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Self- and cross-velocity correlation functions and diffusion coefficients in liquids: A molecular dynamics study of binary mixtures of soft spheres

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Molecular dynamics simulation is applied to the study of the diffusion properties in binary liquid mixtures made up of soft-sphere particles with different sizes and masses. Self- and distinct velocity correlation functions and related diffusion coefficients have been calculated. Special attention has been paid to the dynamic cross correlations which have been computed through recently introduced relative mean molecular velocity correlation functions which are independent on the reference frame. The differences between the distinct velocity correlations and diffusion coefficients in different reference frames (mass-fixed, number-fixed, and solvent-fixed) are discussed.

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I. INTRODUCTION

Self- and distinct diffusion coefficients (DC's) have been suggested as basic pieces for theoretical studies of transport properties in multicomponent liquids [1–4]. The former provide information abut the mobility of molecules. The latter measure the coupling between the velocities of distinct particles. The self- and distinct DC's are defined as time integrals of self- and distinct velocity correction functions (VCF's), respectively (equivalent definitions from the slope of the displacement correlation functions can also be used [3,4]). Although the information given by the DC's is interesting, time-dependent VCF's provide us with more details about atomic motions. The problem is that these functions cannot be determined experimentally and information about them should be obtained by other methods such as molecular dynamics (MD) simulation.

The study of distinct DC's has mainly been focused on electrolyte solutions. Both phenomenological (Onsager) and empirical (electrical transport, interdiffusion) coefficients can be written as linear combinations of self- and distinct DC's [5–7]. Thus distinct DC's of several electrolyte solutions have been obtained from experiments [8–11]. These coefficients supply a helpful link between experiment and theory and have been proposed as suitable parameters to probe the quality of solvent-averaged interionic potentials [3,12]. MD simulations of electrolyte solutions are very costly, and MD studies of distinct VCF's and related DC's have been restricted to binary liquid mixtures of simple liquids and molten salts [4,7,13–15]. Although distinct DC's in some binary nonelectrolyte mixtures of organic and water-organic liquids have been determined [16–18], these data cannot be used for a systematic test of the MD results for simple soft spheres or Lennard-Jones liquids.

One of the major complications in the interpretation of diffusion data in multicomponent liquids is that, unlike the self-properties, distinct VCF's and related DC's depend on the reference frame (RF) [2–7,19,20]. The RF's commonly used in theoretical and experimental works are different [11], and this must be taken into account in comparing results from the two methods. In the case of computer simulations, the identification of the RF corresponding to different simulation methods is problematic. It has been shown that results from ordinary MD simulations at a constant energy and moment should be associated with the barycentric RF [21]. However, when other computer simulations such as MD at constant temperature (and/or pressure) or stochastic simulations are used, the association is not so clearly established [4]. On the other hand, it should be noted that theoretical and computer simulation studies of distinct VCF's have been restricted to the barycentric RF [13–15], and there is very little information about the characteristics of distinct VCF's in different RF's. Distinct DC's in binary nonelectrolyte mixtures for different RF's deduced from experimental data have recently been analyzed by Mills *et al.* [18].

A set of RF-independent collective VCF's between the center of mass of particles of different species, the relative mean molecular VCF's together with the corresponding set of DC's, have been proposed in a recent paper [7] as an alternative to RF-dependent distinct properties. Phenomenological and empirical coefficients as well as the distinct VCF's and DC's in different RF's may be written as combinations of RF-independent properties [7]. However, a MD study of the characteristics of the relative mean molecular VCF's is still lacking.

One of the aims of this paper is to analyze the relative mean molecular VCF's and related DC's from MD simulations of binary mixtures of simple liquids. The dependence of the dynamic cross correlations on the asymmetry of mixtures (differences between the two species) will be discussed. Another objective of this work is to study the distinct properties in three typical RF's (mass fixed, number fixed, and solvent fixed). Because of the dependence of both self-VCF's and self-DC's on the mass and size of particles [4,22,23], we have considered liquid mixtures of species with different masses and sizes. For the sake of simplicity, soft-sphere interatomic potentials have been assumed.

II. MOLECULAR DYNAMICS SIMULATIONS

Systems made up of 500 particles in a cubic box with ordinary periodic boundary conditions have been simulated by MD. Binary mixtures of species 1 and 2 with a mole fraction $x_1=x_2=0.5$ have been considered. The temperature and density are $T=116$ K and $\rho=2.4\times10^{-2}$ Å^{-3}, respectively. Interatomic forces have been obtained from the repulsive part of a Lennard-Jones potential, i.e., the cutoff has been at r corresponding to the minimum of the potential. As may be observed in Table I, three different series of MD runs have been performed. All the systems in the first and second series have the same mean mass ($\overline{m}=m_{\mathrm{Ar}}=39.948$ amu) and mean size ($\overline{\sigma}=\sigma_{\mathrm{Ar}}=3.405$ Å):

$$\overline{m}=x_1m_1+x_2m_2\ , \tag{1}$$

$$\overline{\sigma}^3=x_1\sigma_1^3+x_2\sigma_2^3\ . \tag{2}$$

In the third series all particles have the same size, and all systems have the same reduced mass (μ):

$$\mu=\frac{m_1m_2}{\overline{m}}\ . \tag{3}$$

TABLE I. Description of the simulated systems. Binary mixtures ($x_1=x_2$) of systems of particles (a) with different masses or/and sizes but with the same $\overline{m}=39.95$ amu and $\overline{\sigma}=3.405$ Å. (b) With the same size $\sigma=3.405$ Å, different masses but the same $\overline{m}=39.95$ amu. (c) With the same size $\sigma=3.405$ Å, different masses, but the same $\mu=39.95$ amu.

(a)

System	m_2/m_1	σ_2/σ_1	μ
A	8	1	15.78
B	1	2	39.95
C	8	2	15.78

(b)

System	m_2/m_1	μ
$A8=A$	8	15.78
$A4$	4	25.56
$A2$	2	35.51
$A1$	1	39.95

(c)

System	m_2/m_1	$\overline{m}$
$A8'$	8	101.12
$A4'$	4	62.42
$A2'$	2	44.94
$A1'\equiv A1$	1	39.95

It should be emphasized that the calculation of relative and distinct properties requires performing very long MD runs. The length of the runs in this work is about 4×10^5 time steps of 10^{-2} ps, and the estimated uncertainties for the resulting relative DC's are about 10%. In the case of the self-DC's the uncertainties are smaller ($<5\%$). In all cases the DC's have also been calculated from the slopes of the corresponding displacement correlation functions, and we have observed a satisfactory accordance within error intervals.

III. DEFINITIONS

In a multicomponent system of q species, the mean molecular relative VCF's $\Lambda_{ab}(t)$ [7] (for the sake of simplicity we will call them relative VCF's) are defined as time correlation functions of the relative velocity of the center of mass of species a with respect to the center of mass of species b [it should be noticed that unlike in Ref. [7] the factor x_ax_b has been included in the definition of $\Lambda_{ab}(t)$]

$$\Lambda_{ab}(t)\equiv\tfrac{1}{3}x_ax_b\{N\langle[\mathbf{u}_a(t)-\mathbf{u}_b(t)][\mathbf{u}_a(0)-\mathbf{u}_b(0)]\rangle\}_\infty\ , \tag{4}$$

where { } indicates the thermodynamic limit operation, ⟨ ⟩ denotes the average over the canonical ensemble, and $\mathbf{u}_a(t)$ is the mean molecular velocity of the component a given by

$$\mathbf{u}_a(t)\equiv N_a^{-1}\sum_{ai=1}^{N_a}\mathbf{u}_{ai}(t)\ , \tag{5}$$

where N_a is the number of particles of species a, and $\mathbf{u}_{ai}(t)$ is the velocity of the particle ai of species a in the laboratory RF.

$\Lambda_{ab}(t)$ may be separated into self- $[\Lambda_{ab}^0(t)]$ and distinct $[\Lambda_{ab}^d(t)]$ contributions as follows:

$$\Lambda_{ab}(t)=(1-\delta_{ab})\Lambda_{ab}^0(t)+x_ax_b\Lambda_{ab}^d(t)\ . \tag{6}$$

It should be noted that according to definition (4) the q $\Lambda_{aa}(t)$ functions are equal to zero. The contribution of the self-velocity correlations is

$$\Lambda_{ab}^0(t)=x_b\Lambda_a^s(t)+x_a\Lambda_b^s(t)\ , \tag{7}$$

where $\Lambda_a^s(t)$ and $\Lambda_b^s(t)$ are the well-known velocity autocorrelation functions

$$\Lambda_a^s(t)=\tfrac{1}{3}\{\langle\mathbf{u}_{ai}(t)\cdot\mathbf{u}_{ai}(0)\rangle\}_\infty\ . \tag{8}$$

The contribution of the distinct velocity correlations may be written as

$$\Lambda_{ab}^d(t)=\Lambda_{aa}^{dR}(t)+\Lambda_{bb}^{dR}(t)-2\Lambda_{ab}^{dR}(t)\ , \tag{9}$$

where the right-side terms are distinct VCF's in a given reference frame R (R-RF):

$$\Lambda_{ab}^{dR}(t)=\tfrac{1}{3}\{N\langle\mathbf{u}_{ai}^R(t)\cdot\mathbf{u}_{bj}^R(0)\rangle\}_\infty\ , \tag{10}$$

where $\mathbf{u}_{ai}^R(t)\equiv\mathbf{u}_{ai}(t)-\mathbf{u}^R(t)$ is the velocity of particle ai in the R-RF, and the velocity of R-RF with respect to the laboratory is given by

$$\mathbf{u}^R(t) \equiv \sum_{a=1}^{q} g_a^R \mathbf{u}_a(t) \ , \quad \sum_{a=1}^{q} g_a^R = 1 \ , \tag{11}$$

where g_a^R's are weight factors which define the macroscopic reference velocity (see Table I in Ref. [20]).

The distinct VCF's can be written as combinations of functions which are independent of the RF with coefficients depending on the weight factors [7]:

$$\begin{aligned}\Lambda_{ab}^{dR}(t) = {} & \sum_{c=1}^{q} \frac{(g_c^R)^2}{x_c} \Lambda_c^s(t) \\ & - \left[\frac{g_a^R}{x_a} \Lambda_a^s(t) + \frac{g_b^R}{x_b} \Lambda_b^s(t) \right] \\ & - \frac{1}{2} \left\{ \Lambda_{ab}^d(t) - \sum_{c=1}^{q} g_c^R [\Lambda_{ac}^d(t) + \Lambda_{bc}^d(t)] \right. \\ & \left. + \sum_{c=1}^{q} \sum_{d=1}^{q} g_c^R g_d^R \Lambda_{cd}^d(t) \right\} . \end{aligned} \tag{12}$$

The initial values of the VCF's may be simply obtained from the mass of the particles and the temperature of the system by using the relations [7]

$$\Lambda_{ab}(0) = \Lambda_{ab}^0(0) = \frac{x_a m_a + x_b m_b}{m_a m_b} k_B T \ , \tag{13}$$

$$\Lambda_{ab}^d(0) = 0 \ , \tag{14}$$

$$\Lambda_a^s(0) = \frac{k_B T}{m_a} \ , \tag{15}$$

$$\Lambda_{ab}^{dR}(0) = \left[\sum_{c=1}^{q} \frac{(g_c^R)^2}{x_c m_c} - \left[\frac{g_a^R}{x_a m_a} + \frac{g_b^R}{x_b m_b} \right] \right] k_B T \ . \tag{16}$$

The diffusion coefficients D_{ab}, D_{ab}^0, D_{ab}^d, D_a^s, and D_{ab}^{dR} are defined as the time integrals of the corresponding velocity correlation functions $\Lambda_{ab}(t)$, $\Lambda_{ab}^0(t)$, $\Lambda_{ab}^d(t)$, $\Lambda_a^s(t)$, and $\Lambda_{ab}^{dR}(t)$:

$$D = \int_0^\infty \Lambda(t) dt \ . \tag{17}$$

According to the given definitions, information about the dynamic cross correlations is provided by the $\Lambda_{ab}(t)$, $\Lambda_{ab}^d(t)$, and $\Lambda_{ab}^{dR}(t)$ functions and related diffusion coefficients. We want to emphasize that the only RF-dependent properties defined in this section are the distinct $\Lambda_{ab}^{dR}(t)$ functions and the corresponding D_{ab}^{dR} coefficients.

IV. RESULTS FOR BINARY LIQUID MIXTURES

In a binary system the number of independent VCF's is three [7]. During MD simulations of the binary ($q = 2$) liquid mixtures of soft spheres described in Sec. II, we calculated the $\Lambda_1^s(t)$, $\Lambda_2^s(t)$, and $\Lambda_{12}(t)$ functions. The other VCF's as well as the DC's have been determined using the equations in Sec. III.

It is shown in Ref. [7] that the interdiffusion coefficient in the volume-fixed RF is given by

$$D_{12}^v = \theta D_{12} \ , \tag{18}$$

where θ is the thermodynamic factor (for ideal solutions $\theta = 1$). Equation (18) shows that D_{12}^v depends on both a macroscopic thermodynamic parameter and a "microscopic" transport coefficient. Moreover, it is frequently assumed that for nearly ideal mixtures $D_{12}^v = D_{12}^0$ (the Hartley-Crank approximation). A measure of the deviations of this approximation is given by the coefficient

$$\delta_{12} = x_1 x_2 D_{12}^d / D_{12}^0 \ . \tag{19}$$

It should be noted that δ_{12} vanishes in "mixtures" of two identical species. According to Eq. (6),

$$D_{12} = D_{12}^0 (1 + \delta_{12}) \ . \tag{20}$$

Then the deviations of the Hartley-Crank approximation are given by the thermodynamic coefficient θ and the microscopic coefficient δ_{12}. The results of Mills *et al.* [18] suggest that these two coefficients are correlated, and systems with θ markedly different from the unity are the same as those for which δ_{12} show noticeable deviations from zero.

A. RF-independent VCF's and DC's

The resulting basic functions $\Lambda_1^s(t)$, $\Lambda_2^s(t)$, and $\Lambda_{12}(t)$ and related DC's for the systems in Table I(a) are shown in Fig. 1 and Table II. For the sake of clarity we have represented the normalized functions $[C(t)$

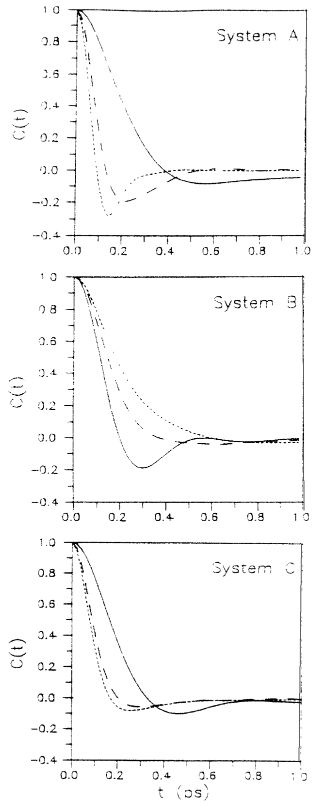

FIG. 1. Normalized self- and relative VCF's for systems *A*, *B*, and *C*: - - -, $C_1^s(t)$; ——, $C_2^s(t)$; — — — —, $C_{12}(t)$.

TABLE II. Non-RF-dependent diffusion coefficients (in 10^{-5} $\text{cm}^2/\text{s}^{-1}$).

	System A	System B	System C
D_1^s	1.95	4.35	6.1
D_2^s	1.75	1.6	1.75
D_{12}^0	1.85	2.95	3.9
D_{12}	1.95	3.2	4.5
D_{12}^d	0.4	1.0	2.3
δ_{12}	0.05	0.1	0.15

$=\Lambda(t)/|\Lambda(0)|$]. It should be pointed out that the initial values do not provide significant information about the atomic motions and can be determined without any MD simulation [Eqs. (13) and (15)].

Results for $C_1^s(t)$ and $C_2^s(t)$ (Fig. 1) are consistent with those in earlier studies [22,23]. In mixtures of species with different masses (system A) the function corresponding to the heavy particles $C_2^s(t)$ has a slower decay and shows a slighter backscattering (negative values). This is a consequence of the velocity persistence of the heavy particles when they collide with lighter ones. Since the light particles always interact with other equal or larger particles, the changes in their velocities are always important and $C_1^s(t)$ shows a more marked backscattering. In the case of mixtures of species with different sizes (system B), the faster decay and deeper backscattering corresponds to $C_2^s(t)$ (for the large particles). This may be associated with the oscillatory motions of the large particles in the cage formed by neighboring like particles. The weaker backscattering for the small particles reflects a dominant diffusive behavior along the interstices among the large ones.

As may also be observed in Fig. 1, the shape of $C_{12}(t)$ is intermediate between $C_1^s(t)$ and $C_2^s(t)$. This suggests that the effects of the distinct correlations in these systems are rather small, and $C_{12}(t)$ will resemble $C_{12}^0(t)$. The differences between these two functions is a measure of the contribution of the correlations between distinct particles, and they are equal to $\delta_{12}(t)=x_1x_2C_{12}^d(t)$, where $C_{12}^d(t)=\Lambda_{12}^d(t)/\Lambda_{12}^0(0)$ [see Eqs. (6) and (13)]. The results for systems A, B, and C are shown in Fig. 2, and they show that $C_{12}^d(t)$ is more important when particles of the two species differ only in mass (system A), and are markedly smaller when particles differ in mass and size (system C). This result is somewhat surprising because earlier findings suggested that the effects of the distinct velocity correlations should increase with the asymmetry of the two species [4,15,20] [$C_{12}^d(t)$ vanishes in "mixtures" of two identical species]. Nevertheless, the comparison of results for systems A and B in Fig. 2 suggests that size differences can balance mass differences. This is consistent with findings for system C.

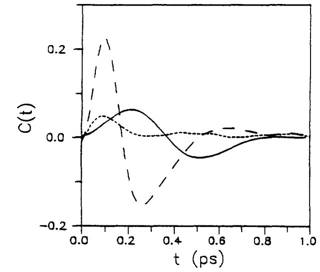

FIG. 2. Distinct contributions to the relative VCF's [$\delta_{12}(t)$]: — — — —, system A; ——, system B; - - -, system C.

Quantitative information about the contribution of the distinct correlations to D_{12} is given by δ_{12}. Results in Table II show that δ_{12} is smaller than 15% for the three systems. Unlike the VCF's the biggest distinct contribution to D_{12} is for system C. This finding is a consequence of the oscillatory shapes of $\delta_{12}(t)$ for systems A and B, and it corroborates the insensitivity of the DC's to the microscopic properties at short time scales [4]. Thus a low value of D_{12}^d does not imply that dynamic cross correlations are negligible. It has been suggested [24] that the positive values obtained for the D_{12}^d coefficients may indicate that particles of the same species have a greater tendency to diffuse together than those of differing species. Nevertheless, it should be pointed out that uncertainties in the values of D_{12}^d and δ_{12} are more important than for the other DC's because they are determined from differences between two coefficients (D_{12} and D_{12}^0) which in general are very close.

B. Distinct VCF's and DC's

In this case of binary mixtures, expressions for the RF-dependent distinct VCF's in terms of the RF-independent VCF's may be deduced from Eqs. (11) and (12):

$$\Lambda_{11}^{dR}(t)=-g_1^R(1+g_2^R)x_1^{-1}\Lambda_1^s(t)+(g_2^R)^2x_2^{-1}\Lambda_2^s(t)+(g_2^R)^2\Lambda_{12}^d(t)\ , \tag{21}$$

$$\Lambda_{12}^{dR}(t)=-g_1^Rg_2^R[x_1^{-1}\Lambda_1^s(t)+x_2^{-1}\Lambda_2^s(t)+\Lambda_{12}^d(t)]\ , \tag{22}$$

$$\Lambda_{22}^{dR}(t)=(g_1^R)^2x_1^{-1}\Lambda_1^s(t)-g_2^R(1+g_1)x_2^{-1}\Lambda_2^s(t)+(g_1^R)^2\Lambda_{12}^d(t)\ . \tag{23}$$

Extending the Hartley-Crank approximation to the VCF's, it may be assumed that for ideal mixtures $\Lambda_{12}^d(t)=0$. Then expressions for the distinct VCF's for ideal mixtures can easily be deduced by removing the $\Lambda_{12}^d(t)$ terms in Eqs. (21)–(23). These functions will be called $\Lambda_{11}^{dR0}(t)$, $\Lambda_{12}^{dR0}(t)$, and $\Lambda_{22}^{dR0}(t)$. It should be noted that both distinct VCF's and related DC's for nearly ideal systems may be determined approximately as combinations of the self-VCF's and DC's, and deviations from ideality are given by $\Lambda_{12}^d(t)$ multiplied by factors which depend on the RF considered.

Limiting expressions of the distinct VCF's as x_1 goes to zero may be deduced from Eqs. (21)–(23). The results are given in the Appendix. Using Eqs. (6) and (21)–(23) it may be readily obtained that

$$\Lambda_{11}^{dR}(t)=(x_1x_2)^{-1}(g_2^R)^2\Lambda_{12}(t)-x_1^{-1}\Lambda_1^s(t)\ , \tag{21'}$$

$$\Lambda_{12}^{dR}(t)=-(x_1x_2)^{-1}g_1^Rg_2^R\Lambda_{12}(t)\ , \tag{22'}$$

$$\Lambda_{22}^{dR}(t)=(x_1x_2)^{-1}(g_1^R)^2\Lambda_{12}(t)-x_2^{-1}\Lambda_2^s(t)\ . \tag{23'}$$

1. *Mass-fixed RF*

The weight factors corresponding to the barycentric or mass-fixed RF ($R \equiv M$) are the mass fractions [20]

$$g_1^M = \frac{x_1 m_1}{\overline{m}} , \quad g_2^M = \frac{x_2 m_2}{\overline{m}} . \tag{24}$$

Equations (21′)-(23′) and (24) have been used to determine the $\Lambda_{11}^{dM}(t)$, $\Lambda_{12}^{dM}(t)$, and $\Lambda_{22}^{dM}(t)$ functions for systems *A*, *B*, and *C*. These functions have been normalized, but their signs have been kept $[C_{ab}^{dM}(t) = \Lambda_{ab}^{dM}(t)/|\Lambda_{ab}^{dM}(0)|]$. In this case it may be readily deduced from (16) that the three functions have the same initial values:

$$\Lambda_{11}^{dM}(0) = \Lambda_{12}^{dM}(0) = \Lambda_{22}^{dM}(0) = -\frac{k_B T}{\overline{m}} . \tag{25}$$

Because of the negative initial values of the distinct VCF's, the corresponding DC's are in general negatives. The resulting normalized distinct VCF's and DC's are shown in Fig. 3 and Table III, respectively. In the three cases $C_{12}^{dM}(t)$ is intermediate between $C_{11}^{dM}(t)$ and $C_{22}^{dM}(t)$, but these two functions are very different for the three systems. $C_{11}^{dM}(t)$ for system *A* (species 1 is lighter than 2) shows a high maximum, and the corresponding DC is positive whereas for system *B* (species 2 is larger than 1) $C_{22}^{dM}(t)$ shows a maximum and D_{22}^{dM} is slightly greater than zero. When species 2 is heavier and larger (system *C*), the mass effects are dominant and the maximum is shown by $C_{11}^{dM}(t)$.

The results for distinct VCF's in the mass-fixed reference frame (MRF) for systems *A* and *C* are compared with those corresponding to the ideal mixture approximations $[\Lambda_{12}^{d}(t) = 0]$ in Figs. 4 and 5. Marked differences may be observed for system *A*, especially for correlations between the like light particles (1-1). However, for system *C*, when species have different sizes and masses, the differences are markedly smaller. This is due to the large values of the $\Lambda_{12}^{d}(t)$ functions for system *A* (Fig. 2). In both systems the differences for the 1-1 functions are greater than for 2-2. However, this cannot be attributed to differences in the microscopic behavior of species 1 and 2, but to the fact that $(g_2^M)^2$ is much larger than $(g_1^M)^2$ [see Eqs. (21) and (23) and Table III]. The distinct DC's (Table III) are in general very close to those corresponding to the ideal mixtures, and the only noticeable difference is between D_{11}^{dM} and D_{11}^{dM0} for system *C* (it should be noted that despite the differences in the VCF's the 1-1 DC's for system *A* are very close).

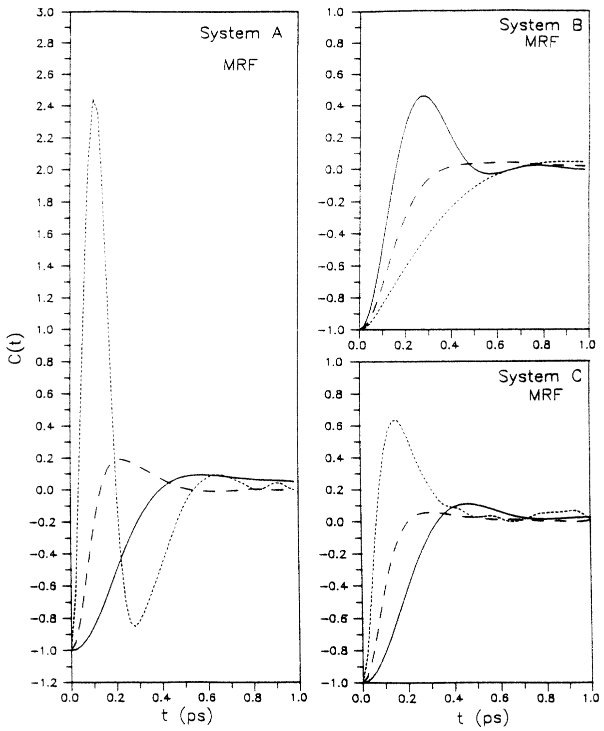

FIG. 3. Normalized (except in sign) distinct VCF's for systems *A*, *B*, and *C* in the mass-fixed RF: - - -, $C_{11}^{dM}(t)$; — — — —, $C_{12}^{dM}(t)$; —— $C_{22}^{dM}(t)$.

2. *Number-fixed RF*

In the case of the molecular or number-fixed RF's ($R \equiv N$), the weight factors are the mole fractions [20]

$$g_1^N = x_1 , \quad g_2^N = x_2 . \tag{26}$$

Then the initial values are

$$\Lambda_{11}^{dN}(0) = \frac{x_2 m_1 - (1+x_2) m_2}{m_1 m_2} k_B T , \tag{27}$$

$$\Lambda_{12}^{dN}(0) = -\frac{x_1 m_1 + x_2 m_2}{m_1 m_2} k_B T , \tag{28}$$

$$\Lambda_{22}^{dN}(0) = \frac{x_1 m_2 - (1+x_1) m_1}{m_1 m_2} k_B T . \tag{29}$$

It follows from (29) that if $x_1 m_2 > (1+x_1) m_1$, the initial value of $\Lambda_{22}^{dN}(t)$ is positive. This condition is fulfilled by

TABLE III. Distinct DC's in different reference frames (in 10^{-5} cm^2/s^{-1}).

System	RF	g_1^R	g_2^R	D_{11}^{dR}	(D_{11}^{dR0})	D_{12}^{dR}	(D_{12}^{dR0})	D_{22}^{dR}	(D_{22}^{dR0})
A	*M*	$\frac{1}{9}$	$\frac{8}{9}$	+2.25	(+1.95)	−0.8	(−0.75)	−3.4	(−3.4)
A	*N*	$\frac{1}{2}$	$\frac{1}{2}$	−1.95	(−2.05)	−1.95	(−1.85)	−1.55	(−1.65)
B	$M \equiv N$	$\frac{1}{2}$	$\frac{1}{2}$	−5.5	(−6.0)	−3.2	(−3.0)	+0.05	(−0.2)
C	*M*	$\frac{1}{9}$	$\frac{8}{9}$	+2.0	(+0.2)	−1.8	(−1.55)	−3.3	(−3.3)
C	*N*	$\frac{1}{2}$	$\frac{1}{2}$	−7.7	(−8.3)	−4.5	(−3.9)	+1.0	(+0.45)
C	*S*	0	1	+5.8	(+3.5)	0	(0)	−3.5	(−3.5)

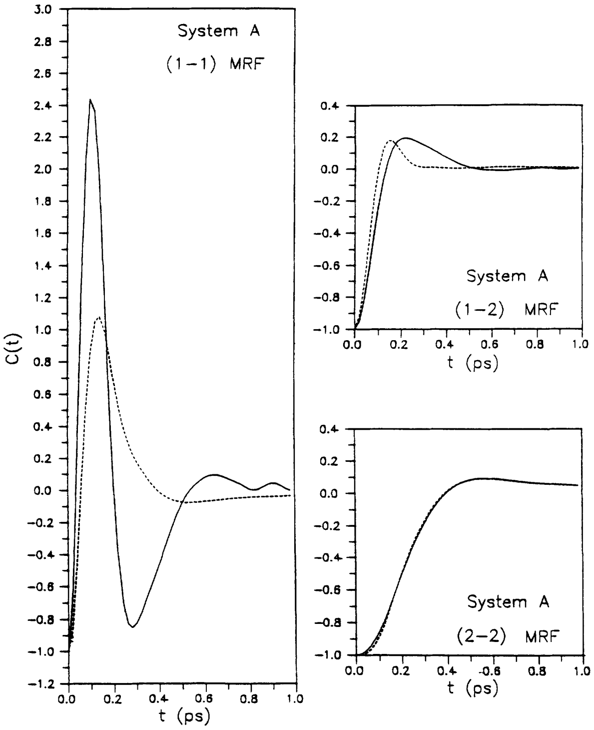

FIG. 4. Comparison of the normalized distinct VCF's for system A in the mass-fixed RF (——) with the ones for the ideal mixture approximation (- - -). $C_{11}^{dM}(t)$ and $C_{11}^{dM0}(t)$ in (a); idem for 1-2 in (b) ; idem for 2-2 in (c).

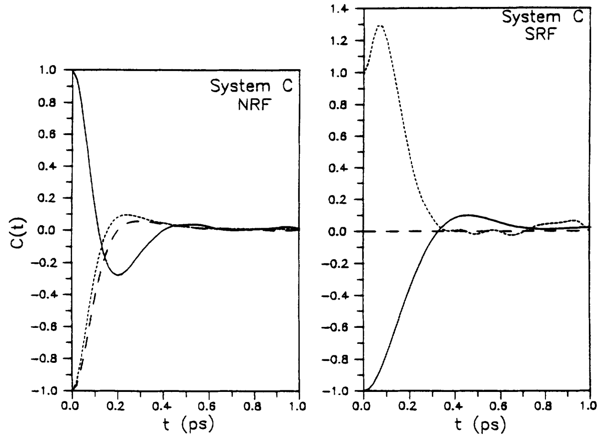

FIG. 6. Normalized (except in sign) distinct VCF's for system C in the number-fixed and solvent-fixed RF's: - - -, $C_{11}^{dR}(t)$; — — — —, $C_{12}^{dR}(t)$; ——, $C_{22}^{dR}(t)$. Left and right figures are for $R\equiv N$ and $R\equiv S$, respectively.

systems A and C. The normalized distinct VCF's (keeping the sign) and DC's for system C are shown in Fig. 6(a) and Table III, respectively. The results are completely different (even in the sign of the DC's) from those in the barycentric RF.

In Figs. 7 and 8, the VCF's for the actual A and C systems in the number-fixed reference frame (NRF) are compared with the VCF's for the corresponding ideal mixture approximation. In this RF, the differences between the results for the 1-1 functions are smaller than in the case of the MRF. Conversely the differences for the 2-2 functions are greater. This is due to the different weight factors corresponding to the two RF's (see Table III). For system C, the effects of the nonideality on the distinct VCF's in the NRF are very small. The distinct DC's for the actual system are also very close to those for the ideal systems (Table III). These findings corroborate that the influence of the dynamic cross correlations on the distinct properties is notoriously modulated by the weight factors associated with the RF's.

3. *Solvent-fixed RF*

If we consider that species 2 plays the role of solvent and is taken as the RF (solvent-fixed or Hittorf RF, $R\equiv S$) the weight factors are [20]

$$g_1^S=0\ ,\quad g_2^S=1\ . \tag{30}$$

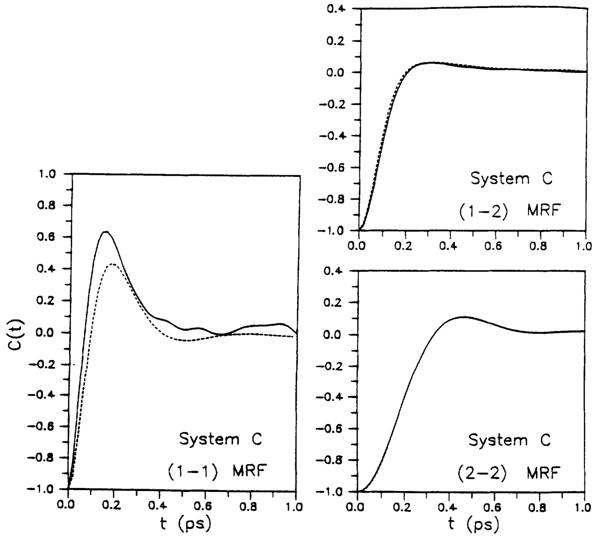

FIG. 5. As Fig. 4, but for system C.

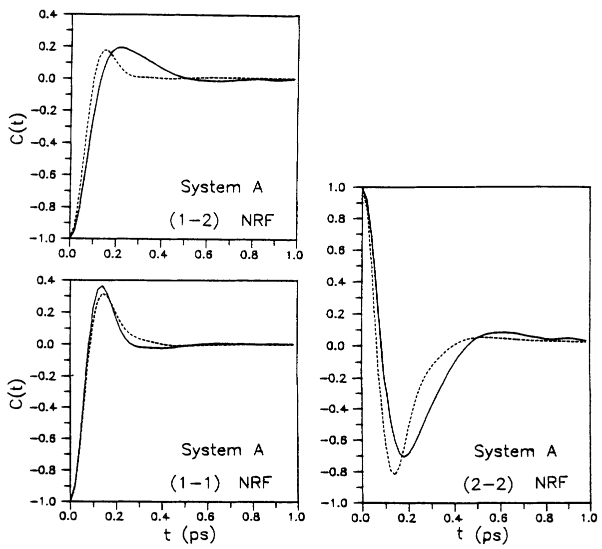

FIG. 7. As Fig. 4, but in the number-fixed RF.

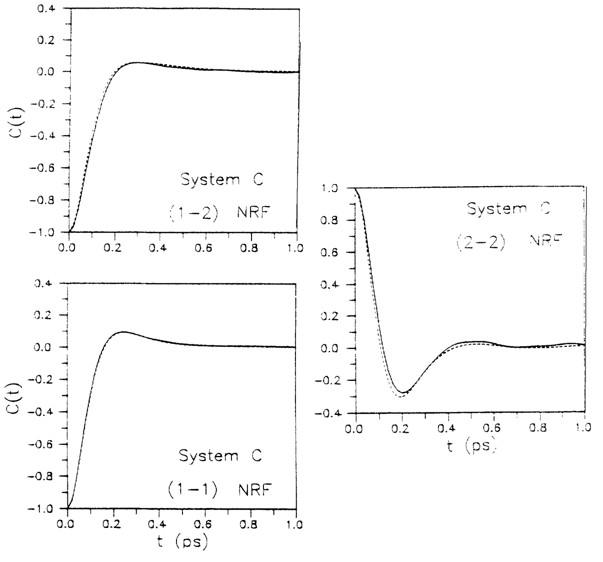

FIG. 8. As Fig. 5, but in the number-fixed RF.

Then the initial values are as follows:

$$\Lambda_{11}^{dS}(0)=(x_2m_2)^{-1}k_BT\ , \tag{31}$$

$$\Lambda_{12}^{dS}(0)=0\ , \tag{32}$$

$$\Lambda_{22}^{dS}(0)=-(x_2m_2)^{-1}k_BT\ . \tag{33}$$

In this RF, $\Lambda_{11}^{dS}(t)=x_2^{-1}\Lambda_2^s(t)+\Lambda_1^d(t)$, and $\Lambda_{12}^{dS}(t)=0$ and $\Lambda_{22}^{dS}(t)=-x_2^{-1}\Lambda_2^s(t)$. The results in this RF are completely different from those in the other two RF's and, in the case of system *C*, they are given in Fig. 6(b) and Table III. It should be noted that $C_{12}^{dS}(t)$ does not show an initial decay but a maximum at $\cong 0.1$ ps. This maximum should be attributed to the contribution of the distinct correlations since, as may be observed in Fig. 2, $\delta_{12}(t)$ also shows a maximum at the same *t* value. A maximum in the distinct VCF's has been also observed in other cases.

The findings for different RF's (Figs. 3–8 and Table III) corroborate the strong dependence of the distinct properties on the RF. Since information about the dynamic characteristics of the system is mixed with the weight factors corresponding to the RF, the distinct properties cannot easily be interpreted. Moreover, it has been shown that the shape of the distinct VCF's is mainly dependent on the RF considered, and is scarcely influenced by the contribution of correlations between different particles.

C. Mass dependence of the self- and cross-VCF's

The results reported in this paper indicate that mass differences between the species in liquid mixtures have a significant influence on their dynamic properties. The self-VCF's and DC's of isotopic liquid mixtures have been analyzed in several MD studies [22,25], but less attention has been paid to the dynamic cross correlations [14]. These facts encouraged us to perform a more systematic study of the mass influence on the VCF's and DC's. We carried out MD simulations of the systems described in Tables I(b)–I(c). In these series the relations of the mass of particles have been changed, but the mean masses $\bar{m}$ or μ have been kept constant. The results for the normalized functions are shown in Figs. 9 and 10. The minima of the self-VCF's of light particles become deeper and shift toward lower times when the relation between the masses of the two species (m_2/m_1) increases. The shift was not observed when the mass of light particles (not the mean mass) was kept constant [22]. The behavior of the self-VCF's of heavy particles is opposite to that of light particles. In the case of $C_{12}(t)$ the behavior as a function of the asymmetry of species is

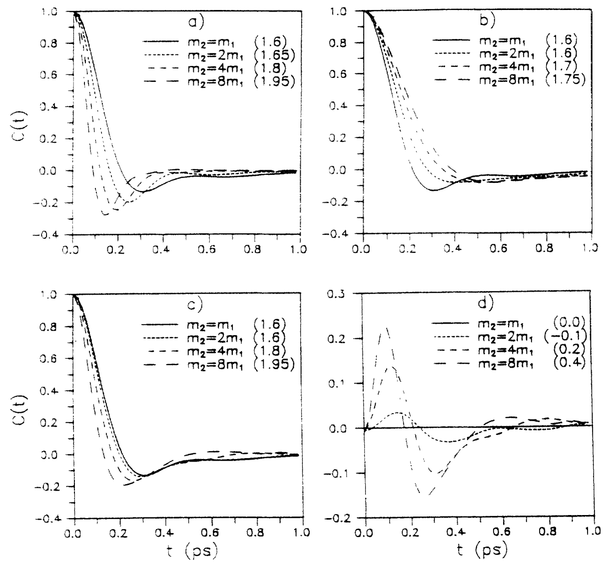

FIG. 9. Self- and cross-normalized VCF's for the systems with the same $\bar{m}$ (*A*8, *A*4, *A*2, and *A*1): $C_1^s(t)$ in (a); $C_2^s(t)$ in (b); $C_{12}(t)$ in (c); $\delta_{12}(t)$ in (d). Numbers in parentheses are the diffusion coefficients in 10^{-5} cm^2/s^{-1}.

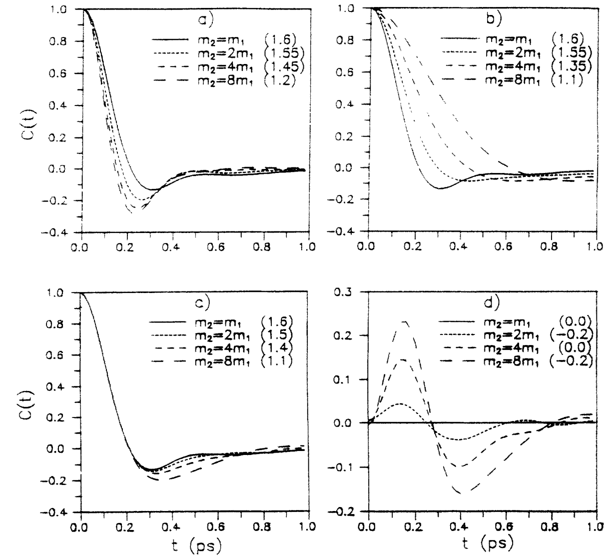

FIG. 10. As Fig. 9, but for the systems with the same μ (*A*8′, *A*4′, *A*2′, and *A*1′).

different depending on whether $\overline{m}$ or μ are kept constant. In the second case, different VCF's show the same initial decay. Moreover, the initial values of the nonnormalized functions for systems with the same μ are the same, as may be readily deduced from (13), taking into account that $q=2$:

$$\Lambda_{ab}(0)=\frac{\overline{m}}{m_1 m_2}=\frac{1}{\mu}\ . \tag{34}$$

The resulting DC's are also shown in Figs. 9 and 10. Although the self-VCF's of the light and heavy particles are markedly different, the self-DC's for each system are quite similar and the D_{12} values are intermediate between D_1^s and D_2^s. So, the distinct contribution δ_{12} is rather small. It may be observed in Figs. 9 and 10 that in general DC's increase when $\overline{m}$ or μ decrease. It is interesting to realize that when μ is kept constant, D_{12} diminishes when the differences between the species become greater, whereas the tendency is opposite when $\overline{m}$ is kept constant. The $\delta_{12}(t)$ functions for the different mass relations are represented in Figs. 9(d) and 10(d), and they show that the influence of distinct correlations increase with the mass asymmetry between the two species.

V. CONCLUDING REMARKS

Results in this paper indicate that one should be very careful with the interpretation of the RF-dependent distinct properties, because both the characteristics of distinct VCF's and the values of distinct DC's are dependent mainly on the dynamic properties of individual particles (self-properties) and the weight factors corresponding to the RF, whereas the influence of correlations between distinct particles is rather small and cannot easily be distinguished. For this reason it should be more useful to characterize the dynamic cross correlations through properties which are independent of the RF, such as the relative VCF's. Three independent VCF's are necessary to calculate all the mass transport properties in a binary mixture. The findings analyzed in this paper suggest that a suitable set of VCF's can be constituted by the non-RF-dependent functions $\Lambda_1^s(t)$, $\Lambda_2^s(t)$, and $\Lambda_{12}(t)$ or $\Lambda_{12}^d(t)$. It should be noted that unlike in earlier papers [3,4,20], distinct VCF's have not been included in the set of basic VCF's.

Specially interesting is the information about the contribution to the transport properties of the correlations between distinct particles provided by $\Lambda_{12}^d(t)$, $\delta_{12}(t)$, D_{12}^d, and δ_{12}. Although these quantities are combinations of the RF-dependent distinct properties, they are independent of the RF. δ_{12} has recently been used by Mills *et al.* [18] as a measure of the self-association in binary nonelectrolyte liquid mixtures.

Finally, we want to point out that this work is part of a more complete study of time correlations in multicomponent liquids. The dependence of these correlations on the interatomic interactions as well as their characteristics in other systems including ternary liquid mixtures of simple liquids, ions in noncharged solvents, and electrolyte solutions, will be analyzed further and the results reported in forthcoming papers.

ACKNOWLEDGMENTS

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APPENDIX

Infinite dilute solutions are systems of great interest in many cases. In this appendix, expressions for some VCF's in an infinite diluted binary system are given. We consider species 1 as the solute and species 2 as the solvent. Thus the limiting expressions for $x_1 \rightarrow 0$ are calculated.

The limiting expression for the relative VCF follows from Eqs. (6) and (7):

$$\Lambda_{12}(t)\rightarrow\Lambda_1^s(t)\ . \tag{A1}$$

In the case of distinct VCF's, a limiting expression independent of the RF can be obtained from Eqs. (23), (24), (26), and (30):

$$\Lambda_{22}^{dR}(t)\rightarrow-\Lambda_2^s(t)\ . \tag{A2}$$

For other distinct VCF's the expressions depend on the RF. For the mass-fixed RF it follows from Eqs. (21), (22), and (24) that

$$\Lambda_{12}^{dM}(t)\rightarrow-m_1 m_2^{-1}\Lambda_1^s(t)\ , \tag{A3}$$

$$\Lambda_{11}^{dM}(t)\rightarrow\Lambda_2^s(t)-2m_1 m_2^{-1}\Lambda_1^s(t)+\Lambda_{12}^d(t)\ . \tag{A4}$$

For the number-fixed RF, using Eqs. (21), (22), and (26),

$$\Lambda_{12}^{dN}(t)\rightarrow-\Lambda_1^s(t)\ , \tag{A5}$$

$$\Lambda_{11}^{dN}(t)\rightarrow\Lambda_2^s(t)-2\Lambda_1^s(t)+\Lambda_{12}^d(t)\ . \tag{A6}$$

For the solvent-fixed RF, from Eqs. (21), (22),and (30) we obtain

$$\Lambda_{12}^{dS}(t)\rightarrow 0\ , \tag{A7}$$

$$\Lambda_{11}^{dS}(t)\rightarrow\Lambda_2^s(t)+\Lambda_{12}^d(t)\ . \tag{A8}$$

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