_\alpha x_\beta(\epsilon_{\alpha\beta}M_{\alpha\beta})^{1/2}\sigma_{\alpha\beta}^{-2}\end{aligned}\right\} \tag{7}$$

where $M_{\alpha\beta} = 2M_\alpha M_\beta\,(M_\alpha + M_\beta)^{-1}$. Other rules such as the two-liquid theory (Prausnitz, 1969), and Evans-Hanley rules (1979), were found to give results similar to the Kays and Van der Waals-Enskog rules, respectively. In the remaining portion of this paper, we discuss only Kays rule and the VdW-Enskog rules specifically, but similar conclusions can be drawn for the Evans-Hanley rules and the two liquid theories.

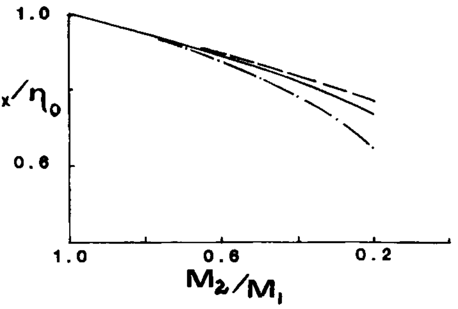

Figure 1. Viscosity of liquid mixtures with variations in M_2/M_1. ——— NEMD; —·—·— Van der Waals-Enskog rules; --- Kays rule.

The two sets of mixing rules given by Eqs. 6 and 7 were then evaluated by obtaining ϵ_x, σ_x, and M_x for the various mixtures studied from these rules, and then carrying out simulations for the hypothetical fluids defined by them. As discussed previously, this provides an unambiguous test for the accuracy of these rules.

Results

Figures 1, 2, and 3 show the results for the shear viscosity of mixtures using NEMD ("exact values") compared with the values obtained using conformal solution theory using the Kays mixing rule and the Van der Waals-Enskog mixing rules. Figure 1 shows the results when $\epsilon_2/\epsilon_1 = 1$, $\sigma_2/\sigma_1 = 1$, and M_2/M_1 varies between 1.0 and 0.2. The results show that the Kays rule overpredicts the viscosity for the entire range but not by much. At the smallest ratio (0.2), it overpredicts by 5%. On the other hand the Van der Waals-Enskog rules underpredict at the smallest ratio by as much as 15%. Figure 2 shows the results when $\sigma_2/\sigma_1 = 1$, $M_2/M_1 = 1$, and ϵ_2/ϵ_1 varies between 1.0 and 0.2. In this case both theories overpredict the viscosity values. Kays overpredicts at the smallest ratio by 19%, while Van der Waals-Enskog overpredicts by 10%. Finally, Figure 3 shows the results when $\epsilon_2/\epsilon_1 = 1$, $M_2/M_1 = 1$, and σ_2/σ_1 varies between 1.0 and 0.2. As could have been expected, while decreasing the M_2/M_1 ratio to 0.2 lowered the viscosity by only 26%, and decreasing the ϵ_2/ϵ_1 to 0.2 reduced the viscosity by only 21%, lowering the σ_2/σ_1 ratio to 0.2 lowers the viscosity by 59%. In addition, both the conformal solution theories overpredict the viscosity in this

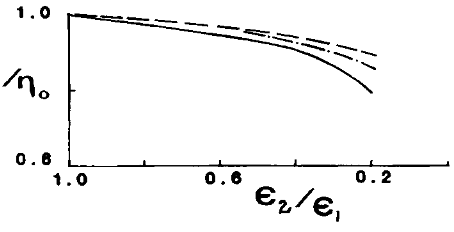

Figure 2. Viscosity of liquid mixtures with variations in ϵ_2/ϵ_1. Curve identification as in Figure 1.

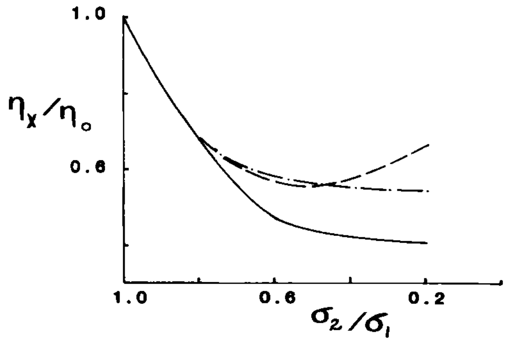

Figure 3. Viscosity of liquid mixtures with variations in σ_2/σ_1. Curve identification as in Figure 1.

case. For $\sigma_2/\sigma_1 = 0.2$, the Kays rule overpredicts by 61%, and Van der Waals-Enskog theory overpredicts by 31%. Finally, at the smallest σ_2/σ_1 ratios, the Kays rule even has the wrong qualitative features. However, it must be understood that $\sigma_2/\sigma_1 = 0.2$ corresponds to a critical volume ratio of 125.

The results show that when only one ratio is different from unity, the Van der Waals-Enskog mixing rules are better than the Kays rule. However, this is not surprising since clearly the Van der Waals-Enskog rules are more complicated, in addition to having a strong theoretical basis. What is certainly surprising is that the Kays rule works as well as it does. For ratios up to 0.4, the Kays rule is in fact as good as, if not better than Van der Waals-Enskog rules, despite its simplicity.

In the next set of simulations we allowed two parameter ratios to vary simultaneously. Since ϵ_2/ϵ_1 had the smallest effect on the viscosity, we kept it at 1.0. Results for varying σ_2/σ_1 and M_2/M_1 are shown in Table 1 (the first three results). First of all it is clear that the interaction between the two ratios is quite complex, and it is unlikely that one could get results for these mixtures by looking at the cases where only one ratio was varied. This is seen by looking at the first two simulations and Figures 1 and 2. The η_x/η_o ratios for $\sigma_2/\sigma_1 = 0.75$ and 1.25 are 0.61 and 1.49, respectively (keeping the other two ratios at 1). For $M_2/M_1 = 0.75$ and 1.25, the η_x/η_o ratios are 0.94 and 1.05, respectively. Assuming that ratios get multiplied (an obvious oversimplification), the ratio for the first point would be 0.61 × 1.05 = 0.64, which is close to the actual result of 0.62. However for the second point this approach would lead to a value of 1.49 × 0.94 = 1.40. The actual value is 2.68. It is not surprising that this rather simplified approach fails, but what is evident is that the interaction of the two parameters is quite complex. As far as the conformal solution theory approach is concerned it appears that both the Van der Waals-Enskog and Kays rules have approximately the same errors. The third point gives much larger errors because the ratios are much larger (or smaller) than the first two points, compared to the reference value of 1.0.

Table 1. Viscosity of Liquid Mixtures from NEMD and CST

Parameter Ratios			Viscosity Ratios η_x/η_o		
ϵ_2/ϵ_1	σ_2/σ_1	M_2/M_1	NEMD	Keys	VdW-E
1.0	0.75	1.25	0.62	0.67	0.73
1.0	1.25	0.75	2.68	2.04	2.51
1.0	0.5	2.5	0.49	0.74	1.03
1.25	0.75	1.25	0.57	0.72	0.68
1.25	1.25	0.75	3.19	2.28	2.80
0.80	0.80	0.80	0.55	0.66	0.67
0.60	0.60	0.60	0.40	0.54	0.56

In the last set of simulations all three parameter ratios were varied simultaneously. In this case there appears to be evidence that the Van der Waals-Enskog rules are better (although not significantly). This improvement primarily results from the better mixing rule for molecular weight that the Enskog theory provides.

Discussion

We have carried NEMD calculations for viscosity of Lennard-Jones mixtures and compared them with conformal solution results using the simpler Kays rule, and the more sophisticated rules based on Van der Waals rules for σ and ϵ, and Enskog dense gas theory for M. Our results are quite surprising because they do not clearly demonstrate that Van der Waals-Enskog rules are significantly better than the Kays rules, as we had expected, despite their theoretical basis and more complicated form. It appears to us that the Kays rule, despite its simple form, is clearly a powerful mixing rule for liquid viscosity, and has been rather underrated by the scientific community. In many cases we found it to be even significantly better than Van der Waals mixing rules. We found similar results when studying surface tension of liquid mixtures (Murad, 1983).

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Notation

L_α = α component of the momentum vector
M_i, M_j = molecular weight of component i and j
M_{ij} = cross-interaction term for M_i and M_j
M_x = (pseudo) molecular weight of mixture
$P_{\alpha\beta}$ = $\alpha\beta$ component of pressure tensor
r_{ij} = vector joining centers of masses of molecules i and j
u_α = α component of translational velocity vector
V = volume of molecular dynamics system.
y = component 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.
ϵ_{ij} = cross-interaction term for ϵ_i and ϵ_j
ϵ_x = (pseudo) energy parameter for mixture
η_o = viscosity of pure fluid
η_x = viscosity of mixture
σ_i, σ_j = size parameter for Lennard-Jones potential for components i and j
σ_{ij} = cross interaction term for σ_i and σ_j
σ_x = (pseudo) size parameter for mixing
ϕ = intermolecular potential

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