Generalized Form for Finite-Size Corrections in Mutual Diffusion Coefficients of Multicomponent Mixtures Obtained from Equilibrium Molecular Dynamics Simulation

Seyed Hossein Jamali, André Bardow, Thijs J. H. Vlugt, and Othonas A. Moultos*

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ABSTRACT: The system-size dependence of computed mutual diffusion coefficients of multicomponent mixtures is investigated, and a generalized correction term is derived. The generalized finite-size correction term was validated for the ternary molecular mixture chloroform/acetone/methanol as well as 28 ternary LJ systems. It is shown that only the diagonal elements of the Fick matrix show system-size dependency. The finite-size effects of these elements can be corrected by adding the term derived by Yeh and Hummer (*J. Phys. Chem. B* **2004**, *108*, 15873–15879). By performing an eigenvalue analysis of the finite-size effects of the matrix of Fick diffusivities we show that the eigenvector matrix of Fick diffusivities does not depend on the size of the simulation box. Only eigenvalues, which describe the speed of diffusion, depend on the size of the system. An analytic relation for finite-size effects of the matrix of Maxwell–Stefan diffusivities was developed. All Maxwell–Stefan diffusivities depend on the system size, and the required correction depends on the matrix of thermodynamic factors.
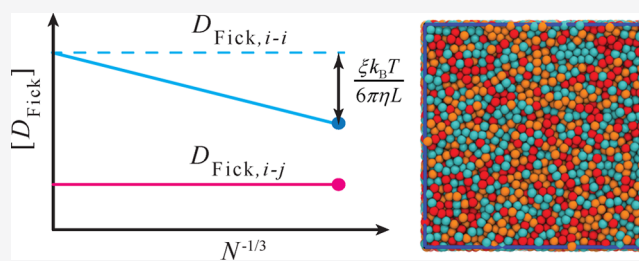
1. INTRODUCTION

The past few decades, Equilibrium Molecular Dynamics (EMD) simulation has emerged as a powerful tool for computing diffusion coefficients of pure components and multicomponent mixtures.[1−18] Typically, system sizes in the order of hundreds to a few thousands molecules are used, combined with periodic boundary conditions.[19,20] As shown in the pioneering work by Dünweg and Kremer almost 30 years ago,[21] the choice of the system size strongly affects computed self-diffusivities, which scale linearly with the inverse of the simulation box size. In early 2000s, Yeh and Hummer[22] (YH) derived an analytic hydrodynamic correction which should be added to self-diffusivities computed from EMD, to obtain diffusivities at the thermodynamic limit, i.e., the quantity measured in experiments. The practically more relevant mass transport due to concentration gradients depends on mutual diffusion coefficients (i.e., Fick and Maxwell–Stefan).[23−25] Very recently, Jamali et al.[26] proposed an empirical correction that should be applied to computed Maxwell–Stefan (MS) diffusivities in binary mixtures. To the best of our knowledge, it is still unknown if and how finite-size corrections should be applied to mutual diffusivities in multicomponent systems. In this study, we show that such corrections should indeed be applied, and we derive a general correction term for mutual diffusion coefficients of multicomponent mixtures computed from EMD. In this way, multicomponent diffusivities can be computed in a reliable way, allowing for quantitative comparison with experiments. The derivation of the new

generalized correction presented in the present study proves the validity of the empirical correction term proposed by Jamali et al.[26] for binary mixtures and provides fundamental understanding of the underlying mechanisms of system size effects in multicomponent mutual diffusion.

The manuscript is organized as follows: Some essential theoretical definitions are provided in the following paragraphs. The generalized correction term for the mutual diffusivities in multicomponent mixtures is derived in the Results and Discussion section, where also the verification of the new correction is shown for 28 ternary Lennard-Jones (LJ) mixtures and for a ternary molecular mixture. In the Conclusions section, the main findings of this study are summarized.

2. BACKGROUND: MUTUAL DIFFUSIVITY AND FINITE-SIZE EFFECTS

Fick (mutual) diffusion coefficients are commonly used to describe transport diffusion in a mixture.[23,24,27] According to Fick's law, the molar flux (J_i) of species i in an n-component

mixture is proportional to the concentration gradients of $(n - 1)$ constituent species (c_j):[23,28]

$$J_i = -\sum_{j=1}^{n-1} D_{ij} \nabla c_j \tag{1}$$

in which D_{ij} denotes Fick diffusion coefficients. For an n-component mixture, the matrix of Fick diffusivities consists of $(n - 1)^2$ elements. The empirical nature of Fick's law has been overcome by the MS formulation of diffusion, according to which the driving force for diffusion is the gradient in chemical potential (μ_i), which is in balance with frictional forces:[23,24,28,29]

$$-\frac{x_i}{RT} \nabla \mu_i = \sum_{j=1;j\neq i}^{n} \frac{x_j J_i - x_i J_j}{c_t Đ_{ij}} \tag{2}$$

where x_i is the mole fraction of species i, c_t is the total concentration, R is the universal gas constant, and T is the temperature of the system. The friction force is due to the difference in the fluxes (velocities) of species i and j, (i.e, $x_j J_i - x_i J_j$). The inverse of the MS diffusion coefficient (i.e., $\frac{1}{Đ_{ij}}$) can be considered as a friction coefficient. For an n-component mixture, $n \cdot (n - 1)/2$ diffusion coefficients are defined. In a homogeneous mixture, D_{ij} and $Đ_{ij}$ describe the same physical phenomenon. These diffusivities are related via the so-called matrix of thermodynamic factors, $[\Gamma]$:[23,24,28]

$$[D_{\text{Fick}}] = [\Delta][\Gamma] \tag{3}$$

where $[D_{\text{Fick}}]$ is the matrix of Fick diffusivities. $[\Delta]$ is the symmetric phenomenological diffusion coefficient matrix which is related to MS diffusivities according to[11,28–30]

$$[B] = [\Delta]^{-1} \tag{4}$$

$$B_{ii} = \frac{x_i}{Đ_{in}} + \sum_{k=1,k\neq i}^{n} \frac{x_k}{Đ_{ik}} \tag{5}$$

$$B_{ij} = -x_i \left(\frac{1}{Đ_{ij}} - \frac{1}{Đ_{in}} \right) \tag{6}$$

where i and j take values from 1 to $n - 1$ and $i \neq j$. $[\Gamma]$ is an asymmetric matrix, whose elements can be computed from[28,31–33]

$$\Gamma_{ij} = \delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j}\bigg|_{T,p,\Sigma} \tag{7}$$

where δ_{ij} is the Kronecker delta and the subscript "T,p,Σ" denotes constant temperature, pressure, and mole fractions of all species, except for the nth species.[28,29,33] More information about the computation of $[\Delta]$ and $[\Gamma]$ from EMD simulations can be found in the literature.[28–30,34–38]

The Brownian motion of molecules in a pure or a multicomponent fluid mixture can be described by the self- (or tracer) diffusivity.[39] In EMD, self-diffusivities are computed from ensemble averages of mean-squared displacements of individual molecules.[28,40] According to the studies of Dünweg and Kremer,[21] and Yeh and Hummer,[22] computed self-diffusivities from EMD $(D_{i,\text{self}}^{\text{MD}})$ scale linearly with the inverse of the simulation box length (L). Based on hydrodynamic arguments, these authors derived an analytic

correction (hereafter referred to as the YH correction, D^{YH}) for the self-diffusivity, $D_{i,\text{self}}$, of species i:

$$D_{i,\text{self}}^{\infty} = D_{i,\text{self}}^{\text{MD}} + D^{\text{YH}}(T, \eta, L) = D_{i,\text{self}}^{\text{MD}} + \frac{\xi k_B T}{6\pi\eta L} \tag{8}$$

in which k_B is the Boltzmann constant, η is the shear viscosity of the system computed from EMD, and $D_{i,\text{self}}^{\infty}$ is the self-diffusivity in the thermodynamic limit. η computed in EMD does not show finite-size effects.[22,26,41] ξ is a constant which depends on the shape of the simulation box[42–45] (for a cubic simulation box,[22] $\xi = 2.837297$). The validity of eq 8 has been extensively verified for various conditions and types of molecules.[22,26,41,46] Moultos et al.[41] showed that the YH correction holds for nonspherical molecules when a minimum number of 250 molecules is used in the simulation. In a recent study,[46] we showed that the YH finite-size correction also holds for self-diffusivities of mixtures. This finding allowed us to develop a method to compute the shear viscosity of a mixture from the computed self-diffusivities of its constituent components.[46]

In our previous work,[26] finite-size effects of binary mutual diffusivities were studied. For a binary mixture, the matrix form of eq 3 reduces to an algebraic equation as there is a single D_{Fick}, $Đ_{\text{MS}}$, and Γ. By performing simulations for more than 200 distinct Lennard-Jones and 9 molecular systems, we derived the following phenomenological correction for the computed (i.e., finite-size) MS diffusivity, $Đ_{\text{MS}}^{\text{MD}}$:[26]

$$Đ_{\text{MS}}^{\infty} = Đ_{\text{MS}}^{\text{MD}} + \left(\frac{1}{\Gamma} \right) D^{\text{YH}} \tag{9}$$

By combining eq 9 and eq 3 for a binary mixture, it can be shown that finite-size effects of the binary Fick diffusion coefficient require the same correction as self-diffusivities:

$$D_{\text{Fick}}^{\infty} - D_{\text{Fick}}^{\text{MD}} = \Gamma Đ_{\text{MS}}^{\infty} - \Gamma Đ_{\text{MS}}^{\text{MD}} = \Gamma(Đ_{\text{MS}}^{\infty} - Đ_{\text{MS}}^{\text{MD}})$$
$$= \Gamma\left(\frac{1}{\Gamma} D^{\text{YH}} \right) = D^{\text{YH}} \tag{10}$$

3. SIMULATION DETAILS

The open-source software package LAMMPS[47] (version 16, Feb. 2016) was used to perform MD simulations for two sets of simulations: ternary Lennard-Jones (LJ) systems and a ternary molecular mixture. To compute transport properties and thermodynamic factors of these systems, the OCTP plugin was used.[48] The scheme used for computing Maxwell–Stefan (MS) diffusivities from Onsager coefficients and thermodynamic factors from Kirkwood–Buff coefficients is described in detail in the main text and Supporting Information of our published papers.[26,28,48,49]

3.1. Molecular Mixture. MD simulations were performed for a ternary mixture of (1) chloroform, (2) acetone, and (3) methanol at 298 K and 1 atm, corresponding to a density of 1025 kg/m³. The mole fractions of these components in the mixtures are 0.3, 0.3, and 0.4, respectively. Similar to the work of Liu et al.,[38] force field parameters for methanol,[50] acetone,[51] and chloroform[52] are obtained from literature. Schematic representations of these molecules are shown in Figure S1 in the Supporting Information, and force field parameters are listed in Table S2 in the Supporting Information. All molecules are considered rigid. The bond lengths and angles are listed in Table S3 in the Supporting Information. LJ interactions are
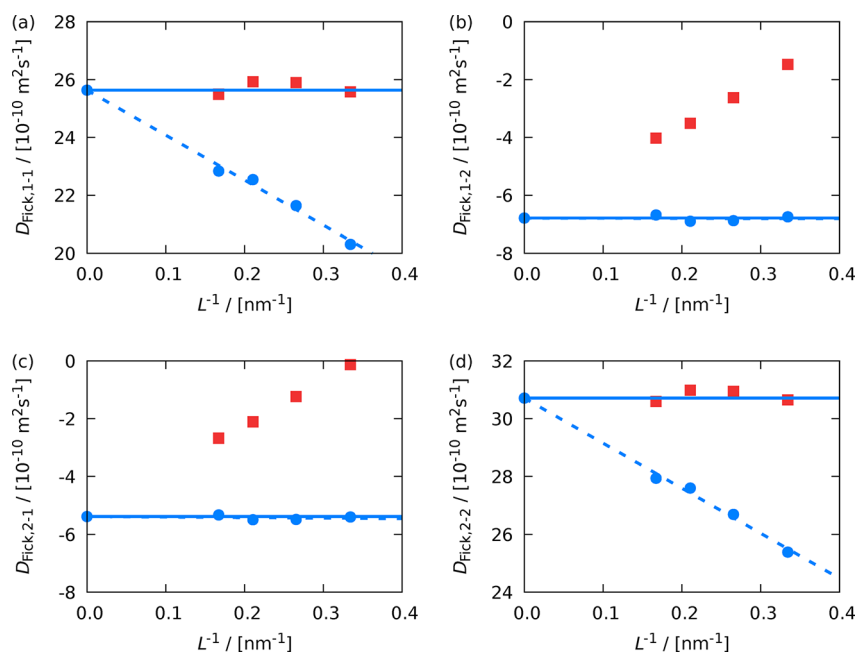
Figure 1. Computed elements of the Fick diffusivity matrix for the ternary mixture of (1) chloroform, (2) acetone, and (3) methanol ($x_{chloroform} = x_{acetone} = 0.3$) as a function of the inverse simulation box length L: (a) Diagonal element $D_{Fick1-1}$, (b) off-diagonal element $D_{Fick1-2}$, (c) off-diagonal element $D_{Fick2-1}$, and (d) diagonal element $D_{Fick2-2}$. Blue circles are the computed diffusion coefficients in MD simulations. Red squares are corrected diffusivities using the YH correction (eq 8). Dashed lines show extrapolation to the thermodynamic limit, and solid lines are the extrapolated values. All data related to Fick diffusion coefficient computations are provided in the Simulation Details section and in the Supporting Information.

truncated at a cutoff radius of 12 Å, and analytic tail corrections are included for the energy and pressure of the system.[20] Long-range electrostatic interactions are considered by using the particle–particle particle–mesh (PPPM) method with a relative precision of 10^{-6}.[20] Diffusion coefficients were computed for four system sizes of 250, 500, 1000, and 2000 molecules. Initial molecular configurations were constructed in PACKMOL,[53] and LAMMPS input files were generated in VMD.[54] A time step of 1 fs was used, and all simulations have a total length of 100 ns. A total of 100 independent simulations were performed to obtain low statistical uncertainties. Thermodynamic factors (Γ) for this system are obtained from the work of Liu et al.[38] Γ_{11}, Γ_{12}, Γ_{21}, and Γ_{22} are 0.61, −0.40, −0.31, and 0.79, respectively.

3.2. Lennard-Jones Systems. In this study, 28 distinct LJ ternary systems are considered. Properties are reported in reduced units, where the LJ energy (ϵ), size (σ), and mass (m) are equal to 1. To create asymmetric systems, the LJ energy parameter of each species is different ($\epsilon_1 = 1.0$, $\epsilon_2 = 0.8$, and $\epsilon_3 = 0.6$), while the sizes and masses for all particles are equal ($\sigma_1 = \sigma_2 = \sigma_3 = \sigma$ and $m_1 = m_2 = m_3 = m$). All 28 ternary LJ systems correspond to homogeneous mixtures away from demixing. Interactions between dissimilar LJ particles are calculated according to the Lorentz–Berthelot mixing rules with an adjustable parameter (k_{ij}) for the energy parameters:[20]

$$\epsilon_{ij} = (1 - k_{ij}) \sqrt{\epsilon_{ii} \cdot \epsilon_{jj}}$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{11}$$

The k_{ij} parameters for the 28 ternary systems are listed in Table S1 in the Supporting Information. LJ interactions are truncated at a cutoff radius of 4σ. Analytic tail corrections are considered for energy and pressure calculations.[20] The mole

fraction of species 1 is 0.4, and species 2 and 3 have mole fractions equal to 0.3. Simulations were performed at a reduced temperature of 0.65 and a reduced pressure of 0.05. The corresponding densities of these systems range from 0.78 to 0.89. Transport properties were computed in the micro-canonical (NVE) ensemble for four system sizes consisting of 500, 1000, 2000, and 4000 LJ particles. To achieve sufficient statistics, 100 independent simulations with different initial configurations were performed for each system. To calculate radial distribution functions (RDFs) and consequently thermodynamic factors, MD simulations were performed in the canonical (NVT) ensemble. The statistical uncertainties of thermodynamic factors were obtained by performing 5 independent simulations, each one consisting of 25000 LJ particles. A time step of 0.001 was used to integrate equations of motion by using the velocity Verlet algorithm.[20] The total simulation lengths for computing transport properties and RDFs are 100 and 10 million timesteps, respectively.

4. RESULTS AND DISCUSSION

4.1. Generalized Correction for the Finite-Size Effects in Fick Diffusivities. Equation 10 is used as the initial step for investigating finite-size effects in multicomponent mixtures. Fick diffusion coefficients were computed for 4 system sizes for the ternary mixture (1) chloroform/(2) acetone/(3) methanol. Simulation details can be found in the Supporting Information. The finite-size effects are shown in Figure 1 for all elements of the Fick diffusivity matrix. The extrapolation to the thermodynamic limit is performed by fitting a line to the 4 finite-size diffusivities. Figure 1 strongly suggests that the off-diagonal elements of the Fick diffusivity matrix do not show any system-size dependence. In sharp contrast, the diagonal elements depend on the size of the simulation box and experience a finite-size effect of the same magnitude as the YH
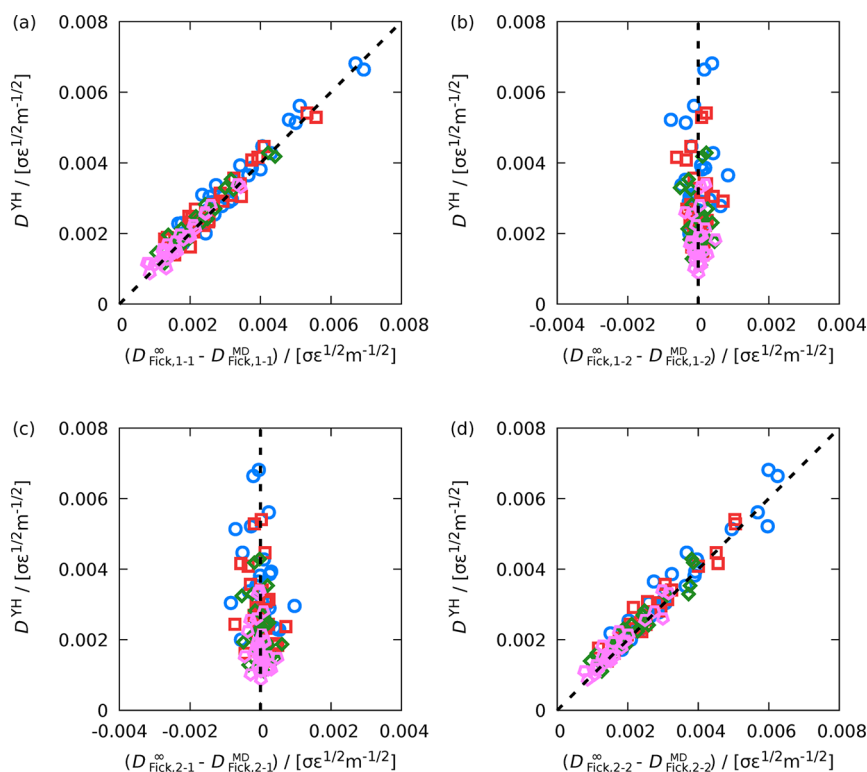
Figure 2. Finite-size corrections required for elements of the Fick diffusivity matrix (a) $D_{Fick,1-1}$, (b) $D_{Fick,1-2}$, (c) $D_{Fick,2-1}$, and $D_{Fick,2-2}$ as a function of the YH correction (D^{YH}, eq 8) for 28 LJ systems containing 500 particles (blue circles), 1000 particles (red squares), 2000 particles (green diamonds), and 4000 particles (magenta pentagons). Reduced temperature is 0.65 and reduced pressure 0.05. The diagonal dashed lines indicate perfect agreement between the YH correction and the required finite size corrections for Fick diffusivities. The vertical dashed lines indicate no finite-size effects of Fick diffusivities. Raw data are provided in the Supporting Information.

correction. Hence, we will hypothesize that the YH correction should be applied to the diagonal elements of the Fick diffusivity matrix, while no finite-size correction is needed for off-diagonal elements:

$$[D_{Fick}^{\infty}] = [D_{Fick}^{MD}] + D^{YH}[I] \tag{12}$$

where $[D_{Fick}^{MD}]$ and $[D_{Fick}^{\infty}]$ are the Fick diffusivity matrices for a finite-size simulation box and in the thermodynamic limit, respectively. $[I]$ is the identity matrix.

To examine the validity of this hypothesis, EMD simulations were performed to obtain the mutual diffusion coefficients of 28 different ternary LJ mixtures. For each mixture, 4 system sizes were simulated. All simulation details are provided in the Supporting Information. The differences between Fick diffusivities for the finite size and for the extrapolation to the thermodynamic limit are shown in Figure 2. Clearly, the results for the LJ and the molecular systems are in-line with our hypothesis (eq 12).

The system-size dependency of multicomponent Fick diffusivities can also be investigated using the eigenvalue $[\hat{D}_{Fick}]$ and modal $[P]$ matrices of the Fick diffusivity matrix $[D_{Fick}]$. $[\hat{D}_{Fick}]$ is a diagonal matrix containing all eigenvalues of the Fick diffusivity matrix, while $[P]$ consists of all eigenvectors.[23] By definition, the modal matrix $[P]$ has the property that[23]

$$[\hat{D}_{Fick}] = [P]^{-1}[D_{Fick}][P] \tag{13}$$

Eigenvalue and modal matrices are important for the linearized theory of multicomponent diffusion.[23,55,56] Importantly, the linearized theory of multicomponent diffusion allows trans-

forming the $(n-1)$ equations of motion to $(n-1)$ pseudobinary eigen-species representing $(n-1)$ hydrodynamic diffusion modes. The speed of these hydrodynamic diffusion modes is expressed by the eigenvalues of the Fick matrix. Thus, we expect that the hydrodynamic YH correction should affect the eigenvalues of the Fick matrix. Techniques like light dynamic light scattering (DLS), that can access hydrodynamic modes, determine the eigenvalues of the Fick matrix in multicomponent mixtures.[57,58]

By definition, the ith eigenvalue of the matrix of finite-size Fick diffusivities ($\hat{D}_{i,Fick}^{MD}$) is calculated from the following equation:

$$|[D_{Fick}^{MD}] - \hat{D}_{i,Fick}^{MD}[I]| = 0 \tag{14}$$

A similar equation can be written for the ith eigenvalue of Fick diffusivities in the thermodynamic limit ($\hat{D}_{i,Fick}^{\infty}$):

$$|[D_{Fick}^{\infty}] - \hat{D}_{i,Fick}^{\infty}[I]| = 0 \tag{15}$$

By combining eq 15 with eqs 12 and 14 we obtain

$$0 = |[D_{Fick}^{\infty}] - \hat{D}_{i,Fick}^{\infty}[I]| = |[D_{Fick}^{MD}] + D^{YH}[I] - \hat{D}_{i,Fick}^{\infty}[I]| \tag{16}$$

$$= |\hat{D}_{i,Fick}^{MD}[I] + D^{YH}[I] - \hat{D}_{i,Fick}^{\infty}[I]| \tag{17}$$

$$= |(\hat{D}_{i,Fick}^{MD} + D^{YH} - \hat{D}_{i,Fick}^{\infty})[I]| \tag{18}$$

The last equation holds only when the term in the parentheses equals zero. Hence, all eigenvalues of the Fick diffusivity matrix need a finite-size correction equal to D^{YH}. This means that the eigenvalue matrix of finite-size Fick diffusivities, $[\hat{D}_{Fick}^{MD}]$, whose
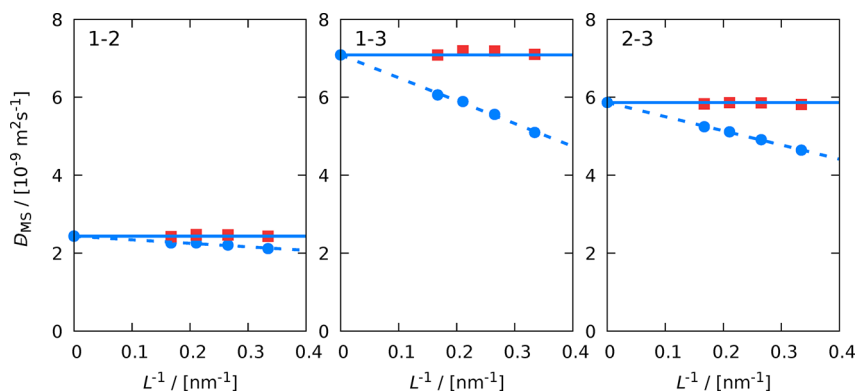
Figure 3. MS diffusion coefficients for a mixture of (1) chloroform, (2) acetone, and (3) methanol ($x_{chloroform} = x_{acetone} = 0.3$) as a function of the simulation box length (L). Blue circles are the computed diffusion coefficients in MD simulations. Red squares are the corrected diffusivities using the proposed correction in eq 30. Dashed lines show extrapolation to the thermodynamic limit, and solid lines are the extrapolated values.
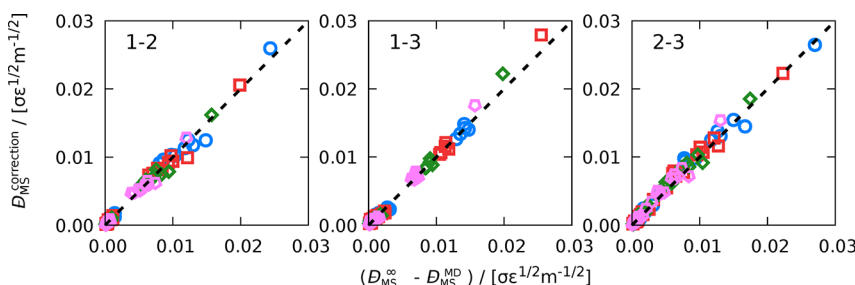
Figure 4. Comparison between finite-size corrections required for MS diffusivities ($Đ_{MS}^{\infty} - Đ_{MS}^{MD}$) and the proposed correction for MS diffusivities ($Đ_{MS}^{correction}$, eq 30, for 28 LJ systems containing 500 particles (blue circles), 1000 particles (red squares), 2000 particles (green diamonds), and 4000 particles (magenta pentagons). Parts 1-2, 1-3, and 2-3 indicate $Đ_{1-2}$, $Đ_{1-3}$, and $Đ_{2-3}$, respectively. Reduced temperature is 0.65 and reduced pressure 0.05. The dashed lines indicate perfect agreement between the proposed correction and the required finite size corrections for MS diffusivities. Raw data are provided in the Supporting Information.

diagonal elements are the eigenvalues of $[D_{Fick}^{MD}]$, should be corrected according to

$$[\hat{D}_{Fick}^{\infty}] = [\hat{D}_{Fick}^{MD}] + D^{YH}[I] \tag{19}$$

Equation 19 is a general expression according to which one should correct the finite size effects of Fick diffusivity computed in EMD. Although the validity of this expression is shown in Figures 1 and 2 for ternary mixtures, the theoretical derivation presented in this section makes it valid for any n-component mixture.

A similar finite-size effect investigation can be performed for the modal matrix, $[P]$. Based on eq 13, for the Fick diffusivity in the thermodynamic limit, we can write

$$[\hat{D}_{Fick}^{\infty}] = [P^{\infty}]^{-1}[D_{Fick}^{\infty}][P^{\infty}] \tag{20}$$

By using eq 12 and simplifying the identity matrix (i.e., $[I] = [P^{\infty}]^{-1}[P^{\infty}]$), one can rewrite eq 20 as

$$[\hat{D}_{Fick}^{\infty}] = [P^{\infty}]^{-1}([D_{Fick}^{MD}] + D^{YH}[I])[P^{\infty}] \tag{21}$$

$$= [P^{\infty}]^{-1}[D_{Fick}^{MD}][P^{\infty}] + D^{YH}[P^{\infty}]^{-1}[I][P^{\infty}] \tag{22}$$

$$= [P^{\infty}]^{-1}[D_{Fick}^{MD}][P^{\infty}] + D^{YH}[I] \tag{23}$$

According to eq 19, the left-hand side of this equation can be substituted by $[\hat{D}_{Fick}^{MD}] + D^{YH}[I]$. Therefore, the terms $D^{YH}[I]$ on both sides of the equation cancel out, and the following relation can be obtained:

$$[\hat{D}_{Fick}^{MD}] = [P^{\infty}]^{-1}[D_{Fick}^{MD}][P^{\infty}] \tag{24}$$

Similarly to eq 20, for finite-size diffusivities computed by EMD, one can write

$$[\hat{D}_{Fick}^{MD}] = [P^{MD}]^{-1}[D_{Fick}^{MD}][P^{MD}] \tag{25}$$

By comparing eqs 24 and 25, one can conclude that $P^{\infty} = P^{MD}$. This means that the modal (eigenvector) matrix of Fick diffusivities does not have any system-size dependency, while according to eq 19 the eigenvalue matrix of Fick diffusivities should be corrected. This finding leads to the conclusion that while the size of the simulation box affects the speed of diffusion (i.e., the eigenvalues), the direction of the diffusion process (i.e., the eigenvectors) is unaffected.

4.2. Generalized Correction for the Finite-Size Effects in Maxwell−Stefan Diffusivities. As Fick and MS diffusivity are connected via the thermodynamic factors (see eq 3), a correction term for the finite-size MS diffusivities can be derived as follows:

$$[D_{Fick}^{\infty}] = [D_{Fick}^{MD}] + D^{YH}[I] \tag{26}$$

$$= [\Delta^{MD}][\Gamma] + D^{YH}[I] \tag{27}$$

$$= [\Delta^{MD}][\Gamma] + D^{YH}[\Gamma]^{-1}[\Gamma] \tag{28}$$

$$= ([\Delta^{MD}] + D^{YH}[\Gamma]^{-1})[\Gamma] \tag{29}$$

and by using $[D_{Fick}^{\infty}] = [\Delta^{\infty}][\Gamma]$ in the equation above leads to

$$[\Delta^{\infty}] = [\Delta^{MD}] + D^{YH}[\Gamma]^{-1} \tag{30}$$

from which the MS diffusivities can be computed. Equation 30 indicates that both the diagonal and off-diagonal elements of

the matrix of MS diffusivities show system-size dependency, in sharp contrast to the Fick diffusivity matrix.

In Figure 3, the results of eq 30 are shown for the finite-size effects of the computed MS diffusivities for the ternary molecular mixture (1) chloroform/(2) acetone/(3) methanol. All three MS diffusivities can be corrected using eq 30, while the magnitudes of the required corrections are different. The validity of this correction was further examined for 28 ternary LJ systems (see Figure 4). For all systems, very good agreement between the computed correction and eq 30 is observed. Figures 3 and 4 clearly show that the correction (i.e., eq 30) can accurately predict the finite-size effects of the matrix of MS diffusivities. It is important to note here that, similarly to eq 19, eq 30 is a generalized expression that can be used for any multicomponent mixture, independently of the number of components.

5. CONCLUSIONS

In this study, we investigated the finite-size dependency of mutual diffusion coefficients of multicomponent mixtures, and a generalized correction is derived, i.e., eq 19. While the off-diagonal elements of the Fick diffusivities do not show any system-size dependency, the diagonal elements should be corrected with the term proposed by Yeh and Hummer for the finite-size self-diffusivities.[22] An eigenvalue analysis of the finite-size effects of the matrix of Fick diffusivities revealed that the eigenvector matrix of Fick diffusivities is unaffected by the size of the simulation box. Only eigenvalues, which describe the speed of diffusion, depend on the size of the system. This is in-line with the hydrodynamic nature of the finite-size effects. An analytic relation for finite-size effects of the matrix of Maxwell−Stefan diffusivities was also developed. The finite-size correction term for the mutual diffusivities was examined for the ternary molecular mixture chloroform/acetone/methanol as well as 28 ternary LJ systems. All simulation results are in good agreement with the proposed corrections for Fick and Maxwell−Stefan mutual diffusion coefficients.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.0c00268.

> Tables with force field parameters for the molecular and LJ mixtures (PDF)

> MD simulation results for different system sizes of the Lennard-Jones and molecular mixtures (XLSX)

AUTHOR INFORMATION

Corresponding Author

Othonas A. Moultos − *Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical, Maritime and Materials Engineering, Delft University of Technology, 2628CB Delft, The Netherlands;* ⓞ orcid.org/0000-0001-7477-9684; Email: o.moultos@tudelft.nl

Authors

Seyed Hossein Jamali − *Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical, Maritime and Materials Engineering, Delft University of Technology, 2628CB Delft, The Netherlands;* ⓞ orcid.org/0000-0002-4198-0901

André Bardow − *Institute of Technical Thermodynamics, RWTH Aachen University, 52056 Aachen, Germany; Energy*

Process Systems Engineering, Department of Mechanical and Process Engineering, ETH Zurich, 8092 Zürich, Switzerland; ⓞ orcid.org/0000-0002-3831-0691

Thijs J. H. Vlugt − *Engineering Thermodynamics, Process & Energy Department, Faculty of Mechanical, Maritime and Materials Engineering, Delft University of Technology, 2628CB Delft, The Netherlands;* ⓞ orcid.org/0000-0003-3059-8712

Complete contact information is available at:
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Notes

The authors declare no competing financial interest.

◼ NOMENCLATURE

Greek letters

η	Shear viscosity (Pa·s)
Γ	Thermodynamic factor (−)
$[\Delta]$	Matrix of phenomenological diffusion coefficient (m²·s⁻¹)
μ_i	Chemical potential of species i (kg·m²·s⁻²·mol⁻¹)
ξ	Constant value for the YH correction (−)
δ_{ij}	Kronecker delta (−)

Roman letters

$Đ_{MS}$	Maxwell−Stefan (MS) diffusivity (m²·s⁻¹)
$Đ_{MS}^{correction}$	Correction to finite-size Maxwell−Stefan (MS) diffusivities (m²·s⁻¹)
$Đ_{ij}$	Maxwell−Stefan (MS) diffusivity between pair $i−j$ (m²·s⁻¹)
$\hat{D}_{i,Fick}$	ith eigenvalue of the matrix of Fick diffusivities (m²·s⁻¹)
$[Đ_{MS}]$	Matrix of Maxwell−Stefan (MS) diffusivities (m²·s⁻¹)
$[\hat{D}_{Fick}]$	Diagonal matrix whose elements are eigenvalues of the matrix of Fick diffusivities (m²·s⁻¹)
$[B]$	Inverse of matrix of phenomenological diffusion coefficient, i.e., $[\Delta]^{-1}$ (m⁻²·s)
$[D_{Fick}]$	Matrix of Fick diffusivities (m²·s⁻¹)
$[I]$	Identity matrix (−)
$[P]$	Modal matrix, i.e., eigenvector matrix of the matrix of Fick diffusivities (−)
c_j	Molar density of species j (mol·m⁻³)
c_t	Total molar density (mol·m⁻³)
D^{YH}	Yeh and Hummer (YH) correction (m²·s⁻¹)
D_{Fick}	Fick diffusivity (m²·s⁻¹)
$D_{i,self}$	Self-diffusivity of species i (m²·s⁻¹)
D_{ij}	element (i, j) of the matrix of Fick diffusivities (m²·s⁻¹)
J_i	Molar flux of species i (mol·m⁻²·s⁻¹)
k_B	Boltzmann constant (1.38064852 × 10⁻²³ m²·kg·s⁻²·K⁻¹)
L	Length of the cubic simulation box (m)
n	Total number of components in the mixture (−)
R	Universal gas constant (8.3145 kg·m²·s⁻²·K⁻¹·mol⁻¹)

T   Temperature (K)

x_i Mole fraction of species i ($-$)

Superscripts

MD   Referring to finite-size properties

∞   Referring to the thermodynamic limit (infinite-size)

■ REFERENCES

(1) Alder, B. J.; Alley, W. E.; Dymond, J. H. Studies in Molecular Dynamics. XIV. Mass and Size Dependence of the Binary Diffusion Coefficient. *J. Chem. Phys.* **1974**, *61*, 1415−1420.

(2) Calvo, F.; Costa, D. Diffusion of Hydrides in Palladium Nanoclusters. A Ring-Polymer Molecular Dynamics Study of Quantum Finite Size Effects. *J. Chem. Theory Comput.* **2010**, *6*, 508−516.

(3) Wang, Y.; Markwick, P. R. L.; de Oliveira, C. A. F.; McCammon, J. A. Enhanced Lipid Diffusion and Mixing in Accelerated Molecular Dynamics. *J. Chem. Theory Comput.* **2011**, *7*, 3199−3207.

(4) Parez, S.; Guevara-Carrion, G.; Hasse, H.; Vrabec, J. Mutual Diffusion in the Ternary Mixture of Water + Methanol + Ethanol and its Binary Subsystems. *Phys. Chem. Chem. Phys.* **2013**, *15*, 3985.

(5) Moultos, O. A.; Tsimpanogiannis, I. N.; Panagiotopoulos, A. Z.; Economou, I. G. Atomistic Molecular Dynamics Simulations of CO_2 Diffusivity in H_2O for a Wide Range of Temperatures and Pressures. *J. Phys. Chem. B* **2014**, *118*, 5532−5541.

(6) Mercier Franco, L. F.; Castier, M.; Economou, I. G. Diffusion in Homogeneous and in Inhomogeneous Media: A New Unified Approach. *J. Chem. Theory Comput.* **2016**, *12*, 5247−5255.

(7) Moultos, O. A.; Tsimpanogiannis, I. N.; Panagiotopoulos, A. Z.; Trusler, J. P. M.; Economou, I. G. Atomistic Molecular Dynamics Simulations of Carbon Dioxide Diffusivity in n-hexane, n-decane, n-hexadecane, Cyclohexane, and Squalane. *J. Phys. Chem. B* **2016**, *120*, 12890−12900.

(8) Moultos, O. A.; Tsimpanogiannis, I. N.; Panagiotopoulos, A. Z.; Economou, I. G. Self-Diffusion Coefficients of the Binary (H_2O + CO_2) Mixture at High Temperatures and Pressures. *J. Chem. Thermodyn.* **2016**, *93*, 424−429.

(9) Guevara-Carrion, G.; Gaponenko, Y.; Janzen, T.; Vrabec, J.; Shevtsova, V. Diffusion in Multicomponent Liquids: From Microscopic to Macroscopic Scales. *J. Phys. Chem. B* **2016**, *120*, 12193−12210.

(10) Jamali, S. H.; Ramdin, M.; Becker, T. M.; Rinwa, S. K.; Buijs, W.; Vlugt, T. J. H. Thermodynamic and Transport Properties of Crown-Ethers: Force Field Development and Molecular Simulations. *J. Phys. Chem. B* **2017**, *121*, 8367−8376.

(11) Janzen, T.; Vrabec, J. Diffusion Coefficients of a Highly Nonideal Ternary Liquid Mixture: Cyclohexane-Toluene-Methanol. *Ind. Eng. Chem. Res.* **2018**, *57*, 16508−16517.

(12) Jamali, S. H.; van Westen, T.; Moultos, O. A.; Vlugt, T. J. H. Optimizing Nonbonded Interactions of the OPLS Force Field for Aqueous Solutions of Carbohydrates: How to Capture Both Thermodynamics and Dynamics. *J. Chem. Theory Comput.* **2018**, *14*, 6690−6700.

(13) Tsimpanogiannis, I. N.; Moultos, O. A.; Franco, L. F. M.; Spera, M. B. M.; Erdös, M.; Economou, I. G. Self-diffusion Coefficient of Bulk and Confined Water: A Critical Review of Classical Molecular Simulation Studies. *Mol. Simul.* **2019**, *45*, 425−453.

(14) Fraaije, J. G.; Van Male, J.; Becherer, P.; Serral Gracià, R. Calculation of Diffusion Coefficients through Coarse-Grained Simulations Using the Automated-Fragmentation-Parametrization Method and the Recovery of Wilke-Chang Statistical Correlation. *J. Chem. Theory Comput.* **2018**, *14*, 479−485.

(15) Giraudet, C.; Klein, T.; Zhao, G.; Rausch, M. H.; Koller, T. M.; Fröba, A. P. Thermal, Mutual, and Self-Diffusivities of Binary Liquid Mixtures Consisting of Gases Dissolved in n-Alkanes at Infinite Dilution. *J. Phys. Chem. B* **2018**, *122*, 3163−3175.

(16) Tsimpanogiannis, I. N.; Jamali, S. H.; Economou, I. G.; Vlugt, T. J. H.; Moultos, O. A. On the Validity of the Stokes-Einstein Relation for Various Water Force Fields. *Mol. Phys.* **2019**, 1−11.

(17) Wu, W.; Klein, T.; Kerscher, M.; Rausch, M. H.; Koller, T. M.; Giraudet, C.; Fröba, A. P. Diffusivities in 1-Alcohols Containing Dissolved H_2, He, N_2, CO, or CO_2 Close to Infinite Dilution. *J. Phys. Chem. B* **2019**, *123*, 8777−8790.

(18) Wu, W.; Klein, T.; Kerscher, M.; Rausch, M. H.; Koller, T. M.; Giraudet, C.; Fröba, A. P. Mutual and Thermal Diffusivities as Well as Fluid-phase Equilibria of Mixtures of 1-Hexanol and Carbon Dioxide. *J. Phys. Chem. B* **2020**, *124*, 2482.

(19) Frenkel, D.; Smit, B. *Understanding Molecular Simulation: From Algorithms to Applications*, 2nd ed.; Academic Press: London, 2002.

(20) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*, 2nd ed.; Oxford University Press: Croydon, 2017.

(21) Dünweg, B.; Kremer, K. Molecular Dynamics Simulation of a Polymer Chain in Solution. *J. Chem. Phys.* **1993**, *99*, 6983−6997.

(22) Yeh, I.-C.; Hummer, G. System-Size Dependence of Diffusion Coefficients and Viscosities from Molecular Dynamics Simulations with Periodic Boundary Conditions. *J. Phys. Chem. B* **2004**, *108*, 15873−15879.

(23) Taylor, R.; Krishna, R. *Multicomponent Mass Transfer*, 1st ed.; John Wiley & Sons: New York, 1993.

(24) Krishna, R.; Wesselingh, J. The Maxwell-Stefan Approach to Mass Transfer. *Chem. Eng. Sci.* **1997**, *52*, 861−911.

(25) Wesselingh, J. A.; Krishna, R. *Mass Transfer in Multicomponent Mixtures*, 1st ed.; VSSD: Delft, 2006.

(26) Jamali, S. H.; Wolff, L.; Becker, T. M.; Bardow, A.; Vlugt, T. J. H.; Moultos, O. A. Finite-size Effects of Binary Mutual Diffusion Coefficients from Molecular Dynamics. *J. Chem. Theory Comput.* **2018**, *14*, 2667−2677.

(27) Bird, R. B. *Transport Phenomena*, 2nd ed.; John Wiley & Sons: New York, 2007.

(28) Liu, X.; Schnell, S. K.; Simon, J.-M.; Krüger, P.; Bedeaux, D.; Kjelstrup, S.; Bardow, A.; Vlugt, T. J. H. Diffusion Coefficients from Molecular Dynamics Simulations in Binary and Ternary Mixtures. *Int. J. Thermophys.* **2013**, *34*, 1169−1196.

(29) Krishna, R.; van Baten, J. M. Describing Diffusion in Fluid Mixtures at Elevated Pressures by Combining the Maxwell-Stefan Formulation with an Equation of State. *Chem. Eng. Sci.* **2016**, *153*, 174−187.

(30) Guevara-Carrion, G.; Gaponenko, Y.; Mialdun, A.; Janzen, T.; Shevtsova, V.; Vrabec, J. Interplay of Structure and Diffusion in Ternary Liquid Mixtures of Benzene + Acetone + Varying Alcohols. *J. Chem. Phys.* **2018**, *149*, 064504.

(31) Taylor, R.; Kooijman, H. A. Composition Derivatives of Activity Coefficient Models (For the Estimation of Thermodynamic Factors in Diffusion). *Chem. Eng. Commun.* **1991**, *102*, 87−106.

(32) Kooijman, H. A.; Taylor, R. Estimation of Diffusion Coefficients in Multicomponent Liquid Systems. *Ind. Eng. Chem. Res.* **1991**, *30*, 1217−1222.

(33) Fingerhut, R.; Herres, G.; Vrabec, J. Thermodynamic Factor of Quaternary Mixtures from Kirkwood-Buff Integration. *Mol. Phys.* **2020**, *118*, e1643046.

(34) Wheeler, D. R.; Newman, J. Molecular Dynamics Simulations of Multicomponent Diffusion. 1. Equilibrium Method. *J. Phys. Chem. B* **2004**, *108*, 18353−18361.

(35) Wheeler, D. R.; Newman, J. Molecular Dynamics Simulations of Multicomponent Diffusion. 2. Nonequilibrium Method. *J. Phys. Chem. B* **2004**, *108*, 18362−18367.

(36) Liu, X.; Bardow, A.; Vlugt, T. J. H. Multicomponent Maxwell-Stefan Diffusivities at Infinite Dilution. *Ind. Eng. Chem. Res.* **2011**, *50*, 4776−4782.

(37) Liu, X.; Schnell, S. K.; Simon, J.-M.; Bedeaux, D.; Kjelstrup, S.; Bardow, A.; Vlugt, T. J. H. Fick Diffusion Coefficients of Liquid Mixtures Directly Obtained from Equilibrium Molecular Dynamics. *J. Phys. Chem. B* **2011**, *115*, 12921−12929.

(38) Liu, X.; Martín-Calvo, A.; McGarrity, E.; Schnell, S. K.; Calero, S.; Simon, J.-M.; Bedeaux, D.; Kjelstrup, S.; Bardow, A.; Vlugt, T. J. H. Fick Diffusion Coefficients in Ternary Liquid Systems from Equilibrium Molecular Dynamics Simulations. *Ind. Eng. Chem. Res.* **2012**, *51*, 10247−10258.

(39) Bian, X.; Kim, C.; Karniadakis, G. E. 111 Years of Brownian Motion. *Soft Matter* **2016**, *12*, 6331−6346.

(40) Pranami, G.; Lamm, M. H. Estimating Error in Diffusion Coefficients Derived from Molecular Dynamics Simulations. *J. Chem. Theory Comput.* **2015**, *11*, 4586−4592.

(41) Moultos, O. A.; Zhang, Y.; Tsimpanogiannis, I. N.; Economou, I. G.; Maginn, E. J. System-Size Corrections for Self-Diffusion Coefficients Calculated from Molecular Dynamics Simulations: The Case of CO_2, n-alkanes, and Poly(Ethylene Glycol) Dimethyl Ethers. *J. Chem. Phys.* **2016**, *145*, 074109.

(42) Botan, A.; Marry, V.; Rotenberg, B. Diffusion in Bulk Liquids: Finite-size Effects in Anisotropic Systems. *Mol. Phys.* **2015**, *113*, 2674−2679.

(43) Vögele, M.; Hummer, G. Divergent Diffusion Coefficients in Simulations of Fluids and Lipid Membranes. *J. Phys. Chem. B* **2016**, *120*, 8722−8732.

(44) Simonnin, P.; Noetinger, B.; Nieto-Draghi, C.; Marry, V.; Rotenberg, B. Diffusion under Confinement: Hydrodynamic Finite-size Effects in Simulation. *J. Chem. Theory Comput.* **2017**, *13*, 2881−2889.

(45) Yang, X.; Zhang, H.; Li, L.; Ji, X. Corrections of the Periodic Boundary Conditions with Rectangular Simulation Boxes on the Diffusion Coefficient, General Aspects. *Mol. Simul.* **2017**, *43*, 1423−1429.

(46) Jamali, S. H.; Hartkamp, R.; Bardas, C.; Söhl, J.; Vlugt, T. J. H.; Moultos, O. A. Shear Viscosity Computed from the Finite-Size Effects of Self-Diffusivity in Equilibrium Molecular Dynamics. *J. Chem. Theory Comput.* **2018**, *14*, 5959−5968.

(47) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.* **1995**, *117*, 1−19.

(48) Jamali, S. H.; Wolff, L.; Becker, T. M.; de Groen, M.; Ramdin, M.; Hartkamp, R.; Bardow, A.; Vlugt, T. J. H.; Moultos, O. A. OCTP: ATool for on-the-Fly Calculation of Transport Properties of Fluids with the Order-n Algorithm in LAMMPS. *J. Chem. Inf. Model.* **2019**, *59*, 1290−1294.

(49) Krüger, P.; Vlugt, T. J. H. Size and Shape Dependence of Finite-volume Kirkwood-Buff Integrals. *Phys. Rev. E: Stat. Phys., Plasmas, Fluids, Relat. Interdiscip. Top.* **2018**, *97*, 051301.

(50) Jorgensen, W. L. Optimized Intermolecular Potential Functions for Liquid Alcohols. *J. Phys. Chem.* **1986**, *90*, 1276−1284.

(51) Tummala, N. R.; Striolo, A. Hydrogen-bond Dynamics for Water Confined in Carbon Tetrachloride-acetone Mixtures. *J. Phys. Chem. B* **2008**, *112*, 10675−10683.

(52) Gupta, R.; Chandra, A. Structural, Single-particle and Pair Dynamical Properties of Acetone-Chloroform Mixtures with Dissolved Solutes. *Chem. Phys.* **2011**, *383*, 41−49.

(53) Martínez, L.; Andrade, R.; Birgin, E. G.; Martínez, J. M. PACKMOL: A Package for Building Initial Configurations for Molecular Dynamics Simulations. *J. Comput. Chem.* **2009**, *30*, 2157−2164.

(54) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual Molecular Dynamics. *J. Mol. Graphics* **1996**, *14*, 33−38.

(55) Toor, H. L. Solution of the Linearized Equations of Multicomponent Mass Transfer: I. *AIChE J.* **1964**, *10*, 448−455.

(56) Stewart, W. E.; Prober, R. Matrix Calculation of Multicomponent Mass Transfer in Isothermal Systems. *Ind. Eng. Chem. Fundam.* **1964**, *3*, 224−235.

(57) Bardow, A. On the Interpretation of Ternary Diffusion Measurements in Low-Molecular Weight Fluids by Dynamic Light Scattering. *Fluid Phase Equilib.* **2007**, *251*, 121−127.

(58) Heller, A.; Giraudet, C.; Makrodimitri, Z. A.; Fleys, M. S. H.; Chen, J.; van der Laan, G. P.; Economou, I. G.; Rausch, M. H.; Fröba, A. P. Diffusivities of Ternary Mixtures of *n*-Alkanes with Dissolved Gases by Dynamic Light Scattering. *J. Phys. Chem. B* **2016**, *120*, 10808−10823.