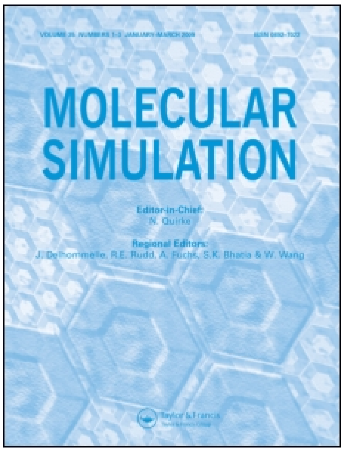

Molecular Simulation

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Molecular Dynamics Simulation of the Maxwell-Stefan Diffusion Coefficients in Lennard-Jones Liquid Mixtures

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To cite this Article van de Ven-Lucassen, Irma M. J. J. , Otten, Anita M. V. J. , Vlugt, Thus J. H. and Kerkhof, Piet J. A. M.(1999) 'Molecular Dynamics Simulation of the Maxwell-Stefan Diffusion Coefficients in Lennard-Jones Liquid Mixtures', Molecular Simulation, 23: 1, 43 — 54

To link to this Article: DOI: 10.1080/08927029908022110

URL: http://dx.doi.org/10.1080/08927029908022110

Molecular Simulation, 1999, Vol. 23, pp. 43–54
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the Gordon and Breach Science
Publishers imprint.
Printed in Malaysia.

MOLECULAR DYNAMICS SIMULATION OF THE MAXWELL-STEFAN DIFFUSION COEFFICIENTS IN LENNARD-JONES LIQUID MIXTURES

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(Received March 1999; accepted April 1999)

Maxwell-Stefan (MS) diffusion coefficients in multicomponent liquids have been determined by the equilibrium molecular dynamics calculation of the appropriate Green-Kubo equation. Simulations were performed for systems of 300 LJ particles at various compositions. The unary system was divided into three components by attaching a colour label to the particles, which plays no role in the dynamics. The binary system argon + krypton was divided into three species by attaching a colour label to the particles of argon. The ternary system consisted of argon, krypton and neon. The results of the calculation of the MS diffusion coefficients in the unary and binary systems agreed well with the literature values. The MS diffusion coefficients of the unary system did not differ significantly from the self-diffusion coefficient. The MS diffusion coefficients of the ternary system behaved as expected from other physical properties.

Keywords: Molecular dynamics; Green-Kubo method; Maxwell-Stefan diffusion coefficients; LJ liquid mixtures

1. INTRODUCTION

Multicomponent diffusion in liquid systems plays an important role in chemical engineering and knowledge of diffusion coefficients is required, for example, for the design of process equipment. However, it is very time

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*Corresponding author.

consuming and difficult to measure diffusion coefficients in multicomponent systems [1, 2]. Simulation techniques like molecular dynamics provide an attractive alternative to determine the diffusion coefficients.

For the calculation of the diffusion coefficients in a binary or ternary mixture of Lennard-Jones particles equilibrium molecular dynamics methods have been developed, in which the correlation function of fluctuating quantities is determined [3 – 6]. The integrals of the correlation functions are related to the diffusion coefficients through the Green-Kubo formalism. In Ref. [6] we have shown that this so-called Green-Kubo method is preferred above a non-equilibrium method, in which the system is driven away from equilibrium and the system response is monitored. The Green-Kubo method was tested by performing simulations in coloured Lennard-Jones mixtures: the particles in the binary and ternary system had identical LJ potential parameters and differed only by a colour label, which plays no role in the dynamics [6]. The purpose of the work presented here is to use the Green-Kubo method by performing simulations in binary and ternary Lennard-Jones mixtures, in which the particles have different LJ potential parameters and different masses.

An outline of the paper is as follows. In Section 2, the main features of the theory for describing diffusion in liquids are given. The details of the simulations are described in Section 3. Section 3.1 presents the MD simulations of the diffusion coefficients in a unary system; Section 3.2 describes the simulations in a binary LJ system, followed by the simulations in a ternary LJ system in Section 3.3. Results are compared with the literature.

2. THEORY

Molecular diffusion in multicomponent systems can be described by the Maxwell-Stefan approach. When temperature T and pressure p are constant, and when there are no external forces acting on the system, the molar fluxes N_i, N_j of components i, j due to the gradient in the chemical potential μ_i of component i are given by

$$\sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_i N_j - x_j N_i}{C_t D_{ij}} = \frac{x_i}{RT} \nabla_{T,p} \mu_i, \tag{1}$$

in which R is the gas constant, x_i the mole fraction of component i and C_t the total molar concentration. D_{ij} is the Maxwell-Stefan diffusion coefficient between components i and j. Because $D_{ij} = D_{ji}$, there are $n(n-1)/2$

independent Maxwell-Stefan diffusion coefficients. An extensive description of the Maxwell-Stefan approach is given in [7].

Maxwell-Stefan diffusion coefficients can be calculated using an equilibrium molecular dynamics (EMD) method based on the Green-Kubo formalism. This Green-Kubo method uses the time correlation functions of fluctuating quantities in an equilibrium system; these time correlation functions are linked to the response to weak perturbations in the equilibrium system by linear response theory [8 – 10]. The Maxwell-Stefan diffusion coefficients D_{12} of a binary system is then given by

$$D_{12} = \frac{x_2}{3n_1}\left(\frac{M_1x_1 + M_2x_2}{M_2x_2}\right)^2 \int_0^\infty \left\langle \sum_{i=1}^{n_1} \boldsymbol{v}_1^i(0) \cdot \sum_{j=1}^{n_1} \boldsymbol{v}_1^j(t) \right\rangle dt, \tag{2}$$

in which t is the simulation time, M_i is the molar mass of component i, n_1 the number of particles of component 1, and $\boldsymbol{v}_1^i$ the velocity of particle i of component 1.

Calculation of the self-diffusion coefficient D_i of component i can be performed simultaneously, using

$$D_i = \frac{1}{3}\int_0^\infty \langle \boldsymbol{v}_i(0) \cdot \boldsymbol{v}_i(t)\rangle dt. \tag{3}$$

The derivation of Eqs. (2) and (3) has been given in [6].

Calculating Ternary Diffusion Coefficients

Diffusion in a ternary system can be described by the independent Maxwell-Stefan diffusion coefficients D_{12}, D_{31} and D_{23}. For the calculation of these ternary diffusion coefficients the following equation has been derived [6]

$$D_{ij} = \frac{n_in_jM(\mathrm{Int}_{iki}\mathrm{Int}_{kjk}\mathrm{Int}_{jij} + \mathrm{Int}_{jki}\mathrm{Int}_{ijk}\mathrm{Int}_{kij})}{3n_iM_i\mathrm{Int}_{iki}\mathrm{Int}_{kjk} + 3n_jM_j\mathrm{Int}_{jki}\mathrm{Int}_{kij} - 3n_kM_k\mathrm{Int}_{kjk}\mathrm{Int}_{kij}} \tag{4}$$

in which $M = M_ix_i + M_jx_j + M_kx_k$ and Int_{ijk} has been defined by

$$\mathrm{Int}_{ijk} = \int_0^\infty \langle(\boldsymbol{u}_i(0) - \boldsymbol{u}_j(0)) \bullet \boldsymbol{u}_k(t)\rangle dt \tag{5}$$

with $\boldsymbol{u}_i$ is the velocity of component i.

Since $\mathrm{Int}_{ijk}(i \neq j \neq k \neq i) = 0$, Eq. (4) simplifies to

$$D_{ij} = \frac{n_jM}{3M_i}\mathrm{Int}_{jij}. \tag{6}$$

3. SIMULATIONS

To investigate the Green-Kubo method, simulations of a Lennard-Jones fluid were performed. We used the truncated and shifted potential

$$U^{tr-sh}(r) = \begin{cases} U^{LJ}(r) - U^{LJ}(R_{\text{cut}}) & r \leq R_{\text{cut}} \\ 0 & r > R_{\text{cut}} \end{cases}. \tag{7}$$

$U^{LJ}(r)$ is the Lennard-Jones potential:

$$U^{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right], \tag{8}$$

in which r is the particle–particle distance, ε the Lennard-Jones energy parameter and σ the Lennard-Jones size parameter. The cross interaction parameters were obtained from the Lorentz-Berthelot rules $\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2}$ and $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$. Using reduced units the reduced pair potential $U^{LJ^*} \equiv U^{LJ}/\varepsilon$ is a dimensionless function of the reduced distance $r^* \equiv r/\sigma$. Other reduced quantities are the reduced time $t^* \equiv (t/\sigma)(\varepsilon/m)^{1/2}$, the reduced density $\rho^* \equiv \rho\sigma^3$, the reduced pressure $p^* = p\sigma^3/\varepsilon$, and the reduced temperature $T^* \equiv Tk_B/\varepsilon$, in which m is the mass of the atoms in the system, and k_B is Boltzmann's constant. In all simulations we will use reduced quantities and we, therefore, omit the superscripts*.

Systems of 300 particles were used in the simulations. Periodic boundary conditions were applied with a cutoff radius of the potential $R_{\text{cut}} = 2.5$ and a timestep $\Delta t = 0.001$. Starting with lattice configurations and random velocities, the total momenta of the systems were set to zero and the systems were equilibrated for 25,000 timesteps at the desired temperature and density. During equilibration the temperature of the systems was scaled to the desired temperature after each timestep. The resulting velocities and coordinates were used as a staring point for further simulations.

3.1. Simulations in a Unary Lennard-Jones System

Simulations were performed on a system of 300 identical Lennard-Jones particles at $T = 0.728$ and $\rho = 0.8442$ in the NVE-ensemble. The system was divided into three species or components by attaching a colour label to a mole fraction x_i of the particles. So, the three species differ only by the colour label, which plays no role in the dynamics. MD simulations of multiples of 25,000 timesteps ($\Delta t = 0.001$) were performed and every 10 timesteps a new time origin was taken for the calculation of the multiple particle autocorrelation function $\sum v_1^i(0) \cdot \sum v_1^j(t)$ of Eq. (2), resulting in 2,350 time origins per run of 25,000 time steps. The MS diffusion coefficients were calculated, using Eq. (6) for several numbers of time origins and for various integration times (maximal 1,500 timesteps). The accuracy of the MS diffusion coefficients in this unary system, as well as in the following binary and ternary systems, was estimated from the standard deviation of the averages of at least 5 consecutive simulations of 250,000 timesteps.

The MS diffusion coefficients became constant for integration times > 1.0 (1000 timesteps). This was independent of the simulation time, as illustrated in Figure 1. For all mole fractions the accuracy of the calculation was not improved significantly, if the simulation time was extended longer than 1250 (Fig. 2). The consistency of the calculations was also tested using the integrals Int_{ijk} of Eq. (5) [6]. Figure 3 shows that the $\Delta\mathrm{Int}_{ijk} = \langle(\boldsymbol{u}_i(0) - \boldsymbol{u}_j(0)) \bullet \boldsymbol{u}_k(t)\rangle$ $(i \neq j \neq k \neq i)$ were oscillating around zero, as expected. The amplitude of the oscillations decreased with increasing number of time origins (simulation time) and became constant for simulation time longer than 1250, as illustrated in Figure 4.

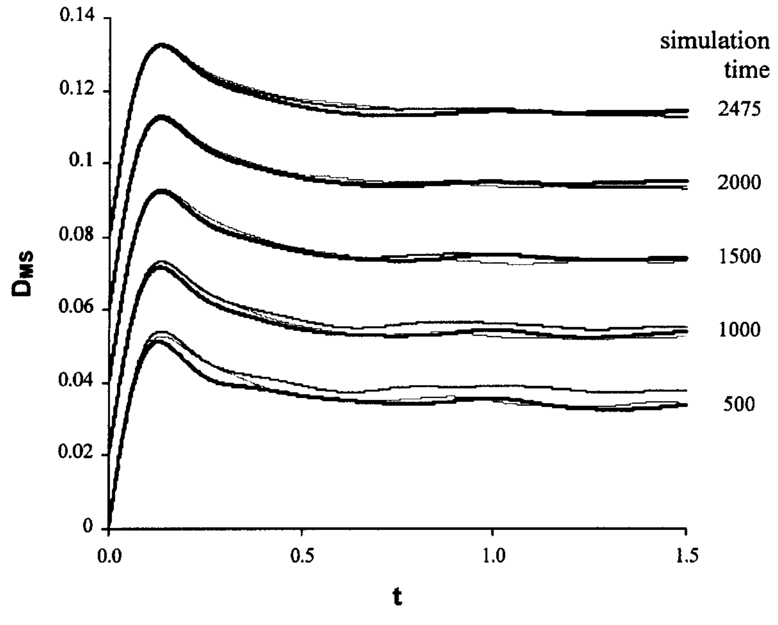

FIGURE 1 Maxwell-Stefan diffusion coefficients as a function of the integration time t for various simulation times (300 LJ particles, $T = 0.728$, $\rho = 0.884$, $x_1 = 0.5$, $x_2 = 0.25$, $x_3 = 0.25$). For clarity, we have shifted the diffusion coefficients with +0.02 subsequently: —, D_{12}; —, D_{31}; —, D_{23}.

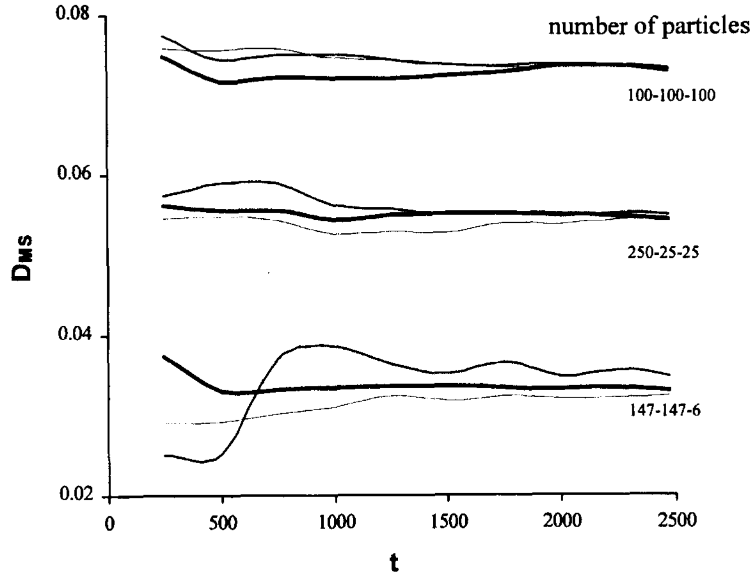

FIGURE 2 Maxwell-Stefan diffusion coefficients as a function of the simulation time t for various numbers of particles (300 LJ particles, $T = 0.728$, $\rho = 0.884$, integration time = 1.0). For clarity, we have shifted the diffusion coefficients with $+0.02$ subsequently: —, D_{12}; —, D_{31}; —, D_{23}.

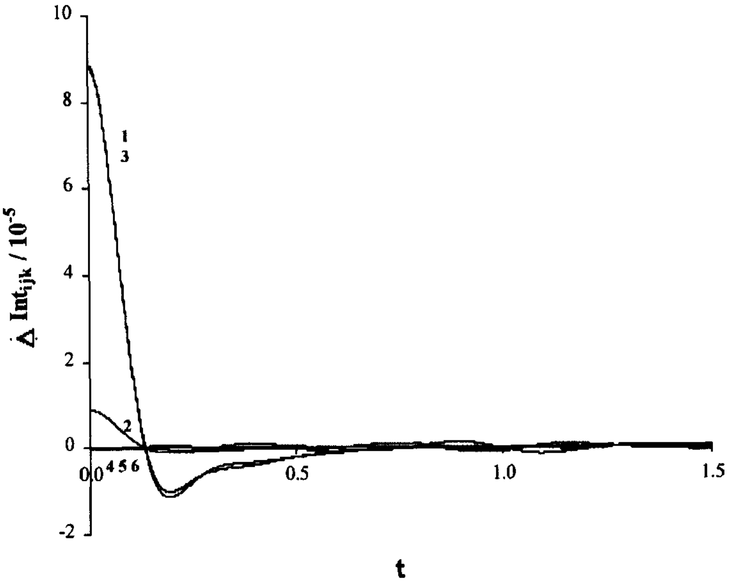

FIGURE 3 $\Delta\text{Int}_{ijk} = \langle (\boldsymbol{u}_i(0) - \boldsymbol{u}_j(0)) \bullet \boldsymbol{u}_k(t) \rangle$ as a function of the integration time t (300 LJ particles, $T = 0.728$, $\rho = 0.884$, $x_1 = 0.5$, $x_2 = 0.25$, $x_3 = 0.25$, simulation time = 1250): (1) ΔInt_{212}; (2) ΔInt_{131}; (3) ΔInt_{323}; (4) ΔInt_{231}; (5) ΔInt_{321}; and (6) ΔInt_{312}.

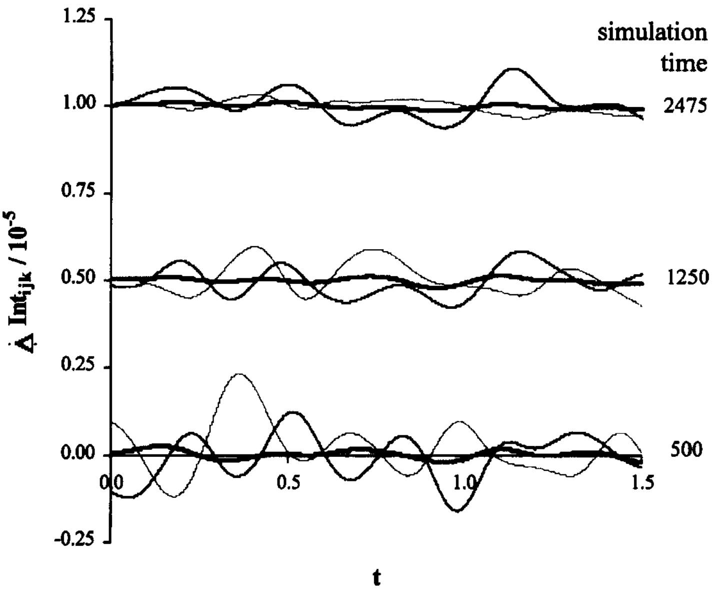

FIGURE 4 $\Delta\mathrm{Int}_{ijk} = \langle(\boldsymbol{u}_i(0) - \boldsymbol{u}_j(0)) \bullet \boldsymbol{u}_k(t)\rangle$ as a function of the integration time t for various simulation times (300 LJ particles, $T = 0.728$, $\rho = 0.884$, $x_1 = 0.5$, $x_2 = 0.25$, $x_3 = 0.25$). For clarity, we have shifted the $\Delta\mathrm{Int}_{ijk}$ with $+0.5$ subsequently): ▬, $\Delta\mathrm{Int}_{231}$; —, $\Delta\mathrm{Int}_{321}$; and —, $\Delta\mathrm{Int}_{312}$.

The results of the simulations with a simulation time of 1250 and an integration time of 1.0 are listed in Table I. The differences between the values of the MS diffusion coefficients at various mole fractions are a measure for the accuracy of Eq. (6) and of the calculations. The results of the simulations of the 300 particles system agree very well with the simulations of the 250 particles system given by [6], as expected.

Naghizadeh and Rice [11] derived a corresponding state relationship for the self-diffusion coefficients of liquid argon, krypton, and xenon:

$$\log D = 0.05 + 0.07p - \frac{1}{T}(1.04 + 0.1p), \tag{9}$$

in which p is the reduced pressure, T is the reduced temperature and D is the reduced self-diffusion coefficient. The LJ energy parameter $\varepsilon = 1.71 \cdot 10^{-21}$ J and the LJ size parameter $\sigma = 3.418 \cdot 10^{-10}$ m of argon used by Nagazideh and Rice [11] differed from the parameters used in our study (Tab. II). The reduced temperature $T = 0.728$ and the reduced pressure $p = 0.98$ of our simulations were therefore recalculated into $T = 0.702$ and $p = 0.95$ for use

TABLE I Ternary diffusion coefficients as a function of the mole fraction coloured component for a unary LJ fluid of 300 particles: $T = 0.728$, $\rho = 0.884$, simulation time = 1250, integration time = 1.0

x_1	x_2	x_3	D_{12}	D_{31}	D_{23}
0.067	0.467	0.467	0.034 ± 0.003	0.032 ± 0.001	0.033 ± 0.002
0.250	0.250	0.500	0.032 ± 0.002	0.034 ± 0.001	0.033 ± 0.002
0.250	0.500	0.250	0.031 ± 0.001	0.0348 ± 0.0007	0.034 ± 0.001
0.333	0.333	0.333	0.032 ± 0.001	0.034 ± 0.001	0.034 ± 0.001
0.467	0.067	0.467	0.0308 ± 0.0007	0.033 ± 0.002	0.031 ± 0.003
0.467	0.467	0.067	0.031 ± 0.001	0.033 ± 0.004	0.0325 ± 0.0009
0.490	0.490	0.020	0.034 ± 0.001	0.036 ± 0.007	0.032 ± 0.002
0.500	0.250	0.250	0.031 ± 0.001	0.034 ± 0.001	0.033 ± 0.002
0.833	0.083	0.083	0.035 ± 0.001	0.036 ± 0.002	0.033 ± 0.001
0.933	0.033	0.033	0.033 ± 0.002	0.033 ± 0.001	0.032 ± 0.002
0.980	0.010	0.010	0.031 ± 0.001	0.035 ± 0.002	0.034 ± 0.001

TABLE II Lennard-Jones parameters and molecular mass

	Substance		
	Ar	*Kr*	*Ne*
$\varepsilon\ [10^{-21}\,\mathrm{J}]$	1.65	2.30	0.19
$\sigma\ [10^{-10}\,\mathrm{m}]$	3.41	3.64	2.75
$m\ [10^{-26}\,\mathrm{kg}]$	6.64	13.92	3.36

in Eq. (9). The self-diffusion coefficient calculated using Eq. (9) $D = 0.032$ agrees very well with the results of our simulations.

3.2. Simulations in a Binary Lennard-Jones System

Simulations were performed for binary systems of 300 LJ particles at $T = 0.8$ and $\rho = 0.7901$ in the NVE ensemble. All reduced units are constructed using the parameters of argon atoms. The first component argon with a mole fraction $(x_1 + x_2)$ was divided into two species by attaching a colour label to a mole fraction x_1 of the particles. The mole fraction of the second component was x_3. For this second component we used the Lennard-Jones parameters describing krypton. The potential parameters used are given in Table II. MD simulations of multiples of 25,000 timesteps ($\Delta t = 0.001$) were performed and every 10 timesteps a new time origin was taken. The MS diffusion coefficients were calculated, using Eq. (6) for several numbers of time origins and for various integration times (maximal 1,500 timesteps).

The MS diffusion coefficients became constant for integration times > 1.0, independent of the simulation time and the mole fractions. The amplitude of the oscillations of $\Delta\mathrm{Int}_{ijk}(i \neq j \neq k \neq i)$ decreased with an increasing number of time origins and became constant for a simulation time > 1750, if the number of the particles of one component was very low. For higher numbers of the particles a simulation time > 1250 was sufficient.

The results of the simulations with an integration time of 1.0 are listed in Table III. The values of the MS diffusion coefficients D_{31} and D_{23} were identical within the simulation error for each system, as expected, since the particles with a mole fraction x_1 and x_2 differed only by colour. Moreover, the MS diffusion coefficients were independent of the mole fraction coloured component for all calculations with $x_3 = 0.5$. The values of the MS diffusion coefficients increased with an increasing mole fraction of argon $(x_1 + x_2)$.

For comparison with the literature values the calculated MS diffusion coefficients had to be converted to Fick diffusion coefficients. For a ternary system the Fick diffusivities and the MS diffusivities are related by [7, 12]

$$[D^f] = [B]^{-1}[\Gamma], \tag{10}$$

in which $[D^f]$ is the 2×2 matrix of the Fick diffusivities and $[\Gamma]$ is the 2×2 matrix of the thermodynamic factors. The elements of the 2×2 matrix $[B]$ are equal to

$$B_{ii} = \frac{x_i}{D_{in}} + \sum_{\substack{k=1\\k\neq i}}^{n} \frac{x_k}{D_{ik}}, \quad i, j = 1, 2; \; n = 3 \tag{11}$$

and

$$B_{ij, i\neq j} = -x_i\left(\frac{1}{D_{ij}} - \frac{1}{D_{in}}\right), \quad i, j = 1, 2; \; n = 3, \tag{12}$$

TABLE III Ternary diffusion coefficients as a function of the mole fraction for a binary LJ fluid Ar(1, 2) + Kr(3) of 300 particles: $T = 0.8$, $\rho = 0.7901$, integration time = 1.0

Simulation time t	x_1	x_2	x_3	D_{12}	D_{31}	D_{23}
2475	0.10	0.40	0.50	0.035 ± 0.001	0.0185 ± 0.0003	0.0211 ± 0.0007
2475	0.25	0.25	0.50	0.037 ± 0.002	0.0194 ± 0.0008	0.022 ± 0.001
2475	0.33	0.17	0.50	0.038 ± 0.002	0.0202 ± 0.0008	0.022 ± 0.001
2475	0.49	0.01	0.50	0.038 ± 0.001	0.0212 ± 0.0007	0.018 ± 0.003
1250	0.33	0.33	0.33	0.042 ± 0.003	0.025 ± 0.001	0.030 ± 0.001
1250	0.10	0.40	0.50	0.034 ± 0.004	0.0187 ± 0.0005	0.020 ± 0.001
1250	0.25	0.25	0.50	0.035 ± 0.003	0.0183 ± 0.0008	0.020 ± 0.001
1250	0.33	0.17	0.50	0.036 ± 0.002	0.0195 ± 0.0009	0.0194 ± 0.0008
1250	0.49	0.01	0.50	0.039 ± 0.002	0.020 ± 0.001	0.024 ± 0.007
1250	0.17	0.17	0.67	0.031 ± 0.002	0.0156 ± 0.0008	0.017 ± 0.001

in which D_{ij} are the MS diffusivities. In an ideal mixture the matrix of the thermodynamic factors $[\Gamma]$ is equal to $[I]$, the identity matrix. For the coloured binary mixture with composition $x_1 = x_2 = 0.25$ and $x_3 = 0.5$ the values of the MS diffusivities were calculated to be $D_{12} = 0.037$ and $D_{31} = D_{23} = 0.020$. The Fick diffusivities $D_{11} = D_{22}$ can then be calculated from Eq. (10), assuming an ideal mixture: $D^f_{11} = D^f_{22} = 0.023$, or in real units $D^{fr}_{11} = D^{fr}_{22} = 1.26 \cdot 10^{-9}\,\text{m}^2 \cdot \text{s}^{-1}$ at 99 K. Schoen and Hoheisel [3] computed the following binary diffusion coefficients: $D^{fr}_{12} = 2.78 \cdot 10^{-9}\,\text{m}^2 \cdot \text{s}^{-1}$ at 116 K, and $D^{fr}_{12} = 2.05 \cdot 10^{-9}\,\text{m}^2 \cdot \text{s}^{-1}$ at 109 K for equimolar mixtures with comparable potential parameters and masses. Assuming an exponential relation $D = A \cdot \exp(-B/T)$ between the diffusion coefficient D and the temperature T[11], the values of Schoen and Hoheisel [3] would result in $D^{fr}_{12} = 1.23 \cdot 10^{-9}\text{m}^2 \cdot \text{s}^{-1}$ at 99 K. This value is in very good agreement with our simulations. Lee [13] performed MD simulations for an equimolar mixture of argon and krypton at 608 K, 266 K, and 117 K. Exponential extrapolation of his results to 99 K would lead to a value of D^{fr}_{12} between $5 \cdot 10^{-10}\text{m}^2 \cdot \text{s}^{-1}$ and $2 \cdot 10^{-9}\text{m}^2 \cdot \text{s}^{-1}$; this extrapolation is very inaccurate but covering our simulations.

3.3. Simulations in a Ternary Lennard-Jones System

Simulations were performed for ternary systems of 300 particles at $T = 0.8$ and $\rho = 0.7901$ in the NVE ensemble. All reduced units are constructed using the parameters of argon atoms. Each system was a liquid mixture of argon, krypton, and neon. The LJ potential parameters used are given in Table II. MD simulations of multiples of 25,000 timesteps ($\Delta t = 0.001$) were performed and every 10 timesteps a new time origin was taken. The MS diffusion coefficients were calculated using Eq. (6) for various simulation times (maximal 2,500,000 timesteps) and for various integration times (maximal 1,500 timesteps).

A simulation time of 2475 was sufficient for the MS diffusion coefficients to become constant. At this simulation time the values of the MS diffusion coefficients were independent of the integration time t for $t > 1.0$. The results of the simulations with a simulation time of 2475 and an integration time of 1.0 are given in Table IV and Figure 5.

The values of the MS diffusion coefficients increase with an increasing mole fraction x_1. An increase of approximately 15% from $x_1 = 0$ to $x_1 = 0.9$ might be explained by the decrease of the pressure values of the simulated systems from 1.7 to 0.47 [11]. The MS diffusion coefficient between argon and neon (D_{31}) is higher than the MS diffusion coefficient between krypton

TABLE IV Ternary diffusion coefficients as a function of the mole fraction for a ternary LJ mixture Ar(1) + Kr(2) + Ne(3) of 300 particles: $T = 0.8$, $\rho = 0.7901$, simulation time = 2475, integration time = 1.0

x_1	x_2	x_3	p	D_{12}	D_{31}	D_{23}
0.003	0.897	0.10	1.72	0.020 ± 0.002	0.069 ± 0.002	0.0401 ± 0.0009
0.01	0.89	0.10	1.69	0.016 ± 0.003	0.066 ± 0.004	0.041 ± 0.002
0.05	0.85	0.10	1.58	0.0182 ± 0.0003	0.068 ± 0.003	0.040 ± 0.002
0.20	0.70	0.10	1.14	0.0235 ± 0.0005	0.087 ± 0.006	0.0446 ± 0.0007
0.40	0.50	0.10	0.82	0.030 ± 0.001	0.103 ± 0.007	0.055 ± 0.002
0.60	0.30	0.10	0.60	0.039 ± 0.001	0.110 ± 0.008	0.060 ± 0.002
0.80	0.10	0.10	0.50	0.0481 ± 0.0009	0.120 ± 0.007	0.0645 ± 0.0007
0.85	0.05	0.10	0.48	0.0514 ± 0.0008	0.125 ± 0.002	0.066 ± 0.002
0.89	0.01	0.10	0.48	0.050 ± 0.001	0.128 ± 0.003	0.064 ± 0.004
0.90	0.00	0.10	0.47		0.131 ± 0.003	

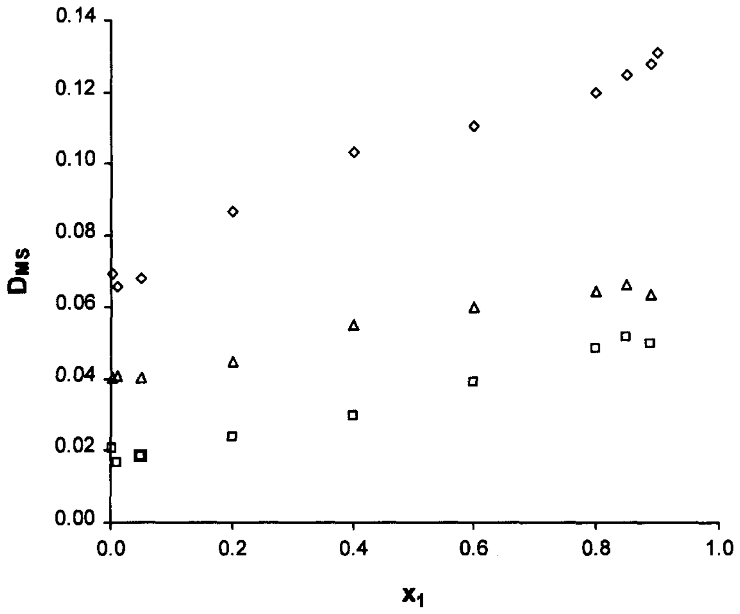

FIGURE 5 Maxwell-Stefan diffusion coefficients of the ternary system Ar(1) + Kr(2) + Ne(3) as a function of the mole fraction Ar (300 LJ particles, $T = 0.8$, $\rho = 0.7901$, integration time = 1.0, $x_3 = 0.1$): □, D_{12}; ◇, D_{31}; Δ, D_{23}.

and neon (D_{23}), which is in his turn higher than the MS diffusion coefficient between argon and krypton (D_{12}). This is in accordance with our expectations, since the MS diffusion coefficients are inversely proportional to the frictional coefficients between the particles [7], and these frictional coefficients will increase with increasing masses of the components.

4. CONCLUSION

Maxwell-Stefan diffusion coefficients in unary, binary and ternary systems of LJ particles can be determined by the Green-Kubo method. For all systems the MS diffusion coefficients became constant for integration times > 1.0. The simulation times required were dependent on the number of different components in the systems, and increased from 1250 for a unary system, and 1750 for a binary system to 2475 for a ternary system. The Maxwell-Stefan diffusion coefficients calculated by Eq. (6) agreed well with the literature values available, or were in accordance with the behaviour as expected from other physical properties.

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