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The mutual diffusion coefficient D_{12} in binary liquid model mixtures. Molecular dynamics calculations based on Lennard-Jones (12-6) potentials

M. Schoen^a & C. Hoheisel^a

^a Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-4630, Bochum, F.R. Germany

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The mutual diffusion coefficient D_{12} in binary liquid model mixtures. Molecular dynamics calculations based on Lennard-Jones (12-6) potentials

I. The method of determination

by M. SCHOEN and C. HOHEISEL

Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum,
D-4630 Bochum, F.R. Germany

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Molecular dynamics calculations have been performed to determine the mutual diffusion coefficient D_{12} i.e. the dynamic cross correlations in a binary model mixture. The mean square displacement as well as the velocity-correlation function of the centre of mass of particles of kind 1 have been used for the determination. From various pilot runs it turned out that using runs of a length of 10^5 time-steps the cross correlations can be very accurately evaluated in terms of D_{12}/D_{12}^0 , where D_{12}^0 is the pure mutual diffusion coefficient available through the two self diffusion coefficients of the mixture. Whilst the overall error for this quotient D_{12}/D_{12}^0 is found to be 3 per cent, the inaccuracy in D_{12} itself is slightly larger because of the additional evaluation of the thermodynamic factor for non-ideal mixtures.

Systematic errors have been discovered in earlier molecular dynamics calculations of the D_{12} , which are primarily due to the use of too short runs. Our calculations resulted in positive cross correlations of 5 per cent for the Ar/Kr model system. This is in contrast to previous molecular dynamics results which yielded 9 per cent negative cross effects for this system.

Extended computations of the D_{12}/D_{12}^0 will be reported in the subsequent paper, where a series of very different model systems is discussed.

1. INTRODUCTION

Whilst one particle dynamic phenomena in model liquids are frequently studied by molecular dynamics calculations (MDC), investigations of the collective properties of such systems are rather scarce. For instance, self diffusion in model liquids is now well understood in terms of computer simulations, whereas the transport coefficients for viscous flow are not yet reliably obtained by equilibrium simulations [1-4].

The reason for this situation stems from the following: a direct way of determining transport coefficients for mass-, momentum- or heat flow by simulations is the evaluation of suitable time dependent correlation functions and subsequent application of the Green-Kubo relations [5]. However, for collective properties of fluids, this simple method apparently encounters appreciable difficulties. The time averages for the value of the correlation function cannot be improved by the number of particles used for the simulation ensemble. So in most cases one is not able to obtain reliable averages for the correlation

functions, even if the MD-run is lengthened by a factor two or three. Moreover, a few of these functions show a significant long time tail, which can neither be obtained by MDC nor approximately estimated by current theories [4].

In view of these aspects there are—not surprisingly—only two MD-studies on the mutual diffusion flow in binary liquid mixtures, which is a collective process. Of these two studies only the second one has regarded the determination of the mutual diffusion coefficient D_{12} as its primary task [6], while the first one generated the D_{12} -coefficients more or less as a byproduct [7].

For us the errors of the D_{12} -values reported by the authors of the second work [6] seemed to be disproportionately large in comparison with their greatly extended averaging procedure. Additionally the determined D_{12} -value was rather far from the value obtained in [7]. Furthermore, the investigation of [6] covered only the Ar/Kr model mixture which is not expected to exhibit appreciable dynamic cross correlations [8]. So we have undertaken a further exhaustive MD study on mutual diffusion in Lennard-Jones liquid mixtures in which we strongly varied the potential parameters.

As our technique of evaluating reliable binary diffusion coefficients from MDC is considered as very substantial it is described in detail in this first part of our report. A subsequent paper will then primarily contain our results on cross correlation effects in various 'Lorentz-Berthelot mixtures' [8].

2. DEFINITIONS OF DIFFUSION COEFFICIENTS IN A BINARY MIXTURE

For a binary mixture we may define four phenomenological transport coefficients, concerning the generalized mass flux: L_{11} , L_{12} , L_{21} , L_{22} , where the first index refers to the flux and the second one refers to the concentration gradient [9]. These four transport coefficients L_{ij} determine two diffusion coefficients corresponding to the two existing currents:

$$D_{11} = \frac{L_{11}}{T} \left(\frac{\partial \mu_1}{\partial x_1} \right)_{T,p} + \frac{L_{12}}{T} \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T,p},$$

$$D_{21} = \frac{L_{21}}{T} \left(\frac{\partial \mu_1}{\partial x_1} \right)_{T,p} + \frac{L_{22}}{T} \left(\frac{\partial \mu_2}{\partial x_1} \right)_{T,p},$$

μ_i is the chemical potential of component i , and x_i is the mole fraction of component i . Using the Onsager relations, $L_{12} = L_{21}$; $L_{22} = L_{11}$, it is easy to show that D_{21} equals $-D_{11}$. So for a binary system there exists only one independent mutual diffusion coefficient, which we shall denote as D_{12} .

Now the phenomenological definition of the self diffusion coefficient (or tracer diffusion coefficient) in a 1-component system may be obtained through the D_{12} -coefficient of the 2-component system in the limits of $x_1 \rightarrow 0$ or $x_2 \rightarrow 0$. We shall designate these self diffusion coefficients of the pure substances by D_1 and D_2 .

These self diffusion coefficients D_i must not be confused with those of a binary mixture, which we are here interested in. The phenomenological definition of the self diffusion coefficients in a *binary mixture* is obtainable exclusively from the definitions of the two independent mutual diffusion coefficients in a *ternary mixture* for the limit $x_3 \rightarrow 0$. We have denoted these self diffusion coefficients as D_{11} and D_{22} , although this notation also appears

in the foregoing equations with a different meaning. However, as in this latter case we refer to self diffusion, it is hoped that the signature remains clear. The explicit expressions for the two independent diffusion coefficients in a ternary system as well as the final relations for the self diffusion coefficients in the binary system lack in the literature. So we regard it as valuable to derive these relations in Appendix 2. From the considerations there it becomes immediately apparent that the self diffusion coefficients D_{11} and D_{22} are one particle quantities and the mutual diffusion coefficient D_{12} is a collective quantity.

Following the considerations of Jolly and Bearman [6] we obtain the D_{12} -coefficient from the Kubo integral over the velocity correlation function of the centre of mass of particles of kind 1 and from the Einstein relation for the mean square displacement of the centre of mass of the particles of type 1. The origin of these formulae is discussed extensively in [10, 11].

$$D_{12} = Q_N \int_t^{t_{\max}} z_{\text{CM}}(\tau) d\tau, \quad (1)$$

$$D_{12} = \frac{1}{2} Q_N \lim_{\tau \rightarrow t_{\max}} \left[\frac{d}{d\tau} r_{\text{CM}}^2(\tau) \right], \quad (2)$$

where

$$z_{\text{CM}}(\tau) = \left\langle \sum_{i=1}^{N_1} \mathbf{u}_i(t) \sum_{i=1}^{N_1} \mathbf{u}_i(t+\tau) \right\rangle,$$

$$r_{\text{CM}}^2(\tau) = \left\langle \left[\sum_{i=1}^{N_1} \mathbf{r}_i(t+\tau) - \sum_{i=1}^{N_1} \mathbf{r}_i(t) \right]^2 \right\rangle$$

and

$$Q_N = \frac{1}{3N} \frac{Q}{c_1 c_2} \left(\frac{m_1}{m_2} c_1 + c_2 \right)^2.$$

$$\left. \begin{array}{ll} N_i & \text{number of particles of type } i, \text{ with } N_1 + N_2 = N \\ c_i & \text{number density of particles of kind } i \\ m_i & \text{mass of particle of kind } i \\ Q & \text{thermodynamic factor} \end{array} \right\} i = 1, 2.$$

The brackets $\langle \dots \rangle$ denote time averages.

The relations (1) and (2) arise basically from a transformation of the co-ordinate system and one obtains finally only summations over particles of type 1 (see also [11]). Equations (1) and (2) are composed of two factors: a thermodynamic factor Q which contains integrals over partial total pair correlation functions, and which is unity for an ideal mixture, and a dynamic factor, which contains the integral over the time dependent correlation functions. Both of these factors can in principle be evaluated by MDC. As we are mainly interested in the dynamic properties of the D_{12} we have eliminated the Q -factor by considering the quantity D_{12}/D_{12}^0 , where D_{12}^0 is the 'pure mutual diffusion coefficient'. This pure mutual diffusion coefficient D_{12}^0 contains no contributions from dynamic cross correlations and can easily be obtained from the relations (1) or (2) by neglecting all cross products in the relevant sums in the

correlation functions (see Appendix 1). The result is a commonly used approximation for D_{12} , which should be exact for infinitely dilute mixtures [12, 13] :

$$D_{12}^0 = Q(x_2 D_{11} + x_1 D_{22}) \tag{3}$$

where, for example

$$D_{11} = \frac{1}{3} \frac{1}{N_1} \int_0^{t_{\max}} \left\langle \sum_{i=1}^{N_1} \mathbf{u}_i(t) \mathbf{u}_i(t + \tau) \right\rangle d\tau.$$

This quantity D_{12}^0 can be determined directly from the two self diffusion coefficients of the mixture and thus is easily accessible by MDC.

Consequently the dominant part of our calculations takes into account this quotient D_{12}/D_{12}^0 , which explicitly indicates the dynamic cross correlations in mixtures without contributions owing to the thermodynamic non-ideality of the system. However, to get the absolute values of D_{12} an evaluation of Q is unavoidable. We show in § 5, that the Q -factor is unfortunately not very accurately determinable by MDC. Nonetheless most of the model mixtures are characterized by small deviations of Q from unity, therefore these errors do not greatly influence the D_{12} .

3. TECHNICAL REMARKS ON THE MDC AND THE QUOTIENT D_{12}/D_{12}^0

To compare our MD results with those of [6] and [7], we have chosen the model system Ar/Kr at the temperature and the density given in these references. The Lennard-Jones potential parameters used for this system are listed on table 1, the temperatures and densities can also be read from this table. Normally the temperature of a MD run will not end up exactly with the pre-selected value, but these small deviations do definitely not influence the D_{12}/D_{12}^0 ratio. Dynamic cross correlations play only a secondary role in this mixture as expected from earlier studies and from the consideration that the $\epsilon_{ij}, \sigma_{ij}$ -parameters are not very different from each other. To emphasize our results concerning the precision of evaluating cross correlation effects, we have additionally used

Table 1. Potential parameters of the Lennard-Jones systems studied.

System	Interaction	$\epsilon/k^\dagger/\text{K}$	$\sigma/10^{-10} \text{ m}$	$m^\ddagger/\text{a.u.}$	n^*	$T^*\S$
Ar/Kr	Ar-Ar(1-1)	119.8	3.405	39.95	0.7901	0.80
	Ar-Kr(1-2)	141.4	3.519			
	Kr-Kr(2-2)	167.0	3.633	83.8		
1	1-1	212.2	3.591	61.88	0.83	0.74
	1-2	141.4	3.591			
	2-2	94.4	3.591	61.88		
2	1-1				0.85	0.79
	1-2	(see system 1)				
	2-2					

† Boltzmann constant.
 ‡ Atomic masses.
 § Density and temperature in reduced units, see [20].

model mixtures with appreciably larger $\epsilon_{22}/\epsilon_{11}$ -ratios and applying the Lorentz-Berthelot combining rules $\sigma_{12}=0.5 (\sigma_{11} + \sigma_{22})$, $\epsilon_{12}=(\epsilon_{11} \cdot \epsilon_{22})^{1/2}$.

The decisive difference between our simulations and those of [6] and [7] is that we utilize MD runs of a factor 10 longer and that cross correlations are calculated by both the velocity correlation function (VCF) and the mean square displacement (MSD) of the centre of mass (CM) of particle kind 1. We furthermore investigate systematically the particle and average number dependence of the cross correlations. These latter studies are reported specifically in the §§ 4.2 and 4.3.

The computation of the self diffusion coefficients (SDC) is not critical : we obtained the corresponding MSD and velocity autocorrelation functions (VACF) from averages over 60 independent time origins from 300–400 particle configurations—generated by runs of $4\text{--}5 \times 10^{-11}$ s—following each trajectory up to 30–60 time intervals. Table 2 lists the minimum distances between time origins used. So we worked with averages of 7680 events at least for the correlation functions and obtained SDC values from MSD and VACF, which deviated 3 per cent at best. For concentrations other than equimolar composition, one has to take care of the effect of the reduced particle number of one component. In these instances we enlarged the size of the ensemble [13].

Table 2. Minimum intervals between consecutive time origins Δt_{OR} for the averaging process to evaluate the various time correlation functions.

Function	$\Delta t_{\text{OR}} \times 10^{14}/\text{s}$
VACF	27
CM-VCF	27
MSD	20
CM-MSD	20

Table 3. Details of the MD runs.

Particle numbers	256–2048 (standard : 864)
Cube length	24.1 Å (256)–48.4 Å (2048)
Equilibration time-steps	600
Number of integration steps	4000–230000 (standard : 50000)
Time step	10^{-14} s
Cutoff radii†	$r_{\text{c}\uparrow} = 3.1 \sigma_{ij}$, $r_{\text{c}} = 2.5 \sigma_{ij} \left. \vphantom{\begin{matrix} i, j \\ i < j \end{matrix}} \right\} i, j = 1, 2$
CPU time per 100 integration steps	2.75 s (256), 13.6 s (864)

† Radius for neighbour list.
‡ Selected with respect to the interaction potentials 1–1, 1–2, 2–2.

The primary task was however the accurate computation of the CM correlation functions to yield D_{12} coefficients with high precision. As in this case the statistics cannot be improved by the number of particles, one has to provide the averages for the correlation functions solely by collecting the relevant data from independent time origins.

Assuming a small particle number of 100 one has to evaluate about 6000 averages to reach a statistical error comparable with that of the one particle correlation functions. These 6000 values should have to be taken from about 60 000 particle configurations to ensure the time origin independence. Consequently one would end up with runs of lengths 6×10^5 time steps to get collective correlation functions with statistical errors comparable with those for the one particle correlation functions. Such conditions would be prohibitive for a systematic investigation of cross correlations in mixtures. On the other hand, the averages for the one particle time dependent correlation functions are commonly chosen superfluously large, so that an appreciable reduction of the number of time origins seems to be possible. Consequently we have attempted to find out the optimal averaging conditions which guarantee agreement between the D_{12} from the CM-VCF and the D_{12} from the CM-MSD within 2–3 per cent and an overall error for D_{12}/D_{12}^0 smaller than 5 per cent.

In the subsequent sections we shall report various aspects of these pilot calculations and an analysis of the averaging procedure adopted by Jolly and Bearman [6].

Using the vector computer Cyber 205 we were able to produce 100 000 time steps within 4 h for a 864 particle system [14]. So an extensive variation of the MD conditions was possible for a detailed study of the features of cross

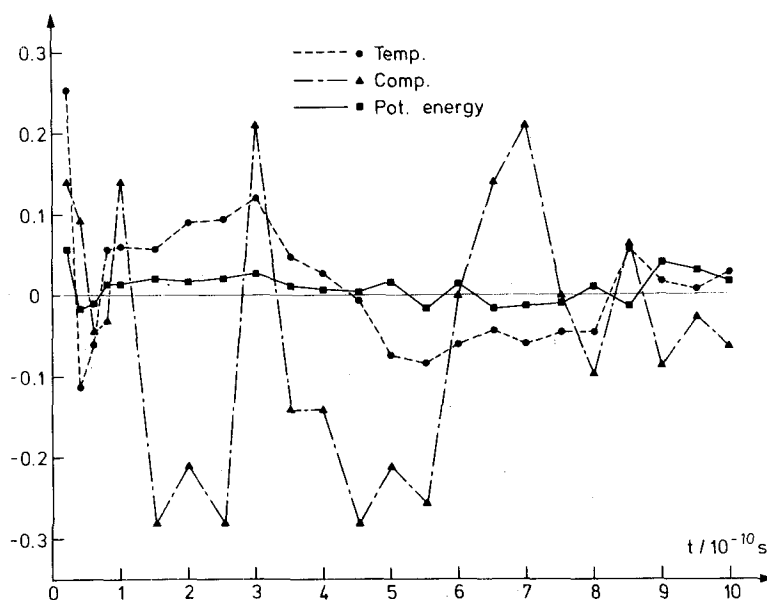


Figure 1. Time evolution of a 864 particle system over 10^5 time steps.

correlations. Although the method of molecular dynamics is now well established [15], we have to comment on our calculations with respect to the greatly extended lengths of our runs.

The Störmer–Verlet integration algorithm which was utilized sufficed to conserve the total energy of the mixture system to better than 0.001 per cent for 230 000 integration steps. For illustration we present the behaviour of a 500 particle system on figure 1, where the evolution of the mean values of the temperature, the compressibility factor and of the potential energy are displayed as a function of time. Details of the conditions of these runs are additionally gathered on table 3.

4. THE EVALUATION OF CROSS CORRELATION EFFECTS FOR BINARY MIXTURES IN TERMS OF D_{12}/D_{12}^0

4.1. Basic aspects

To get a single value of the quotient D_{12}/D_{12}^0 we determined a set of six coefficients independently evaluated through one MD run. These six numbers are the following :

- D_{11} SDC from mean square displacement (MSD) of particles of kind 1,
- D_{11} SDC from the velocity autocorrelation function (VACF) of particles of kind 1,
- D_{22} SDC from MSD of particles of kind 2,
- D_{22} SDC from VACF of particles of kind 2,
- D_{12} binary diffusion coefficient (BDC) (excluding the factor Q , see § 2) from the MSD of the centre of mass of particles of kind 1,
- D_{12} BDC from VCF of the centre of mass (CM–VCF) of particles of kind 1.

4.2. Uncorrelated time origins

In order to manage with a minimum of configurations for the evaluation of the CM correlation functions we tested the independence of the initial time origins used for the averaging procedure. Ideally one would require a time interval between nearest time origins of length comparable with the decay time of the relevant correlation function.

For the VACF, this would correspond to a time of about 60 time steps with a step width of 1×10^{-14} s. As the time integration of the VACF has to be performed at intervals of $1-4 \times 10^{-14}$ s to yield reliable diffusion coefficients, these large time spans cannot be achieved in MDC. Similar considerations hold for the CM correlation functions provided that there is no significant long time behaviour for these latter. For the MSD (or CM–MSD) the selection of the interval between independent time origins is not quite so difficult. Since in this case only the ‘long time’ slope is desired, the time positions at which these functions are actually computed can be spread broadly, for instance, at time intervals of $10-15 \times 10^{-14}$ s. So here one is able to reduce the number of MD-integration steps by simply enlarging the step width. This is often possible for the model systems with spherically symmetric interactions because it is known that a time step of 1×10^{-14} s for the model system argon is unnecessarily small [16].

Our pilot runs using 'short' averaging procedures (960 time origins) indicated the following :

- (i) The time interval Δt_{OR} between time origins should be at least the time during which the corresponding normalized correlation function has decayed to a value of $1/e$.
- (ii) Smaller time intervals than those defined in (i) affect the average value of the correlation function appreciably. Larger intervals do not improve the mean significantly.
- (iii) For the models applied herein, this time interval is $\Delta t_{\text{OR}} \approx 30 \times 10^{-14}$ s (see table 2).

We illustrate our investigations in table 4, where the D_{12} is calculated for various Δt_{OR} .

Table 4. Diffusion coefficients of the Ar-Kr system calculated from VACF and CM-VCF at various time intervals Δt_{OR} ($N=256$, 960 averaging steps for CM-VCF).

$\Delta t_{\text{OR}} \times 10^{14}/\text{s}$	D_{11}^\dagger	D_{22}^\dagger	D_{12}^\dagger
3	3.15	2.42	2.69
6	2.75	2.18	2.95
9	2.85	2.16	2.54
12	3.02	2.56	2.28
15	3.07	2.32	2.14
21	2.90	2.49	2.87
27	2.96	2.43	2.71
33	2.98	2.49	2.86

† Diffusion coefficient in $10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

Note, that the MSD is describable by the self term of the van-Hove-function [17], $G_s(r, t)$. Consequently one has to use this correlation function to get an optimal Δt_{OR} for the MSD. A reasonable estimate for the Δt_{OR} is however also accessible by the initial non-linear behaviour of the MSD, which we have exploited for the determination of Δt_{OR} [18].

4.3. Number of averaging steps

In continuation of the systematic pilot calculations, we investigated the form of the CM correlation functions as a function of the number of averages for an optimized time difference between nearest time origins. Though the computed CM correlation functions exhibited a smooth behaviour, their structure changed on increasing the number of averaging events. Figures 2-5 display typical examples of CM-MSD and CM-VCF at two very different levels of averaging. Together with the collective correlation functions we have plotted the one particle correlation functions for comparison. It is evident from these figures that especially the behaviour of the functions for the longer times changes remarkably with the number of averaging steps. Consequently the diffusion coefficients computed from these functions must vary unacceptably widely.

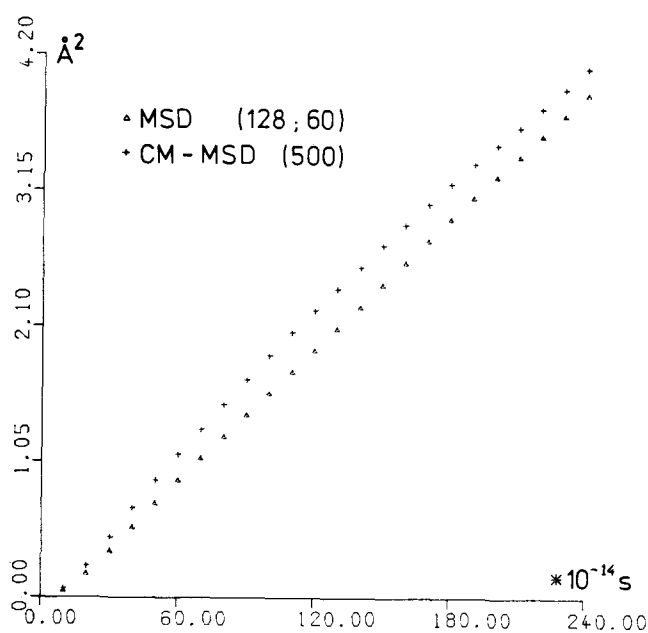


Figure 2. Mean square displacement of particles of type 1 averaged by 128×60 events. Mean square displacement of the centre of mass of particles of type 1 averaged by 500 time-origins.

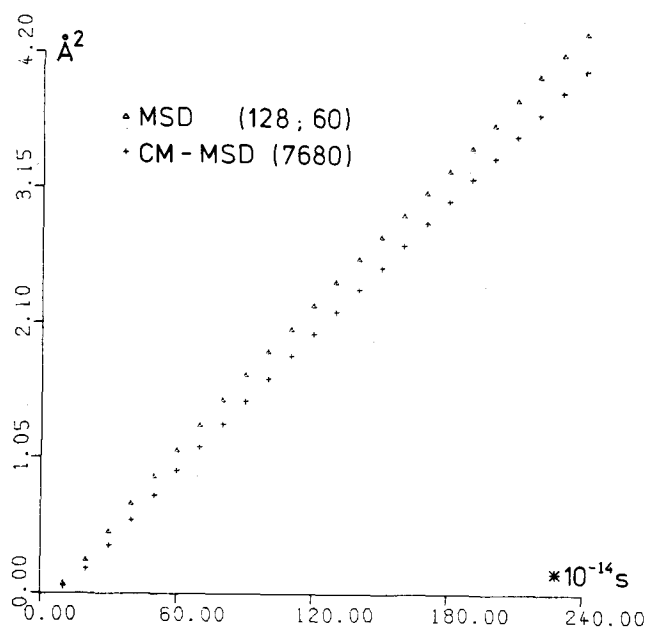


Figure 3. As figure 2, but with 7680 time origins for the centre of mass function.

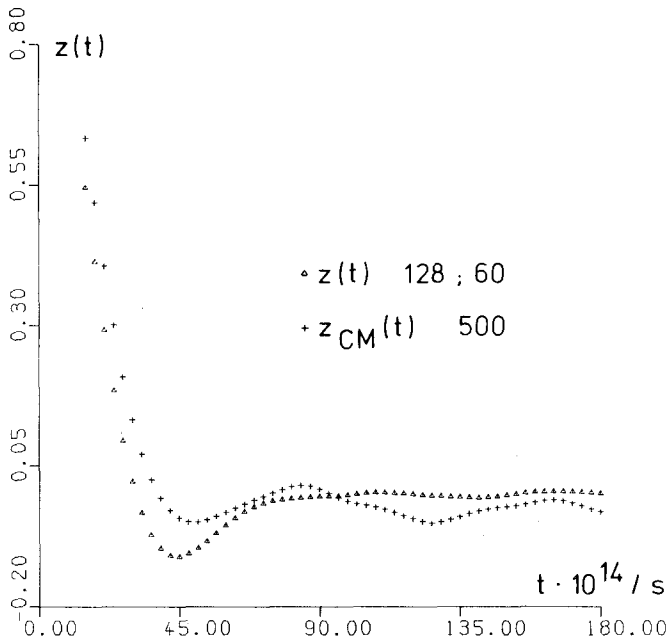


Figure 4. Normalized velocity autocorrelation function $z(t)$ of particles of type 1 averaged by 128×60 events. Normalized velocity correlation function $z_{CM}(t)$ of the centre of mass of particles of type 1 averaged by 500 time origins.

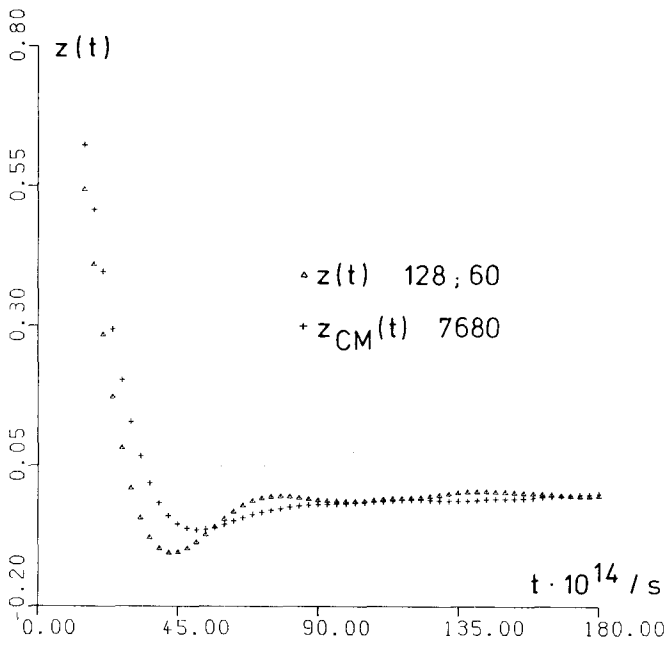


Figure 5. As figure 4, but with 7680 time origins for $z_{CM}(t)$.

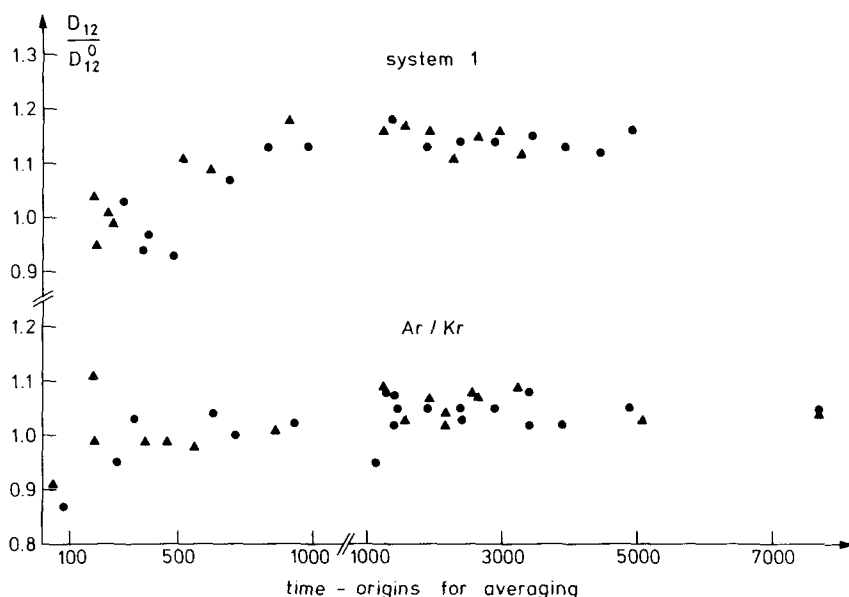


Figure 6. D_{12}/D_{12}^0 for the Ar/Kr system and system 1 dependent on the number of time origins used for the D_{12} -determination.

In figure 6 we show the resulting quotient D_{12}/D_{12}^0 for the Ar/Kr system as a function of the number of independent time origins used for the average. The values computed from the CM-VCF are separately plotted from those generated by the CM-MSD. Table 5 presents the corresponding sets of 6 diffusion coefficients. It is worth mentioning here the independence of the MD runs for this test. Each set of diffusion coefficients has been obtained by a new MD run using new starting configurations. Consequently these numbers indicate the overall error included in the calculations. As the Ar/Kr model exhibits only small cross correlation effects, we extended our pilot calculations on to a system of more pronounced cross effects. Figure 6 and table 6 show the results for this latter system. Both the plots on figure 6 clearly indicate a range from 1500–2500 time origins to be sufficient for the determination of the quotient D_{12}/D_{12}^0 accurate to 3 per cent. In view of this we have chosen at least 2000 independent time origins for the averaging procedure. To reach this averaging level, we are forced to use MD runs of 50 000 time steps or more.

4.4. Particle number dependence

For completion of the test run series, we investigated the particle number dependence of the D_{12}/D_{12}^0 ratio using the appropriate averaging level and the time origin distance.

On the one hand, this investigation is crucial, as it indicates how far the quantity under study deviates from the thermodynamic limit which is ideally to be computed. On the other hand it can be only poorly performed for a 3-dimensional system. Though in our tests we have utilized already an extremely large particle number of 2048, it is a long way to 10^{20} particles in a macroscopic system, as an unknown referee of this paper mentioned with good

Table 5. Diffusion coefficients for the equimolar Ar–Kr system.

T/K	$D_{11}^\dagger(\text{MSD})$	$D_{22}^\dagger(\text{MSD})$	$D_{12}^\dagger(\text{CM-MSD})$	Number of averaging steps	$D_{11}^\dagger(\text{VACF})$	$D_{22}^\dagger(\text{VACF})$	$D_{12}^\dagger(\text{CM-VCF})$	Number of averaging steps
115.96	2.98	2.45	2.35	80	—	—	—	—
115.89	2.91	2.45	2.54	275	—	—	—	—
115.71	3.00	2.54	2.86	335	—	—	—	—
115.82	2.98	2.47	2.83	625	2.83	2.34	2.34	35
115.58	3.02	2.41	2.71	710	—	—	—	—
115.82	2.98	2.47	2.77	930	2.83	2.34	2.87	187
115.89	2.91	2.45	2.54	1135	2.96	2.43	2.66	187
115.74	2.98	2.33	2.86	1310	2.95	2.34	2.61	460
115.74	2.98	2.39	2.90	1375	—	—	—	—
115.44	2.99	2.52	2.81	1410	2.90	2.56	2.69	560
115.81	2.97	2.40	2.81	1430	2.96	2.43	2.71	863
115.79	2.94	2.42	2.82	1885	2.98	2.32	2.90	1246
115.79	2.94	2.42	2.81	1885	2.98	2.32	2.62	387
115.71	2.94	2.47	2.84	2350	2.94	2.49	2.80	1576
115.77	2.95	2.48	2.80	2380	2.98	2.48	2.78	2176
115.73	2.91	2.43	2.81	2875	3.06	2.42	2.93	1912
116.81	3.10	2.47	2.83	3385	3.16	2.49	3.01	2245
115.73	2.92	2.46	2.89	3385	2.94	2.47	2.81	2245
115.81	3.05	2.58	2.86	3870	2.96	2.60	2.99	2578
115.74	2.95	2.40	2.80	4870	2.89	2.44	2.90	3241
116.38	3.00	2.54	2.89	7680	2.98	2.52	2.83	5088
115.42	—	—	—	—	3.02	2.51	2.88	7680

$^\dagger 10^{-5} \text{ cm}^2 \text{ s}^{-1}$.

Table 6. Diffusion coefficients for the equimolar system 1 (see table 5).

T/K	Number of averaging steps					Number of averaging steps		
	$D_{11}(\text{MSD})$	$D_{22}(\text{MSD})$	$D_{12}(\text{CM-MSD})$	$D_{11}(\text{VACF})$	$D_{22}(\text{VACF})$	$D_{12}(\text{CM-VCF})$		
108.97	2.04	1.77	1.97	2.11	1.65	1.79	204	
108.78	2.16	1.74	1.84	2.02	1.81	1.99	190	
108.98	2.13	1.73	1.88	2.16	1.67	1.89	260	
108.99	2.15	1.74	1.85	2.03	1.80	1.93	244	
109.01	2.16	1.70	2.06	2.12	1.74	2.26	460	
109.02	2.02	1.66	2.07	2.11	1.67	2.10	524	
109.20	2.04	1.63	2.08	2.11	1.67	2.06	624	
109.04	2.01	1.66	2.17	1.82	1.46	1.94	960	
109.03	2.16	1.60	2.12	2.11	1.53	2.11	1240	
109.01	2.01	1.73	2.12	1.90	1.65	2.08	1596	
108.98	2.07	1.66	2.12	1.89	1.68	2.07	1906	
108.96	2.09	1.68	2.13	2.07	1.69	2.17	2622	
108.95	2.06	1.67	2.09	1.98	1.52	2.03	2958	
108.95	2.02	1.72	2.16	2.04	1.69	2.09	3294	

reason. Nonetheless we are able to exploit experience from earlier simulations on other quantities and from the material of our present calculations, to conclude that the D_{12}/D_{12}^0 ratio is not far from the thermodynamic limit. The figure 7 shows plots of this quotient against the particle number for two different model mixtures. Table 7 contains the corresponding sets of diffusion coefficients. Evidently from these plots there is only a negligible particle number dependence observable. If the BDC were to have a noticeably different particle number dependence from the SDC, this would result in a significant variation of the D_{12}/D_{12}^0 ratio. The argument that those differences possibly would become apparent for much larger particle ensembles can be countered by the following observations :

- (i) Figures 3 and 5 show that the collective correlation functions have no distinct tail for 256 particle ensembles (the slope of the CM-MSD does not change ; the CM-VCF decays within 100 time steps, for the high averaging level).
- (ii) The behaviour of CM functions computed for larger systems fall in line with those plotted on figures 3 and 5.
- (iii) A 2048-particle system allows a calculation of the correlation functions up to 5×10^{-12} s. Within this time interval the CM-MSD exhibits a strictly linear form indicating again no remarkable long time behaviour of these collective correlation function, as is seen from figure 8.
- (iv) The structure of the CM correlation functions resembles rather precisely that of the one particle correlation functions. Comparable properties for the former can therefore be expected (see figures 3 and 5).

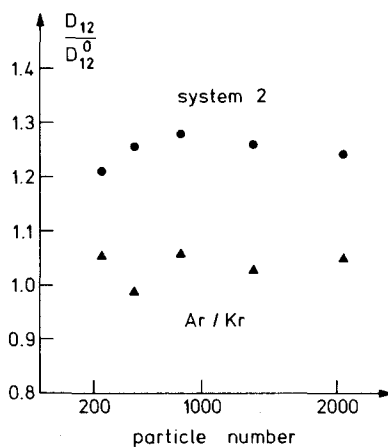


Figure 7. Particle number dependence of D_{12}/D_{12}^0 for the Ar/Kr system and system 2.

4.5. Averaging in terms of a lot of short MD-runs

The D_{12} -results for the Ar/Kr system of Jolly and Bearman [6] disagree slightly but significantly with our results. Whereas these authors find small negative cross correlations of 9 per cent, we observe positive correlation effects of 5 per cent. Furthermore, positive cross correlations support considerations about the relative strength of the 1-2 potential, whilst negative effects do not. A detailed discussion of this can be found in the subsequent paper [8].

Table 7. The diffusion coefficients of system 2 and the Ar-Kr system for various particle numbers. The values for D_{12} are obtained by averaging over 1500 time origins (see table 5).

System	T/K	N	D_{11} (MSD)	D_{22} (MSD)	D_{12} (CM-MSD)	D_{11} (VACF)	D_{22} (VACF)	D_{12} (CM-VCF)
Ar-Kr	119.4	256	3.10	2.22	2.86	2.98	2.24	2.69
	115.4	500	2.91	2.43	2.77	2.92	2.40	2.84
	115.7	864	2.98	2.43	2.87	2.95	2.44	2.85
	114.5	1372	2.93	2.45	2.74	2.90	2.50	2.81
	114.45	2048	2.98	2.45	2.86	2.94	2.46	2.84
2	108.07	256	1.80	1.42	1.99	1.86	1.49	2.00
	111.04	500	1.94	1.55	2.16	1.90	1.51	2.11
	112.12	864	2.12	1.71	2.42	2.26	1.73	2.59
	111.16	1372	2.10	1.74	2.37	2.08	1.71	2.54
	111.45	2048	2.11	1.70	2.33	2.15	1.63	2.39

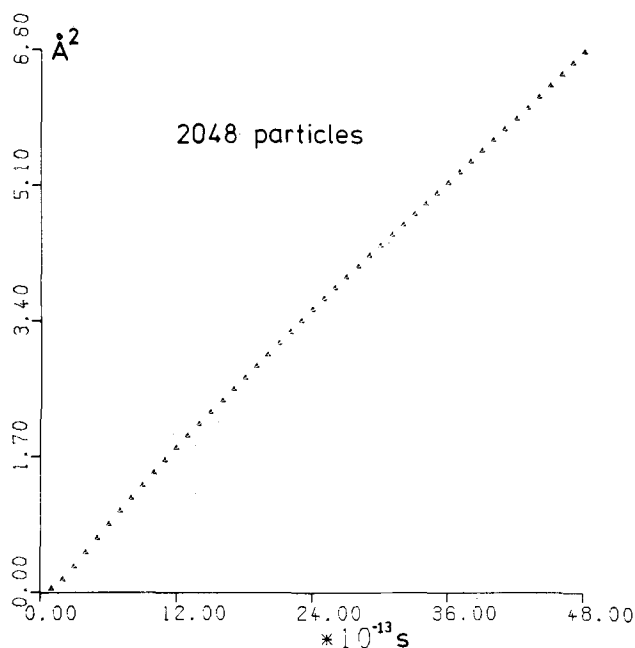


Figure 8. Mean square displacement of the centre of mass of particles of kind 1 for a 2048 particle ensemble.

In our opinion these small differences in D_{12} are due to a systematic error implicitly involved in the evaluation method adopted by Jolly and Bearman (hereafter referenced through JB). JB computed the CM-MSD from a great number of short MD runs separately and finally averaged over the D_{12} -coefficients obtained by the slopes of these separate CM-MSD. A single run of 7500 steps gives, however, only an average of about 350 independent time origins, which is too low to reproduce the correct structure of the CM-function. This is readily seen from figure 1 of JB, where the CM-MSD exhibits two different slopes between 0–175 and 175–350 $\times 10^{-14}$ s. (The CM-VCF shown on figure 2 displays oscillations for the larger times, however, this function was not used for the D_{12} -determination.)

As the short runs produce unreliable D_{12} -values, the average over 10–30 of these data can only partly balance this defect. This has been proven by an additional pilot series, where we have determined the quotient D_{12}/D_{12}^0 for the Ar/Kr-system precisely in the way proposed by JB. Table 8 shows clearly the agreement between this value and that of JB but the disagreement with our definite result. We conclude therefore that the method of JB is not suitable to reproduce very accurate D_{12} -coefficients by MDC.

A final technical remark should be in order. Whilst for the dynamic one particle correlation functions a storing of the entire set of coordinates of the particles on tape or disc in preselected time intervals seems to be reasonable, for the collective properties this is a waste of storage and I/O time, as from one configuration of coordinates only a few single numbers are computed for the

Table 8. D_{12}/D_{12}^0 for the Ar-Kr system of 864 particles using short runs of 7500 integration steps (see table 5).

T/K	$D_{11}(\text{MSD})$	$D_{22}(\text{MSD})$	$D_{12}(\text{CM-MSD})$	D_{12}/D_{12}^0	$D_{11}(\text{VACF})$	$D_{22}(\text{VACF})$	$D_{12}(\text{CM-VCF})$	D_{12}/D_{12}^0
115.11	2.96	2.48	2.24	0.82	3.13	2.60	2.42	0.84
115.28	3.01	2.56	2.66	0.96	2.90	2.57	2.51	0.92
115.45	3.07	2.54	2.64	0.94	2.94	2.48	2.74	1.01
114.01	2.95	2.52	2.82	1.03	3.16	2.44	3.17	1.13
113.27	2.92	2.45	2.99	1.11	3.12	2.48	3.32	1.19
114.62	2.98	2.39	2.29	0.85	3.15	2.34	2.30	0.84
115.36	3.00	2.46	3.04	1.11	3.06	2.42	2.60	0.95
112.84	2.84	2.35	2.35	0.91	2.71	2.39	2.61	1.02
115.92	3.12	2.58	2.73	0.96	3.02	2.50	2.44	0.88
114.86	2.95	2.38	2.39	0.90	2.91	2.43	2.85	1.07

D_{12}/D_{12}^0 , this work, using 10 short runs 0.97
 D_{12}/D_{12}^0 of [6] 0.91
 D_{12}/D_{12}^0 , this work, using long runs 1.05

collective correlation functions. Consequently, one may advantageously compute these numbers during the run and store blocks of these numbers to make subsequent calculations possible.

In our case we have stored 300–400 configurations of particle-coordinates for the one particle properties and 10 or 20 blocks of 1500 numbers for the collective properties.

5. THE THERMODYNAMIC FACTOR Q

If the absolute value of the mutual diffusion coefficient is required rather than the cross correlation effect, an evaluation of the thermodynamic factor Q is obligatory. JB have shown that this factor is available by MD by integration of the partial pair correlation functions, which are corrected for their large- r behaviour.

$$\left. \begin{aligned} Q &= \frac{1}{1 + (c_1 c_2 / (c_1 + c_2))(G_{11} + G_{22} - 2G_{12})}, \\ G_{ij} &= \int h_{ij}(r) \, dr \quad (j \geq i, i = 1, 2), \end{aligned} \right\} \quad (3)$$

where c_i are the number densities of the particle kinds and $h_{ij}(r)$ are the total pair correlation functions as defined by

$$h_{ij}(r) = g_{ij}(r) - 1$$

It is easily seen that for an ideal mixture, which has three equivalent $g_{ij}(r)$ functions, the thermodynamic factor equals 1. JB determined $Q = 0.97$ for the Ar/Kr system with an error of 0.08 corroborating the assumption of near ideality for this model (see § 2). Our attempt to compute Q led to the same result of unity for Ar/Kr with a small tendency to a smaller value. We hesitate however to give error bars, since we have not corrected the $g_{ij}(r)$ for large r . Nevertheless we believe that the error is smaller than 10 per cent, for we have used $g_{ij}(r)$ -functions up to 21 Å, that is six coordination-shells. It must however be noted, that the desired difference $G'_{11} + G'_{22} - 2G'_{12}$ fluctuates strongly with distance due to the enormous increase of the particle number as function of the integration radius (see table 9).

We have further estimated the Q -factor from the sum of the local mole fractions x_{ii} minus one :

$$Q \approx \frac{1}{x_{11}(r_M) + x_{22}(r_M)} = \frac{1}{x_s(r_M)}, \quad (4)$$

where $x_{ii}(r)$ are defined by a quotient of the number of neighbours of particles of type i and j around the origin particle i [18, 19]. The distance r_M has to be chosen so as to represent an average value of $x_s(r)$ within the first two coordination shells. The selection of r_M is not critical even if the value $x_s(r)$ oscillates. One has only to take care of the fact that reliable values of $x_{ii}(r)$ cannot be obtained for very short distances, where any of the $g_{ij}(r)$ functions has not yet reached its maximum.

On the basis of the local mole fractions we have evaluated the Q -factor for a few mixture types studied in our work. We shall report the investigation of these models in the consecutive paper. Table 10 lists the Q -factor obtained by (4) together with the number of JB and our directly computed value.

Table 9. Q -factor from relation (3) of § 5 as a function of the integration distance.

System	r/σ_{11}	$G'_{11} + G'_{22} - 2G'_{12}$	$Q(r/\sigma_{11})$
Ar/Kr (2048)	1.17	-0.170	1.030
	1.37	-0.067	1.011
	1.61	0.020	0.996
	1.81	0.041	0.993
	2.01	-0.099	1.018
	2.21	-0.247	1.046
	2.41	-0.368	1.070
	2.65	-0.373	1.071
	2.81	-0.336	1.064
	3.01	-0.319	1.060
	3.21	-0.340	1.065
	3.41	-0.183	1.034
	3.61	-0.061	1.011
	3.81	0.127	0.973
	4.01	0.290	0.951
	4.21	0.492	0.919
	4.57	0.655	0.895
	4.81	0.524	0.915
	5.01	0.401	0.933
	5.15	0.474	0.922
	5.41	0.624	0.900
	5.65	0.555	0.910
	5.81	0.326	0.945
	6.01	0.225	0.961
	6.21	0.124	0.978
	6.41	-0.131	1.024
	6.51	-0.278	1.052
	6.71	-0.380	1.073
	6.83	-0.491	1.096

Table 10. Estimated Q -factor for different Lennard-Jones systems with 1-2 interaction from Lorentz-Berthelot combining rules.

System	From rel (2)	From rel (4)	From [6]
Ar/Kr	0.973	0.997	0.97
(1.0/1.5)		0.996	
(1.0/2.0)		0.987	
(1.0/2.75)		0.967	
(1.0/3.0)		0.964	
$(\mu/\nu) = \left(\frac{\sigma_{22}}{\sigma_{11}} \sqrt{\frac{\epsilon_{22}}{\epsilon_{11}}} \right)$; Lorentz-Berthelot 1-2 parameters.			

It appears evident from the table that the factor Q is close to unity throughout the spectrum of mixture types taken into account. The agreement between the directly computed value and the number estimated by the local mole fractions is satisfactory. Similarly, the result from JB falls exactly in line with our number.

We must however admit that Lorentz–Berthelot mixtures of type

$$\left(\frac{\sigma_{22}}{\sigma_{11}} \geq 1 ; \frac{\epsilon_{22}}{\epsilon_{11}} \ll 1 \right)$$

are excluded from our comparisons. For these mixtures, significant departures of the Q -factor from unity have to be expected, as here the effect of the ratios σ_{22}/σ_{11} and $\epsilon_{22}/\epsilon_{11}$ on the non-ideality of the system is cumulative [20].

6. CONCLUSIONS

We have unambiguously shown that a determination of cross correlation effects in binary liquid model mixtures by MDC is possible in terms of the quantity D_{12}/D_{12}^0 .

The D_{12}^0 is defined as the pure mutual diffusion coefficient available from the SDC of the component particles of the mixture. MD-runs of length 5×10^4 time steps provide reliable D_{12}/D_{12}^0 quotients with an overall error of only 3 per cent. The absolute value of the D_{12} has a slightly larger error as in this case the thermodynamic factor Q has additionally to be evaluated for the non-ideal mixture. As neither a significant particle number dependence nor a noticeable potential cutoff dependence could be observed for the D_{12}/D_{12}^0 quantity, MD calculations based on small particle ensembles should already reproduce good D_{12} -values provided the number of averages is large enough. 5×10^4 integration steps can however be performed on conventional computers using 108 or 256 particles.

Our detailed study has moreover revealed some deficiencies of earlier computations on cross correlations [6, 7], although this previous work on D_{12} yielded values, which are not far from our results. The values of Jaccuci and McDonald are in perfect agreement with our data. As these latter authors have not reported their errors precisely, this accordance may be fortuitous. An extended comparison of our values with those of Jaccuci *et al.* and JB will follow in the subsequent paper [8]. In this following paper a systematic investigation is reported of cross effects in various Lennard-Jones model mixtures, where for the 1–2 interaction potential the Lorentz–Berthelot combining rules have been invoked.

APPENDIX 1

The mutual diffusion coefficient D_{12} in a binary mixture is given by the Green–Kubo integral over the velocity correlation function of the centre of mass of particles of kind 1 as

$$D_{12} = \frac{Q}{3Nc_1c_2} \left(\frac{m_1}{m_2} c_1 + c_2 \right)^2 \int_0^\infty z_{\text{CM}}(\tau) d\tau \quad (\text{A } 1)$$

with

$$z_{\text{CM}}(\tau) = \left\langle \sum_{i=1}^{N_1} \mathbf{u}_i(t) \sum_{i=1}^{N_1} \mathbf{u}_i(t+\tau) \right\rangle \quad (\text{A } 2)$$

where the angular brackets denote an average over an appropriate equilibrium ensemble. This equation may be rewritten in the centre of mass frame of the total system with the help of the well known expression [21].

$$\mathbf{u}_0(t) = \frac{m_1 \sum_{i=1}^{N_1} \mathbf{u}_i(t) + m_2 \sum_{j=1}^{N_2} \mathbf{u}_j(t)}{N_1 m_1 + N_2 m_2} \quad (\text{A } 3)$$

where $\mathbf{u}_0(t)$ is the velocity of the centre of mass of the total system at time t , which generally is chosen to be zero for the MD ensemble. One then gets

$$\begin{aligned} D_{12} &= \frac{Q}{3Nc_1c_2} \int_t^\infty \left\langle \left[c_2 \sum_{i=1}^{N_1} \mathbf{u}_i(t) - c_1 \sum_{j=1}^{N_2} \mathbf{u}_j(t) \right] \right. \\ &\quad \times \left. \left[c_2 \sum_{i=1}^{N_1} \mathbf{u}_i(t+\tau) - c_1 \sum_{j=1}^{N_2} \mathbf{u}_j(t+\tau) \right] \right\rangle d\tau \\ &= \frac{Q}{3Nc_1c_2} \int_t^\infty \left\langle c_2^2 \sum_{i=1}^{N_1} \sum_{k=1}^{N_1} \mathbf{u}_i(t) \mathbf{u}_k(t+\tau) - c_1c_2 \sum_{i=1}^{N_1} \sum_{l=1}^{N_2} \mathbf{u}_i(t) \mathbf{u}_l(t+\tau) \right. \\ &\quad \left. - c_1c_2 \sum_{j=1}^{N_2} \sum_{k=1}^{N_1} \mathbf{u}_j(t) \mathbf{u}_k(t+\tau) + c_1^2 \sum_{j=1}^{N_2} \sum_{l=1}^{N_2} \mathbf{u}_j(t) \mathbf{u}_l(t+\tau) \right\rangle d\tau. \quad (\text{A } 4) \end{aligned}$$

It may be seen from (A 4) that there are two different types of cross correlations which contribute to the Green-Kubo integral

- (i) Cross correlations between different particles of the same mixture component (terms with c_i^2 ($i=1, 2$)).
- (ii) Cross correlations between particles of different mixture components (terms with c_1c_2).

Equation (A 4) can now be simplified by neglecting both types of cross correlations completely, thus obtaining

$$\begin{aligned} D_{12}^0 &= x_2 \frac{Q}{3N_1} \int_t^\infty \left\langle \sum_{i=1}^{N_1} \mathbf{u}_i(t) \mathbf{u}_i(t+\tau) \right\rangle d\tau \\ &\quad + x_1 \frac{Q}{3N_2} \int_t^\infty \left\langle \sum_{j=1}^{N_2} \mathbf{u}_j(t) \mathbf{u}_j(t+\tau) \right\rangle d\tau \quad (\text{A } 5) \\ &= Q(x_2 D_{11} + x_1 D_{22}). \end{aligned}$$

We have thereby arrived at (3) of § 2.

APPENDIX 2

Phenomenological definition of diffusion coefficients in mixtures

The diffusive mass flux \mathbf{J}_s of a component s in a mixture of r components relative to the fluid's centre of mass is given by

$$-\mathbf{J}_s = \frac{L_{sq}}{T} \nabla(\ln T) + \sum_{t=1}^r \frac{L_{st}}{T} (\nabla \mu_t)_{T,p}, \quad (\text{A } 6)$$

where the chemical potential of component t is denoted by μ_t and the phenomenological transport coefficients are denoted by L , with L_{sq} referring to thermal and L_{st} referring to isothermal diffusion. In a system of r components at least $(r-1)$ fluxes \mathbf{J}_s or $(r-1)$ phenomenological coefficients L_{st} may be chosen independently. So we have two further relations :

$$\sum_{s=1}^r \mathbf{J}_s = \mathbf{0} \quad (\text{A } 7)$$

and

$$\sum_{t=1}^r L_{st} = 0, \quad (\text{A } 8)$$

where the first index refers to the flux and the second one refers to the component. Considering isothermal diffusion only (A 6) may be rewritten as

$$-\mathbf{J}_s = \sum_{t=1}^{r-1} D_{st} \nabla x_t. \quad (\text{A } 9)$$

The mutual diffusion coefficient D_{st} is now given in terms of the derivative of the chemical potential and the phenomenological transport coefficients

$$D_{st} = \sum_{v=1}^r \frac{L_{sv}}{T} \left(\frac{\partial \mu_v}{\partial x_t} \right)_{T,p}. \quad (\text{A } 10)$$

In the case of a ternary system (A 9) may be written as

$$\left. \begin{aligned} -\mathbf{J}_1 &= D_{11} \nabla x_1 + D_{12} \nabla x_2, \\ -\mathbf{J}_2 &= D_{21} \nabla x_1 + D_{22} \nabla x_2, \\ -\mathbf{J}_3 &= D_{31} \nabla x_1 + D_{32} \nabla x_2, \end{aligned} \right\} \quad (\text{A } 11)$$

with six diffusion coefficients. Using the Gibbs–Duhem equation

$$\sum_{t=1}^r x_t \left(\frac{\partial \mu_t}{\partial x_t} \right)_{T,p} \nabla x_t = \mathbf{0} \quad (\text{A } 12)$$

and (A 10) together with

$$x_1 + x_2 + x_3 = 1, \quad (\text{A } 13)$$

one gets

$$\left. \begin{aligned} TD_{11} &= \left[\left(\frac{x_1}{x_2} L_{12} - L_{11} \right) \left(\frac{\partial \mu_1}{\partial x_3} \right)_{T,p} + \left(\frac{x_3}{x_2} L_{12} - L_{13} \right) \left(\frac{\partial \mu_3}{\partial x_3} \right)_{T,p} \right] = TD_{12}, \\ TD_{21} &= \left[\left(\frac{x_1}{x_2} L_{22} - L_{21} \right) \left(\frac{\partial \mu_1}{\partial x_3} \right)_{T,p} + \left(\frac{x_3}{x_2} L_{22} - L_{23} \right) \left(\frac{\partial \mu_3}{\partial x_3} \right)_{T,p} \right] = TD_{22}, \\ TD_{31} &= \left[\left(\frac{x_1}{x_2} L_{32} - L_{31} \right) \left(\frac{\partial \mu_1}{\partial x_3} \right)_{T,p} + \left(\frac{x_3}{x_2} L_{32} - L_{33} \right) \left(\frac{\partial \mu_3}{\partial x_3} \right)_{T,p} \right] = TD_{32}. \end{aligned} \right\} \quad (\text{A } 14)$$

In the latter equations the number of independent mutual diffusion coefficients is reduced to three. Finally one obtains only two independent coefficients when (A 7) is exploited additionally :

$$D_{11} + D_{21} = -D_{31}. \quad (\text{A } 15)$$

We turn now to the self diffusion in a binary mixture, which may be regarded as a limiting case of the mutual diffusion in a ternary system. For component 1 not different from component 3 and $x_3 \rightarrow 0$, we may substitute L_{13} , L_{23} and μ_3 in (A 14) by L_{11} , L_{21} and μ_1 .

$$\text{Using } \mu_t = \mu_t^* + RT \ln f_t x_t \quad (\text{A } 16)$$

μ_t^* ; standard chemical potential of component t ,

f_t ; activity coefficient of component t ,

R ; gas constant,

it is easy to show, that

$$\lim_{x_3 \rightarrow 0} \left(\frac{\partial \mu_1}{\partial x_3} \right)_{T,p} = \lim_{x_3 \rightarrow 0} RT \left[\frac{1}{x_1 f_1} \left\{ x_1 \left(\frac{\partial f_1}{\partial x_3} \right)_{T,p} - f_1 \right\} \right] = -\frac{RT}{x_1}. \quad (\text{A } 17)$$

Together with (A 8), (A 17) can now be used to derive

$$D_{11}^\infty = RL_{11} \frac{1+x_2}{x_1 x_2} \quad (\text{A } 18)$$

from (A 14). (A 18) is the definition of the self diffusion coefficient of *component 1* in a binary mixture. The definition of the self diffusion coefficient of *component 2* can be derived in a similar way, assuming that now component 2 is identical with component 3. We finally arrive at an equation similar to (A 18) which differs only by a term $1+x_1$ instead of $1+x_2$.

In contrast the mutual diffusion coefficient for a binary mixture is given by the expression [9]

$$D = RL_{11} \frac{1}{x_1 x_2 f_1} \left[x_1 \left(\frac{\partial f_1}{\partial x_2} \right)_{T,p} - f_1 \right]. \quad (\text{A } 19)$$

Comparing (A 18) and (A 19) it is evident that the mutual diffusion coefficient in a binary mixture is a two particle quantity due to the term $(\partial f_1 / \partial x_2)_{T,p}$.

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