



Fick Diffusion Coefficients in Ternary Liquid Systems from Equilibrium Molecular Dynamics Simulations

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Supporting Information

ABSTRACT: An approach for computing Fick diffusivities directly from equilibrium molecular dynamics (MD) simulations is presented and demonstrated for a ternary chloroform–acetone–methanol liquid mixture. In our approach, Fick diffusivities are calculated from the Maxwell–Stefan (MS) diffusivities and the so-called matrix of thermodynamic factors. MS diffusivities describe the friction between different molecular species and can be directly computed from MD simulations. The thermodynamic factor describes the deviation from ideal mixing behavior and is difficult to extract from both experiments and simulations. Here, we show that the thermodynamic factor in ternary systems can be obtained from density fluctuations in small subsystems embedded in a larger simulation box. Since the computation uses the Kirkwood–Buff coefficients, the present approach provides a general route toward the thermodynamics of the mixture. In experiments, Fick diffusion coefficients are measured, while previously equilibrium molecular dynamics simulation only provided MS transport diffusivities. Our approach provides an efficient and accurate route to predict multicomponent diffusion coefficients in liquids based on a consistent molecular picture and therefore bridges the gap between theory and experiment.

1. INTRODUCTION

Chemical engineers often need to compute properties of systems undergoing multicomponent mass transfer. Diffusion is often rate-limiting for mass transport in liquids. Transport diffusion is a process by which mass transfer occurs due to a gradient in chemical potential or concentration as the driving force. The presence of three or more components in a liquid mixture introduces phenomena that cannot be described by the well-known first law of Fick for binary systems.¹ A consistent methodology to accurately describe and predict mass transfer in multicomponent systems is therefore required. Two theories are commonly used to describe the mass transport: generalized Fick's law and the Maxwell–Stefan approach.

Generalized Fick's law in an n -component system with respect to a molar reference frame is given by^{1–3}

$$J_i = -c_t \sum_{j=1}^{n-1} D_{ij} \nabla x_j \quad (1)$$

in which J_i is the diffusion flux, c_t is the total molar concentration, D_{ij} are Fick diffusivities, and ∇x_j is the gradient in mole fraction of component j . Transformations between fluxes in other reference frames can be easily performed.^{1,2,4} From eq 1 it follows directly that the elements of the matrix of Fick diffusivities $[D]$ depend on the labeling of the components.

In an n -component system, transport diffusion is thus described by $(n - 1)^2$ Fick diffusion coefficients. It is important to note that the matrix of Fick diffusivities $[D]$ is not symmetric

and the elements often strongly depend on concentration.² Also, in multicomponent systems, the elements of the matrix $[D]$ are unrelated to their binary counterparts. The off-diagonal Fick diffusivities D_{ij} with $i \neq j$, can even be negative.¹

The Maxwell–Stefan (MS) approach provides a physically based comprehensive framework for describing multicomponent mass transport.^{1,2,4,5} The approach relates the driving force for diffusion of component i (i.e. the chemical potential gradient $\nabla \mu_i$ at constant temperature and pressure) to friction forces of molecules of component i with molecules of other components:

$$-\frac{1}{RT} \nabla_{T,p} \mu_i = \sum_{j=1, j \neq i}^n \frac{x_j (u_i - u_j)}{D_{ij}} \quad (2)$$

in which R and T are the gas constant and absolute temperature, respectively. x_j is the mole fraction of component j . The friction force between components i and j is proportional to the difference in average velocities of the components, $(u_i - u_j)$. The MS diffusivity D_{ij} can be considered as an inverse friction coefficient describing the magnitude of the friction between components i and j . MS diffusivities do not depend on a reference frame. The MS diffusivities are symmetric, $D_{ij} = D_{ji}$, and

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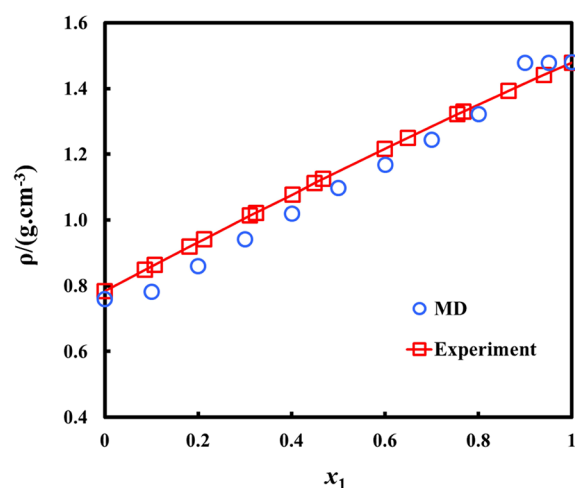


Figure 1. Densities of chloroform (1)–acetone (2) mixtures at 298 K, 1 atm. Circles are the computed densities by this work using MD simulations. Squares are the experimental densities measured by Karr et al.⁵⁸

therefore, $n(n-1)/2$ MS diffusivities D_{ij} are sufficient to describe diffusion in an n -component system. However, it is difficult to obtain MS diffusivities from experiments as chemical potentials cannot be measured directly. In contrast, obtaining MS diffusivities from molecular dynamics (MD) simulations is a natural choice but often requires large amounts of CPU time.^{6–17} It is important to note that the MS diffusivities are also concentration dependent. In our earlier work, we developed the multicomponent Darken model for describing this concentration dependence of MS diffusivities.¹¹ The multicomponent Darken model accurately predicts the MS diffusivities for ideal diffusing mixtures.¹¹

As generalized Fick's law and the MS theory describe the same physical process, their coefficients are related. In an n -component system in a molar reference frame, this relation is^{1,2,4,7}

$$[D] = [B]^{-1}[\Gamma] \quad (3)$$

in which $[D]$ is the $(n-1) \times (n-1)$ matrix of Fick diffusivities. The elements of the matrix $[B]$ are given by^{1,3,7,18}

$$B_{ii} = \frac{x_i}{D_m} + \sum_{j=1, j \neq i}^n \frac{x_j}{D_{ij}} \quad \text{with } i = 1, \dots, (n-1) \quad (4)$$

$$B_{ij} = -x_i \left(\frac{1}{D_{ij}} - \frac{1}{D_m} \right) \quad \text{with } i, j = 1, \dots, (n-1) \text{ and } i \neq j \quad (5)$$

The elements of the so-called matrix of thermodynamic factors $[\Gamma]$ are defined by^{1–3,7}

$$\Gamma_{ij} = \delta_{ij} + x_i \left(\frac{\partial \ln \gamma_i}{\partial x_j} \right)_{T,p,\Sigma} \quad (6)$$

in which δ_{ij} is the Kronecker delta and γ_i is the activity coefficient of component i in the mixture. The symbol Σ indicates that the partial differentiation of $\ln \gamma_i$ with respect to mole fraction x_j is carried out at constant mole fraction of all other components except the n th one, so that $\sum_{i=1}^n x_i = 1$ during the differentiation. The constrained derivative of eq 6 can be written as a function of unconstrained derivatives as follows:

Table 1. Densities of Pure Chloroform, Acetone, and Methanol at 298 K, 1 atm

component	$\rho/(\text{g}\cdot\text{mL}^{-1})$	
	this work (MD)	experiment
acetone	0.76	0.78 ^{a,b} , 0.79 ^c
methanol	0.75	0.79 ^{a,b}
CHCl ₃	1.48	1.47 ^d

^aExperiments by Campbell et al.⁶² ^bExperiments by Noda et al.⁶³

^cExperiments reported in ref 64. ^dExperiments reported in ref 58.

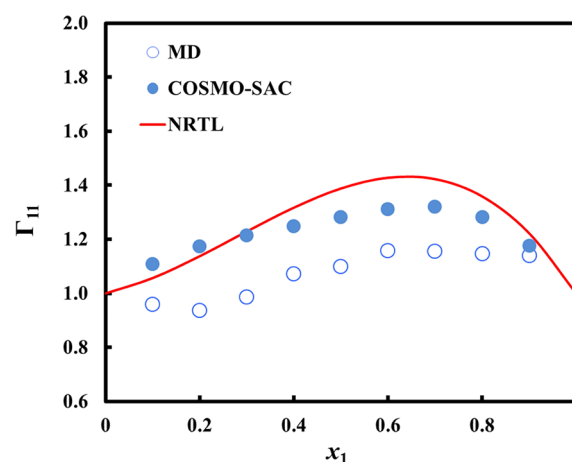


Figure 2. Thermodynamic factor Γ_{11} in the binary system chloroform (1)–acetone (2) at 298 K, 1 atm. Open symbols are the computed Γ_{11} in this work using MD simulations. Filled symbols are the computed Γ_{11} using COSMO-SAC. The solid line represents Γ_{11} calculated from the NRTL model fitted to experimental VLE data of ref 59.

$$\left. \frac{\partial \ln \gamma_i}{\partial x_j} \right|_{T,p,\Sigma} = \left. \frac{\partial \ln \gamma_i}{\partial x_j} \right|_{T,p,j'} - \left. \frac{\partial \ln \gamma_i}{\partial x_n} \right|_{T,p,n'} \quad (7)$$

Here, the prime symbols in the derivative evaluations indicate that the mole fractions of all other components are held constant. For any system in the limit of infinite dilution, the values of $[\Gamma]$ are known, i.e., $\Gamma_{ii}^{x_i \rightarrow 0} = 1$, $\Gamma_{ij,i \neq j}^{x_i \rightarrow 0} = 0$. For a binary system, eqs 3–6 reduce to^{1,2}

$$D_{11} = \Gamma_{11} D_{12} \quad (8)$$

in which the thermodynamic factor Γ_{11} is given by^{1,2}

$$\Gamma_{11} = 1 + x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,p,\Sigma} \quad (9)$$

Equation 3 clearly shows the gap between molecular simulations and experiments. In experiments, Fick diffusion coefficients are measured while equilibrium MD simulations usually provide MS diffusivities.^{9,19–23} The two worlds are related via the matrix of thermodynamic factors $[\Gamma]$, but this is usually known only with relatively large uncertainties.^{18,24} To obtain the matrix of thermodynamic factors, the experimental vapor–liquid equilibrium data can be fitted using excess Gibbs energy models, e.g. Margules, van Laar, NRTL, etc.²⁵ Several models may provide estimates of $\ln \gamma_i$ that give equally good fits to the vapor–liquid equilibrium data. However, the thermodynamic factor Γ_{ij} involves the first derivative of the activity coefficient $\ln \gamma_i$ with respect to the composition. Errors of the size of 20% and larger are expected for this derivative.²⁶

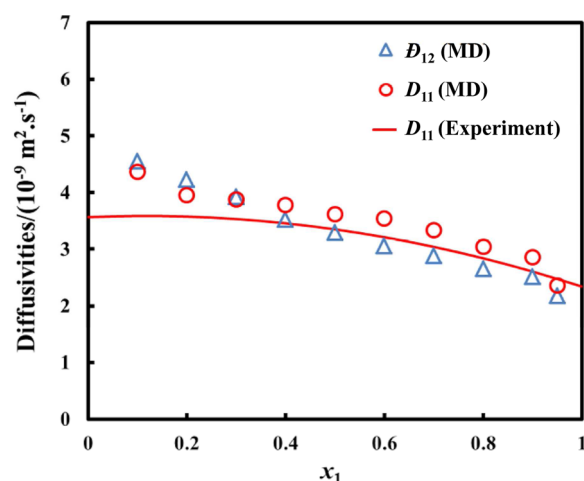


Figure 3. Computed MS diffusivities D_{12} and Fick diffusivities D_{11} in the binary system chloroform (1)–acetone (2) at 298 K, 1 atm. Open symbols represent Fick diffusivities calculated using the computed thermodynamic factor Γ_{11} and MS diffusivities D_{12} from MD simulations. The error bars of computed diffusivities are smaller than the symbol size.

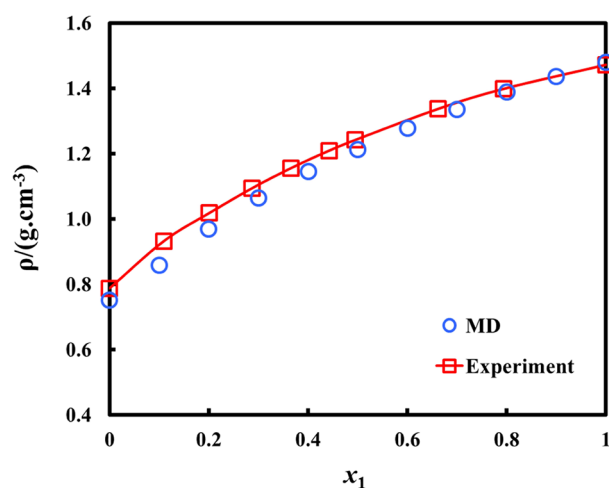


Figure 4. Densities of chloroform (1)–methanol (2) mixtures at 298 K, 1 atm. Circles are the computed densities from this work using MD simulations. Squares are the experimental densities taken from ref 60.

Currently used approaches for computing Fick diffusivities from molecular simulation suffer from inconsistencies or other problems:

- Direct calculation of Fick diffusivities using nonequilibrium MD (NEMD) requires significant efforts and very high concentration gradients.^{27–29} This approach is usually not accurate and quite impractical as the concentration dependence of Fick diffusivities is not easily captured.
- Combining MS diffusivities obtained from equilibrium MD simulations with experimentally obtained equations of state or models for the excess Gibbs energy is inconsistent, as experiments and molecular models in principle provide different values for the thermodynamic factor.^{22,30,31}
- Currently used molecular simulation techniques to determine the thermodynamic factor of liquid mixtures

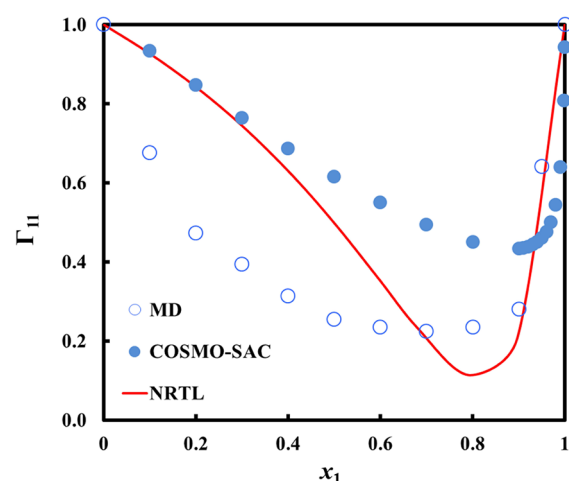


Figure 5. Thermodynamic factor Γ_{11} in the binary system chloroform (1)–methanol (2) at 298 K, 1 atm. Open symbols are the computed Γ_{11} by this work using MD simulations. Filled symbols represent Γ_{11} computed using COSMO-SAC. The solid line represents Γ_{11} calculated from the NRTL model fitted to experimental VLE data of ref 59.

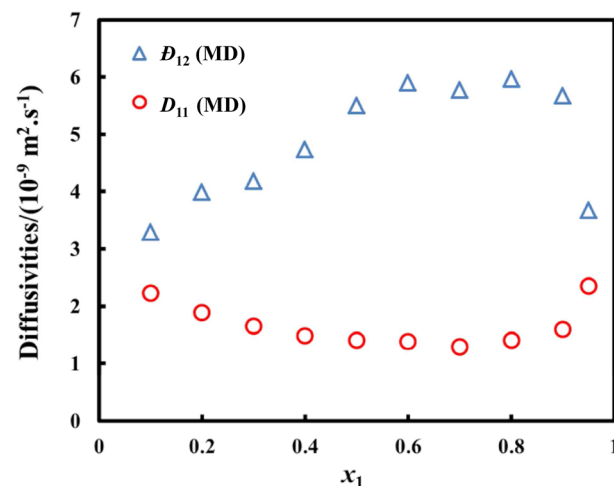


Figure 6. Computed MS diffusivity D_{12} and Fick diffusivities D_{11} in the binary system chloroform (1)–methanol (2) at 298 K, 1 atm. Fick diffusivities calculated using the computed thermodynamic factor Γ_{11} and MS diffusivities D_{12} from MD simulations. The error bars of computed diffusivities are smaller than the symbol size.

are quite inefficient.^{21,32} To the best of our knowledge, these techniques have only been applied to binary mixtures.

Recently, we developed a consistent methodology to calculate binary Fick diffusivities using MS diffusivities D_{ij} and thermodynamic factors $[\Gamma]$ from equilibrium MD simulations.^{33,34} Thermodynamic factors can be computed by studying density fluctuations in small subvolumes inside a larger simulation box and correcting for finite-size effects.^{32,35} In our earlier work, this approach was validated for the binary systems acetone–methanol and acetone–tetrachloromethane.^{33,34} In these simulations, all molecules were treated as rigid bodies interacting through Lennard-Jones (LJ) and electrostatic interactions. Our MD results for these systems quantitatively agree with the experimental data for binary Fick diffusion coefficients D_{11} as well for the thermodynamic factor Γ_{11} .^{33,34} Our approach thus bridges the gap between diffusion experiments and molecular simulations. In this work, this approach is extended and validated

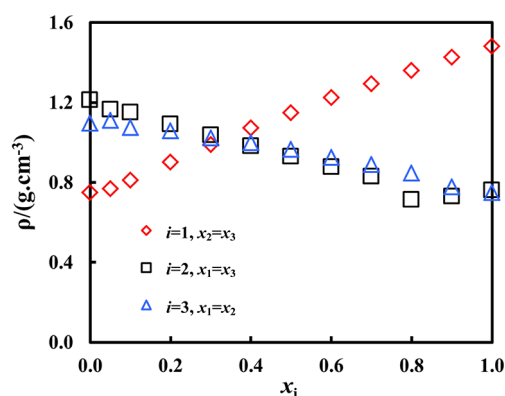


Figure 7. Densities of chloroform (1)–acetone (2)–methanol (3) mixtures at 298 K, 1 atm, computed from MD. The densities are plotted as a function of the mole fraction of one of the components, while keeping the mole fractions of the other components equal to each other.

for the ternary system chloroform–acetone–methanol. Our MD results show good agreement with experiments. Even with simple molecular models taken from standard classical force fields, i.e. excluding polarization effect, we shall see that it is possible to predict Fick diffusivities with reasonable accuracy. This may suggest that the use of more realistic/complex force fields is not needed for predicting transport diffusivities of typical small molecules.

This paper is organized as follows. In section 2, we explain how to obtain the MS diffusivities and thermodynamic factors from equilibrium MD simulations. The details of the simulations are addressed in section 3. In section 4, we validate the methodology for computing Fick diffusivities for the ternary system chloroform–acetone–methanol. Our findings are summarized in section 5.

2. COMPUTATION OF DIFFUSION COEFFICIENTS AND THERMODYNAMIC FACTORS

2.1. Obtaining Diffusion Coefficients from MD Simulations.

In equilibrium MD simulations, representative trajectories of a system consisting of interacting molecules are obtained.^{36–38} From these trajectories, transport properties can be computed.³⁶ The self-diffusivity is related to the motion of individual molecules and can be calculated using the average displacements of molecules of type i as described by the Einstein equation:³⁶

$$D_{i,\text{self}} = \frac{1}{6N_i} \lim_{m \rightarrow \infty} \frac{1}{m \cdot \Delta t} \left\langle \left(\sum_{l=1}^{N_i} (r_{l,i}(t + m \cdot \Delta t) - r_{l,i}(t))^2 \right) \right\rangle \quad (10)$$

Here, N_i is the total number of molecules of component i , m is the number of time steps and Δt is the time step used in MD simulations. $r_{l,i}(t)$ is the position of the l -th molecule of type i at time t .

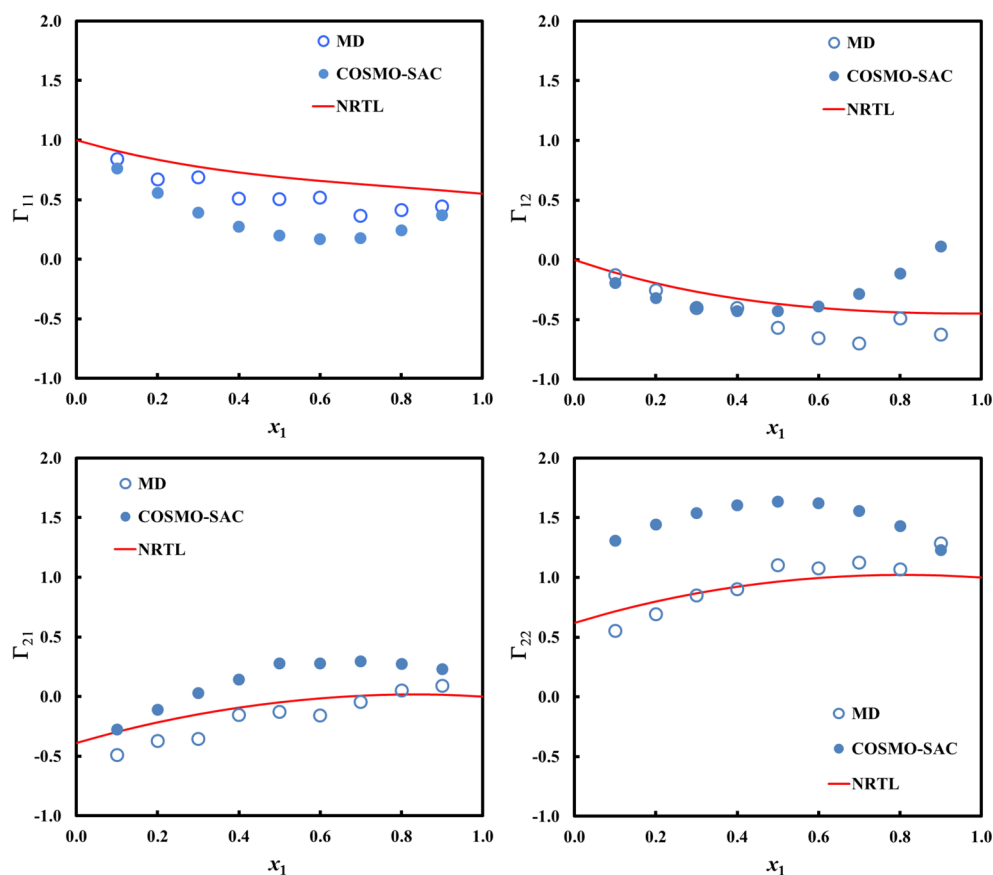


Figure 8. Thermodynamic factor Γ_{ij} in the ternary system chloroform (1)–acetone (2)–methanol (3) at 1 atm. Open circles are the computed values of Γ_{ij} using MD simulations at 298 K. Filled circles are the computed values of Γ_{ij} using COSMO-SAC at 298 K. Solid lines represent Γ_{ij} calculated from the NRTL model fitted to experimental VLE data at 303 K of ref 61. x_1 is varied while keeping $x_2 = x_3$.

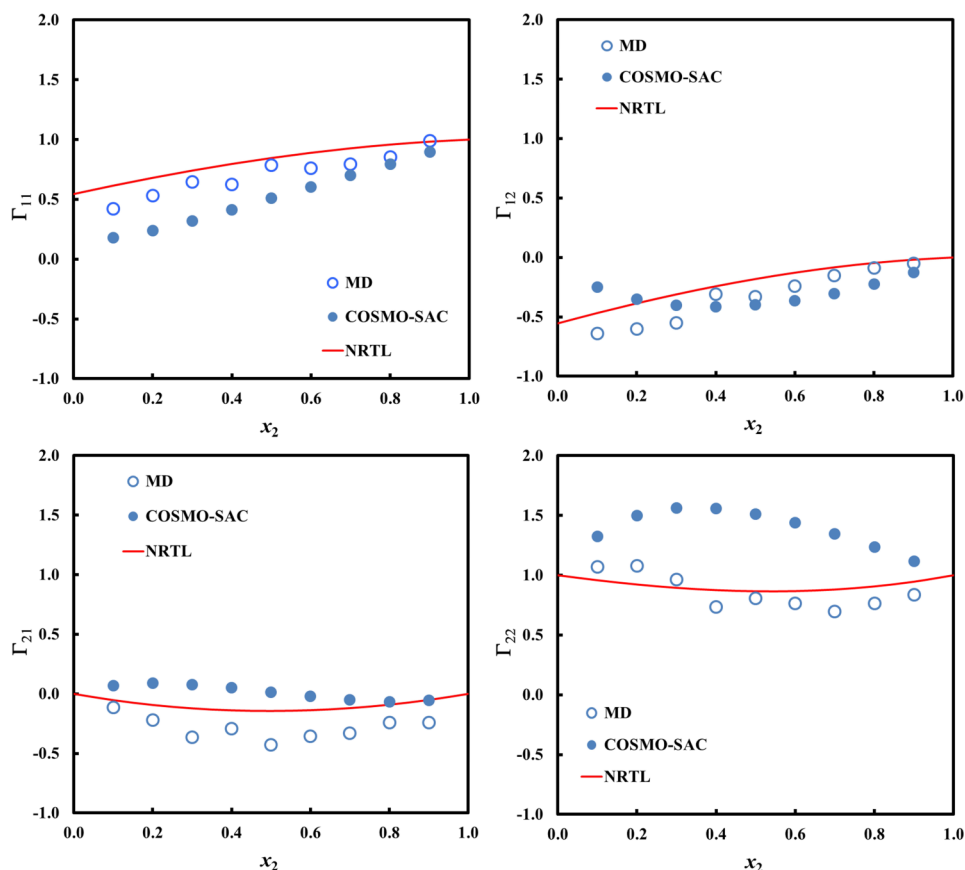


Figure 9. Thermodynamic factor Γ_{ij} in the ternary system chloroform (1)–acetone (2)–methanol (3) at 1 atm. Open circles are the computed values of Γ_{ij} using MD simulations at 298 K. Filled circles are the computed values of Γ_{ij} using COSMO-SAC at 298 K. Solid lines represent Γ_{ij} calculated from the NRTL model fitted to experimental VLE data at 303 K of ref 61. x_2 is varied while keeping $x_1 = x_3$.

MS diffusivities D_{ij} are calculated as follows: first, the Onsager coefficients Λ_{ij} are calculated:⁷

$$\Lambda_{ij} = \frac{1}{6} \lim_{m \rightarrow \infty} \frac{1}{N m \Delta t} \left(\left\langle \sum_{l=1}^{N_i} (r_{l,i}(t + m \Delta t) - r_{l,i}(t)) \right\rangle \right. \\ \left. \times \left(\sum_{k=1}^{N_j} (r_{k,j}(t + m \Delta t) - r_{k,j}(t)) \right) \right) \quad (11)$$

in which N is the total number of molecules and n is the number of components. The Onsager coefficients are constrained by $\sum_{i=1}^n M_i \Lambda_{ij} = 0$ in which M_i is the molar mass of component i .⁷ Furthermore, by definition $\Lambda_{ij} = \Lambda_{ji}$. Using the computed values for Λ_{ij} and the mixture composition, MS diffusivities can be computed. The mean-squared displacement and Onsager coefficients were updated with different frequencies according to the order- n algorithm described in refs 36 and 39. The expressions relating the Onsager coefficients Λ_{ij} to the MS diffusivities in binary, ternary, and quaternary systems can be found in refs 7 and 11.

2.2. Obtaining Thermodynamic Factors from MD Simulations. The elements of the matrix of thermodynamic factors $[\Gamma]$ can be expressed as density fluctuations in the grand-canonical ensemble, as derived by Kirkwood and Buff^{40,41} in 1951. The natural method for obtaining these averages are grand-canonical Monte Carlo (GCMC) simulations.³⁶ However, GCMC simulations of liquid mixtures at room temperature are quite challenging as the insertion and deletion of molecules is very inefficient for dense liquids.³⁶ There is some recent

improvement in this area but these simulations remain quite inefficient.^{42,43} Kirkwood and Buff showed that density fluctuations in the grand-canonical ensemble are related to the integrals of radial distribution functions over volume, resulting in the following expression for the so-called Kirkwood–Buff (KB) coefficients for components i and j :^{40,41}

$$G_{ij} = V \frac{\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle}{\langle N_i \rangle \langle N_j \rangle} - \frac{\delta_{ij}}{c_i} \quad (12)$$

$$= 4\pi \int_0^\infty [g_{ij}(r) - 1] r^2 dr \quad (13)$$

In these equations, V is the volume and c_i is the number density of component i , defined by $\langle N_i \rangle / V$. The brackets $\langle \dots \rangle$ denote an ensemble average in the grand-canonical ensemble. $g_{ij}(r)$ is the radial distribution function for molecules of type i and j in the grand-canonical ensemble, and it is natural to define the distance r between two molecules as either the distance between their centers of mass or the distance between their central atoms. As the choice of ensemble is irrelevant for large systems, in practice $g_{ij}(r)$ is computed in the NpT or NVT ensemble. In binary mixtures, the thermodynamic factor Γ_{11} is related to the KB coefficients G_{ij} by⁴⁰

$$\Gamma_{11} = 1 - x_1 \frac{c_2(G_{11} + G_{22} - 2G_{12})}{x_1 c_2(G_{11} + G_{22} - 2G_{12})} \quad (14)$$

In ternary systems, the elements of thermodynamic factor $[\Gamma]$ are related to the KB coefficients G_{ij} by^{41,44}

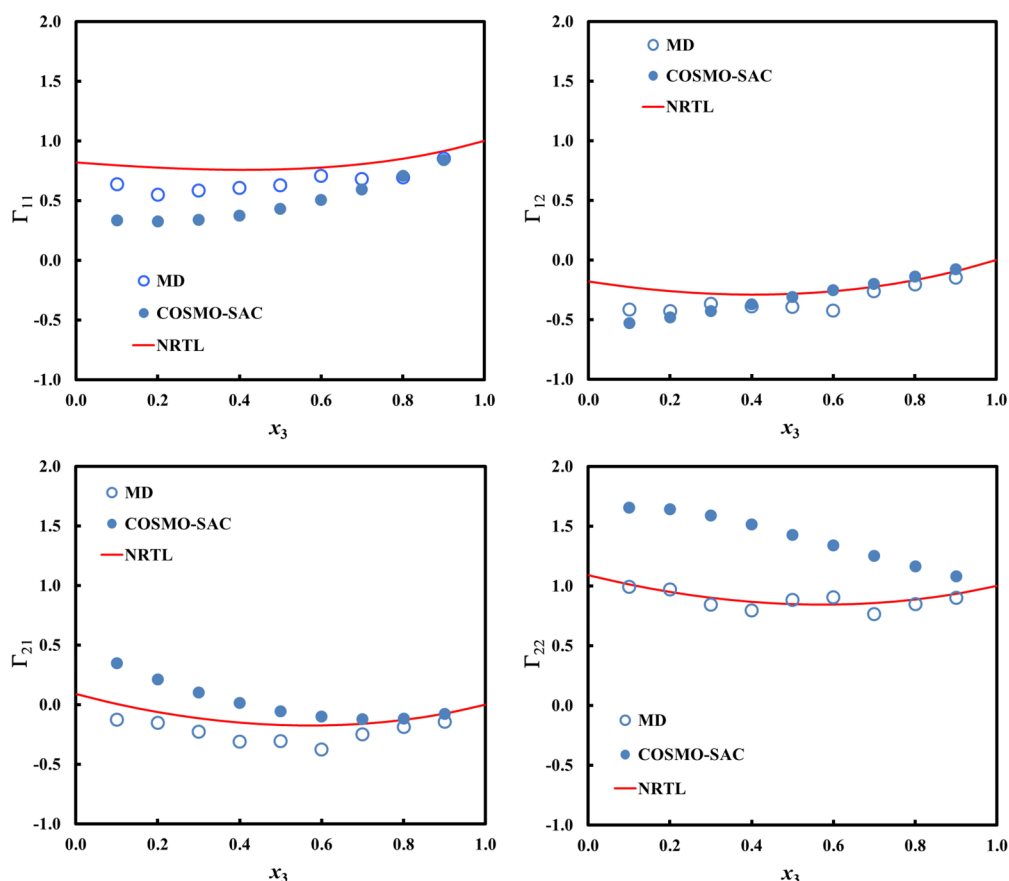


Figure 10. Thermodynamic factor Γ_{ij} in the ternary system chloroform (1)–acetone (2)–methanol (3) at 1 atm. Open circles are the computed values of Γ_{ij} using MD simulations at 298 K. Filled circles are the computed values of Γ_{ij} using COSMO-SAC at 298 K. Solid lines represent Γ_{ij} calculated from the NRTL model fitted to experimental VLE data at 303 K of ref 61. x_3 is varied while keeping $x_1 = x_2$.

$$\Gamma_{11} = -\frac{1}{\eta}[-c_2c_3G_{22} - c_2 + 2c_2c_3G_{23} - c_2c_3G_{33} - c_3 + c_1(c_2G_{12} - c_2G_{22} - 1 + c_2G_{23} - c_2G_{13})] \quad (15)$$

$$\Gamma_{12} = -\frac{c_1}{\eta}(c_2G_{12} + c_3G_{12} - c_2G_{13} - c_3G_{13} - c_2G_{22} + c_2G_{23} - c_3G_{23} + c_3G_{33}) \quad (16)$$

$$\Gamma_{21} = \frac{c_2}{\eta}(c_1G_{11} - c_1G_{12} - c_3G_{12} - c_1G_{13} + c_3G_{13} + c_1G_{23} + c_3G_{23} - c_3G_{33}) \quad (17)$$

$$\Gamma_{22} = \frac{1}{\eta}(c_1c_3G_{11} + c_1 - 2c_1c_3G_{13} + c_1c_3G_{33} + c_3 + c_2(c_1G_{11} - c_1G_{12} - c_1G_{13} + 1 + c_1G_{23})) \quad (18)$$

in which

$$\eta = c_1 + c_2 + c_3 + c_1c_2\Delta_{12} + c_2c_3\Delta_{23} + c_1c_3\Delta_{13} - \frac{1}{4}c_1c_2c_3(\Delta_{12}^2 + \Delta_{23}^2 + \Delta_{13}^2 - 2\Delta_{13}\Delta_{23} - 2\Delta_{12}\Delta_{13} - 2\Delta_{12}\Delta_{23}) \quad (19)$$

and

$$\Delta_{ij} = G_{ii} + G_{jj} - 2G_{ij} \quad (20)$$

The KB coefficients allow the computation of the thermodynamic factor from MD simulations and thus avoid the insertion and deletion of particles as needed in simulations in the grand-canonical ensemble. It is important to consider the convergence of the integrals in eq 13. For infinitely large systems, $g_{ij}(r) \rightarrow 1$ for $r \rightarrow \infty$. For finite systems with periodic boundary conditions, however, $g_{ij}(r)$ does not converge to 1 for $r \rightarrow \infty$ resulting in a divergence of G_{ij} .⁴¹ Recently, several studies showed that the obtained value of G_{ij} using eq 13 depends on the system size.^{32,45} In the Supporting Information, we show that the integrals of the radial distribution function over volume strongly vary with system size for a binary Weeks–Chandler–Andersen (WCA) fluid and for a binary system of acetone–methanol. To improve the convergence of G_{ij} , a natural choice is to make the system larger and to use longer simulations. However, this is computationally inefficient and thus seriously hinders the direct estimation of KB coefficients from simulations. Recently, some effort has been made in computing the KB coefficients using different methods. Wedberg et al. accounted for finite size effects in simulations by introducing tail corrections to the correlation functions based on integral equation theory.⁴⁶ These corrections are based on the hypernetted chain closure which is accurate at high densities. This method requires the optimization of two parameters, the joining radius and the tail approximation. Nichols et al. discussed the effects of truncation of the KB integrals.⁴⁷ In addition, a method for estimating the KB integrals using the Fourier transformed atomic positions is described by these authors. This method is shown to account for the corners

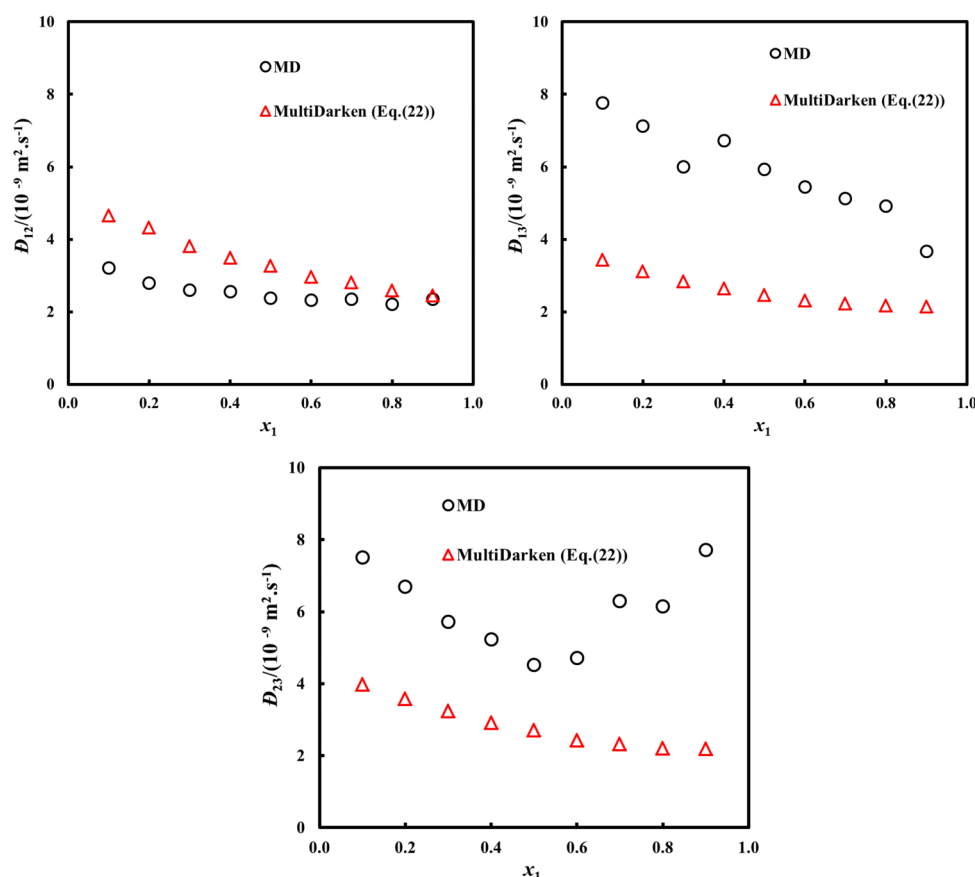


Figure 11. Comparison of the computed MS diffusivities \bar{D}_{ij} and the predicted MS diffusivities \bar{D}_{ij} in the ternary system chloroform (1)–acetone (2)–methanol (3) at 298 K, 1 atm. x_1 varies while keeping $x_2 = x_3$. Circles are the computed \bar{D}_{ij} using MD simulations. Triangles are the predicted \bar{D}_{ij} using multicomponent Darken equation (eq 22). The computed self-diffusivities from MD simulations are used to parametrize eq 22 and listed in Table S2 of the Supporting Information.

of the simulation box and is less sensitive to cutoff effects than the traditional method of eq 13. An empirical method for extrapolating the partial volume, compressibility, and activity coefficients for binary mixtures through the use of seven parameters was also presented. Mukherji et al. obtained the KB coefficients by coupling a small all-atom region to a very large coarse-grained reservoir. Exchanging molecules between the small system and the reservoir is allowed via a hybrid region. The difficulties of this approach are that the system should be very large and the thermodynamic force which ensures the thermodynamic equilibrium over the whole system should be calculated for each concentration.⁴⁵ The simplest and in the past frequently used approach is to simply use a switching function to force the radial distribution function $g(r)$ to converge to 1 for large distance r . However, it turns out that the final result depends on the choice of the switching function.^{45,48}

Recently, we found that the average particle fluctuations in eq 12 can also be calculated by considering a large system in which smaller subvolumes are embedded. These subvolumes can exchange particles and energy with the simulation box and therefore a subvolume can be considered as a system in the grand-canonical ensemble. However, corrections should be taken due to the finite size effect originating from the boundaries of the subvolumes:^{32,35,49}

$$G_{ij}(L) = G_{ij}^{\infty} + \frac{(\text{constant})}{L} \quad (21)$$

In this equation, L is the linear length of subvolume in one dimension. The KB coefficient in the thermodynamic limit (G_{ij}^{∞}) can thus be

obtained by simple extrapolation to $L \rightarrow \infty$. This approach allows for the use of much smaller systems. More details concerning this method can be found in the Supporting Information of this work.

2.3. Obtaining Thermodynamic Factors from COSMO-SAC. An alternative method to predict the thermodynamic factors for a mixture is through a model for the activity coefficients γ_i .⁵⁰ The COSMO-SAC theory is a quantum-mechanically based predictive model for the activity coefficients.^{51,52} In brief, the molecules are represented by a set of screening charge densities known as their σ -profiles. These profiles are generated by placing each molecule in a conducting or dielectric cavity and compute a charge distribution using density functional theory (DFT) which completely screens the molecular charge distribution from the outside. The resulting σ -profiles represent “fingerprints” of each of the molecules which can be used to model a solution by mixing them in their appropriate mole fractions. Since COSMO-SAC is an activity coefficient model, the dispersion is assumed to cancel in the reference fluid. The outcome of this modeling is the activity coefficients of each species as a function of their concentration. The thermodynamic factors Γ_{ij} then follow from numerical differentiation using eqs 6 and 7. This predictive excess Gibbs energy model is used as a benchmark and reference in this work.

3. SIMULATION DETAILS

In the ternary mixture chloroform–acetone–methanol, the OPLS force field was used for acetone and methanol.^{53,54} A nonpolarizable five-site model for chloroform was used.⁵⁵ All components are treated as rigid molecules. The LJ potentials

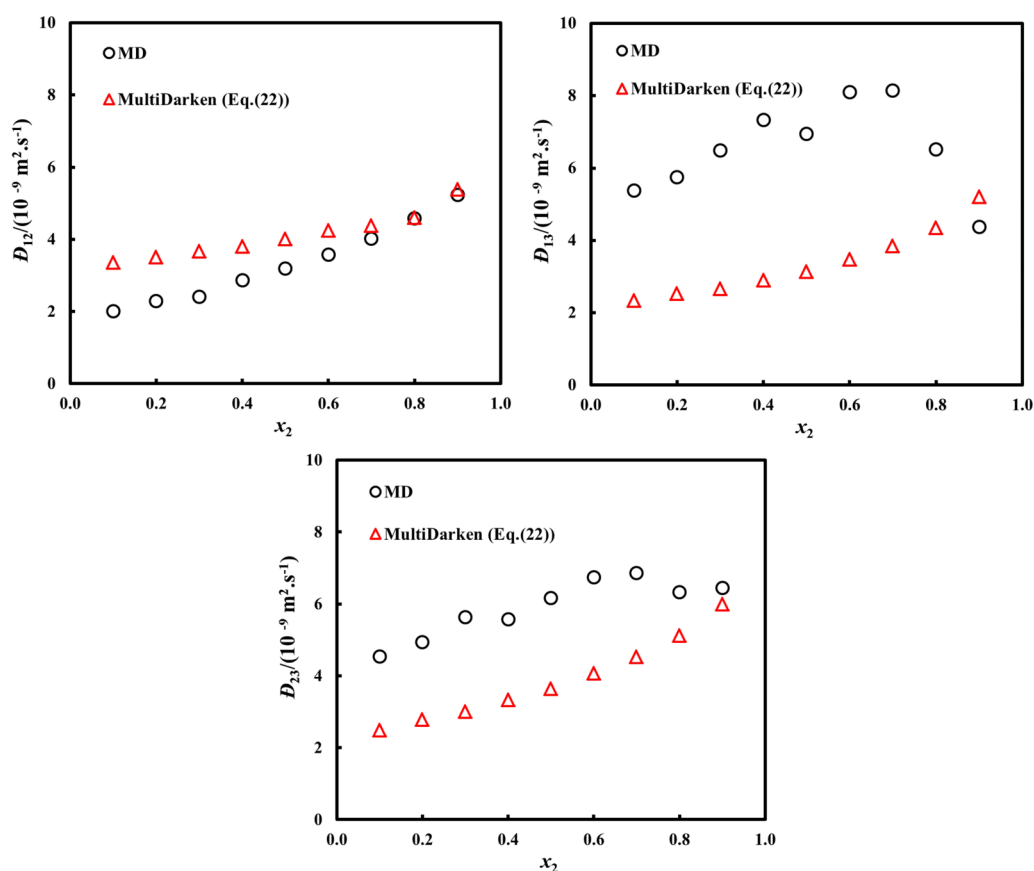


Figure 12. Comparison of the computed MS diffusivities \bar{D}_{ij} and the predicted MS diffusivities \bar{D}_{ij} in the ternary system chloroform (1)–acetone (2)–methanol (3) at 298 K, 1 atm. x_2 varies while keeping $x_1 = x_3$. Circles are the computed \bar{D}_{ij} using MD simulations. Triangles are the predicted \bar{D}_{ij} using multicomponent Darken equation (eq 22). The computed self-diffusivities from MD simulations are used to parametrize eq 22 and listed in Table S2 of the Supporting Information.

describe the intermolecular nonbonded interactions which are truncated and shifted at 10 Å. The Lorentz–Berthelot mixing rules are applied to obtain the LJ interaction between unlike atoms.³⁷ Electrostatic interactions are handled by Ewald summation using a relative precision⁵⁶ of 10^{-5} . The force field parameters as well as the parameters defining the geometries of the molecules can be found in the Supporting Information of this work. Three dimensional periodic boundary conditions consistent with a cubic box were applied to obtain properties corresponding to bulk systems. MD simulations were carried out at a temperature of 298 K and a pressure of 1 atm. Systems were first equilibrated in an NpT ensemble with a Nosé–Hoover thermostat and barostat using the time constants of 0.1 and 1 ps, respectively. The equations of motion were integrated using the leapfrog Verlet algorithm with a time step of 1 fs. The MS diffusion coefficients are obtained from equilibrium MD simulations in the NVT ensemble using the Nosé–Hoover thermostat at a density corresponding to a pressure of 1 atm.³⁶ The box sizes were typically around $(28 \text{ Å})^3$ resulting in a total number of molecules of the order of 200. The simulations for extracting diffusion coefficients were run for at least 100 ns to obtain MS diffusivities with an accuracy of around 5%. KB coefficients required for the calculation of thermodynamic factors were obtained from MD simulations in the NpT ensemble. Temperature and pressure were controlled using the Nosé–Hoover thermostat and barostat, respectively. In these simulations, the box size needs to be larger, see also section 2.2. The box size was typically fluctuating around $(85 \text{ Å})^3$. The maximum number of

molecules used in these simulations was typically 7000. Simulation runs of at least 5 ns were needed to obtain accurate values of the thermodynamic factors. The error bars of the computed thermodynamic factors are less than 3%.

The COSMO-SAC computations were performed with the 2011.03 release ADF Theoretical Chemistry software.⁵⁷ The COSMO surfaces were calculated using BP functionals and the TZP bases.⁵⁷ The standard values of the parameters for the model were used in all calculations.⁵² To obtain accurate numerical derivatives, calculations for the logarithmic activities of each mixture were performed at mole fraction intervals of at most 0.05 in each component. The unconstrained derivatives from eq 7 were then calculated in MATLAB directly from these activities using a central differencing scheme. In the case of the ternary system, the derivatives were computed using a barycentric coordinate system. The constrained derivatives were then computed using eq 6.

4. RESULT AND DISCUSSION

To study the diffusion in the ternary mixture chloroform–acetone–methanol, three binary mixtures are relevant: chloroform–acetone, chloroform–methanol, and acetone–methanol. As ternary experimental data of diffusion coefficients are lacking for the ternary system chloroform–methanol–acetone, we validated our method in the relevant binary mixtures and predicted the ternary diffusion coefficients assuming that the quality of our method in ternary mixtures is similar to that of binary systems. The binary system acetone–methanol has been studied in our previous

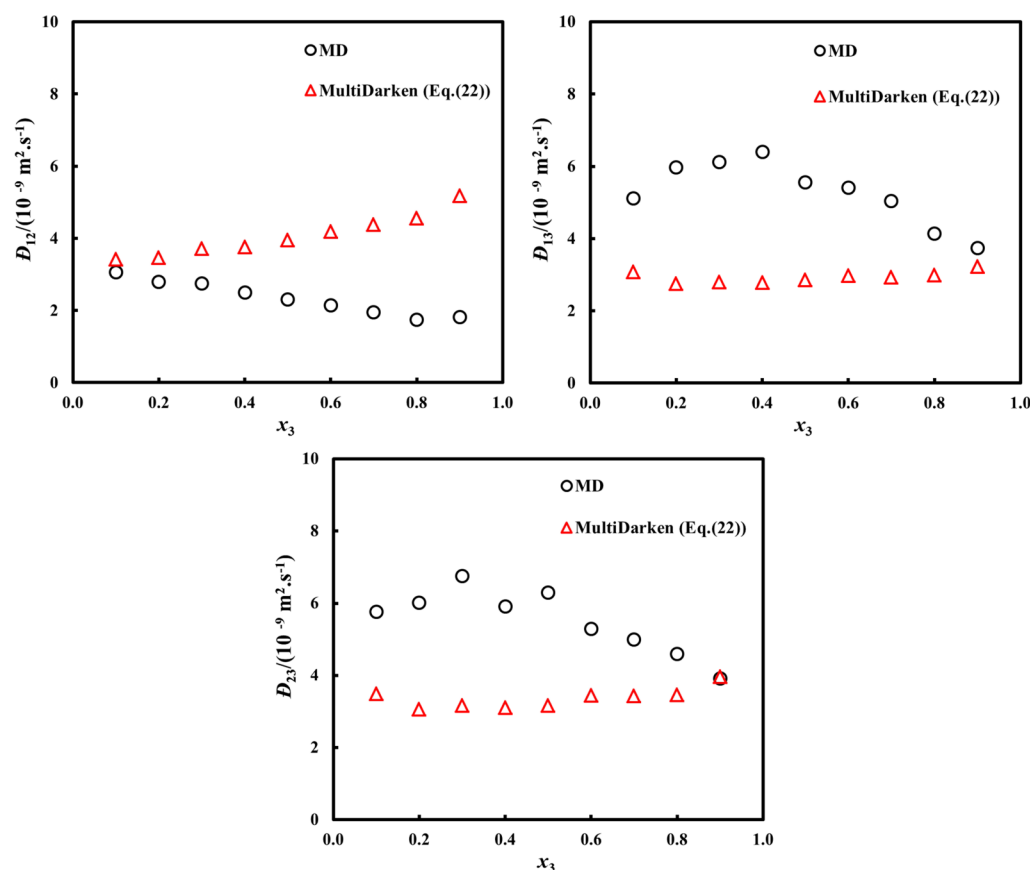


Figure 13. Comparison of the computed MS diffusivities D_{ij} and the predicted MS diffusivities D_{ij} in the ternary system chloroform (1)–acetone (2)–methanol (3) at 298 K, 1 atm. x_3 varies while keeping $x_1 = x_2$. Circles are the computed D_{ij} using MD simulations. Triangles are the predicted D_{ij} using multicomponent Darken equation eq 22. The computed self-diffusivities from MD simulations are used to parametrize (eq 22) and listed in Table S2 of the Supporting Information.

work.^{33,34} The computed Fick diffusivity D_{11} and thermodynamic factor Γ_{11} quantitatively agree with the experiments.^{33,34}

4.1. Chloroform–Acetone. Karr et al. measured the densities of chloroform–acetone mixtures at 298 K, 1 atm.⁵⁸ In Figure 1, the computed densities using MD simulations are compared to the experiments as a function of the composition. The computed mixture densities show a slightly stronger dependence on mixture composition suggesting a lower density of pure acetone and a higher density of pure chloroform. This is also shown in Table 1 in which computed pure-component densities are compared to the experimental ones.

Figure 2 shows the thermodynamic factor Γ_{11} obtained from experiments and MD simulation in the binary mixture chloroform–acetone for various compositions. In ref 59, the vapor–liquid equilibrium (VLE) data are provided from which the activity coefficients γ_i can be calculated. By fitting these activity coefficients γ_i using an excess Gibbs energy model, i.e. the NRTL model, the thermodynamic factor Γ_{11} was obtained. Compared to the experiment, Γ_{11} obtained from COSMO-SAC shows good agreement. The computed Γ_{11} using MD simulations is somewhat lower.

Using the computed MS diffusivity D_{12} and the thermodynamic factor Γ_{11} from MD simulations, we calculate the Fick diffusivity D_{11} as a function of composition, see Figure 3. A good agreement of Fick diffusivity D_{11} between experiments and MD simulations is seen. The very good agreement is partially due to error cancellation: the computed value of Γ_{11} is lower than in experiments implying larger values of the computed MS dif-

fusivity D_{12} . This is reasonable since the computed mixture densities are lower than in the experiments and larger values of diffusion coefficients are thus expected.

4.2. Chloroform–Methanol. In the binary mixture chloroform–methanol, the computed mixture densities agree very well with the experiments;⁶⁰ see Figure 4. Figure 5 shows thermodynamic factor Γ_{11} as a function of composition for the same binary mixture. COSMO-SAC accurately predicts Γ_{11} when the concentration of chloroform is low. As the concentration of chloroform increases, Γ_{11} computed using MD simulations is closer to the experimental data.⁵⁹ Figure 6 shows the computed MS diffusivity D_{12} and Fick diffusivity D_{11} from MD simulations. The Fick diffusivity D_{11} is calculated using the computed MS diffusivity D_{12} and the thermodynamic factor Γ_{11} . We observe that the MS diffusivity D_{12} increases as the concentration of chloroform increases. However, the increasing chloroform concentration drives the mixture away from ideal mixing behavior resulting in a reduced concentration dependence of Fick diffusivity D_{11} . The Fick diffusivity D_{11} has a minimum value around a concentration of $x_1 = 0.7$, while the MS diffusivity D_{12} displays a maximum in the same concentration range. The MS diffusivity D_{12} ranges from 3×10^{-9} to $6 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ and the Fick diffusivity D_{11} ranges from 1.5×10^{-9} to $2.5 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$.

4.3. Chloroform–Acetone–Methanol. Figure 7 shows the computed densities in chloroform–acetone–methanol mixtures at 298 K, 1 atm. We observe a linear relation between mixture densities and composition. Figure 8–10 show the thermodynamic factors Γ_{ij} in the ternary mixtures as a function of the

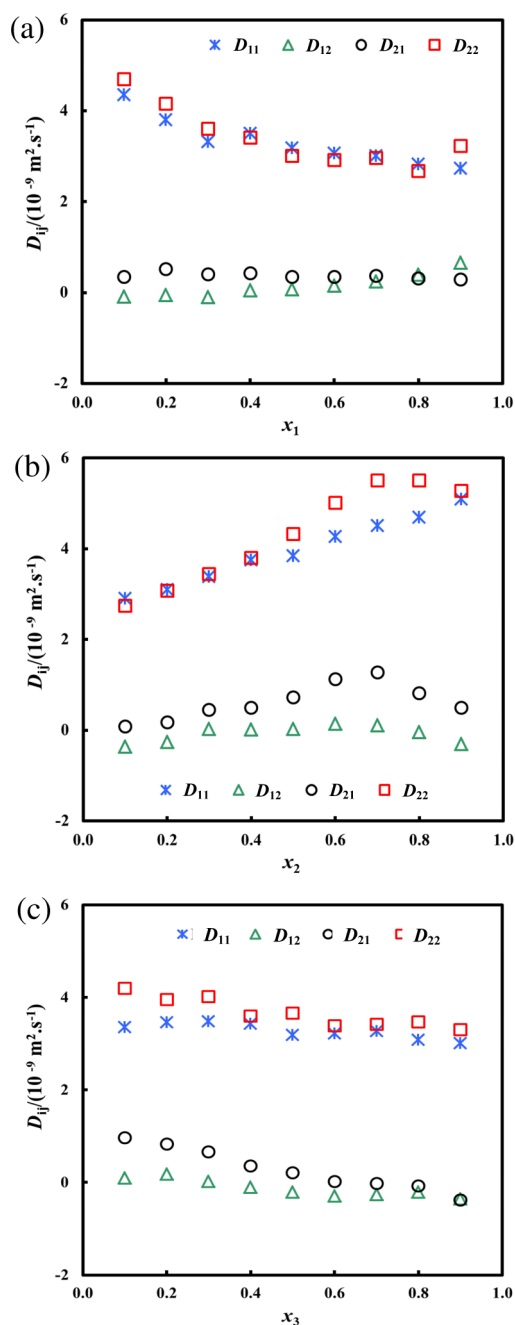


Figure 14. Fick diffusivities D_{ij} in the ternary system chloroform (1)–acetone (2)–methanol (3) at 298 K, 1 atm. Fick diffusivities D_{ij} are calculated using the computed MS diffusivities \bar{D}_{ij} and thermodynamic factors Γ_{ij} : (a) x_1 varies while keeping $x_2 = x_3$; (b) x_2 varies while keeping $x_1 = x_3$; (c) x_3 varies while keeping $x_1 = x_2$.

composition. Data are reported for Γ_{ij} as a function of x_i while keeping $x_j = x_k$ (with $i \neq j \neq k$). Oracz et al. measured the vapor–liquid equilibrium for this ternary mixtures at 303 K.⁶¹ This VLE data were converted to the matrix of thermodynamic factors Γ_{ij} using the NRTL model.^{1,18} The ternary VLE data are very well described by the NRTL model. The computed Γ_{ij} using MD simulation show quantitative agreement with the experimental data and the results from COSMO-SAC deviate from the experiments. We feel that the agreement is very good considering the fact that simple molecular interaction models were used in the MD simulations, i.e. polarization effects are not accounted for.

MS diffusivities \bar{D}_{ij} can not be measured directly in experiments. However, it is possible to predict MS diffusivities \bar{D}_{ij} using easily obtained self-diffusivities $D_{i,\text{self}}$. For this purpose, we have proposed a multicomponent Darken model.¹¹ In this model, we neglect the velocity cross-correlations between unlike molecules.¹¹ The resulting multicomponent Darken equation is

$$\bar{D}_{ij} = D_{i,\text{self}} D_{j,\text{self}} \sum_{i=1}^n \frac{x_i}{D_{i,\text{self}}} \quad (22)$$

in which $D_{i,\text{self}}$ is the self-diffusivity of component i in the mixtures. The computed self-diffusivities $D_{i,\text{self}}$ in the ternary system chloroform–acetone–methanol can be found in the Supporting Information of this work. The multicomponent Darken equation has been shown to allow for the most robust and accurate prediction of diffusion coefficients in ideal diffusing mixtures where the neglect of velocity cross-correlations is justified.^{10,11} Figures 11–13 show the computed MS diffusivities \bar{D}_{ij} and the predicted MS diffusivities \hat{D}_{ij} . From these figures, it can be seen that the concentration dependence of MS diffusivities \bar{D}_{ij} is not well captured by the multicomponent Darken equation. The MS diffusivities are either underestimated or overestimated by the multicomponent Darken equation suggesting that the correlations of different molecules are important in the chloroform–acetone–methanol system. The deviation of the predicted \hat{D}_{ij} using the multicomponent Darken equation from the computed \bar{D}_{ij} was already observed for the binary mixtures acetone–methanol and acetone–tetrachloromethane.^{33,34} The comparison to the multicomponent Darken equation demonstrates the potential of molecular simulations for the prediction of multicomponent Fick diffusion coefficients as the molecular models also allow the prediction of nonideal systems.

Figure 14 shows the computed Fick diffusivities D_{ij} using the computed MS diffusivities \bar{D}_{ij} and thermodynamic factors Γ_{ij} as a function of composition. It can be observed that: (1) the diagonal Fick diffusivities are always positive and the off-diagonal Fick diffusivities may be negative; (2) the diagonal Fick diffusivities are about 1 order of magnitude larger than the off-diagonal Fick diffusivities suggesting the diffusion flux of component i mainly depends on its own concentration gradient while the concentration gradients of other components play a minor role. This behavior is in accordance with the bound placed on off-diagonal coefficients by the entropy production for ternary diffusion.⁴ It is important to note that the values of $[\Gamma]$ and $[D]$ depend on the labeling of the components. This problem does not apply for MS diffusivities. The computed ternary Fick diffusivities can be considered as true predictions as they directly originate from the force field.

5. CONCLUSION

In this work, we present a consistent method for computing ternary Fick diffusivities from equilibrium MD simulations. For this purpose, MS diffusivities and thermodynamic factors are computed to calculate the matrix of Fick diffusivities. Our approach is applied to a ternary mixture chloroform–acetone–methanol. Even though a simple molecular model is used, the computed thermodynamic factors $[\Gamma]$ are in close agreement with experiments. This findings suggests that the fluctuation method is well-suited for computing thermodynamic properties of mixtures in general since the framework relies on the Kirkwood–Buff coefficients which become now accessible in practical computations. Validation data for diffusion is only

available for two binary subsystems. Here, MD results and experiments do agree well. Therefore, we expect that the computed Fick diffusivities should also be comparable with experiments. The presented approach allows for an efficient and consistent prediction of multicomponent Fick diffusion coefficients from molecular models.

■ ASSOCIATED CONTENT

■ Supporting Information

We provide (1) the force field parameters as well as the parameters defining the geometries of the molecules simulated in this work; (2) the integrals of radial distribution functions over volume as a function of the system size; (3) details concerning the fluctuation method to compute KB coefficients; (4) the self-diffusivities in the ternary mixture chloroform–acetone–methanol at 298 K, 1 atm; (5) computed Kirkwood–Buff coefficients as a function of the cutoff radius used in the simulation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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