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Molecular-dynamics study of the velocity-autocorrelation function and the self-diffusion coefficient in multicomponent mixtures

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A detailed molecular-dynamics study is presented concerning the dynamic one-particle properties of binary and ternary mixtures of hard-sphere-like particles. We have studied the self-diffusion coefficient for each component of the mixture as a function of the density, and as a function of the difference in particle diameter. The results are compared with the predictions of the Enskog theory. At moderate densities positive deviations from the Enskog theory are found; at high densities we find negative deviations. It is observed that the amplitudes of these deviations differ for each component of the mixture. For moderate densities it is shown that these amplitudes have a particle-diameter dependence that is similar to that of the amplitudes of the long-time tails of the velocity-autocorrelation functions. This finding indicates that the vortex processes that give rise to the long-time tails are also responsible for the nonexponential decay of the velocity-autocorrelation function at shorter times.

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INTRODUCTION

The velocity-autocorrelation function (VAF) and its Green-Kubo integral, the self-diffusion coefficient, have been studied extensively for the one-component fluid of hard spheres. Considerably less attention has been paid to the behavior of the VAF of hard-sphere mixtures. The first molecular-dynamics (MD) studies concerning the calculation of transport properties of one-component hard-sphere fluids were performed by Alder and coworkers [1–3]. They found that at high densities a VAF has a significant negative part. As a result, the self-diffusion coefficient is significantly smaller than the value predicted by the Enskog theory.

The same MD studies [1–3] have also revealed significant discrepancies between the MD and the Enskog values of the self-diffusion coefficients at moderate densities. In the density range $0.4 \leq \rho\sigma^3 \leq 0.7$ it was found that the self-diffusion coefficient exceeds the Enskog value by 10–30%. This is due to a slowly decaying nonexponential tail of the VAF. Several groups [4–7] have derived an expression for the asymptotic decay of this long-time tail that has been tested against more detailed computer calculations [8–10]. The most convincing support for the presence of the long-time tails has been obtained recently by Frenkel and Ernst [10] for the case of lattice-gas cellular automata. In their work they have used explicitly the indistinguishability of the "particles" after a collision, which is characteristic for the cellular automata. Such an approach is not possible for mixtures where the particles are defined to be distinguishable.

Up to this moment the discussion concerning the VAF of hard-sphere fluids has been concentrated on proving the existence of the long-time tails. However, it is important to remember that the discrepancy between the observed self-diffusion coefficient and its Enskog value is mainly caused by the contribution of the nonexponential tail of the VAF to the Green-Kubo integral at relatively short times where the asymptotic behavior of the VAF has not yet been reached [1,3,5,9].

Less is known about the behavior of the VAF of hard-sphere mixtures. Herman and Alder [11] have performed a MD study concerning a test particle that differs only in mass from the other particles. They found that the amplitude of the asymptotic tail of the VAF depends on the ratio of the masses of the test particle and the other particles. Jackson, Rowlinson, and van Swol [12] have studied the self-diffusion coefficient in binary mixtures, but they did not compare their results with the Enskog theory. Erpenbeck [13] has done MD calculations of transport properties of an equimolar isotopic mixture of hard spheres, but he did not consider the self-diffusion coefficient.

In this paper we present the results of MD calculations of several binary and ternary mixtures of particles that differ in size, but not in mass. We have studied the density dependence of the self-diffusion coefficients, as well as their dependence on the relative particle size. We will also propose a relationship between the self-diffusion coefficients and the asymptotic tail of the VAF for mixtures at moderate densities. These results indicate that the dynamic processes that cause the long-time tail are also responsible for the nonexponential decay of the VAF at shorter times.

COMPUTATIONAL

We have performed MD calculations in the NVE ensemble of binary mixtures and three ternary mixtures of spherical particles of different sizes. The particles of component 1 have a diameter of $\sigma_{11}=2.6984$ Å. In the calculations for the binary mixtures the diameter of the particles of the second component vary between 2.6984 Å $\leq \sigma_{22} \leq 5.3968$ Å $=2\sigma_{11}$. In the case of the ternary mixtures the particles of the second component have a diameter $\sigma_{22}=3.4$ Å and those of the third component are $\sigma_{33}=4.2834$ Å. The masses of all particles are the same

(40 a.u.). We have used the following interaction potential:

$$V_{ij}(r)=\varepsilon(\sigma_{ij}/r)^n, \quad n=42 \ . \qquad (1)$$

For the interactions between unlike particles we assume additivity: $\sigma_{ij}=(\sigma_{ii}+\sigma_{jj})/2$. The energy parameter ε is chosen to be equal to the product of the Boltzmann constant k_B and the temperature T. This "hard-soft-sphere" potential yields results that to a very good approximation are equal to those that are calculated using a genuine hard-sphere potential [14].

The equations of motion are integrated using the Stoermer-Verlet scheme, using a time step of either 10^{-14} or 0.5×10^{-14}s. The total length of a single run varies between 4.5×10^{-11} and 1.6×10^{-10}s, depending on the density of the system.

The binary mixtures are of equimolar composition. We have further studied the three ternary mixtures with the mole fraction ratios $x_i{:}x_j{:}x_k=1{:}1{:}2$. All the mixtures are studied in the density range $0.5\le\rho_{1-\text{fluid}}\le0.85$. Here $\rho_{1-\text{fluid}}$ is the 1-fluid density, which is defined as

$$\rho_{1-\text{fluid}}=(N/V)\sigma_x^3, \quad \sigma_x^3=\sum_{i,j=1}^{s} x_i x_j \sigma_{ij}^3 \ , \qquad (2)$$

where s denotes the number of components in the mixture. In most cases the system consists of 500 particles. Additional calculations have been performed with systems of 2048 particles in order to be able to account accurately for the tail of the VAF.

RESULTS AND DISCUSSION

Self-diffusion coefficients

We have determined the self-diffusion coefficient by evaluating the slope of the mean-square displacement and by integrating the VAF [15]. The difference between the results obtained by those two methods is less than 5%. Unless stated otherwise, the values of the self-diffusion coefficients that will be presented here are average values obtained from the two methods. The self-diffusion coefficients are compared with the predictions of the kinetic theory. Al-Chalabi and McLaughin [16] have given the first-order Enskog expression for the self-diffusion coefficient in a binary mixture of hard spheres. Their expression can be straightforwardly generalized to multicomponent mixtures

$$D_{i,E}=k_BT\left[\frac{16\pi}{3}\sum_{j=1}^{s}\sigma_{ij}^2\rho_j g_{ij}(\sigma_{ij})\left[\frac{k_BT\mu_{ij}}{2\pi}\right]^{1/2}\right]^{-1} , \qquad (3)$$

where ρ_j represents the number density of component j and μ_{ij} is the reduced mass $\mu_{ij}=m_im_j/(m_i+m_j)$. The value of the pair distribution function at contact $g_{ij}(\sigma_{ij})$ is calculated using the expression that is consistent with the Carnahan-Starling equation for mixtures [17,18].

For the following discussion it is convenient to introduce a reduced self-diffusion coefficient that is equal to the ratio of the self-diffusion coefficient that is obtained by MD and the first-order Enskog value that is calculated using Eq. (3),

$$D_i^*=D_{i,\text{MD}}/D_{i,E} \ . \qquad (4)$$

In Figs. 1–4 we show for several equimolar binary mixtures the density dependence of the reduced self-diffusion coefficients. In the case of the pseudomixture $(\sigma_{11}=\sigma_{22})$ we find that our results are in good agreement with those of Alder and co-workers [1–3] for genuine hard spheres. This can be seen in Fig. 1. It should be noted that the values for D^* of Alder and co-workers have been confirmed recently by Erpenbeck and Wood [19]. In Figs. 2–4 the results for mixtures of particles with different diameters are shown. The tendencies in Figs. 1–4 are the same. At high densities $(\rho_{1-\text{fluid}}>0.8)$ we find for both components a value of the reduced self-diffusion coefficient $D_i^*<1$, and that D_i^* decreases with increasing density. This effect has been discussed by Alder and Wainwright [1] for the one-component fluid. Their qualitative explanation of this phenomenon is as follows. Due to the high density a tagged particle is closed in by its neighbors. Therefore, the collisions of the tagged particle with its neighbors lead, on average, to a reversal of its velocity [20]. As a result, the diffusive motion of the tagged particle is slowed down. This is

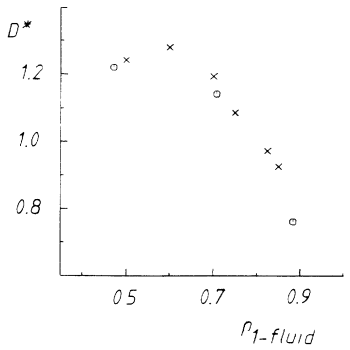

FIG. 1. Density dependence of the reduced self-diffusion coefficient $D_i^*=D_{i,\text{MD}}/D_{i,E}$ of the binary pseudomixture $\sigma_{11}=\sigma_{22}$. ×, our results; ○, results of Ref. [3]. $N=500$.

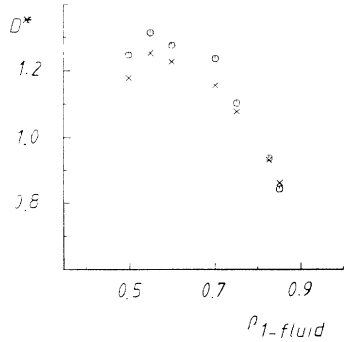

FIG. 2. Density dependence of the reduced self-diffusion coefficient $D_i^*=D_{i,\text{MD}}/D_{i,E}$ of the equimolar binary mixture with $\sigma_{11}=2.6984$ Å and $\sigma_{22}=3.400$ Å. ×, component 1; ○, component 2. $N=500$.

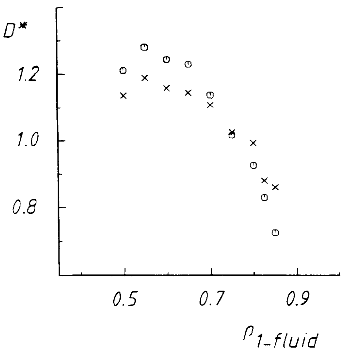

FIG. 3. Same as Fig. 2, but with $\sigma_{11}=2.6984$ Å and $\sigma_{22}=4.2834$ Å.

called the backscattering effect. In the case of the binary mixture we find at a given (high) density that the reduced self-diffusion coefficient D_i^* has the highest value for the component with the smallest diameter, and that this difference between D_1^* and D_2^* becomes more pronounced as the difference in size of the two species of particles increases. This result indicates that the small particles are able to move through the cavities left by the rigid coarse ordering of the large particles.

At moderate densities the situation is reversed. In the density range $0.5<\rho_{1-\text{fluid}}<0.65$ we find for the reduced self-diffusion coefficients values $D_i^*>1$. Furthermore, we find that the largest particles of the mixture have the largest value for D_i^*. Again the difference between D_1^* and D_2^* seems to be more pronounced as the difference in the size of the two species of particles increases, although at these densities this dependence of D_i^* on the particle diameter is not as clearly observable as in the high-density region. The positive deviation of the self-diffusion coefficient from its Enskog value was first observed by Alder and Wainwright [1] in a one-component fluid. They have explained it qualitatively [2] in terms of an average vortex flow pattern around a tagged particle that moves through the fluid. The persistence of velocity of the tagged particle is increased by the additional driving force caused by the surrounding particles. This may give rise to an increase of the self-diffusion coefficient. The difference between D_1^* and D_2^* that we observe in the mixtures suggests that the large particles are more involved in this process than the small particles. Closely related to this vortex model is the observed algebraic decay of the VAF at long times. This will be discussed in the next section.

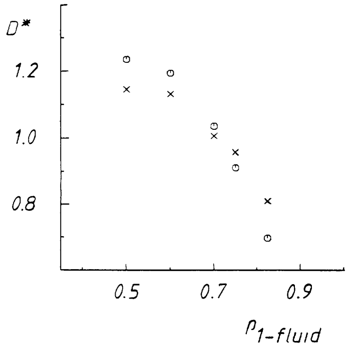

FIG. 4. Same as Fig. 2, but with $\sigma_{11}=2.6984$ Å and $\sigma_{22}=5.3968$ Å.

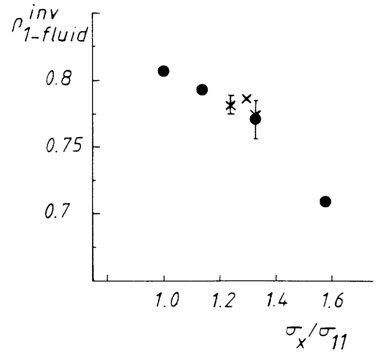

FIG. 5. σ_x dependence of the density at which $D^*>1$ changes to $D^*<1$. ●, binary mixtures; ×, ternary mixtures. $N=500$

The one-fluid density at which the reduced self-diffusion coefficients change from values larger than 1 to values smaller than 1 appears to be dependent on the ratio of the diameters of the different particles. In the case of the pseudomixture ($\sigma_{11}=\sigma_{22}$) we find that this crossover occurs at $\rho_{1-\text{fluid}}=0.81$, whereas for mixtures with the largest difference in the two diameters ($\sigma_{11}=0.5\sigma_{22}$) we find this crossover at $\rho_{1-\text{fluid}}=0.71$, as illustrated in Fig. 5. This dependence on the relative particle size implies that the one-fluid density is not a proper scaling function for corresponding state comparisons of transport properties of different mixtures at densities at which the backscattering effect contributes to the VAF.

We conclude this section by presenting the results for the self-diffusion coefficients of three-component mixtures. In Fig. 6 we show the density dependence of the self-diffusion coefficient in the mixture with $x_1=x_2=0.5x_3$. We have obtained similar results for the mixtures with $x_1=x_3=0.5x_2$ and $x_2=x_3=0.5x_1$. The results for the three-component mixtures are consistent

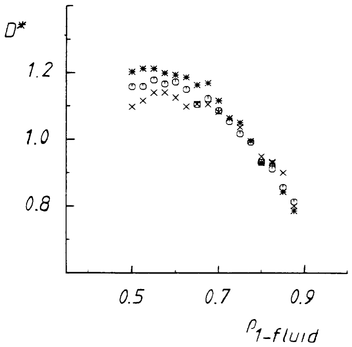

FIG. 6. Density dependence of the reduced self-diffusion coefficient of the ternary mixture with $x_1=x_2=0.25$ and $x_3=0.5$, $\sigma_{11}=2.6984$ Å, $\sigma_{22}=3.4000$ Å, and $\sigma_{33}=4.2834$ Å. ×, component 1; ○, component 2; $*$, component 3. $N=500$.

with the results for the binary mixtures, as discussed above. In the high-density region we find values of the reduced self-diffusion coefficients that are smaller than 1. However, in contrast to the binary mixture, we find for the three-component mixtures no large discrepancy between the different reduced self-diffusion coefficients at high densities. This indicates that the space in the cavities between the large particles is taken by the medium-sized particles, thus limiting the space in which the small particles can move. In the moderate density range we find that the largest particles have the largest D_i^* values and that the smallest particles have the smallest values. The 1-fluid density at which the crossover occurs from $D_i^* > 1$ to $D_i^* < 1$ is independent of the composition of the ternary mixture. This is due to the $\sigma_{x}-$ parameter, which has about the same value for the three mixtures studied here (see also Fig. 5).

The results presented above are for mixtures in which all components have the same mass. However, it is to be expected that more or less similar results can be obtained for mixtures of particles that differ also in mass. See, for example, the results for isotopic mixtures of Herman and Alder [11]. In the next section we will discuss how deviations from the Enskog theory manifest themselves in the form of the VAF.

Velocity-autocorrelation function

The Enskog theory predicts in the first order a VAF with an exponential decay

$$\langle v_i(0)v_i(t)\rangle = \exp\left[\frac{-tm_i}{k_B T D_i}\right] . \quad (5)$$

Alder and Wainwright [2] found significant deviations from the exponential decay of the VAF. At moderate densities they discovered that the VAF has a slowly decaying tail. They proposed that the VAF of fluids at moderate densities has an algebraic long-time decay

$$\langle v(0)v(t)\rangle|_{t\to\infty} = \alpha(t/t_0)^{-(d/2)} . \quad (6)$$

Here α is an amplitude, d is the dimension of the system (in our case $d=3$), and t_0 is the mean free time of the particle.

The discovery of the long-time tail initiated a considerable amount of theoretical and computational work. Several groups have found expressions for the asymptotic behavior of all the relevant current autocorrelation functions for one-component fluids using hydrodynamics [4], modified kinetic theory [5], and mode coupling techniques [6]. These expressions are supposed to be valid for times longer than $10t_0$ [5]. However, as shown clearly by Alder and co-workers [1,3], the nonexponential part of the VAF has its largest contribution to the self-diffusion coefficient around $5t_0$.

The argument that links the presence of long-time tails with a positive deviation for the self-diffusion coefficients from the predictions of the Enskog theory is that the vortex model discussed above is a hydrodynamic model. Therefore, the vortex motion should affect the long-time behavior of the correlation functions. Here we attempt to obtain support for Alder's qualitative explanation [2] for the positive deviation from the Enskog theory.

For mixtures the one-component expression for the long-time tail cannot be used. This is because for mixtures one also has to consider the conservation law of concentration and then quantities like the osmotic compressibility may enter the expression for the long-time tail. Wood [7] has discussed the long-time tails for binary mixtures, but unfortunately, he did not consider the VAF.

In order to study the tail of the VAF in binary mixtures, we have performed several MD runs with 2048-particle systems. In these calculations the mixtures have a density of $\rho_{1-\text{fluid}}=0.5$. For each mixture we have averaged the VAF over six independent runs in order to obtain the required small statistical uncertainty for the VAF tail. Each MD run has a length of 1.6×10^{-10}s. For our analysis we have normalized the real-time axis of the VAF of component i with respect to the mean free time of component i,

$$t_{0i} = \left[(8\pi k_B T)^{1/2} \sum_{j=1}^{s} \sigma_{ij}^2 \rho_j g_{ij}(\sigma_{ij}) \mu_{ij}^{-1/2} \right]^{-1} . \quad (7)$$

In Table I we have presented the values of t_{0i} for the mixtures under consideration. It should be noted that, in the special case studied here in which all the particles have the same mass, the mean free time is closely related to the self-diffusion coefficient [see Eq. (3)]. The conversion from the t axis to the t/t_0 axis causes the VAF to decay initially on the same scale. This is illustrated in Fig. 7 for the mixture with $\sigma_{11}=2.6984$ Å and $\sigma_{22}=4.2834$ Å. In Fig. 7(b) a clear difference can be seen between the amplitudes of the tails of the two VAF's. As mentioned earlier, integration of the VAF yields the self-diffusion coefficient. We have integrated both VAF's up to the 1.5×10^{-11}s self-diffusion coefficient. In the case of the VAF's shown in Fig. 7, we have shown in Fig. 8 how the integral of the VAF

$$D_i^*(t/t_{0i}) = \frac{k_B T t_{0i}}{D_{i,E} m_i} \int_0^{t/t_{0i}} d(t/t_{0i}) \langle v_i(0) v_i(t/t_{0i})\rangle \quad (8)$$

converges for large times to the value of D_{0i}^*. Figure 8 also demonstrates clearly that a significant positive deviation from the Enskog value has been obtained as early as $t/t_0=10$. This indicates that processes that play on a relatively short time (i.e., $t/t_0 < 10$) do give rise to an important positive deviation of the self-diffusion coefficient from its Enskog value. Similar results have been obtained for the other mixtures studied here. In the case of

TABLE I. Mean free times t_{0i} for each component of the mixture. $x_1=x_2=0.5$, $\rho_{1-\text{fluid}}=0.5$.

σ_{11} (Å)	σ_{22} (Å)	t_{01} 10^{-13}s	t_{02} 10^{-13}s
2.6984	2.6984	2.233	2.233
2.6984	3.4000	2.939	2.227
2.6984	4.2834	3.997	2.314
2.6984	5.3968	5.515	2.475

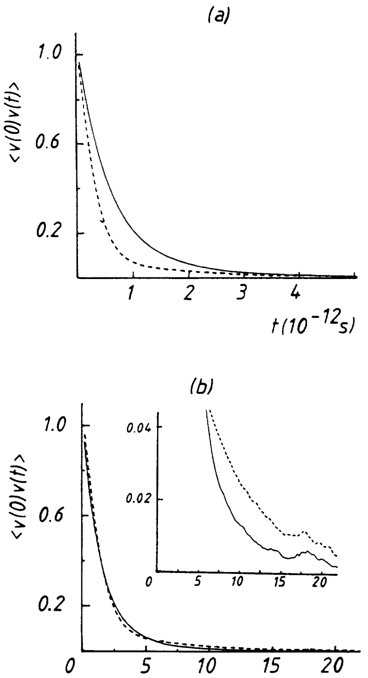

FIG. 7. VAF's of the equimolar binary mixture with $\sigma_{11}=2.6982$ Å and $\sigma_{22}=4.2834$ Å. Solid line, component 1; dashed line, component 2; $\rho_{1-\text{fluid}}=0.50$, $N=2048$. (a) Real-time axis; (b) collision time axis; at the inset a magnification of the tails of the VAF's are shown.

the one-component fluid this was already shown by Alder and co-workers [1,3].

When the vortex model of Alder and Wainwright [2] indeed does explain the positive deviation of the self-diffusion coefficient from its Enskog value, then it should be possible to relate the amplitudes of the long-time tails to the non-Enskog part of the reduced self-diffusion coefficients D_i^*-1. In the following, we will try to obtain a relationship between the amplitude of the long-time tails and D_i^*-1.

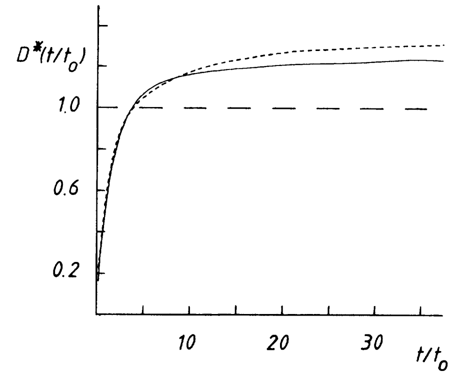

FIG. 8. Time dependence of the integral $D_i^*(t/t_0)$ of the equimolar binary mixture with $\sigma_{11}=2.6982$ Å and $\sigma_{22}=4.2834$ Å. Solid line, component 1; dashed line, component 2; the horizontal long-dashed line, the first-order Enskog value $D_i^*=1$; $\rho_{1-\text{fluid}}=0.50$, $N=2048$.

The long-time behavior of the VAF can be studied best when the exponential Enskog contribution, as given by Eq. (5), is subtracted from our MD results. Next, the resulting non-Enskog part is multiplied with $(t/t_0)^{3/2}$ [10]. In Fig. 9 we show the resulting functions for all binary

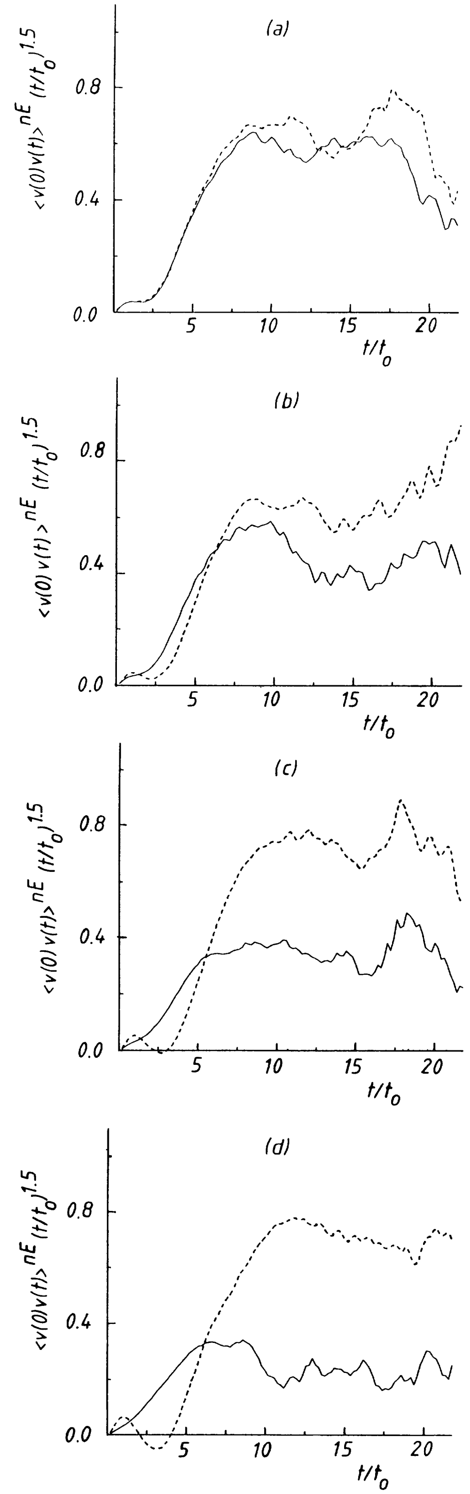

FIG. 9. Non-Enskog part of the VAF's multiplied with $(t/t_0)^{1.5}$. Solid line, component 1; dashed line, component 2; $\rho_{1-\text{fluid}}=0.50$, $N=2048$. $\sigma_{11}=2.6982$ Å and (a) $\sigma_{22}=2.6982$ Å, (b) $\sigma_{22}=3.4000$ Å, (c) $\sigma_{22}=4.2834$ Å, and (d) $\sigma_{22}=5.3968$ Å.

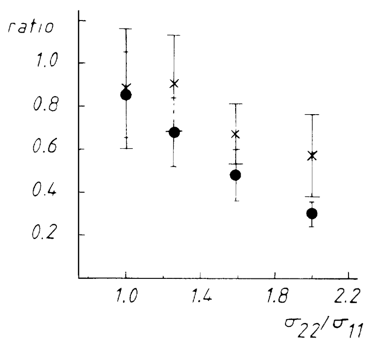

FIG. 10. Diameter-ratio dependence of the ratio of non-Enskog quantities. ×, $(D_1^*-1)/(D_2^*-1)$; ●, α_1/α_2. $\rho_{1-\text{fluid}}=0.50$, $N=2048$.

mixtures that are considered here. Several conclusions can be drawn from Fig. 9. First, the non-Enskog contribution to the Green-Kubo integral is the largest around $t/t_0=7$. Second, the algebraic $(t/t_0)^{-3/2}$ decay occurs at times larger than $t/t_0=10$. For these times the amplitude ratio α_1/α_2 of the long-time tails is nearly constant. At times larger than $t/t_0=20$ our results are unreliable due to statistical noise. We have calculated the amplitudes α_1 and α_2 in the time interval $10\leq t/t_{0i}\leq 20$ from our data using Eq. (6). The ratio of these amplitudes can be compared with the ratio of the non-Enskog factors of the self-diffusion coefficients $(D_1^*-1)/(D_2^*-1)$.

In Fig. 10 we show the $(\sigma_{22}/\sigma_{11})$ dependence of the amplitude ratio of the long-time tail α_1/α_2 and the ratio $(D_1^*-1)/(D_2^*-1)$. The values of the self-diffusion coefficients used here are those that are obtained by the integration of the VAF's (see Table II). The uncertainty margin in the values of the self-diffusion coefficients is obtained from the standard deviation of D_i in the six independent MD runs, while the standard deviation of α_i is obtained from the fit of Eq. (6) to the VAF. It should be noted that the manner on which the results are presented in Fig. 10 causes an artificial proportional increase in the standard deviations. In all cases we find that $(D_1^*-1)/(D_2^*-1)$ and α_1/α_2 are of the same order of magnitude. The ratio $(D_1^*-1)/(D_2^*-1)$ is always somewhat larger than α_1/α_2. The reason for this difference is unclear. It might be that the usage of the interaction potential defined in Eq. (1) affects the short-time behavior of the VAF. Another possibility might be that the Carnahan-Starling approximation for the contact values $g_{ij}(\sigma_{ij})$ that are used in the calculation of the Enskog value of the self-diffusion coefficient are responsible for the defect. A small error (of the order of 5%) may give rise to such a difference. Nonetheless, it is important to note that $(D_1^*-1)/(D_2^*-1)$ and α_1/α_2 both decrease more or less in the same manner in which the diameter ratio increases. Furthermore, from the values of D_i^* and α_i, as given in Table II, more detailed information can be obtained. The values of D_2^* and α_2 are constant within the error bars, whereas D_1^* and α_1 both decrease as σ_{22} increases. This indicates that the processes that give rise to the long-time tail of the VAF of the large particles are not affected by the presence of the small particles. The situation is different when the VAF of the small particles is considered. The processes that give rise to the long-time tail of the VAF of the small particles are disturbed by the presence of the large particles. The results indicate that the presence of the large particles causes some sort of screening of the vortex flow pattern around the small particles. The last conclusion that can be drawn from Table I is that the ratio $(D_2^*-1)/\alpha_2$ is constant, and that $(D_1^*-1)/\alpha_1$ is almost constant when the relatively large uncertainty margins are taken into account. This finding indicates that is it possible to calculate D_2 (and possibly also D_1) once the self-diffusion coefficient of the one-component fluid and an accurate expression for α_i are known. This last statement is only valid at densities at which the backscattering effect can be neglected.

In the discussion presented above, we have not mentioned the possible influence of the finite system size. The magnitude of the correction term due to an extrapolation is proportional to $1/N$. Using the accurate extrapolation performed by Erpenbeck and Wood [19], we estimate that such a correction to D_i^* for the extrapolation from $N=2048$ to ∞ is less than 1%. This is less than the numerical uncertainty of the results presented in Table II. Furthermore, since we are comparing D_i^* ($N=2048$) with α_i ($N=2048$) we do not expect that an extrapolation to the thermodynamic limit will affect the conclusions. All our observations concerning the behavior of D_i^* and α_i indicate that the processes that give rise to the long-time tails of the VAF's also are responsible for the positive deviation of the self-diffusion coefficient from its Enskog value. Thus our results give support for the vortex model introduced by Alder and Wainwright [2] as an explanation for the behavior of the self-diffusion coefficient at moderate densities.

Finally, we will consider the VAF in the high-density regime. In Fig. 11 we have plotted the VAF's of an equimolar binary mixture ($\sigma_{11}=2.6984$ Å, $\sigma_{22}=4.2834$

TABLE II. Reduced self-diffusion coefficients and the amplitudes of the long-time tails for four equimolar binary mixtures at $\rho_{1-\text{fluid}}=0.5$. $N=2048$.

σ_{11} (Å)	σ_{22} (Å)	D_1^*	D_2^*	α_1	α_2
2.6984	2.6984	1.284±0.038	1.322±0.046	0.568±0.062	0.666±0.068
2.6984	3.4000	1.289±0.044	1.319±0.027	0.433±0.057	0.638±0.054
2.6984	4.2834	1.214±0.015	1.319±0.036	0.358±0.058	0.745±0.053
2.6984	5.3968	1.179±0.033	1.314±0.036	0.216±0.029	0.715±0.042

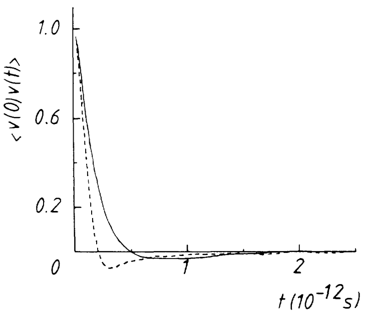

FIG. 11. VAF's of the equimolar binary mixture with $\sigma_{11}=2.6982$ Å and $\sigma_{22}=4.2834$ Å. Solid line, component 1; dashed line, component 2; $\rho_{1-\text{fluid}}=0.85$, $N=500$.

Å) at a density $\rho_{1-\text{fluid}}=0.85$. It can be seen that both autocorrelation functions have a significant negative part at intermediate times. The VAF of the large particles has the negative well at shorter times than the VAF of the small particles. A similar behavior can be found when both VAF's are plotted as a function of the collision time t/t_0. This result indicates that the large particles are earlier involved in the backscattering process than the small particles. This observation supports the claim we made in the previous section, that the small particles are able to move through the coarse network created by the ordering of the large particles.

CONCLUSIONS

We have shown that for component i of a multicomponent mixture, the deviation of the self-diffusion coefficient D_i from its Enskog value depends on the diameter ratio σ_{ii}/σ_{jj}. In the case of mixtures at moderate densities we have found a positive deviation, which is the smallest for the smallest particles present in the mixture. This observation has enabled us to obtain a relationship between the ratio of the non-Enskog contributions to the self-diffusion coefficients and the amplitudes of the long-time tails of the VAF's. This relationship gives support for the vortex model introduced by Alder and co-workers as an explanation for the positive deviation of the self-diffusion coefficient from its Enskog value [2]. Our results for the mixtures at moderate densities imply that the vortex flow pattern is the largest around the largest particles of the mixture. The vortex motion around the smallest particles is hindered by the presence of the large particles.

At high densities we found that the self-diffusion coefficient has a negative deviation from its Enskog value. The deviation is most negative for the largest particles in the mixture. This indicates that the small particles are able to move relatively freely through the coarse network of large particles. The mobility of the smallest particles is reduced when particles of intermediate size are added to the mixture.

Finally, we have shown that the 1-fluid density is not a proper scaling parameter for corresponding state comparisons of the transport properties of different mixtures. Such comparisons can only be made when those mixtures have almost the same σ_x/σ_{11} values, or at densities at which the backscattering effect does not contribute to the shape of the VAF.

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