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The Open-Access Journal for the Basic Principles of Diffusion Theory, Experiment and Application

Maxwell-Stefan Diffusivities and Velocity Cross-Correlations in Dilute Ternary Systems

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Abstract

The Maxwell-Stefan (MS) approach is commonly used for describing mass transport by diffusion in gases and liquids since it correctly accounts for the chemical potential gradient as driving force. It is well known that MS diffusivities are concentration dependent which should be taken into account in practical applications. Unfortunately, it is difficult to obtain MS diffusivities both from experiments and molecular simulations. Therefore, there is a considerable interest in predictive models describing the concentration dependence of MS diffusivities. MS diffusivities can be expressed as functions of (1) easily obtainable self-diffusivities, and (2) the integrals of velocity cross-correlations. By assuming that the latter terms are small, we recently derived the multicomponent Darken equation. The objectives of the present study are twofold: First, we present a validation of the multicomponent Darken equation in ternary systems. Second, we investigate the dependence of velocity cross-correlations on concentration and system size. A linear relation between the velocity cross-correlations and 1/*N* is found ("*N*" being the total number of molecules in the system). Two types of systems are studied: (1) Weeks-Chandler-Andersen (WCA) fluids in which only repulsive interactions are considered; (2) the ternary system water-DMSO-methanol in which atoms are interacting using both Lennard-Jones and electrostatic potentials.

Keywords: Maxwell-Stefan diffusivities, self-diffusivities, multicomponent Darken equation, velocity cross-correlations

1. Introduction

To describe multicomponent mass transport by diffusion in gases and liquids, the Maxwell-Stefan (MS) approach is commonly used as it provides a convenient description of diffusion in an *n*-component system. The key point of this approach is that the driving force for diffusion of component *i* (*i.e.* the gradient in its chemical potential, $\nabla\mu_i$) is balanced by a frictional force, resulting in the following equation [1, 2, 3]

$$-\frac{1}{RT}\nabla\mu_i = \sum_{j=1,\, j\neq i}^{n} \frac{x_j\left(u_i - u_j\right)}{Đ_{ij}}. \qquad \text{Eq. (1)}$$

In this equation, the friction force between components *i* and *j* is proportional to the difference in average velocities of the components, (u_i-u_j). *R* and *T* represent the gas constant and absolute temperature, respectively. x_j is the mole fraction of component *j*. The MS diffusivity $Đ_{ij}$ thus acts as an inverse friction coefficient describing the magnitude of the friction between components *i* and *j*. The following reasons make the use of MS diffusivities popular in chemical engineering: (1) MS diffusivities depend less on the concentration compared to Fick diffusivities; (2) In a system containing *n* components, $n\cdot(n\text{-}1)/2$ MS diffusivities are sufficient to describe mass transport, in contrast $(n\text{-}1)^2$ Fick diffusivities are necessary. Thus, in the MS approach less parameters are needed for $n>2$; (3) MS diffusivities in multicomponent systems can be related to binary diffusivities which is very useful for developing predictive models. In sharp contrast to this, multicomponent Fick diffusivities are not related to their binary counterparts.

Unfortunately, it is difficult to obtain MS diffusivities from experiments as the chemical potential cannot be measured directly [4]. Obtaining MS diffusivities from molecular simulations requires extensive amount of CPU time [5]. Predictive models for MS diffusivities based on easily obtainable parameters, *e.g.* self-diffusivities, are therefore desired.

MS diffusivities can be expressed as functions of self-diffusivities and the integrals of velocity cross-correlations. In our previous study, we recently derived a rigorous model for the prediction of MS diffusivities in multicomponent systems by assuming that the latter terms are small [6]. As the result can be considered as an extension of the well-known binary Darken equation [7], we named it the multicomponent Darken equation. The multicomponent Darken equation requires self-diffusivities in mixtures which can be easily obtained from both experiments and molecular simulations. In this study, we investigate the validity of our multicomponent Darken equation using Molecular Dynamics (MD) simulations. The remainder of this paper is organized as follows. In Section 2, we briefly describe how to derive the multicomponent Darken equation. In Section 3, we present the details of our MD simulations. In Section 4, we validate the multicomponent Darken equation in ternary systems including Weeks-Chandler-Andersen (WCA) fluids and H_2O-DMSO-CH_3OH mixtures using MD simulations. Furthermore, we investigate the dependence of velocity cross-correlations on concentration and system size. Our conclusions are summarized in Section 5.

2. Multicomponent Darken Equation

MS diffusivities can be expressed as functions of concentration and the Onsager coefficients Λ_{ij} which are calculated from the motion of the molecules in MD simulations [8, 9]

$$\Lambda_{ij} = \frac{1}{3N}\int_0^\infty dt \left\langle \sum_{l=1}^{N_i} v_{l,i}(0) \cdot \sum_{p=1}^{N_j} v_{p,j}(t) \right\rangle, \qquad \text{Eq. (2)}$$

in which N is the total number of molecules. N_i is the number of molecules of component i, $v_{l,i}(t)$ is the velocity of l^{th} molecule of component i at time t.

For $i = j$, we split the calculation of Λ_{ii} into a self-part and a cross-part,

$$\begin{aligned}\Lambda_{ii} &\approx \frac{1}{3N}\int_0^\infty N_i dt \left\langle v_{l,i}(0)\cdot v_{l,i}(t)\right\rangle + \frac{1}{3N}\int_0^\infty N_i (N_i - 1) dt \left\langle v_{l,i}(0)\cdot v_{g,i}(t)\right\rangle \\ &= \frac{N_i}{N} C_{ii} + \frac{N_i (N_i - 1)}{3N} C_{ii}^*,\end{aligned} \qquad \text{Eq. (3)}$$

in which C_{ii} and C_{ii}^* represent the velocity correlations of identical molecules and distinct molecules, respectively:

$$C_{ii} = \frac{1}{3}\int_0^\infty dt \left\langle v_i(0)\cdot v_i(t)\right\rangle = D_{i,\mathbf{self}}, \qquad \text{Eq. (4)}$$

$$C_{ii}^* = \int_0^\infty dt \left\langle v_{l,i}(0)\cdot v_{g,i}(t)\right\rangle. \qquad \text{Eq. (5)}$$

In Eqs. (3, 5), l and g represent different molecules of component i. The term C_{ii} is equal to the self-diffusivity $D_{i,\mathrm{self}}$ of component i. For $i \neq j$, as velocity correlations between different molecules are on average identical, Eq. (2) becomes

$$\Lambda_{ij} \approx \frac{N_i N_j}{3N} C_{ij}. \qquad \text{Eq. (6)}$$

in which C_{ij} represents integrals of velocity cross-correlations between different molecules (l, g) of different type (i, j)

$$C_{ij} = \int_0^\infty dt \left\langle v_{l,i}(0)\cdot v_{g,j}(t)\right\rangle. \qquad \text{Eq. (7)}$$

For infinitely diluted systems in which particles are not or weakly associated (*e.g.* WCA systems, the system n-hexane-toluene-cyclohexane), it has been shown that the terms $C_{ij,i\neq j}$ and C_{ii}^* are small compared to C_{ii} [10]. This assumption ultimately leads to a Darken-like equation for a general n-component system [6]

$$Đ_{ij} = D_{i,\mathbf{self}} \cdot D_{j,\mathbf{self}} \sum_{k=1}^{n} \frac{x_k}{D_{k,\mathbf{self}}}, \qquad \text{Eq. (8)}$$

In the remainder of this manuscript, we refer to Eq. (8) as the *multicomponent Darken equation*. For binary systems, Eq. (8) reduces to the well-known binary Darken equation [7]:

$$Đ_{ij} = x_i D_{j,\mathbf{self}} + x_j D_{i,\mathbf{self}}. \qquad \text{Eq. (9)}$$

3. Molecular Dynamics Simulations

The multicomponent Darken equation (Eq. (8)) described in Section 2 was tested for two systems: (1) WCA fluids; (2) water-DMSO-methanol systems in which particles interact using both Lennard-Jones (LJ) and electrostatic interactions. Three dimensional periodic boundary conditions consistent with a cubic box were applied to obtain properties corresponding to bulk systems.

In the WCA systems, all components only differ in molar mass. For convenience, we express all quantities in reduced units by setting the LJ parameters σ and ε as units for length and energy, respectively [9]. The mass of the lightest component (M_1) is set as unit of mass. With these conventions, the units of energy, temperature, number density, and time are: ε, ε/k_B, σ^{-3}, $\sigma/(M_1/\varepsilon)^{½}$ respectively (k_B being the Boltzmann constant). The WCA potential is constructed by truncating and shifting the LJ potential at $2^{1/6}\sigma$. A linked-cell algorithm is applied to improve the efficiency of the simulations. Self- and MS diffusivities were obtained from simulations in the microcanonical (NVE) ensemble. The equation of motion was integrated using a time step of $\Delta t = 0.001$ (in reduced units as described above) and typically 10^9 steps were needed to obtain diffusivities from MD simulations.

For the water-DMSO-methanol systems, intermolecular interactions are described by LJ and electrostatic potentials. LJ potentials are truncated and shifted at 12Å. Electrostatic interactions are handled by the Ewald summation using a relative precision of 10^{-4}. Methanol and DMSO are described using TraPPE-UA model in which the CH_3 groups are considered as united atoms [11, 12]. A flexible simple point charge (SPC-FW) model is used to describe water [13]. The Lorentz-Berthelot mixing rules are applied to calculate the LJ parameters for the interactions of unlike atoms. The simulations were carried out as follows: initial configurations were generated and equilibrated in the NPT ensemble at a temperature of T = 298K and a pressure of p = 1atm. The Nosé-Hoover thermostat and barostat were used with a time constants of 0.2 and 1 ps, respectively. A time step of 1 fs was used for integrating the equation of motion. When the average density of the systems did not change with time, we used the equilibrated system at this average density for computing the self- and MS diffusivities in NVE ensemble.

The statistic errors for all computed MS diffusivities were less than 5%. The errors in computed self-diffusivities were around 2%.

4. Results and Discussion

4.1 MS diffusivities

Table 1 shows a comparison between computed and predicted MS diffusivities in ternary WCA systems. In WCA systems, only repulsive interactions are present. The simulations were carried out at a temperature of T = 2 and a density of ρ = 0.7 (all in reduced units). This density is much higher than our previous work [6, 10]. The mole fractions of components 1 and 2 are kept equal and the mole fraction of the third component varies. The multicomponent Darken equation (Eq. (8)) is used to predict the MS diffusivities. The self-diffusivities required in the multicomponent Darken equation were also computed using MD simulations. The absolute differences between simulation results and predictions are calculated and normalized with the simulation results. The averaged absolute differences are used to evaluate the quality of multicomponent Darken equation.

We observe at all concentrations, that MS diffusivities can be accurately predicted by the multicomponent Darken equation with a maximal deviation of 6%. It is important to note that this deviation becomes smaller when a mixture is approaching infinite dilution. Recall the assumptions made in the derivation of the multicomponent Darken equation: we assume that velocity self-correlations are much larger than the velocity cross-correlations of nonidentical molecules. This assumption is more reasonable at infinite dilution leading to more accurate predictions. Notably, all predictions are within the simulation accuracy indicating excellent agreement with the theory.

Table 1: Computed self- and MS diffusivities in ternary WCA systems. MS diffusivities are also predicted using Eq. (8). Simulation details: $T = 2$, $\rho = 0.7$, $M_1 = 1$, $M_2 = 4$, $M_3 = 16$, $x_1 = x_2$.

x_3	$D_{1,self}^{a}$	$D_{2,self}^{a}$	$D_{3,self}^{a}$	$Đ_{12}^{a}$	$Đ_{13}^{a}$	$Đ_{23}^{a}$	$Đ_{12}^{b}$	$Đ_{13}^{b}$	$Đ_{23}^{b}$	AAD^{c}
0.60	0.106	0.090	0.077	0.110	0.106	0.087	0.114	0.097	0.082	6%
0.89	0.082	0.073	0.063	0.089	0.082	0.074	0.093	0.080	0.071	4%
0.95	0.075	0.068	0.060	0.086	0.081	0.069	0.084	0.074	0.068	4%

[a] Computed diffusion coefficients using MD simulations
[b] Prediction of MS diffusivities using Eq. (8)
[c] Averaged absolute difference of MS diffusivities normalized with simulation results

Table 2 provides a comparison between the computed and predicted MS diffusivities in the system H_2O-DMSO-CH_3OH at a temperature of $T = 298$K and a pressure of $p = 1$atm. In this system, both LJ and electrostatic interactions are present. We tested the multicomponent Darken equation in a diluted mixture which is close to a pure component system. The deviation from simulation result is 8% in this system. Considering the statistic errors in simulations (5%), the predictions using Eq. (8) are very accurate for this system.

Table 2: Computed self- and MS diffusivities/($10^{-8}m^2s^{-1}$) in H_2O-DMSO-CH_3OH systems at 298K, 1atm. MS diffusivities are also predicted using Eq. (8). Here, “1” represents DMSO, “2” represent H_2O, and “3” represents CH_3OH. $x_1 = x_3 = 0.045$.

x_2	$D_{1,self}^{a}$	$D_{2,self}^{a}$	$D_{3,self}^{a}$	$Đ_{12}^{a}$	$Đ_{13}^{a}$	$Đ_{23}^{a}$	$Đ_{12}^{b}$	$Đ_{13}^{b}$	$Đ_{23}^{b}$	AAD^{c}
0.91	0.102	0.200	0.169	0.125	0.094	0.168	0.106	0.091	0.178	8%

[a] Computed diffusion coefficients using MD simulations
[b] Prediction of MS diffusivities using Eq. (8)
[c] Averaged absolute difference normalized with simulation results

4.2 Velocity Cross-Correlations

Figure 1 shows the values of the velocity cross-correlations C_{ij} in ternary WCA systems. A linear relation between C_{ij} and $1/N$ was found (“N” being the total number of molecules in the system). There are two ways to understand this observation. First, we can explain this observation from the original definition of C_{ij}. We rewrite Eq. (6) as

$$\Lambda_{ij} \approx \frac{1}{3} x_i x_j N C_{ij} \text{.} \qquad \text{Eq. (10)}$$

By definition, Λ_{ij} should be an intensive quantity [10]. This is confirmed numerically in table 3.

Table 3: Computed Onsager coefficients/($10^{-8}m^2s^{-1}$) in H_2O-DMSO-CH_3OH systems at 298K, 1atm. Here, "1" represents DMSO, "2" represent H_2O, and "3" represents CH_3OH. N_i is the number of molecules of component *i*.

N_1	N_2	N_3	Λ_{11}	Λ_{12}	Λ_{13}	Λ_{22}	Λ_{23}	Λ_{33}
30	600	30	0.0938	-0.3595	-0.0233	0.0903	-0.0097	0.1429
40	800	40	0.0907	-0.3464	-0.0207	0.0902	-0.0096	0.1467
50	1000	50	0.0922	-0.4022	-0.0218	0.1134	-0.0076	0.1452
65	1300	65	0.0954	-0.4373	-0.0202	0.1050	-0.0071	0.1467
75	1500	75	0.1054	-0.4373	-0.0212	0.1050	-0.0071	0.1567
85	1700	85	0.0947	-0.4446	-0.0237	0.1127	-0.0085	0.1461
100	2000	100	0.1015	-0.4588	-0.0217	0.1229	-0.0063	0.1545

At a constant composition of the mixture, clearly, C_{ij} is inversely proportional to *N*. This can also be understood in a second, more intuitive way. In principle, there are two contributions to C_{ij} : (1) contributions due to the presence of molecules of type *j* which are close to molecules of type *i*; (2) contributions due to the presence of molecules of type *j* which are far away from molecules of type *i*. The contribution from the latter will be essentially zero. The overall value of C_{ij} thus equals

$$C_{ij} = \frac{C_{ij}^{*} \cdot N_j^c + 0 \cdot \left(N_j - N_j^c\right)}{N_j} = \frac{C_{ij}^{*} \cdot N_j^c}{x_j} \cdot \frac{1}{N} = \left(\text{constant}\right) \times \frac{1}{N} \text{.} \qquad \text{Eq. (11)}$$

in which C_{ij}^* represents contributions from neighboring molecules of type *i* and *j*. N_j^c is the number of molecules of type *j* which close to molecules of type *i*. Both C_{ij}^* and N_j^c are independent of the system size. Eq. (11) shows that at same concentration, the velocity correlations in a larger system will be smaller than velocity correlations in a small system. A large number of molecules of components *i* and *j* leads in practice to more linear scaling as the statistics of Λ_{ij} (and therefore C_{ij}, see Eqs. (2) and (10)) are better, *i.e.* see the data for C_{13} and C_{23} in Figure 1.

Figure 2 shows the velocity cross-correlations C_{ij} in the H_2O-DMSO-CH_3OH systems. The mixture composition is fixed at $x_{\mathrm{DMSO}} = x_{\mathrm{CH3OH}} = 0.045$ and $x_{\mathrm{H2O}} = 0.91$. Seven systems with different sizes are considered. We observed that C_{ij} nicely scales with $1/N$ and it approaches zero in the thermodynamic limit. The fact that we observe straight lines also strongly suggests that finite-size effects are minimal.

5. Conclusions

The Maxwell-Stefan approach conveniently describes the mass transport in multicomponent liquids systems. It is well known that MS diffusivities are concentration dependent. For practical applications, it is useful to develop a model describing this concentration dependence. Recently, we derived a multicomponent Darken equation for the prediction of MS diffusivities. In binary mixtures, the well-known Darken equation is successfully recovered by our model. In this work, we validated the multicomponent Darken equation in ternary systems. We show that in systems in which particles are not associating, the multicomponent Darken equation is accurate. In systems in which particles are strongly associating, the multicomponent Darken equation still provides reasonable predictions for diluted systems. In addition, we investigated the dependence of velocity cross-correlations on the concentration and the systems size. A linear relation between velocity cross-correlations and $1/N$ was found ("N" being the total number of molecules in a system) suggesting that finite-size effects are minimal. In simple systems, velocity cross-correlations are usually small and therefore they can be neglected. However, in more complex systems, understanding these correlations is important to improve the predictions of the multicomponent Darken model.

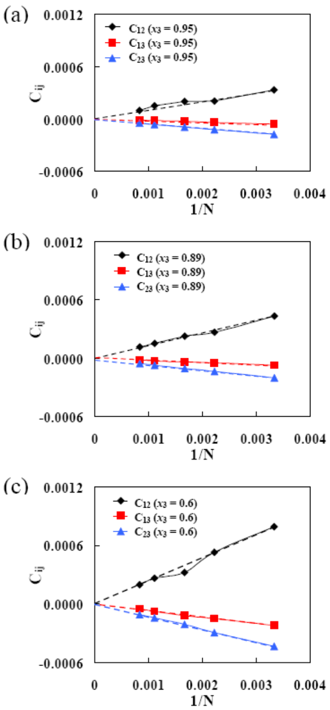

Figure 1: Computed velocity cross-correlations C_{ij} in ternary WCA systems. Simulation details: $T = 2$, $\rho = 0.7$, $M_1 = 1$, $M_2 = 4$, $M_3 = 16$. (a) $x_1 = x_2 = 0.025$. (b) $x_1 = x_2 = 0.055$. (c) $x_1 = x_2 = 0.2$.

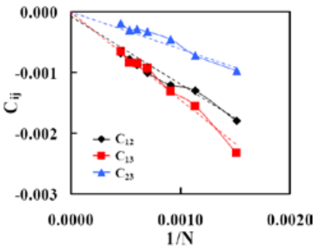

Figure 2: Computed velocity cross correlations C_{ij} in H_2O-DMSO-CH_3OH system at 298K, 1atm. Here, "1" represents DMSO, "2" represent H_2O, and "3" represents CH_3OH. $x_1 = x_3 = 0.045$.

Acknowledgements

This work was performed as part of the Cluster of Excellence ``Tailor-Made Fuels from Biomass", which is funded by the Excellence Initiative by the German federal and state governments to promote science and research at German universities. This work was also sponsored by the Stichting Nationale Computerfaciliteiten (National Computing Facilities Foundation, NCF) for the use of supercomputing facilities, with financial support from the Nederlandse Organisatie voor Wetenschappelijk onderzoek (Netherlands Organization for Scientific Research, NWO).

References

[1] R. Taylor, R. Krishna, Multicomponent mass transfer, Wiley: New York, NY, 1993

[2] J.A. Wesselingh, R. Krishna, Elements of mass transfer, Ellis Hoewood: Chichester, 1990

[3] R. Krishna, J.A. Wesselingh, Chem. Eng. Sci, 52 (1997) 861-911.

[4] A. Bardow, E. Kriesten, M.A. Voda, F. Casanova, B. Blümich, W. Marquardt, Fluid Phase Equilibria, 278 (2009) 27-35.

[5] X. Liu, T.J.H. Vlugt, A. Bardow, Fluid Phase Equilibria, 301 (2011) 110-117.

[6] X. Liu, T.J.H. Vlugt, A. Bardow, Ind. Eng. Chem. Res., 50 (2011) 10350-10358

[7] L.S. Darken, Transactions of the American Institute of Mining and Metallurgical Engineers 175 (1948) 184-201

[8] R. Krishna, J.M. van Baten, Ind. Eng. Chem. Res., 44 (2005) 6939-6947

[9] D. Frenkel, B. Smit, Understanding molecular simulations, Academic Press: San Diego, 2002

[10] X. Liu, A. Bardow, T.J.H. Vlugt, Ind. Eng. Chem. Res, 50 (2011) 4776-4782

[11] B. Chen, J.J. Potoff, J.I. Siepmann, J. Phys. Chem. B 105 (2001) 3093-3104

[12] M. Chalaris, S. Marinakis, D. Dellis, Fluid Phase Equilibria 267 (2008) 47-60

[13] Y.J. Wu, H.L. Tepper, G.A. Voth, J. Chem. Phys 124 (2006) 024503