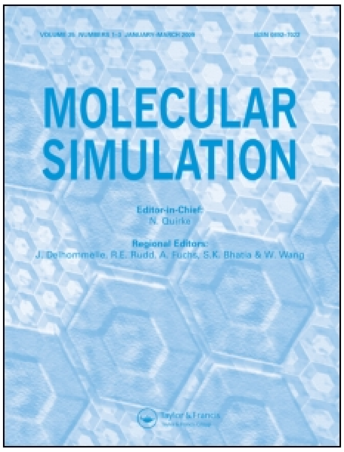

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

Development of a model for the Description of Intra-diffusion in Homogeneous Liquid Lennard-Jones Mixtures

Tatiana Merzliak[a]; Andreas Pfennig[a]
[a] Lehrstuhl für Thermische Verfahrenstechnik, RWTH Aachen University, Aachen, Germany

To cite this Article Merzliak, Tatiana and Pfennig, Andreas(2004) 'Development of a model for the Description of Intra-diffusion in Homogeneous Liquid Lennard-Jones Mixtures', Molecular Simulation, 30: 7, 459 — 468
To link to this Article: DOI: 10.1080/08927020410001680750
URL: http://dx.doi.org/10.1080/08927020410001680750

Molecular Simulation, Vol. 30 (7), 15 June 2004, pp. 459–468

Development of a model for the Description of Intra-diffusion in Homogeneous Liquid Lennard–Jones Mixtures

TATIANA MERZLIAK* and ANDREAS PFENNIG

Lehrstuhl für Thermische Verfahrenstechnik, RWTH Aachen University, Wüllnerstraße 5, D-52062 Aachen, Germany

(Received May 2003; In final form February 2004)

A model for calculation of intra-diffusion coefficients of homogeneous liquid 1-centre Lennard–Jones (LJ) mixtures is proposed. As starting point for deriving this model we have chosen the model of Liu *et al.* [*Chem. Eng. Sci.* 53, (1998), 2403–2422] suggested for calculation of the self-diffusion coefficients of pure LJ model fluids. This model was extended to liquid mixtures by introducing suitable combining and mixing rules for description of different characteristics of the mixture components. The five parameters of the model were determined from data obtained by molecular-dynamics (MD) simulations performed in this work. To generate a database for intra-diffusion coefficients the method of optimal experiment design is employed. This method is applied to plan simulations in such a way as to obtain optimal estimates of the model parameters. The parameters were determined based on the range of temperatures $90 < T < 350$ K and mass densities $200 < \rho_M < 2580$ kg/m^3 with the total average absolute deviation of 5.56%. The suggested model was tested on the data available in literature concerning intra-diffusivities of 1-centre LJ liquid mixtures. The prediction accuracy of 42 data points is 13.08%. Further work will be directed at further optimisation of model structure and model parameters.

Keywords: Intra-diffusion; Homogeneous liquid mixture; Lennard–Jones mixture; Molecular-dynamics

INTRODUCTION

From an engineering point of view studying diffusion processes in liquid mixtures is an important task, since mass transfer plays a key role in thermal separation processes. Today available computer power allows supplementing real-world experiments by their computer analogue with the help of Monte-Carlo techniques or molecular-dynamics (MD) simulations to gain detailed insight into a wide variety of phenomena. Here we apply MD to investigate the principal influence of a wide variety of molecular parameters and system conditions on diffusion processes.

Several authors have already studied diffusion in pure liquids by MD for different intermolecular-potential functions, reaching from hard spheres (HS) to Lennard–Jones (LJ) particles which may be regarded as resembling simple real substances that are already relatively accurate. This data pool allows determining model equations for diffusion coefficients, depending on the properties of the particle-interaction potential and the properties of the system. Results of such model development is discussed in detail in Refs. [1–3]. Thus, a good basis has been worked out for the subsequent development of more general models which appeared in literature relatively recently. For example, self-diffusion models for LJ liquids have been derived [3–7]. Such models designed for self-diffusion coefficients of pure LJ liquids allow predictions with an accuracy comparable to a physical experiment [3–5,7].

The diffusive motion of each component in homogeneous liquid mixtures—intra-diffusion—has been investigated by computer experiment to a far lesser extent. There are some papers reporting intra-diffusion coefficients obtained from MD simulations for the LJ mixtures [8–13]. The number of publications in which models for the description of intra-diffusion coefficients are developed is also limited [8,9,14–16].

---

*Corresponding author. Tel.: +49-241-80-95490. Fax: +49-241-80-92332. E-mail: secretary@tvt.rwth-aachen.de

ISSN 0892-7022 print/ISSN 1029-0435 online
DOI: 10.1080/08927020410001680750

The goal of this work is to carry out further research on the diffusive mobility of the components in homogeneous liquid mixtures in dependence on temperature, concentration and individual characteristics of the particles. Based on these results an adequate model is to be developed for the description of intra-diffusion coefficients. To this end an extended database for intra-diffusion coefficients is established on the basis of the MD simulations which easily allows fitting of model parameters. The present work is focussed on mixtures of single-centre LJ particles.

As a starting point for the development of the model, the approach of Liu *et al.* [3] was chosen which describes self-diffusion coefficients in dense pure LJ liquids. This model appears to be highly attractive because of two reasons. Firstly, the different expressions have a physical interpretation and secondly, the number of adjusted numerical parameters is roughly half of that of models which show comparable accuracy in the description of data [5,7]. Also, the model of Liu *et al.* has been tested on a large amount of data for pure substances.

MODEL

We begin with the model of Liu *et al.* [3] for the self-diffusion coefficient of pure LJ systems:

$$D_{0,\mathrm{LJ}} = \frac{3}{8}\frac{1}{\rho\sigma_{\mathrm{eff}}^{2}}\left(\frac{kT}{\pi m}\right)^{1/2}\exp\left(-\frac{\gamma\rho^{*}}{\rho_{\mathrm{s}}-\rho^{*}}\right)\exp\left(-\frac{\alpha_{\mathrm{LJ}}}{T^{*}}\right) \tag{1}$$

with

$$\sigma_{\mathrm{eff}} = 2^{1/6}\sigma_{\mathrm{LJ}}\left[1+\left(\frac{T^{*}}{T_{0}^{*}}\right)^{1/2}\right]^{-1/6}, \tag{2}$$

$$T^{*} = kT/\varepsilon_{\mathrm{LJ}}, \tag{3}$$

$$\rho^{*} = \rho\sigma_{\mathrm{LJ}}^{3}, \tag{4}$$

and

$$\gamma = 0.75, \tag{5}$$

$$\rho_{s} = 1.2588, \tag{6}$$

$$\alpha_{\mathrm{LJ}} = 0.27862, \tag{7}$$

$$T_{0}^{*} = 0.72197 \quad \text{for } 0.30 < \rho^{*} < 1.05 \text{ and } 0.74 < T^{*} < 5.10. \tag{8}$$

Here, ρ is the number density, k the Boltzmann constant, m the mass of the molecule, T the temperature and ρ^{*} the reduced density. γ, ρ_{s}, α_{LJ} and T_{0}^{*} are numerical coefficients. Their values, except that of γ, were fitted to self-diffusion coefficients from MD simulations available in the literature for various model liquids, namely hard spheres HS, Weeks–Chandler–Anderson particles (WCA) and LJ molecules. σ_{LJ} and $\varepsilon_{\mathrm{LJ}}$ are the molecular parameters of LJ particles. They are also the adjustable model parameters if Eqs. (1)–(8) are used for describing the self-diffusion coefficients in real liquid mixtures. The leading expression of Eq. (1) stems from the kinetic theory of dilute gases, the first exponential accounts for the molecular volume and was fitted to HS results while the second exponential accounts for energetic interactions and was adjusted for pure WCA and LJ fluids.

The model of Liu *et al.* was originally developed for pure liquid LJ systems. Here it is to be extended to LJ mixtures by introducing suitable combining and mixing rules which account for the different relation of particle size and mixture density, which depends on system conditions and the molecular parameters in the mixture. They not only describe the effective particle size and the particle–particle interaction energies, but also the effective densities, the effective reduced temperatures and the inverse masses for each component of the mixture. The proposed equations for the intra-diffusion coefficients are as follows:

$$D_{i,\mathrm{LJ}} = \frac{3}{8}\,\frac{1}{\rho\sigma_{\mathrm{mix},i}^{(2)}}\left(\frac{kT}{\pi\, m_{\mathrm{eff},i}}\right)^{1/2}\exp\left(-\frac{\theta_{4}\rho_{\mathrm{eff},i}^{*}}{\theta_{2}-\rho_{\mathrm{eff},i}^{*}}\right) \times\exp\left(-\frac{\theta_{3}}{T_{\mathrm{mix},i}^{*}}\right) \tag{9}$$

with

$$\rho_{\mathrm{eff},i}^{*} = \rho\sigma_{\mathrm{mix},i}^{(\mathrm{a})}\sigma_{\mathrm{mix}}^{(\mathrm{b})}, \tag{10}$$

$$\sigma_{\mathrm{mix},i}^{(\mathrm{a})} = \sum_{j=1}^{N} x_{j}\sigma_{\mathrm{eff},j,i}^{(3-\theta_{1})}, \tag{11}$$

$$\sigma_{\mathrm{mix}}^{(\mathrm{b})} = \sum_{i=1}^{N}\sum_{j=1}^{N} x_{i}x_{j}\sigma_{\mathrm{eff},j,i}^{\theta_{1}}, \tag{12}$$

$$\sigma_{\mathrm{mix},i}^{(2)} = \sum_{j=1}^{N} x_{j}\sigma_{\mathrm{eff},j,i}^{2}, \tag{13}$$

$$\sigma_{\mathrm{eff},i,j} = 2^{1/6}\sigma_{\mathrm{LJ},i,j}\left[1+\left(\frac{t_{\mathrm{eff},i,j}^{*}}{\theta_{5}}\right)^{1/2}\right]^{-1/6}, \tag{14}$$

$$t_{\mathrm{eff},i,j}^{*} = \frac{kT}{\varepsilon_{\mathrm{LJ},i,j}}, \tag{15}$$

$$T_{\mathrm{mix},i}^{*} = \sum_{j=1}^{N} x_{j}t_{\mathrm{eff},j,i}^{*}, \tag{16}$$

$$m_{\mathrm{eff},i}^{-1/2} = \frac{1}{2}\sum_{j=1}^{N} x_{j}\left(m_{i}^{-1/2}+m_{j}^{-1/2}\right). \tag{17}$$

Here, θ_1, θ_2, θ_3, θ_4, θ_5 are the model parameters, which are independent of the particular mixture being studied. Indices i and j number the components of mixture $i,j = 1,\ldots,N$, m_i is the particle mass, $\sigma_{\mathrm{LJ},i,i}$ and $\varepsilon_{\mathrm{LJ},i,i}$ are the LJ parameters of the pure components, $\sigma_{\mathrm{LJ},i,j}$ and $\varepsilon_{\mathrm{LJ},i,j}$ are the cross LJ parameters in the mixture, x_i is the mole fraction, ρ the number density of the mixture, $\rho^*_{\mathrm{eff},i}$ $t^*_{\mathrm{eff},i,j}$, $m_{\mathrm{eff},i}$ are the reduced density, the reduced temperature and the effective mass corresponding to each component or interaction between the particles in the mixture, respectively.

The suggested equations describe the dependence of the intra-diffusion coefficients on composition, temperature and density of the mixture. In the limiting case of $x_i \rightarrow 1$, Eqs. (9)–(17) reduce to the expressions of Liu *et al.* for the self-diffusion coefficients of the corresponding pure components i. Then the description of pure components are consistently included in the model.

The different mixing and combining rules were introduced in accordance with physical reasoning. From kinetic gas theory the value $\sigma^{(2)}_{\mathrm{mix},i}$ in Eq. (9) represents an effective collision cross-section in the process of the particle collisions. With the assumption that the average collision frequency of a given particle of type i with a j-particle is proportional to x_j and the corresponding collision cross-section described by $\sigma^2_{\mathrm{eff},j,i}$ Eq. (13) for calculation of $\sigma^{(2)}_{\mathrm{mix},i}$ results. Similarly, the $m_i^{-1/2}$ in models for diffusion coefficients are a measure for the velocity with which two molecules of type i are approaching each other. Thus for the mixture, the corresponding measure for the relative velocity of molecules of different types is $(m_i^{-1/2} + m_j^{-1/2})/2$. If it is again assumed that the collision frequencies are proportional to x_j Eq. (17) results for the effective mass. Based on similar arguments the average energy of interaction of component i is characterised by $T^*_{\mathrm{mix},i}$ determined with Eq. (16).

In a mixture of components significantly differing in size, the smaller molecules will require smaller voids for a diffusive move as compared to the larger molecules. Thus, in a system with an equilibrated void-size distribution the smaller molecules have a larger apparent free volume for diffusion. This difference in molecular mobility is accounted for by the effective densities $\rho^*_{\mathrm{eff},i}$ for each mixture component. Different approaches for describing this effect may be possible. We have chosen to use a quadratic mixing rule for $\sigma^{\theta_1}_{\mathrm{eff},j,i}$, where θ_1 is a parameter with a value between 0 and 3. If θ_1 is close to 2, $\sigma^{(b)}_{\mathrm{mix}}$ can be regarded as an average measure for the free area of passages between molecules and $\sigma^{(a)}_{\mathrm{mix},i}$ represents the average collision diameter of particles of type i. Both contributions are combined to yield the dimensionless value of $\rho^*_{\mathrm{eff},i}$.

The thermodynamic parameters of the mixture together with the particle masses and the LJ-potential parameters are the independent variables $\bar{w}_l = \bar{w}_l(m^l_1, \sigma^l_{1,1}, \varepsilon^l_{1,1}, m^l_2, \sigma^l_{2,2}, \varepsilon^l_{2,2}, \sigma^l_{1,2}, \varepsilon^l_{1,2}, \rho^l, T^l, x^l_i)$ of the model function given by Eq. (9). Here, $l = 1, 2, \ldots, M$, where M is the number of the MD simulation data points for the diffusion coefficients. The parameter set $\bar{\Theta} = (\theta_1, \theta_2, \theta_3, \theta_4, \theta_5)$ of the model function was determined from MD simulation data for self- and intra-diffusion coefficients obtained in this work as described in the following section.

THE DATABASE

To determine the model parameters $\bar{\Theta}$ it is necessary to have self- and intra-diffusion coefficients calculated for various sets of the independent variables $\bar{w}$. Thus, MD simulations were performed in order to generate a sufficient database. Since such computer simulations are very time consuming the number of necessary simulations was reduced with the help of optimal experimental design [17,18]. This method ensures that the conditions for each computer simulation are chosen such that the uncertainty in the estimated parameters is minimised. The optimal design procedure applied is described as follows. First, a model function $D_i = D_i(\bar{w}, \bar{\Theta})$ for each component i of the mixture is chosen together with a first estimate of the parameters $\bar{\Theta}_n$. Thus, some few (n) simulations have to be performed to initialise the procedure. According to the method of optimal experimental design [17] the conditions for simulation $n+1$ have then to be considered in the matrix of sensitivity coefficients:

$$\mathbf{F}_i = \begin{pmatrix} \left(\frac{\partial D_i}{\partial \theta_1}\right)_{\bar{w}_1} & \left(\frac{\partial D_i}{\partial \theta_2}\right)_{\bar{w}_1} & \left(\frac{\partial D_i}{\partial \theta_3}\right)_{\bar{w}_1} & \cdots & \left(\frac{\partial D_i}{\partial \theta_p}\right)_{\bar{w}_1} \\ \left(\frac{\partial D_i}{\partial \theta_1}\right)_{\bar{w}_2} & \left(\frac{\partial D_i}{\partial \theta_2}\right)_{\bar{w}_2} & \left(\frac{\partial D_i}{\partial \theta_3}\right)_{\bar{w}_2} & \cdots & \left(\frac{\partial D_i}{\partial \theta_p}\right)_{\bar{w}_2} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \left(\frac{\partial D_i}{\partial \theta_1}\right)_{\bar{w}_n} & \left(\frac{\partial D_i}{\partial \theta_2}\right)_{\bar{w}_n} & \left(\frac{\partial D_i}{\partial \theta_3}\right)_{\bar{w}_n} & \cdots & \left(\frac{\partial D_i}{\partial \theta_p}\right)_{\bar{w}_n} \\ \left(\frac{\partial D_i}{\partial \theta_1}\right)_{\bar{w}_{n+1}} & \left(\frac{\partial D_i}{\partial \theta_2}\right)_{\bar{w}_{n+1}} & \left(\frac{\partial D_i}{\partial \theta_3}\right)_{\bar{w}_{n+1}} & \cdots & \left(\frac{\partial D_i}{\partial \theta_p}\right)_{\bar{w}_{n+1}} \end{pmatrix} \qquad (18)$$

where p is the number of the model parameters and the derivatives are calculated with the estimate $\bar{\Theta}_n$ obtained from the results of the first n simulations. As a first approximation it is further assumed that from the MD simulations the diffusion coefficient is determined with a mean-square deviation δ_i which is the same for all simulated data. The validity of this approximation can be checked from the data given in Table I. In future work the individual δ_i determined in each MD simulation will be included in the evaluation. Then the information matrix $\mathbf{Q}$ for

TABLE I The protocol of the optimal experimental design procedure for the mixture $Ar + CH_4$

k	x_{Ar}	p (MPa)	T (K)	ρ_M (kg/m^3)	$D_1^{MD}(\delta_{D_1})$ (m^2/Gs)	$D_2^{MD}(\delta_{D_2})$ (m^2/Gs)	$\theta_1(\delta_{\theta_{1,k}})$	$\theta_2(\delta_{\theta_{2,k}})$	$\theta_3(\delta_{\theta_{3,k}})$	$\theta_4(\delta_{\theta_{4,k}})$	SSQ $(10^{-19}\,m^4/Gs^2)$	$det\ \mathbf{C}$ (10^{-7})
0	0.1	0.3252	110.80	483.0	4.356(±0.054)	4.279(±0.043)	2.9841	0.8914	1.1317	0.0223	0.04314	
	0.3	0.0125	110.68	617.0	4.428(±0.055)	4.360(±0.045)						
	0.5	0.1356	110.52	755.5	4.548(±0.053)	4.452(±0.028)						
1	0.9	0.2345	110.58	1033.0	4.860(±0.060)	4.644(±0.163)	1.6999 (±1.1037)	1.2602 (±0.7451)	0.3329 (±1.1870)	0.7190 (±2.5565)	0.1977	0.5863
2	0.1	0.3252	110.80	483.0	4.349(±0.031)	4.258(±0.060)	1.9590 (±1.2047)	1.1650 (±0.6278)	0.5876 (±1.3095)	0.4175 (±1.4935)	0.1480	0.1102
3	0.1	0.3252	110.80	483.0	4.356(±0.054)	4.279(±0.043)	2.2973 (±1.0861)	1.0557 (±0.4339)	0.8203 (±0.7311)	0.1943 (±0.6323)	0.1193	0.0107
4	0.9	0.2345	110.58	1033.0	4.858(±0.045)	4.627(±0.136)	1.7177 (±0.96645)	1.2632 (±0.6385)	0.3456 (±1.5898)	0.7137 (±2.1820)	0.1685	0.0661
5	0.487	0.3292	110.48	747.74	4.547(±0.028)	4.438(±0.033)	1.9754 (±0.8167)	1.1221 (±0.4116)	0.6624 (±0.8158)	0.3294 (±0.8463)	0.1430	0.0071

δ_Y the standard deviation of the value Y. $\mathrm{SSQ} = (1/(M - N_p))\sum_i^M \left|D_i^{\mathrm{model}} - D_i^{\mathrm{MD}}\right|^2$, where N_p is the number of fitted parameter.

the step $n + 1$ is defined as follows:

$$\mathbf{Q} = \sum_{i=1}^{N} \mathbf{F}_i^T \mathbf{F}_i / \delta_i^2. \qquad (19)$$

Here, $\mathbf{F}_i^T$ is the transposed $\mathbf{F}_i$ matrix for the component i of the mixtures. The matrix elements of $\mathbf{Q}$ are functions of the unknown set of independent variables for the simulation $n + 1$, $\bar{w}_{n+1}$, thus $\mathbf{Q} = \mathbf{Q}(\bar{w}_{n+1})$. Then in order to obtain the optimal values of the independent variables $\bar{w}_{n+1}$ some measure of the information matrix has to be maximized. We have chosen to apply the following condition [17]:

$$\det \mathbf{Q} = \max_{\bar{w}_{n+1}} |\mathbf{Q}(\bar{w}_{n+1})|. \qquad (20)$$

To obtain the optimal set of independent variables $\bar{w}_{n+1}$ requires to determine the maximum of the determinant of the information matrix $\mathbf{Q}$ or the minimum of the determinant of the covariance matrix $\mathbf{C} = \mathbf{Q}^{-1}$. Simultaneously, the minimum for a confidence domain of the model parameter estimates $\bar{\Theta}$ with respect to the set of values $\bar{w}_1, \ldots, \bar{w}_n, \bar{w}_{n+1}$ is reached. Then the optimal $\bar{w}_{n+1}$ is determined and new diffusion coefficients $D_{i,n+1}$ are calculated with a MD simulation at $\bar{w}_{n+1}$ and supplied to the database. Based on this larger database a new set of model parameters $\bar{\Theta}_{n+1}$ is determined with a least-square minimisation. With the new parameter set the cycle in the procedure of optimal experimental design for step $n + 1$ is finished; the next step then proceeds accordingly. There does not exist a strict criterion for terminating this procedure. A possible criterion could, e.g. be that the confidence interval of the model parameters $\bar{\Theta}$ is decreased below a certain value.

To give an impression of the background of this method an example of the optimal experimental design for the binary mixture $Ar + CH_4$ is considered with the molecular parameters specified in the first line of Table II together with Lorentz–Berthelot mixing rules. This liquid system is regarded at a realistic pressure which should lie between 0 and 0.5 MPa at constant temperature of 110.5 K. Under these conditions only the composition can be varied independently, thus the number of independent variables reduced to unity. During experimental design the mole fraction of Argon was allowed to vary between 0.1 and 0.9. The density is implicitly given by pressure, temperature and composition. This mass density was here determined from a correlation which was obtained from corresponding MD simulations for the limited pressure range specified:

$$\rho_{\mathrm{M}} = 412.2(\pm 1.61) + 689(\pm 2.8)x_{\mathrm{Ar}}. \qquad (21)$$

The procedure of experimental design is documented in Fig. 1 and Table I and explained in

TABLE II Characteristics of the systems simulated in this work

	System	σ_{11} (10^{-10} m)	σ_{22} (10^{-10} m)	ε_{11} (K)	ε_{22} (K)	M_1 (kg/kmol)	M_2 (kg/kmol)	T (K)	X_1	ρ_M (kg/m^3)	p (MPa)	Deviation from Eq. (23) (%)	Deviation from Eq. (24) (%)	M
1	Ar + CH_4	3.504	3.730	117.7	147.95	39.948	16.043	110.5	0.1–0.9	483–1033	0.01–0.47	0	0	5
2	Ar + CH_4	3.504	3.730	117.7	147.95	39.948	16.043	90–140	0.5	739–824.7	0.07–46.6	0	0	23
3	Ar + CH_4	3.504	3.730	117.7	147.95	39.948	16.043	250	0.5	300–600	17.1–66.4	0	0	4
4	Ar + CH_4	3.504	3.730	117.7	147.95	39.948	16.043	300	0.5	200–1300	8.2–485	0	0	27
5	Ar + CH_4	3.504	3.730	117.7	147.95	39.948	16.043	350	0.5–0.9	200, 300	20.5–32.8	0	0	6
6	Ar + $CH_4^{(1)}$	3.504	4.0296	117.7	147.95	39.948	19.974	110.5	0.1–0.9	465–1015.5	0.02–0.29	0	0	5
7	Ar + $CH_4^{(2)}$	3.504	3.730	117.7	147.95	39.948	39.948	110.5	0.3–0.7	1062–1092	0.24–0.61	0	0	3
8	Ar + $CH_4^{(3)}$	3.504	3.730	117.7	147.95	39.948	99.471	110.5	0.3–0.7	1585–2169	0.29–0.97	0	0	3
9	Ar + $CH_4^{(4)}$	3.504	1.752–4.1157	117.7	147.95	39.948	16.043	110.5	0.5	639.7–1500	0.12–0.52	0	0	8
10	Ar + $CH_4^{(5)}$	3.504	3.730	117.7	82.32–188.32	39.948	16.043	110.5	0.5	573–802.5	0.04–0.56	0	0	6
11	Ar + $CH_4^{(6)}$	3.504	3.730	117.7	88.77–177.54	39.948	16.043	110.39–111.05	0.5	702–778.6	0.47–1.45	0	+29 – −8.7	3
12	Ar + Ar	3.504	3.504	117.7	117.7	39.948	39.948	111	0.5	790–1253	0.19–1.10	0	− 50 – +50	3
13	$A_1 + A_2$	3.5375	3.5375	100.0	200.0	61.875	61.875	126–165	0.5	1740.78	10.9–25.4	0	− 20 – +20	5
14	A + B	2.9479	4.1271	141.45	141.45	61.875	61.875	134.38	0.5	1442–1921	8.0–23.0	− 10 – +10	0	5
15	$Ar^{(1)}$	3.405		119.8		39.950		100	1	1294.15	0.67	0	0	1
16	Ar	3.504		117.7		39.948		110.7–300	1	1100–300	0.34–42.6	0	0	5
17	CH_4	3.730		147.95		16.043		110.5–305	1	300–416	0.15–70.5	0	0	4
18	$CH_4^{(2)}$	3.730		147.95		39.948		110.84	1	1036.31	0.99	0	0	1
19	$CH_4^{(3)}$	3.730		147.95		99.471		110.42	1	2580.43	0.05	0	0	1
20	$CH_4^{(7)}$	2.984 –4.1157		147.95		16.043		110.5	1	309.5–811	0.09–0.5	0	0	4
21	CF_4	4.747		141.40		88.0048		160–200	1	700–1200	0.87–74.57	0	0	17
22	N_2	3.636		101.6		28.013		100–300	1	700–868	56.8–335.9	0	0	6

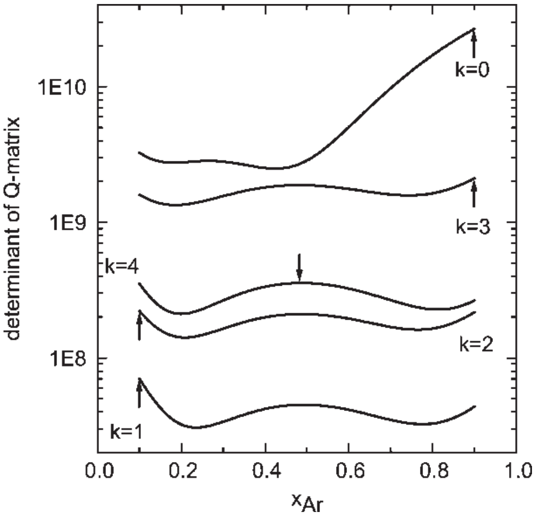

FIGURE 1 Dependence of the information matrix determinant on the mole fraction of argon in the mixture Ar + CH_4 for some steps of optimal experimental design.

the following. To begin with three MD simulations were performed at $x_{\mathrm{Ar}} = 0.1$, 0.3 and 0.5. From the diffusion coefficients obtained by these simulations a first estimate of model parameters $\theta_{i,k}$ ($i = 1, \ldots, 4$; $k = 0$ where k indicates the step of experimental design procedure) is obtained with a least squares minimisation (LMDIF from Ref. [19]). Here $\theta_{5,0}$ was fixed to the value given by Liu *et al.* [Eq. (8)], since this parameter scales the temperature dependence which was not evaluated in these first simulations. With these parameters $\theta_{i,0}$ the procedure of optimal experimental design was started by evaluating the determinant of the **Q**-matrix as a function of composition as shown in Fig. 1. The maximum in step $k = 0$ was determined which is indicated by the corresponding arrow in Fig. 1. Then the mixture at this composition was simulated with MD and the diffusion coefficients evaluated. These new data were then included in the estimation of $\theta_{i,1}$ with which the experimental design then proceeds. Five steps of optimal experimental design were performed as shown in Fig. 1. The thermodynamic conditions of the MD simulations together with the diffusion coefficients, the resulting parameter and their standard deviations (δ_{D_i} and $\delta_{\theta_{i,k}}$) are given in Table I. Here the determinant of the covariance matrix **C** as well as the sums of squares (SSQ, defined below the Table I) are included in the table. From Table I it can be seen that the estimates of the parameters $\theta_{i,k}$ change significantly in each step of the experimental design procedure. Simultaneously, the confidence domain of the estimates of the parameters is rapidly and significantly reduced as can be seen from the determinant of the **C**-matrix (det **C**) as well as the $\delta_{\theta_{i,k}}$.

It should be noted though that the procedure of optimal experimental design was only set up parallel to the first simulations for parameter estimation. Thus, the large number of data points has been simulated where the independent variables were chosen based on physical reasoning, e.g. systematically varying major variables.

SIMULATION DETAILS

In this work the MD simulations were carried out in an NVT ensemble for homogeneous LJ mixtures and pure LJ liquids [20]. The equations of motion of the particles are integrated with a predictor–corrector method of order 5. The particles interacted with a one-centre Lennard–Jones (6, 12) potential:

$$u_{i,j}(r) = 4\varepsilon_{i,j}\left(\left(\frac{\sigma_{i,j}}{r}\right)^{12} - \left(\frac{\sigma_{i,j}}{r}\right)^{6}\right), \qquad (22)$$

where r is the distance between two particles, $\varepsilon_{i,j}$ is the energy parameter $\sigma_{i,j}$ is the diameter parameter between particles of components i and j. In the case of mixtures the LJ potential parameters for the cross interaction were calculated mainly with the Lorentz–Berthelot combining rules:

$$\sigma_{i,j} = \frac{\sigma_{i,i} + \sigma_{j,j}}{2}, \qquad (23)$$

$$\varepsilon_{i,j} = (\varepsilon_{i,i}\varepsilon_{j,j})^{1/2}. \qquad (24)$$

To include systems which are more realistic 4 systems (Table II) were chosen which deviate from Eqs. (23) and (24). The interaction energies were assumed to be pairwise additive. The simulations were performed for 256 particles in a cubic box with periodic boundary conditions. The time step was 3×10^{-15} s in all simulations. 200,000 time steps were used to arrive at thermodynamic equilibrium, and between 300,000 and 1,200,000 time steps to evaluate diffusion coefficients and thermodynamic properties of the system. The self- and intra-diffusion coefficients were calculated by direct evaluation on the mean square displacement of the particles:

$$D_i = \lim_{\tau \to \infty} \frac{1}{6\tau} \langle (\mathbf{r}_i(t_0 + \tau) - \mathbf{r}_i(t_0))^2 \rangle. \qquad (25)$$

Here $\mathbf{r}_i$ is the position vector of particle i, τ the time interval of the observation, and t_0 the initial time of observation. In the simulations the evaluation of Eq. (25) was performed simultaneously for various values of τ as shown in Fig. 2. The value of D_i was then determined from the corresponding plateau value of each component.

The ranges of thermodynamic parameters of systems simulated in this work are listed in Table II. Figure 3 shows a distribution of the simulated states within the range of the values of mass densities ρ_{M} and temperatures T. The diffusion coefficients were determined for each thermodynamic state and collected in the database (database 1), which

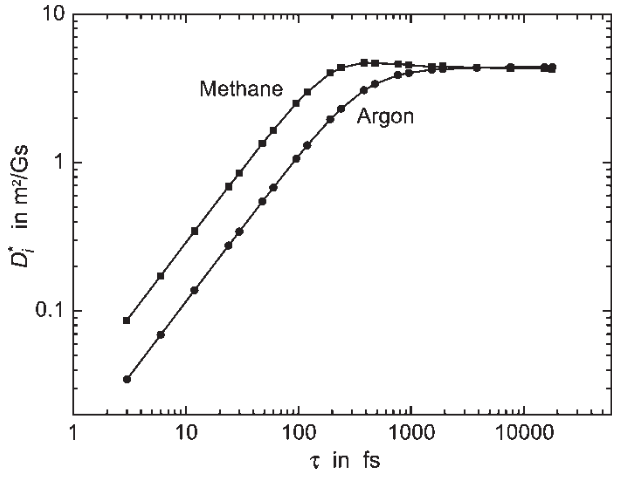

FIGURE 2 Evaluation of intra-diffusion coefficients with the Eq. (25) in an equimolar liquid mixture of argon and methane.

was used in this work for fitting of the model parameters $\bar{\Theta}$. Figure 3 also contains points corresponding to literature data for binary mixtures [8–12]. These literature data from database 2 were not used for determination of the model parameters, but exclusively to test the suggested model.

RESULTS AND DISCUSSION

The parameter set $\bar{\Theta} = (\theta_1, \ldots, \theta_5)$ for Eqs. (9)–(17) was found by least-squares minimisation. As a result the following values were obtained:

$$\begin{aligned}\theta_1 &= 2.159807,\\ \theta_2 &= 1.156846,\\ \theta_3 &= 0.414496,\\ \theta_4 &= 0.610344,\\ \theta_5 &= 0.564022.\end{aligned} \tag{26}$$

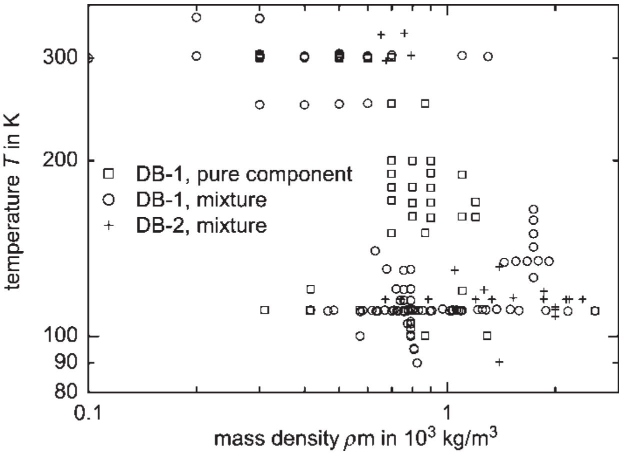

FIGURE 3 Distribution of the simulated states within the range of the values of mass density ρ_M and temperature T for database 1 (DB-1) and the literature data in database 2 (DB-2).

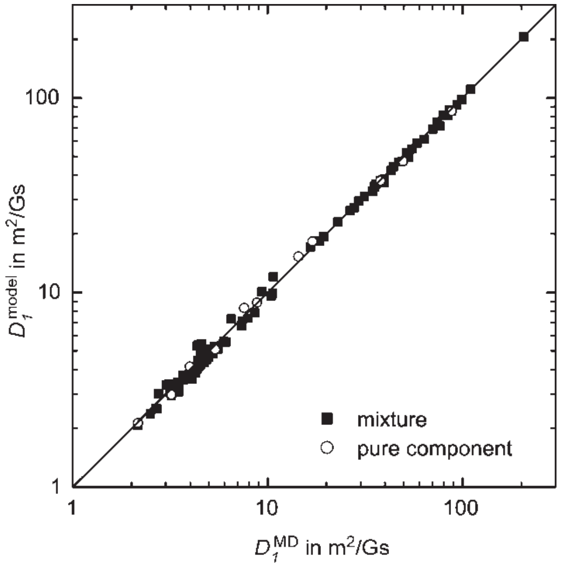

FIGURE 4 Comparison of self- and intra-diffusion coefficients of component 1 calculated with Eqs. (9)–(17) with those in database 1.

with an average absolute deviation (AAD) of 5.56%. Comparison of the diffusion coefficients calculated with our model to those obtained by MD simulation is shown in Figs. 4 and 5. Here the pure-component diffusion coefficients are included only in one of the figures according to their component index which was attributed arbitrarily to improve readability of the figures. Of course the pure component values could in principle be included in either figure. As can be seen the proposed model describes the data points of database 1 very well.

As seen in Fig. 5 there are only four points indicated by the numbers 1–4, in which the calculated values of the intra-diffusion coefficients have perceptibly larger deviations from the MD values. These points are related to an equimolar

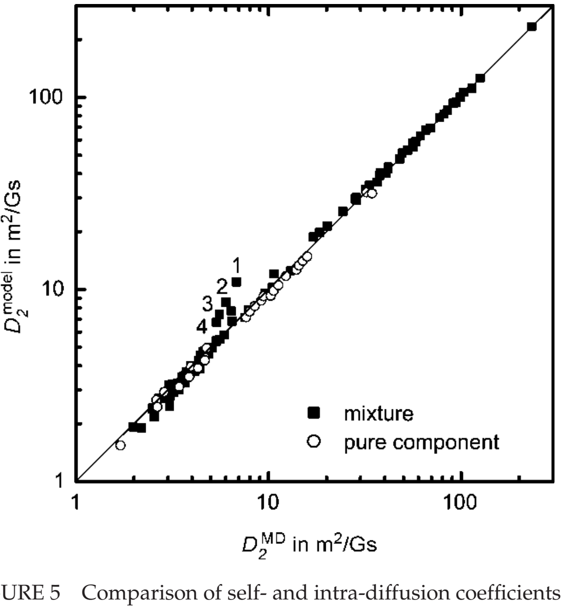

FIGURE 5 Comparison of self- and intra-diffusion coefficients of component 2 calculated with Eqs. (9)–(17) with those in database 1.

TABLE III Characteristics of the database 2 together with the RD for the intra-diffusion coefficients calculated with Eqs. (9)–(17)

	σ_{11} (10^{-10} m)	σ_{22} (10^{-10} m)	ε_{11} (K)	ε_{22} (K)	M_1 (10^{-3} kg/mol)	M_2 (10^{-3} kg/mol)	T (K)	X_1	ρ_M (kg/m^3)	D_1 (m^2/Gs)	RD (%)*	D_2 (m^2/Gs)	RD (%)	Source
1	3.405	3.633	119.80	167.00	39.948	83.800	115.70	0.10	2384.11	1.770	14.27	1.41	15.54	[8]
2	3.405	3.633	119.80	167.00	39.948	83.800	115.70	0.25	2186.64	2.120	13.65	1.79	18.19	[8]
3	3.405	3.633	119.80	167.00	39.948	83.800	115.70	0.50	1857.52	3.010	3.29	2.40	17.88	[8]
4	3.405	3.633	119.80	167.00	39.948	83.800	116.30	0.75	1528.40	3.910	0.65	3.25	21.36	[8]
5	3.405	3.633	119.80	167.00	39.948	83.800	115.60	0.90	1330.93	4.570	4.71	3.64	20.39	[8]
6	3.405	2.800	119.80	36.20	39.948	20.179	90.30	0.97	1396.56	2.110	13.77	3.63	39.28	[8]
7	3.405	2.800	119.80	36.20	39.948	20.179	131.50	0.97	1396.56	3.440	4.15	5.59	42.03	[8]
8	3.405	2.800	119.80	36.20	39.948	20.179	129.70	0.97	1049.19	8.040	5.19	12.84	20.32	[8]
9	5.190	5.460	444.00	392.00	70.138	72.151	297.00	0.50	675.04	3.359	11.37	3.232	18.80	[9]
10	5.190	5.460	444.00	392.00	70.138	72.151	329.00	0.50	653.42	4.721	8.46	4.543	14.20	[9]
11	3.405	3.633	119.80	167.00	39.948	9.524	115.61	0.50	742.77	4.9227	13.79	4.760	3.92	[10]
12	3.405	3.633	119.80	167.00	39.948	19.043	115.61	0.50	885.70	4.3230	13.49	3.961	13.62	[10]
13	3.405	3.633	119.80	167.00	39.948	39.948	115.61	0.50	1199.57	3.7306	9.86	3.256	21.35	[10]
14	3.405	3.633	119.80	167.00	39.948	83.799	115.61	0.50	1857.95	3.1558	1.69	2.610	24.66	[10]
15	3.405	3.405	119.80	119.80	39.948	79.896	115.61	0.50	2142.64	2.216	0.13	2.125	12.09	[10]
16	3.400	3.400	120.00	120.00	26.600	53.200	120.00	0.50	1264.31	4.439	7.76	4.172	3.46	[11]
17	3.400	3.400	120.00	120.00	20.000	60.000	120.00	0.50	1267.48	4.903	8.57	4.217	3.59	[11]
18	3.405	3.633	119.80	167.00	39.950	83.800	115.70	0.50	1860.00	2.980	3.78	2.43	19.37	[12]
19	3.405	3.633	119.80	167.00	39.950	83.800	108.07	0.50	2001.01	1.800	9.54	1.42	17.48	[12]
20	3.405	3.633	119.80	167.00	39.950	83.800	111.04	0.50	2001.01	1.940	6.40	1.55	20.41	[12]
21	3.405	3.633	119.80	167.00	39.950	83.800	112.12	0.50	2001.01	2.120	1.04	1.71	26.53	[12]
ARD†											7.37		18.78	

*Relative deviation $\mathrm{RD}_i = 100^* \left| D_i^{\mathrm{MD}} - D_i^{\mathrm{model}} \right| / D_i^{\mathrm{MD}}$. †Average relative deviation $\mathrm{ARD} = (1/M) \sum_i^M \mathrm{RD}_i$.

mixtures (Table II, line IX) in which σ_{22} for some simulations was chosen to be very small.

Equations (9)–(17) together with the coefficients in Eq. (26) were employed for calculation of intra-diffusion coefficients for database 2 corresponding to literature data. The 21 binary mixtures evaluated are listed in Table III. Only mixtures with extremely high mass densities above $3000\,\mathrm{kg/m^3}$ as well as isotope mixtures in which one of the component had an unphysically high molecular mass compared to its molecular size were excluded from consideration. The deviations of the calculated intra-diffusion coefficients for each of the two components from the values taken from the literature are also listed in Table III. The model suggested in the present work describes these 42 data points with the total AAD of 13.08%, but as seen in Table III the model generally predicts the diffusion coefficients of the first component considerably better than that of the second component. An analysis of the effective reduced densities $\rho^*_{\mathrm{eff},i}$ for the systems of database 2 showed that in several cases the values of $\rho^*_{\mathrm{eff},2}$ take values which are extreme as compared to those for the data of database 1 to which the model parameters were fitted. For component 1 and $\rho^*_{\mathrm{eff},1}$ this is the case in much fewer cases. Thus, the asymmetry in the fitting quality does not correspond to any physical reason but rather depicts the asymmetric choice of molecular parameters in the literature. Also the accuracy of the determination of the intra-diffusion coefficients with MD simulation has to be considered. For example, the largest deviations occur for the diffusion coefficients of Ne in mixtures Ar + Ne at a mole fraction of Ne $x_2 = 0.03$ (systems 6–8 in Table III). This small content of Ne in the mixture might influence the accuracy of the diffusion coefficient which is unfortunately not reported in Ref. [8].

Comparing the suggested model to an independent data set for intra-diffusion coefficients taken from the literature turned out to be very effective. First of all, the results obtained for the first component of the considered mixtures show that the model gives physically correct results with quite good accuracy of the intra-diffusion coefficient when molecular properties and thermodynamic characteristics of mixture components lie within the wide range used for fitting of the model parameters. At the same time an analysis of causes of a less precise prediction of the intra-diffusion coefficients for the second component permits us to define directions of the following work with the goal to further develop the model. The procedure of optimal experimental design will be applied together with a suitable equation of state to find the most sensible conditions with respect to all independent variables for the MD simulations.

CONCLUSION

In this work, a model for calculation of the intra-diffusion coefficients in homogeneous liquid mixtures consisting of 1-centre LJ particles is proposed. The five coefficients of the model were fitted to a database 1 of intra-diffusion coefficients with an average absolute deviation of 5.56%. The database 1 was obtained from MD simulations for the homogeneous liquid mixtures and pure substances over a wide range of the mass densities $200\,\mathrm{kg/m^3} < \rho_{\mathrm{M}} < 2580\,\mathrm{kg/m^3}$ and temperatures $90\,\mathrm{K} < T < 350\,\mathrm{K}$.

The method of optimal experimental design with respect to optimal determination of model parameters was considered and applied in planning the computer experiments for selecting conditions of MD simulations. The goal was to reduce the computational effort to obtain a reliable database.

The model was then applied to calculate the intra-diffusion coefficients for the 1-centre LJ mixtures for which data points were found in the literature. Comparison of the calculated intra-diffusion coefficients to the data available showed that the suggested model is able to predict the diffusion coefficients with an accuracy of 13.08%.

Acknowledgements

We are grateful for the support for implementation of the procedure of experimental design by Dipl.–Ing André Bardon of the chair of process systems engineering at the RWTH Aachen University. This project was funded by the German Science foundation in the framework of the collaborative research center 540 'model-based experimental analysis of kinetic phenomena in fluid multi-phase reactive systems'.

References

[1] Tyrrell, H.J.V. and Harris, K.R. (1984) *Diffusion in Liquids* (Butterworths, London).

[2] Heyes, D.M. (1998) *The Liquid State: Applications of Molecular Simulations* (Wiley, New York).

[3] Liu, H., Silva, C.M. and Macedo, E.A. (1998) "Unified approach to the self-diffusion coefficients of dense fluids over wide ranges of temperature and pressure—hard-sphere, square-well, Lennard-Jones and real substances", *Chem. Eng. Sci.* **53**, 2403–2422.

[4] Silva, C.M., Liu, H. and Macedo, E.A. (1998) "Models for self-diffusion coefficients of dense fluids, including hydrogen-bonding substances", *Chem. Eng. Sci.* **53**, 2423–2429.

[5] Zhu, Yu., Lu, X., Zhou, J., Whang, Y. and Shi, J. (2002) "Prediction of diffusion coefficients for gas, liquid and supercritical fluid: application to pure real fluids and infinite dilute binary solutions based on the simulation of Lennard–Jones fluid", *Fluid Phase Equilib.* **194–197**, 1141–1159.

[6] Yu, Y.X. and Gao, G.H. (1999) "Self-diffusion coefficient equation for polyatomic fluid", *Fluid Phase Equilib.* **166**, 111–124.

[7] Dariva, C., Coelho, L.A.F. and Oliveira, J.V. (1999) "A kinetic approach for predicting diffusivities in dense fluid mixtures", *Fluid Phase Equilib.* **158–160**, 1045–1054.

[8] Jacussi, G. and Mc Donald, I.R. (1975) "Structure and diffusion in mixtures of rare-gas liquids", *Physika A* **80**, 607–625.

[9] Enninghorst, A., Waune, F.D. and Zeidler, M.D. (1996) "Density dependence of self-diffusion in liquid pentanes and pentane mixtures", *Molec. Phys.* **88**, 437–452.

[10] Bearman, R.J. and Jolly, D.L. (1981) "Mass dependence of the self diffusion coefficients in two equimolar binary Lennard–Jones systems determined through molecular dynamics simulation", *Molec. Phys.* **44**, 665–675.

[11] Van den Berg, H.P. and Hoheisel, C. (1990) "Dynamic cross correlation in isotopic two-component liquids: molecular-dynamics calculation results compared with predictions of kinetic theory", *Phys. Rev., A* **42**, 3368–3373.

[12] Schoen, M. and Hoheisel, C. (1984) "The mutual diffusion coefficient D_{12} in binary liquid model mixtures. Molecular dynamics calculations based on Lennard–Jones (12-6) potentials. 1. The method of determination", *Molec. Phys.* **52**, 33–56.

[13] Ebbsiö, I., Schofild, P., Sköld, K. and Waller, I. (1974) "Diffusion in liquid mixtures of isotopes", *J. Phys. C: Solid State Phys.* **7**, 3891–3908.

[14] Jacob, A.C. and Zeidler, M.D. (2003) "Self-diffusion in binary mixtures: the system benzene/cyclohexane at high pressures", *Phys. Chem. Chem. Phys.* **5**, 538–542.

[15] Kerl, K. and Willeke, M. (1999) "Investigation of the mass dependence of self-diffusion coefficients by molecular dynamics calculations: binary and ternary isotopic mixtures of atoms", *Molec. Phys.* **96**, 1169–1183.

[16] Kerl, K. and Willeke, M. (1999) "Investigation of the mass dependence of self-diffusion coefficients by molecular dynamics calculations: binary non-isotopic mixtures of atoms", *Molec. Phys.* **97**, 1255–1262.

[17] Asprey, S.P., Macchietto, S. and Pantelides, C.C. (2000) "Robust optimal designs for dynamic experiments", In: Biegler, L.T., Brambilla, A. and Scali, C., eds, *Proc. of ADCHEM'2000*, Vol. II, pp 869–874.

[18] Radon, F. (2002) "Optimale, sequentielle Versuchsplanung von binären Dampf-Flüssig-Gleichgewichtsexperimenten", Project Thesis (Lehrstuhl für Prozesstechnik, RWTH Aachen).

[19] Garbow, B.S., Hillstrom, K.E. and More, J.J. (1980) *Minpack Project* (Argonne National Laboratory, Argonne, IL, USA).

[20] Allen, M.P. and Tildesley, D.J. (1987) *Computer Simulation of Liquids* (Clarendon Press, Oxford).