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Viscosity of a mixture of soft spheres

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The viscosity of a 50% mixture of soft spheres (i.e., particles which interact according to the force law $\phi = d/r^{12}$) has been simulated by applying nonequilibrium molecular dynamics to a system of 108 particles. Results for several size (actually d) and mass differences are given and compared with the predictions of a conformal-solution Van der Waals 1 theory. To construct this theory, it was necessary to derive a mixing rule for the mass. Overall, agreement between theory and simulation is satisfactory to size differences of about 14% and to mass differences of about 5%. It is pointed out that nonequilibrium molecular dynamics is a powerful technique and appears well suited to this particular application: The simulated viscosity of the mixture can be obtained to within about 5% accuracy for the 108-particle system by applying a shear to the system and following its behavior for about 7000 time steps.

I. INTRODUCTION

Although few computer simulations of a dense gas or liquid mixture in nonequilibrium have been discussed,[1] they would be especially worthwhile since simulation gives insight into the behavior of the real fluid and complements theoretical studies so well. The purpose of this article, therefore, is to report some results obtained via nonequilibrium molecular dynamics (NEMD). Specifically we have computed the viscosity of a binary mixture of soft spheres for several size and mass ratios. In addition a conformal-solution theory for viscosity is proposed.

There are two introductory remarks. The first is that nonequilibrium molecular dynamics is a relatively new technique which has several significant advantages over standard equilibrium molecular dynamics (MD). For example, to obtain the viscosity from the latter method, one examines the fluctuations in the fluid at equilibrium and calculates the coefficient from the Green-Kubo expression. But a large system is necessary and fluctuations have to be followed for an exceptionally long time to get results which approach the accuracy which one would expect from an experiment.[2] With the former technique, however, rather than examine a system *only* at equilibrium, the model system is studied in a nonequilibrium state after imposing an external force, in this case a homogeneous shear.[3-5] It turns out that many properties of the system are weakly dependent on system size and can be obtained to within an acceptable accuracy from a manageable number of time steps. Nonequilibrium molecular dynamics has been reviewed in detail by Hoover and Ashurst[3] and applied recently by one of us to obtain the frequency dependence of shear viscosity.[4,5]

The second remark emphasizes that the soft-sphere system was the logical choice for this preliminary study of a mixture. For instance, (a) it was very helpful that the properties of the pure fluid are known: the equilibrium properties were discussed in Ref. 6 and the viscosity has been computed by Ashurst and Hoover.[3,7] (b) The soft-sphere potential has[6,8] characteristics which simplify the computer simulation and the analysis of the results. As an example a soft-sphere mixture should exhibit only a single fluid phase, with no problems due to gas-liquid or liquid-liquid phase separation. (c) One might expect the behavior of the viscosity to be close to that of a real mixture, certainly at high temperatures.[9] (d) The conformal-solution concept has been examined critically for an equilibrium mixture of soft spheres in Ref. 10.

The organization of the paper is as follows: the simulation is outlined briefly in Sec. II and some results for a special mixture in which cross interactions are zero are given in Sec. III. Results from this particular mixture are one indication of the validity of the simulation procedure. A conformal-solution theory is proposed for viscosity in Sec. IV. Viscosities from the simulation for various interaction and mass differences are reported in Sec. V and compared to the conformal-solution expression. Finally Sec. VI gives some conclusions.

II. COMPUTER SIMULATION

The description of NEMD for viscosity used here—a homogeneous-shear method, has been published in Ref. 4. Nonequilibrium molecular dynamics in general has been reviewed in depth in Refs. 3 and 7. Only an outline, therefore, is needed.[11]

We considered a binary mixture of soft spheres with masses m and αm, respectively. All intermolecular interactions (ϕ) were of the form

$$\phi(r)=d/r^{12}, \tag{1}$$

so that with the index of repulsion fixed, ϕ is a function only of the parameter d. It is, however, also convenient to write Eq. (1) in terms of the usual energy (σ) and length (ϵ) parameters:

$$\phi(r)=\epsilon(\sigma/r)^{12}. \tag{1$'$}$$

Designating the particles by 1 and 2, like and unlike interactions were expressed in terms of d_{11} and the parameters β and γ:

$$\phi_{11}=d_{11}/r^{12},\ \phi_{12}=\beta d_{11}/r^{12},\ \phi_{22}=\gamma d_{11}/r^{12}. \tag{2}$$

For the simulation, the potentials were truncated[12] at a reduced cutoff distance which corresponded to 1.5 for the ϕ_{11} interaction and 1.5 $\beta^{1/12}$ and 1.5 $\gamma^{1/12}$ for the ϕ_{12} and ϕ_{22} interactions, respectively.

The system of volume V was constructed with 108(N) ($\rho=N/V$, where ρ is the density) particles with species 1 labled by an odd particle number, and species 2 by an even particle number. Thus $N_1=N_2=\frac{1}{2}N$ or, in number fractions (x_i): $x_1=x_2=\frac{1}{2}$.

Following Ashurst and Hoover,[3] the system was studied at a density-to-temperature ratio X:

$$X=\frac{N}{\sqrt{2}\,V}\left(\frac{d}{kT}\right)^{1/4}=\frac{N}{\sqrt{2}\,V}\,\sigma^3\left(\frac{\epsilon}{kT}\right)^{1/4}, \tag{3}$$

with T the temperature and k Boltzmann's constant. In terms of the usual reduced density and temperature

$$X=\rho^*/\sqrt{2}\,T^{*1/4} \tag{3$'$}$$

where $\rho^*=(N/V)\sigma^3$ and $T^*=Tk/\epsilon$, defining σ and ϵ by Eq. (1′). In this work we equated X to ρ^* so that T^*, the redundant variable, was fixed at 0.25.

With X ($=\rho^*$) set at a particular value and with the molecular parameters α, β, and γ given, the simulation proceeded as described in Ref. 4 allowing, of course, for the two species 1 and 2. Briefly, the particles were given initial velocities and positions at zero time and the equation of motion solved as a function of time step Δt^* (see Table I). Having verified the system was well behaved, specifically that the energy was constant (variation to within 0.1% over a projected 10 000 time steps), a strain rate ω^* was imposed in the x-y plane: $\omega=\partial u_x/\partial y$ (Table I).

TABLE I. Some dimensionless variables in terms of ϵ, σ, and d. See Eqs. (1) and (1′). In this work, (ϵ/kT) is constant.

Variable	Dimensionless	Real
Length	r^*	$r=r^*\sigma$ $=r^*(d/kT)^{1/12}$
Time	Δt^*	$\Delta t=\Delta t^*\sigma(m/\epsilon)^{1/2}$ $=\Delta t^*(d/kT)^{1/12}(m/kT)^{1/2}$
Velocity	v^*	$v=v^*(\epsilon/m)^{1/2}$ $=v^*(kT/m)^{1/2}$
Shear Rate	ω^*	$\omega=\omega^*\sigma^{-1}(\epsilon/m)^{1/2}$ $=\omega^*(d/kT)^{-1/12}(kT/m)^{1/2}$
Viscosity	η^*	$\eta=\eta^*(m\epsilon)^{1/2}/\sigma^2$ $=\eta^* m^{1/2}(kT)^{2/3}/d^{1/6}$
Pressure	p^*	$p=p^*\epsilon/\sigma^3$ $=p^*(kT)(d/kT)^{-1/4}$

The viscosity coefficient (η) follows from the pressure tensor $\overleftrightarrow{\mathrm{P}}$:

$$\overleftrightarrow{\mathrm{P}}=\frac{1}{V}\left(\sum_i m_i[\vec{v}_i-\vec{u}(\vec{r}_i)][\vec{v}_i-\vec{u}(\vec{r}_i)]+\frac{1}{2}\sum_{i\neq j}\vec{R}_{ij}\frac{\partial\phi_{ij}}{\partial\vec{r}_i}\right) \tag{4}$$

since

$$P_{xy}=-\eta\frac{\partial u_x}{\partial y}. \tag{5}$$

In Eq. (4), the summation is over i with $m_i\equiv m$ for i odd and $m_i\equiv\alpha m$ for i even. Similarly ϕ_{ij} is determined from Eq. (2) noting that i can be odd or even. $\vec{v}_i$ is the velocity of particle i, $\vec{u}(\vec{r}_i)$ the streaming velocity at $\vec{r}_i$, and $\vec{R}_{ij}=\vec{r}_j-\vec{r}_i$.

Values of X were varied between 0.3 and 0.8 (close to a melting density[6]). Reduced shear rates were set between 0.1 and 0.3, although for most of the runs $\omega^*=0.2$. In general, about 7000 time steps with $\Delta t^*\approx 0.006$ were sufficient to give a consistent value of the viscosity which was estimated to be accurate to about ±5% (Sec. II A). In fact we found we could usually obtain a viscosity to within 6% after only 3500 time steps.

A. Comment on the effect of strain rate

At first sight one could perhaps criticize NEDM for viscosity because the strain rates required are often very large in real terms and it would seem impossible to obtain a Newtonian viscosity from the technique. Fortunately, however, experience indicates the effect of the magnitude of the strain is small for a soft-sphere system,[3,7,13,14] and in fact is unimportant if the parameter X is less than 0.6. For large values of X, the effect is as shown in Fig. 1, which illustrates the vari-

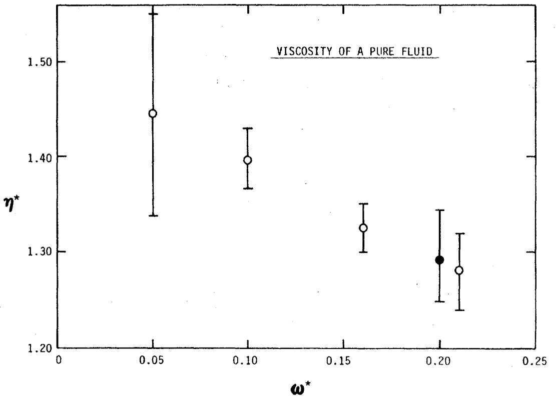

FIG. 1. Viscosity of a pure soft-sphere fluid at $X = 0.6$ as a function of strain rate ω^*. Open circles from Ref. 7, filled circle; this work. Note: numerical results reported here were made compatable to those of Ref. 7 by the factor (ϵ/kT), since $(\epsilon/kT) = 1$ in that reference but here, kT/ϵ was fixed at 0.25. Specifically, ω^* (this work) $= \omega^*(\text{Ref. 7}) \times 4^{7/12}$.

ation of the viscosity with strain rate at $X = 0.6$.

A convincing argument that our results are valid even for apparently large values of the strain rate can be made by considering the hydrostatic pressure. The pressure (and temperature) is independent of strain provided one works in the linear region, i.e., stress is linearly proportional to strain. For instance, if $\overleftrightarrow{\omega}^s$ is the symmetric traceless strain rate tensor and $g(r)$ the nonequilibrium radial distribution function, then an irreducible Taylor expansion of $g(r)$ in the strain rate can be performed so that in the linear region[15,16]

$$g(\vec{r}; \overleftrightarrow{\omega}^s) = g_0(r) + \nu(r) \frac{\vec{r}\vec{r} - \frac{1}{3} r^2 \overleftrightarrow{I}}{r^2} : \overleftrightarrow{\omega}^s , \tag{6}$$

where $\overleftrightarrow{I}$ is the unit tensor, $g_0(r)$ is the equilibrium radial distribution function, and $\nu(r)$ is an unknown scalar function of r. The potential contribution to the hydrostatic pressure is therefore

$$p_\phi(\overleftrightarrow{\omega}^s) = -\frac{\rho^2}{6} \int r \frac{\partial \phi}{\partial r} g(\vec{r}; \overleftrightarrow{\omega}^s) d\vec{r} \tag{7}$$

$$= p_\phi(\overleftrightarrow{\omega}^s = 0) - \frac{\rho^2}{6} \int r \frac{\partial \phi}{\partial r} \nu(r) \frac{\vec{r}\vec{r} - \frac{1}{3} r^2 \overleftrightarrow{I}}{r^2} d\vec{r} : \overleftrightarrow{\omega}^s \tag{8a}$$

$$= p_\phi(\overleftrightarrow{\omega}^s = 0) , \tag{8b}$$

since the second term of Eq. (8a) vanishes.[16]

We have verified by calculation that the pressure is at most very weakly dependent on the strain. For the illustration shown in Fig. 1, for example, we determined p^* $(\omega^* = 0.2) = 1.437$. By comparison the equilibrium run gave p^* $(\omega^* = 0) = 1.425$.

The argument can in fact be reversed. We have found that the value of the pressure obtained from NEMD (i.e., with a nonzero strain) for a given number of time steps, has less statistical uncertainty than the corresponding value determined by MD at equilibrium. This is especially true for mixtures whose components differ in mass and size (d).

III. RESULTS FOR A NONINTERACTIVE MIXTURE

If $\beta = 0$ [Eq. (2)] one has a mixture[17] in which each component behaves as though it alone occupies volume V. For $x_1 = x_2 = \frac{1}{2}$, the mixture properties at a ratio X are related simply to those of a pure substance ($\alpha = 1$, $\gamma = 1$, $\beta = 1$) at $\frac{1}{2}X$. For example, we have for the viscosity

$$\eta_{\text{mix}}(X) = \eta_{\text{pure}}(\tfrac{1}{2}X)(1 + \sqrt{\alpha}) \tag{9}$$

and for the hydrostatic pressure

$$p_{\text{mix}}(X) = 2 p_{\text{pure}}(\tfrac{1}{2}X) . \tag{10}$$

The computer simulation can thus be appraised by investigating a mixture with $\beta = 0$. In this study, mixture results at $X = 0.6$ were compared with those for a pure fluid at $X = 0.3$ for two values of α: $\alpha = 1$ and $\alpha = 10$. For all calculations $\omega^* = 0.2$. The comparison is summarized in Table II.

The agreement between corresponding values in the two columns of Table II is very satisfactory. We note further that, within computational error, the pressure for the pure fluid agrees with the $\omega^* = 0$ value from Ref. 6, and that the viscosity agrees with the interpolated value from Ref. 7. See also Fig. 1.

Overall, our computer procedure is judges to give a viscosity with an accuracy of 5% for runs of about 7000 time steps with $\Delta t^* \approx 0.006$. While this assessment is based on a system of 108 particles interacting with a potential truncated at 1.5 r^*, preliminary simulations with a larger cutoff distance of 2.5 r^* indicate the viscosity changes by less than 1%. As remarked, the results are also not very sensitive to the size of the system.

IV. CONFORMAL SOLUTION THEORY

Our simulation procedure is suitable to test unambigously a transport theory. A conformal-solution approach is especially appropriate since the simulation satisfies the basic corresponding-states criteria; namely, a single-force law is obeyed for all interactions,

$$\phi_{ij} = \epsilon_{ij} f(r/\sigma_{ij}) ; \tag{11}$$

the total potential is the sum of all pairs, and classical mechanics is assumed. In addition, the

TABLE II. Test of the computer simulation for a binary mixture with $\gamma=1$, but $\beta=0$, at $X=0.6$ for $\alpha=1$ and 10, respectively. The viscosity and pressure are compared to values from a pure fluid at $X=0.3$ according to Eqs. (9) and (10). All calculations for $\omega^*=0.2$

	Mixture at X $\alpha=1$	From the pure fluid at $\frac{1}{2}X$
Hydrostatic pressure	0.493	2 $\times$0.235= 0.470[a]
Total Viscosity	0.619	2 $\times$0.298= 0.596[b]
Kinetic Viscosity	0.296	2 $\times$0.136= 0.272
	$\alpha=10$	
Hydrostatic pressure	0.52[c]	2 $\times$0.235= 0.470
Total Viscosity	1.24	4.162$\times$0.298= 1.24
Kinetic Viscosity	0.57	4.162$\times$0.136= 0.57

[a] The Monte Carlo value[6] at $X=0.3$ is 0.464.

[b] Ref. 7 gives 0.64.

[c] From results with $\omega=0.2$.

parameter d_{12} (i.e., σ_{12} and ϵ_{12}) is entered directly. Here we will consider the Van der Waals one-fluid (VdW1) model since it is well established for a mixture in equilibrium.[18]

A. Mixing rule for the mass

Attempts to extend[19] the conformal-solution concept to a nonequilibrium mixture have emphasized some difficulties. First there is no consistent relationship between the transport properties in constrast to the situation for the equilibrium properties which follow from the free energy; second, a one-fluid idea seems inappropriate for properties such as the diffusion coefficient[20]; and third, one needs a mixing rule for the mass.[19]

In this latter case a mixing rule for the mass can be derived from the formal expression for the pressure tensor using an approach analogous to that of Henderson[18] as follows. Let us consider the potential contribution to the symmetric traceless part of the pressure tensor $\overleftrightarrow{\sigma}^3$ (the kinetic contribution is very small in the liquid) for a pure fluid:

$$\overleftrightarrow{\sigma}^s_\phi=-\left(\frac{\rho^2}{2}\sum\vec{r}\nu(r)\frac{\partial\phi}{\partial\vec{r}}(\hat{r}\hat{r}-\tfrac{1}{3}\overleftrightarrow{I})d\vec{r}\right):\overleftrightarrow{\omega}^s, \tag{12}$$

where $\hat{r}=\vec{r}/r$. After carrying out the integration[16] and comparing the result to the constitutive Eq. (5),

$$\overleftrightarrow{\sigma}^s=-2\eta\overleftrightarrow{\omega}^s, \tag{5'}$$

one obtains

$$\eta_\phi=\frac{2\pi}{15}\rho^2\int_0^\infty r^3\frac{\partial\phi}{\partial r}\nu(r)dr. \tag{13}$$

For a mixture this equation becomes

$$\eta_\phi=\frac{2\pi}{15}\rho^2\sum_{i,j}x_ix_j\int_0^\infty r^3\frac{\partial\phi_{ij}}{\partial r}\nu_{ij}(r)dr. \tag{14}$$

By analogy with the equilibrium VdW1 theory we assume that the ν_{ij} (like ϕ_{ij}) are simply rescaled transformations of one another, hence

$$\eta_\phi=\frac{2\pi}{15}\rho^2\sum_{ij}x_ix_j\sigma^4_{ij}\sqrt{\epsilon_{ij}M_{ij}}\int_0^\infty r^{*3}\frac{d\phi^*}{dr^*}\nu^*(r^*)dr^* \tag{15}$$

(ν has units of time).

Equating Eq. (15) with the corresponding expression for a pure fluid gives a mixing rule

$$\sigma^4_x\sqrt{\epsilon_xM_x}=\sum_{ij}x_ix_j\sigma^4_{ij}\sqrt{\epsilon_{ij}M_{ij}}. \tag{16}$$

The mass M_{ij} is given by

$$M_{ij}=2m_im_j/(m_i+m_j) \tag{17}$$

assuming that the relaxation of $g_{ij}(\vec{r},\overleftrightarrow{\omega}^s)$ is governed by ϵ_{ij} and σ_{ij} and by the reduced mass of an i,j pair of particles. We, therefore, suggest that Eq. (16) and

$$\sigma^3_x=\sum_{ij}x_ix_j\sigma^3_{ij}, \tag{18}$$

$$\epsilon_x\sigma^3_x=\sum_{ij}x_ix_j\epsilon_{ij}\sigma^3_{ij} \tag{19}$$

form a consistent set of mixing rules for the viscosity. For a soft sphere the rules simplify to become

$$d^{1/4}_x=\sum_{ij}x_ix_jd^{1/4}_{ij} \tag{20}$$

and

$$d^{1/3}_x\sqrt{M_x}=\sum_{ij}x_ix_jd^{1/3}_{ij}\sqrt{M}_{ij}. \tag{21}$$

B. Viscosity expression

The one-fluid expression for the viscosity of a mixture of soft spheres, η_x, at state parameter X is

$$\eta_x(X)=\eta_0(X'_0)\left(\frac{d_0}{d_x}\right)^{1/6}\left(\frac{M_x}{M_0}\right)^{1/2}, \tag{22}$$

where $\eta_0(X'_0)$ is the viscosity of a reference substance (pure soft-sphere fluid) evaluated at X_0' to correspond to X [for example, in terms of density ρ_x; $\rho_0' = \rho_x (d_x/d_0)^{1/4}$].

In this work the reference viscosity is that of the fluid with the potential parameter d_{11}, [Eq. (2)], and with unit mass for convenience. Using Eqs. (20) and (21), and Eq. (2), the viscosity equation for a 50% mixture can be written

$$\eta_x(X) = 4\eta_0(X_0^1)\left[\frac{1+\gamma^{1/3}\sqrt{\alpha}+2\beta^{1/3}\sqrt{2\alpha/(1+\alpha)}}{(1+\gamma^{1/4}+2\beta^{1/4})^2}.\right] \quad (23)$$

Note that Eq. (23) reduces to Eq. (9) if $\gamma = 1$ and $\alpha = 1$ but $\beta = 0$.

V. RESULTS FOR INTERACTION AND MASS DIFFERENCES

Simulated viscosities are presented and compared to the conformal-solution expression, [Eq. (23)], in this section.

A. Dilute-gas mixture

We are interested here in the dense system but it is necessary to verify that the conformal-solution approach is satisfactory for a dilute-gas mixture, hence we first tabulate some values for the dilute-gas 50% mixture in Table III. For convenience the species are taken to have equal masses ($\alpha = 1$). Shown are mixture viscosities from the Chapman-Enskog expression[21] normalized by the viscosity of the pure soft-sphere dilute gas. The corresponding results from the VdW1 equation (23) are given in the second column. It is clear the agreement between the two sets is very close, for example Eq. (23) is correct in the limit of $\gamma = 1$ but with $\beta = 0$, and further., both the Chapman-Enskog and VdW1 values tend to zero as β tends to infinity with $\gamma = 1$, or as γ tends to infinity with $\beta = 1$.

TABLE III. Comparison between the Van der Waals one-fluid (VdW1) equation, Eq. (23) and the Chapman-Enskog (CE) expression for the dilute-gas equal mass 50% mixture; $X = 0$. In both examples the values have been reduced by the Chapman-Enskog viscosity of a soft-sphere dilute gas.

$\beta(\gamma=1)$	CE	VdW1
0	2	.2
0.2	1.133	1.138
1	1	1
5	0.867	0.870
$\gamma(\beta=1)$		
0	1.066	1.065
1	1	1
5	0.932	0.932

B. Dense mixtures

Simulated viscosities and hydrostatic pressures are presented in Tables IV–VI under conditions selected to demonstrate how these properties vary with the parameters β and γ and the mass difference α. In order to compare the results with the conformal-solution equation in a consistent manner, we selected the reference pure fluid [Eq. (22)] such that $X_0' = 0.6$ at the reduced strain rate of 0.2. From simulation η_0 (0.6) was found to be 1.245 ± 0.050 and the hydrostatic pressure (p_0) to be 1.44 ± 0.01. Simulations, therefore, were carried out at a value of X determined from the relation

$$0.6 = \tfrac{1}{4} X (1 + \gamma^{1/4} + 2\beta^{1/4}) .$$

In two examples shown in Table IV, X_0' was selected to be 0.8 with corresponding values of η_0 (0.8) = 4.40 obtained by extrapolation from results reported in Ref. 7, and a pressure of 2.81 from Ref. 6. These results were considered to include a high X or density.

Table IV presents the viscosities and pressures at fixed $\alpha = 1$. The heading VdW1 gives the viscosity from Eq. (23) and the pressure from the relation $p = p_0 X / X_0'$. Based on the estimated errors in the viscosity and pressure both for a given run

TABLE IV. Variation of the viscosity and pressure for 50% mixture with β and γ. Calculations carried out at $\omega^* = 0.2$. In all cases $\alpha = 1$. The simulations were run at a density-to-temperature ratio X such that $X_0' = 0.6$ or 0.8, see text.

	Viscosity		Pressure	
	VdW1	Simulated	VdW1	Simulated
	$X_0' = 0.6$			
$\beta(\gamma=1)$ [a]				
0.2	1.42	1.32	1.72	1.58
1.0		1.24		1.44
5.0	1.08	1.02	1.15	0.98
	$X_0' = 0.8$			
$\beta(\gamma=1)$				
0.2	4.54	4.64	4.50	4.07
1.0		4.40 [b]		2.81 [c]
5.0	3.84	3.47	3.01	2.57
	$X_0' = 0.6$			
$\gamma(\beta=1)$				
0.2	1.33	1.25	1.57	1.53
1.0		1.24		1.44
5.0	1.16	1.22	1.28	1.22

[a] Reference 22.

[b] From Ref. 7.

[c] From Ref. 6 ($\omega^* = 0$).

TABLE V. Variation of the mixture viscosity with mass (α) with β, $\gamma=1$ at $X_0'=0.6$, $\omega^*=0.2$. Note the pressure is independent (to within computational error) of the mass as expected.

α	Viscosity VdW1	Viscosity Simulated	Pressure (1.44 for $\alpha=1$)
10	2.13	2.17	1.44
20	2.56	2.30	1.40
100	4.30	3.50	1.42

and for the reference pure fluid, we judge acceptable agreement between the simulated results and the conformal-solution VdW1 theory to be within ±8% for the viscosity and ±10% for the pressure. It is seen, therefore, that the conformal-solution theory is generally satisfactory. Table V gives the results from the simulation and VdW1 for the variation of the viscosity with mass only ($\beta=\gamma=1$). We include the pressure—which should be constant at 1.44—mainly to verify that our simulation is satisfactory even though α is very large. Agreement between theory and simulation is acceptable if $\alpha<20$. Finally results for the mixture with parameters β, γ, and α not equal to 1 are given in Table VI. Here, one observes that the VdW1 theory is not satisfactory.

TABLE VI. Results for a mixture with $\gamma=0.2$ and 5.0 (with $\beta=1$ in both cases) for $\alpha=5$ and 10, respectively: $X_0'=0.6$ and $\omega^*=0.2$.

γ	Viscosity VdW1	Viscosity Simulated	Pressure VdW1	Pressure Simulated
	$\alpha=5$			
0.2	1.81	1.92	1.57	1.57
5.0	1.82	1.81	1.28	1.24
	$\alpha=10$			
0.2	2.05	2.50	1.57	1.55
5.0	2.24	2.03	1.28	1.25

VI. CONCLUSION

We have simulated a binary mixture of soft spheres by considering a 108-particle system with components whose masses differ by a parameter α and which obey the force laws $\phi_{11}=d_{11}\, r^{12}$, $\phi_{12}=\beta d_{11}/r^{12}$, and $\phi_{22}=\gamma d_{11}/r^{12}$, respectively. The shear viscosity has been computed by the method of nonequilibrium molecular dynamics[3-5] and our first conclusion is that the computer technique is most satisfactory for this purpose: reliable results (viscosity to about 5%) were obtained without excessive computer time (about 7000 time steps) and with the relatively small system of 108 particles.

We have further extended the well-known Van der Waals one-fluid conformal-solution theory of mixtures to the viscosity by proposing a mixing rule for mass. Predictions from this theory were compared to the simulated results. Our conclusions on the comparisons is not clear-cut. It does appear that the theory is satisfactory for a mixture whose components have equal mass ($\alpha=1$) with β and γ in the range 0.2–5.0. In terms of a "Lennard-Jones σ," this range can be regarded as representing molecules whose sizes differ by about 14% (see Ref. 18). Also the theory is very satisfactory for a mixture whose components differ only by the mass (i.e., $\beta=\gamma=1$) for at least a mass difference of 20. However, there is some evidence that the theory will fail to agree with simulation if the mass difference is about 10 with γ (or β) not set equal to 1. It is very possible that the mass-mixing rule is too approximate, but it is also possible that the concept of the conformal-solution theory is not valid for all the values of β, γ, and α considered here. Clearly the theory eventually has to fail if the mixture has components which have very different masses and/or interaction parameters. We are currently investigating mixtures which indeed are composed of such different species.[23]

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[11] In the homogeneous procedure, the effect of the strain rate (ω) is entered by considering an oblique coordinate system with the x and y axes inclined at an angle θ. In the time Δt, $\theta = \frac{1}{2}\pi - \tan^{-1}(1/\omega\Delta t)$. The periodic images have to be adjusted for this system. See Fig. 9 of Ref. 3. Evans (Ref. 4) has introduced a significant variation: after every time step, the velocity of each particle is adjusted to ensure the strain rate is numerically correct and the strain profile is linear. It is possible the kinetic contribution to the viscosity may be affected by this procedure. This point is under investigation.

[12] Contributions to the thermodynamic properties of the system at molecular separations exceeding 1.5 were shown to be small: generally less than 1.0% in the pressure, for example.

[13] The effect of the magnitude of the shear rate has been discussed by Ashurst and Hoover. The effect is small if $X < 0.6$. See Fig. 12 of Ref. 3.

[14] W. T. Ashurst and W. G. Hoover, Phys. Lett. 61A, 175 (1977).

[15] J. H. Irving and J. G. Kirkwood, J. Chem. Phys. 18, 817 (1950).

[16] H. S. Green, Hand. Phys. 10, 1 (1960). One can prove the second term of Eq. (8) vanishes by several methods but a particularly convenient proof follows from the use of isotopic Cartesian tensors. See Appendix A of R. F. Snider and C. F. Curtiss, Phys. Fluids 1, 122 (1958); also, J. A. R. Coope, R. F. Snider, and F. R. McCourt, J. Chem. Phys. 43, 2269 (1965). It is perhaps worthwhile to note that the second term of Eq. (8) vanishes while the term of Eq. (12) does not.

[17] E. A. Guggenheim, *Mixtures* (Oxford, New York, 1952).

[18] D. Henderson and P. J. Leonard, in ***Physical Chemistry***, edited by D. Henderson (Academic, New York, 1971), Vol. VIII B, Chap. 7. It is well established that the VdW1 approach is satisfactory at equilibrium. Comparisons between conformal-solution theory and simulation are summarized by Henderson and Leonard for a Lennard-Jones mixture. The soft-sphere mixture has been discussed by Leland, Rowlinson, and Sather (Ref. 10) who compare conformal-solution theory with Percus-Yevick results.

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[22] Note that the variations with β ($\gamma = 1$) show directly the "excess" viscosity $\Delta\eta$: $\Delta\eta = \eta_{\text{mix}} - \sum_i x_i \eta_i$.

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