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Dynamic cross correlation in isotopic two-component liquids: Molecular-dynamics calculation results compared with predictions of kinetic theory

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For thermodynamically ideal two-component systems, as for example isotopic systems, the mass effect on the mutual diffusion coefficient is negligibly small for mass ratios of order 2. For higher mass ratios a significant influence on the diffusion coefficient may be expected. We present here accurate molecular-dynamics calculation results for the hard soft sphere and the Lennard-Jones liquids, which indicate quantitatively the mass-ratio effect on the mutual diffusion coefficient. The predictions of the Enskog kinetic theory are found to give the correct trend and order of magnitude of these effects but overestimate them at all the mass ratios studied. Both systems, the hard soft sphere liquid (the softness of the interaction is so small that it can be regarded as a hard one) and the Lennard-Jones liquid, show appreciable mass-ratio dependence of the diffusion coefficient only for ratios larger than 10, in agreement with our previous numerical work [Schoen and Hoheisel, Mol. Phys. **52**, 1029 (1984); **53**, 1367 (1984); **57**, 65 (1986)].

I. INTRODUCTION

Dynamic cross correlations in binary liquid mixtures of very nonideal character have widely been studied by molecular-dynamics (MD) calculations.[1,2] In thermodynamically ideal two-component systems whose component particles differ only in mass, the so-called isotopic mixtures, cross correlations are generally negligible. However, for isotopic systems of very large mass ratio, these cross effects can play a significant role. They accelerate the mutual diffusion process relative to the self-diffusion processes. Recently self-diffusion has been carefully studied for isotopic liquid mixtures.[3] Although significant mass influence was found in these studies, the results provide only indirect information on dynamic cross correlation.

Hence an extensive MD investigation of cross correlation in isotopic binary mixtures seemed to be in order. Such a study seemed of particular interest, because kinetic theoretical predictions exist for these systems[4] and to the best of our knowledge they have not been compared with exact computer results until now. Our calculations include the hard soft sphere (HSS; the softness of the interaction is so small that it can be regarded as a hard interaction) and the Lennard-Jones (LJ) two-component system. The former is equivalent to the hard-sphere system[5] and thus allows application of theoretical approaches developed for HS systems. The latter shows the influence of attractive forces on the cross correlation, when it is compared with the HSS system.

II. DYNAMIC CROSS CORRELATION AND DEMIXING IN TWO-COMPONENT SYSTEMS

For "molecular-dynamics ensembles," where the particle number N, the volume V, and the total energy E are fixed and the total linear momentum $\mathbf{p}$ is zero, the mutual diffusion coefficient D_{12} of a binary system may be written as follows:

$$D_{12}=\frac{Q}{3N}\frac{1}{m_1w_1m_2w_2}\int_0^\infty\langle\mathbf{J}_m(0)\cdot\mathbf{J}_m(t)\rangle dt\ , \tag{1}$$

where $\mathbf{J}_m(t)$ is the mass current defined by the following expression:

$$\mathbf{J}_m(t)=m_1\sum_{i=1}^{N_1}\mathbf{v}_i^{(1)}(t)\ . \tag{2}$$

Here the velocity of particle i of kind 1 is denoted by $\mathbf{v}_i^{(1)}$, the particle masses of the species are denoted by m_1 and m_2, and the mass fractions by w_1 and w_2. The total number of particles is assumed to be $N=N_1+N_2$. The Q factor appearing in the first equation represents a thermodynamic factor, which is unity for a thermodynamically ideal mixture.[6] The angular brackets indicate the average over the NVE $\mathbf{p}=0$ ensemble.

It can then be shown that for a pseudomixture, in which particles of species 1 and 2 can only be distinguished by numbers, Eq. (1) reduces to an expression containing velocity-autocorrelation functions rather than the mass-current autocorrelation function (MCAF).[1] We have for such a system

$$\begin{aligned}D_{12}^0&=Q\left[x_2\int_0^\infty\langle\mathbf{v}_i^{(1)}(0)\cdot\mathbf{v}_i^{(1)}(t)\rangle dt\right.\\&\qquad\left.+x_1\int_0^\infty\langle\mathbf{v}_i^{(2)}(0)\cdot\mathbf{v}_i^{(2)}(t)\rangle dt\right]\\&=Q(x_2D_1+x_1D_2)\ ,\end{aligned}\tag{3}$$

where we have introduced the self-diffusion coefficients D_1 and D_2 and the mole fraction x_1 and x_2 of the components.[6]

We see that in thermodynamically and dynamically ideal mixtures (pseudomixture) the mutual diffusion coefficient is just composed of the self-diffusion coefficients. Thus the diffusion process is solely characterized by velocity autocorrelations.

For nonideal mixtures, the mass-current autocorrelation function given in Eq. (1) appears to contain additional velocity cross correlations responsible for deviations of the mutual diffusion coefficient from the ideal diffusion coefficient D_{12}^0. The so-called dynamic cross-correlation ratio D_{12}/D_{12}^0 may therefore serve as a suitable measure of dynamic cross correlation in binary systems. A further advantage of the use of this dynamic quantity is its explicit independence of the thermodynamic factor Q which drops out as Eq. (1) and (3) show immediately.

However, an interesting alternative, completely equivalent description of the dynamic behavior of a binary mixture may be given by direct analysis of autocorrelation and cross-correlation terms in the mass-current autocorrelation functions. This has been given in a general manner by Raineri and Friedman[7] and applied to computer calculations by the present authors.[8]

Here it is satisfactory to define the so-called self-terms and distinct terms of the mass-current autocorrelation functions which will be exploited in a later section to analyze the dynamic character of the mixture. We write

$$\gamma^s(t)=\tfrac{1}{3}\langle \mathbf{v}_i^{(1)}(0)\cdot\mathbf{v}_i^{(1)}(t)\rangle \ ,$$

$$\gamma^d(t)=\tfrac{1}{3}\langle N_1\mathbf{v}_i^{(1)}(0)\cdot\mathbf{v}_j^{(1)}(t)\rangle \ ,$$

with $j\neq i$. Note that for a pseudomixture $\gamma^s(t)$ cancels $\gamma^d(t)$ at any time to order $(1/N)$. For nonideal mixtures the sum function $\gamma^s(t)+\gamma^d(t)$ is well suited to characterize the dynamic behavior of the mixture.

A final general comment on phase separation and association in a mixture may be in order. Using the dynamic ratio D_{12}/D_{12}^0, one can classify thermodynamically nonideal mixtures in those showing demixing or associating tendencies dependent on whether the D_{12}/D_{12}^0 value is larger or smaller than unity.[1] In particular, phase separation is well detectable in mixtures of very different molecular interactions. However, in the present work we investigate thermodynamically ideal mixtures only differing in the particle mass of the components. These mixtures behave thermodynamically like a pure fluid. They cannot show any structural demixing or associating tendency. So, when we speak of "dynamical demixing" in the following text, we think of *nonequilibrium states,* where these pure dynamical effects could play a role. We think, for instance, of thermodynamically unstable "metastable states" near the boundary of phase stability. For these latter states, pure dynamic demixing effects could influence the behavior of the liquid.

III. KINETIC THEORY

Using the definition of partial friction coefficients[9] in a binary mixture Al-Chalabi and McLaughlin[4] obtained self-diffusion and the mutual-diffusion coefficients of a hard-sphere mixture in the Enskog approximation.[10] In particular, they derived simple formulas for isotopic HS mixtures. Considering these expressions for the self-diffusion coefficients D_1 and D_2, as well as for the mutual-diffusion coefficient D_{12}, we find the following simple relation for the dynamic cross-correlation ratio, $D_{12}/(x_1D_2+x_2D_1)$:

$$\frac{D_{12}}{x_1D_2+x_2D_1}=\frac{(1/S)^{1/2}}{\dfrac{x_2}{x_1+x_2(S)^{1/2}}+\dfrac{x_1}{x_2(R)_+^{1/2}(S)^{1/2}x_1}} \ , \tag{4}$$

where x_1 and x_2 denote the mole fractions and R the mass ratio m_2/m_1 of the two molecular species with the additional abbreviation

$$S=2R/(1+R) \ .$$

We see immediately from Eq. (4) that for $R=1$ the dynamic cross-correlation ratio, which we shall denote by D_{12}/D_{12}^0 in what follows, equals 1, as it should. The asymptotic case of $R\rightarrow\infty$ can also be determined by Eq. (4), yielding

$$\frac{D_{12}}{D_{12}^0}=1+\frac{1}{(2)^{1/2}}\frac{x_1}{x_2}, \quad R\rightarrow\infty \ .$$

For equimolar composition, we then find the value of 1.7. From earlier studies[1,11] we know that dynamic ratios close to 2.0 lead to demixing of the system. So phase separation might not occur in isotopic mixtures, at least not in "Enskog-type" fluids. We shall, however, return to this point in our final discussion.

IV. MD CALCULATIONS

The MD calculations were performed in the manner described extensively in Ref. 6. Some useful technical details of the present computations are gathered in Table I. As we are interested here in very small effects, it was obligatory to perform a lot of different runs for the same mass ratio to achieve the required low statistical error. Furthermore, it was necessary to examine the reproducibility of the results depending on the time step applied. In most cases, an integration time step of 0.5×10^{-14} s sufficed. However, for the larger mass ratios and the hard–soft-sphere potential a reduction to 0.25×10^{-14} s was unavoidable. We studied mass ratios up to $R=20$ very accurately, but performed some test runs for much larger R. As the runs for these latter R values indicated large statistical uncertainties, we did not attempt to reach a better accuracy by increasing the number of runs. The results, which we obtained for the smaller R, sufficed for what we intended to show. The statistical uncertainty of the dynamic cross-correlation ratio computed in this work is smaller than 3%, which has been accounted for in the smoothed curves, drawn by graphical interpolation through the final data, presented in the figures. The "cross-correlation functions" illustrated in the figures have larger statistical uncertainties of 5–10 %, because they stem from single runs only.

V. POTENTIALS AND STATES

For the comparison with kinetic theory we have used the "42" HSS potential function given by the expression

$$u_{\mathrm{HSS}}=\varepsilon(\sigma/r)^{42} \ ,$$

TABLE I. Technical details of the MD computations.

Number of particles	108 256 (standard: 108)
Number of integration time steps	10^5
Number of runs per mass ratio	3–6
Time step	0.25×10^{-14} s, 0.5×10^{-14} s
Integration scheme	Stoermer-Verlet
Ensemble	$NVE\mathbf{p}$ (V volume, E energy, and $\mathbf{p}$ total momentum of a system)
Number of uncorrelated averaging events	10 000 (for D_1 and D_2) 6000 (for D_{12})
Cutoff radius for the LJ potential	2.5σ
Computation time per 1000 steps (Cyber 205)	1.8 s (108 particles)

where ε denotes the energy and σ the volume parameter. Because we study isotopic mixtures, the potential function is identical for all pair interactions. The fluid modeled by this HSS potential has practically the properties of the genuine HS system as shown in recent publications.[5,12] To obtain information about the influence of attractive interactions, we also studied the common (12-6) LJ potential with corresponding ε and σ parameters. The chosen potential parameters are listed in Table II.

Particle masses and mass ratios as well as the density of the states investigated are given in Table III. Equimolar mixtures were considered throughout the computations, and a reduced temperature of $kT/\varepsilon=1$ was achieved in each run with a precision of about 5%. Temperature variations within the 5% range had a negligible influence on the results. The results for other than liquid densities have an accuracy of about 5%, as they have solely been used to discern tendencies.

VI. RESULTS FOR THE HSS MIXTURE

The dynamic cross-correlation ratio D_{12}/D_{12}^0 obtained by MD are plotted as a function of the mass ratio R in Fig. 1. It is evident from this figure that the mass effect on D_{12}/D_{12}^0 is small, leading to an enlargement of D_{12}/D_{12}^0 on the order of 10% for mass ratios around 20. The slope of the curve is practically constant but would also be consistent with a square-root function predicted by kinetic theory.

Kinetic theory results obtained from Eq. (1) and the smoothed MD values for the cross-correlation ratio are presented in Fig. 2. Apparently, the Enskog theory predicts a too high cross-correlation effect, at least for the liquid density considered. However, as the deviation is of the order of 10%, the kinetic theoretical results can be regarded as satisfactory. Some preliminary MD results for smaller densities are summarized in Table IV. The numbers given in this table indicate an increase of D_{12}/D_{12} with decreasing density. Thus agreement between MD and kinetic theory seems to improve slightly, since D_{12}/D_{12}^0 predicted by the Enskog approach has no density dependence. It would, however, be extremely expensive to prove this unambiguously by MD calculations. For completeness, we have gathered the computed self-diffusion coefficients as well as the mutual ones for the density 0.75 in Table V.

TABLE II. Potential parameters.

Type	σ (10^{-10} m)	ε/k[a] (K)
HSS	3.4	120
LJ	3.4	120

[a] k denotes Boltzmann's constant.

VII. RESULTS FOR THE LJ MIXTURE

Figure 3 contains the computed D_{12}/D_{12}^0 ratio for the two-component LJ liquid. As in the case of the HSS system, the mass effect on the cross-correlation ratio is small. It reaches appreciable values solely for the higher

TABLE III. Equimolar isotopic systems studied at $kT/\varepsilon=1$ for $(N/V)\sigma^3=0.75$.

System	R $\left(=\dfrac{m_2}{m_1}\right)$	m_1 (a.u.)
HSS	4	16
	7	10
	9	8
	12	6.15
	15	5
	18	4.21
LJ	2	26.6
	3	20
	7	10
	9	8
	15	5
	19.5	3.90

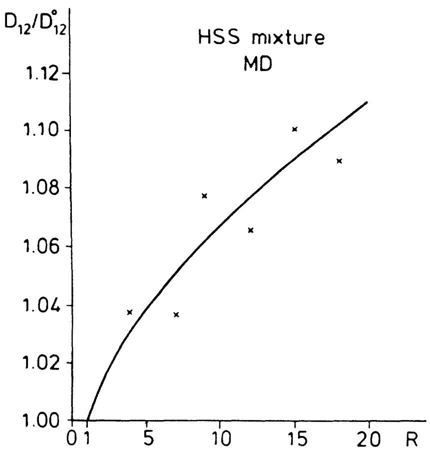

FIG. 1. Dynamic cross-correlation ratio for the equimolar isotopic HSS system as a function of the mass ratio. $n^*=0.75$; $T^*=1$. The line represents a graphical interpolation.

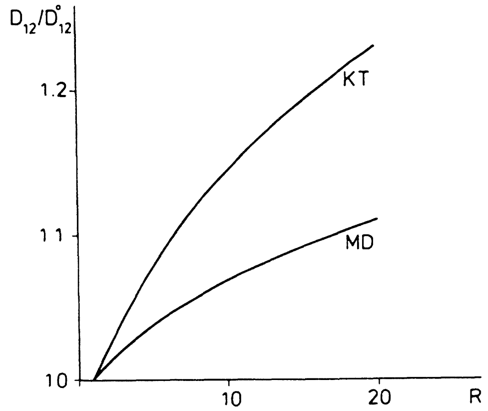

FIG. 2. Dynamic cross-correlation ratio for the equimolar isotopic HSS system as function of the mass ratio. KT, kinetic theory; MD, molecular-dynamics calculations.

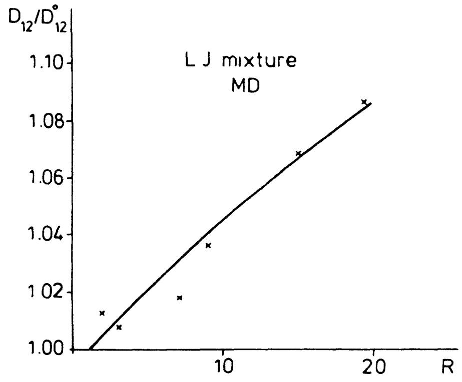

FIG. 3. As in Fig. 1 but for the isotopic LJ system.

TABLE IV. Preliminary MD results for the HSS system at smaller densities than considered in Figs. 1 and 2 for $R=15$.

$\frac{N}{V}\sigma^3$	D_{12}/D^0_{12}
0.75	1.09±0.02 (from Fig. 1)
0.70	1.15±0.1
0.65	1.20±0.1

R values. On comparing Figs. 1 and 3, we see that the dependence of the cross correlation on the mass ratio is very similar in both systems. Apparently, the attractive tail of the LJ potential has only a little influence upon cross correlation. Hence, we may conclude that the present findings concerning dynamic cross correlation in isotopic mixtures are of general validity and might also hold for molecular liquid mixtures. Accordingly, the kinetic theoretical predictions of cross effects apply to HS as well as LJ mixtures. This is in agreement with recent MD investigation of the separation factor in isotopic mixtures.[13,14]

VIII. DISCUSSION AND CONCLUSIONS

Before we summarize a number of conclusions which can be drawn from the present results, we may discuss our findings in the light of recently defined self- and distinct terms of the mass current to describe the mutual diffusion process in mixtures.[7,8] Using the latter determinology (see Sec. II) we can analyze reliably the character of a binary mixture by the sum function $\gamma(t)$:

$$\gamma(t)=\gamma^s(t)+\gamma^d(t) ,$$

where $\gamma^s(t)$ and $\gamma^d(t)$ are the self- and distinct velocity time-correlation functions associated with the mass-current autocorrelation function of component 1 of the mixture system. After Refs. 13 and 14, $\gamma(t)$ is identical to 0 for a thermodynamically and dynamically ideal system, larger than 0 for a system of demixing character, and smaller than 0 for a system of associative character, at least in a certain short-time interval. Relying on these properties of $\gamma(t)$, we should expect that the purely dynamical effects arising from hindered momentum exchange between particles of unlike species are reflected in the time behavior of $\gamma(t)$. This is in fact nicely confirmed by the plots of $\gamma(t)$ presented in Figs. 4 and 5. The figures show curves for different mass ratio and different density. Evidently, the sum function, display a large positive peak at short times in all cases. The height of the peak is largest for the highest mass ratio and depends on density. The positive peak of $\gamma(t)$ indicates undoubtedly the demixing tendency of isotopic mixtures, consistent with the conclusions to be drawn from the D_{12}/D^0_{12} values, which are larger than 1 for mass ratios larger than 1.

Thus we see that the reduced momentum exchange between particles of unequal mass prevents the thermodynamically ideal system from behaving dynamically ideally also. Whether the isotopic system of very large mass ratio may show dynamic demixing depends on the

TABLE V. Self-diffusion and mutual-diffusion coefficients computed for the equimolar isotopic HSS and LJ mixtures, with $(N/V)\sigma^3=0.75$ and $kT/\varepsilon=1$.

System	R	D_1 (10^{-5} cm^{2}s^{-1})	D_2 (10^{-5} cm^{2}s^{-1})	D_{12} (10^{-5} cm^{2}s^{-1})
HSS	4	5.106	4.500	5.253
	7	5.721	4.618	5.492
	9	6.142	4.709	5.841
	12	6.323	4.813	5.933
	15	6.701	4.940	6.408
	18	7.181	5.118	6.694
LJ	2	4.439	4.172	4.361
	4	4.903	4.217	4.581
	7	5.459	4.348	4.988
	9	5.742	4.459	5.203
	15	6.705	4.750	6.117
	19.5	6.888	4.853	6.374

asymptotic behavior of those systems. Using the prediction of kinetic theory for the asymptotic value of D_{12}/D_{12}^0, we find 1.7.

On the other hand, the limiting value of D_{12}/D_{12}^0 determined in Refs. 1 and 2 for the boundary of phase stability is ≈2.0. Therefore, dynamic demixing in isotopic mixtures seems to be impossible. The exact D_{12}/D_{12}^0 ratios presented in this report have probably a considerably smaller asymptotic limit. Hence dynamic demixing is even more unlikely to occur in real isotopic mixtures.

The important results of our work may be summarized as follows: dynamic cross correlation is of the order of 10% for isotopic mixtures of mass ratios larger than 10. Due to the hindered momentum exchange between particles of different mass, one always finds positive cross correlation, which means that the mutual diffusion

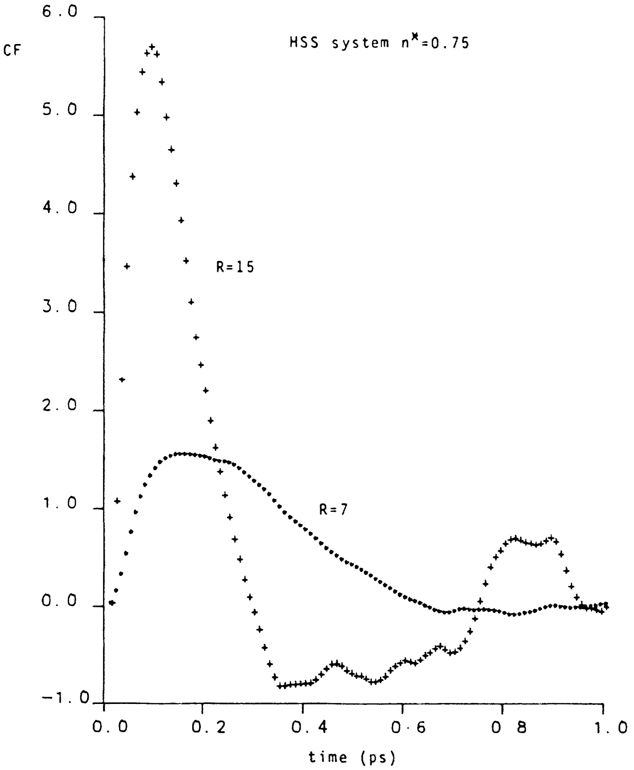

FIG. 4. Sum of the normalized self- and distinct-velocity correlation function for the equimolar isotopic HSS system of mass ratios 7 and 15. $n^*=0.75$, $T^*=1$.

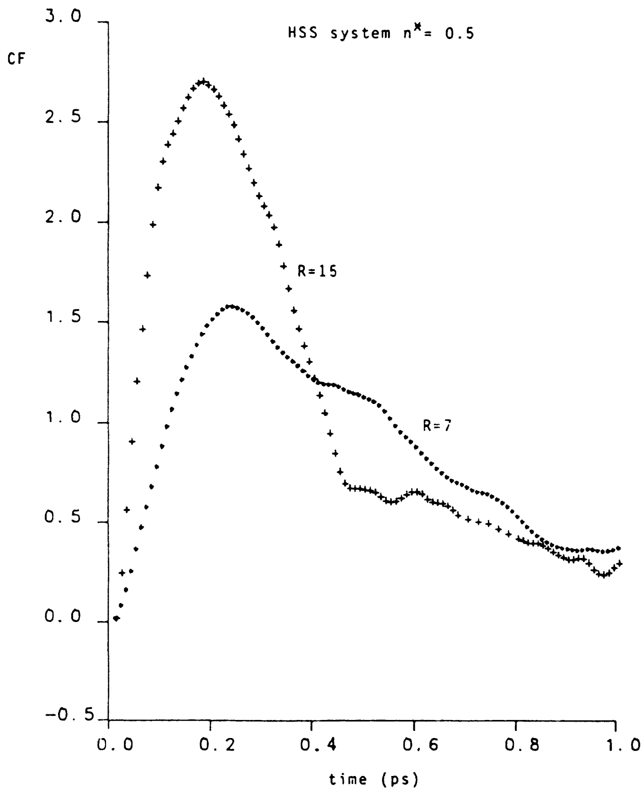

FIG. 5. As in Fig. 4 but for $n^*=0.5$.

coefficient becomes larger than the weighted sum of the self-diffusion coefficients of the mixture. Density and interaction potential effects are small and possibly completely insignificant. Kinetic theory gives a rather good account of the diffusive behavior of these mixtures, although the predictions for the dynamic cross-correlation ratio D_{12}/D_{12}^0 are somewhat too large compared with the exact data.

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