

Investigation of Transport and Structural Properties of Binary fluid Mixtures in the Near-Critical-Region via Molecular Dynamics Simulations

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Abstract - Performing experiments in the near-critical region of a system, for accessing accurate dynamical and structural properties, pose a great challenge. However, molecular dynamics simulation studies complement experiments by providing access to accurate macroscopic properties, virtually at any thermodynamic state, provided a reliable force field (FF) is employed for calculating atomistic level interactions. A recent study by Guevara-Carrion et al. (2019) presented an anomaly of the simulated Fick diffusion coefficient in the near-critical region around the Widom line for the methane and carbon dioxide fluid mixtures, investigated using FFs calibrated based on data obtained at vapour-liquid equilibrium (VLE) conditions. A similar trend for simulated Fick diffusion coefficient of the same binary mixture was reported in a study by Higgoda et al. (2019) by employing FFs calibrated using data obtained via *ab initio* calculations. The reason for these anomalous concentration-dependent trends of the Fick diffusivity has not yet clearly been understood. For in-depth understanding, equilibrium molecular dynamic simulations were performed, using the most recent *ms2* release 4.0 molecular simulation engine, for binary fluid mixtures of methane and carbon dioxide at 295 K and 10 MPa, with varying methane concentrations from 5% to 95%. Fully rigid VLE data-based FFs were employed to calculate Fick diffusivity by calculating Maxwell-Stefan diffusivity and thermodynamic factor. Self-diffusion coefficient and viscosity of the same binary mixtures were also calculated for judging the predictive capabilities of FFs. The simulated structural and dynamical properties were compared with the few available experimental values in the literature and other simulated data obtained via the GROMACS simulation engine. The latter comparison enabled verification of the predictive capabilities of the VLE-based FFs in the compressed liquid and supercritical fluid region via *ms2* engine, for accessing equilibrium and transport properties. The investigations performed in this work revealed that the observed anomalous concentration-dependent behaviour of Fick diffusivity can be explained by the separate analysis of the thermodynamic and kinetic contributions.

Keywords: Equilibrium Molecular Dynamics, Binary mixtures, Fick diffusion coefficient, Methane, Carbon Dioxide

1. Introduction

Study on natural gas systems is important to make economic and ecological decisions in many industrial applications. Binary gas mixtures consisting of methane (CH₄) and carbon dioxide (CO₂) are important fluid systems since its applications are found in Supercritical extraction [1], CO₂ capture and storage [2], enhanced oil recovery [3]–[5] and so forth. Since many of these applications require separation of CO₂ from CH₄ to improve the process efficiency [2]–[4] accurate thermophysical properties of the fluid mixtures are needed to characterize the mass and momentum transfer processes.

The mass transfer of binary mixtures is characterized by the Fick diffusion coefficient D_{11} and the momentum transfer by the shear viscosity η . Therefore, the availability of accurate data or models to estimate data of the above-mentioned properties is vital. However, the experimental data which characterizes mass and momentum transfer processes in fluid

mixtures, especially in the near-critical region, is scarce most likely due to the high cost and complex experimental procedures [5], [6]. In corroboration to that, only a limited number of experimental Fick diffusion coefficient data of CH₄-CO₂ binary fluid mixtures are reported in the literature [7]–[10]. Therefore, demand for reliable predictive mechanisms of transport properties has increased in recent years [6].

Molecular dynamics (MD) simulation methods have been widely applied during recent years due to wide accessibility to computational resources and the free availability of efficient simulation engines [11], [12]. MD simulations are carried out under equilibrium or non-equilibrium conditions to predict the thermophysical properties employing effective potentials, also referred to as force fields (FFs). Several researchers have attempted to predict the transport properties of CH₄-CO₂ mixtures employing MD simulations over the years. In a recent study by Vella [13] on binary mixtures of CH₄ and CO₂, D_{11} was deduced by combining the Darken relation for accessing Maxwell-Stefan (MS) diffusion coefficient D_{12} using self-diffusion coefficients simulated with the TraPPE FFs [14], [15] with values for thermodynamic factor Γ_{11} calculated from an Equation of state (EoS). At 0.1 MPa and close to infinite dilution of CO₂, deviations of the calculated D_{11} data from experimental results within 13% were found. Guevara-Carrion et al. [16] have evaluated D_{11} in binary mixtures of CH₄ and CO₂ across the Widom line via separate calculations of the D_{12} and Γ_{11} by MD simulations. A recent study by Higgoda et al. [17] evaluated the performance of the new *ab-initio* (AI) based FFs in comparison with the TraPPE FFs using CH₄ and CO₂ binary mixtures. In their study, MD simulations were carried out at pressures between 0.1 and 12 MPa and temperatures between 293 K and 355 K to predict D_{11} considering separate simulations for the analysis of D_{12} and Γ_{11} also considering system size effects.

The accuracy of the simulated dynamical properties depends on the quality of the FFs which relates to the underlying sources employed for the calibration of the FF parameters. Vapour-liquid equilibrium (VLE) based FFs are known to predict dynamical properties accurately over a wide range of system densities [18], [19]. The Transferable Potentials for Phase Equilibria widely known as TraPPE [14], [15] is commonly used to model fluid mixtures containing CH₄ and CO₂ and have been shown to predict equilibrium properties accurately. These FF parameters, which can be transferred with a certain class of fluid and developed in the form of united atom (UA) nature, provide a convenient approach in performing MD simulations by accurately predicting equilibrium properties [20], [21]. However, such FFs can have limitations when used for calculating transport properties such as the Fick diffusion coefficient [13] and the viscosity [20]–[22] of fluid mixtures. On the other hand, pair-specific VLE-based FFs are shown to have better predictive capabilities for equilibrium and transport properties overboard range of fluid states [18]. In this study, we aim to employ such pair-specific FFs to calculate transport properties in binary fluid mixtures at large system densities in the supercritical and compressed liquid states.

According to the previous studies [16], [17] a significant deviation has been observed between experimental and simulation data, near the critical point at large system densities of the binary mixture of CH₄ and CO₂. The reason for these anomalous concentration-dependent trends of the Fick diffusion coefficient has not yet been clearly understood. Hence, equilibrium molecular dynamic (EMD) simulations were performed, using the recent *ms2* release 4.0 molecular simulation engine [23], for binary fluid mixtures of CH₄ and CO₂ at 295 K and 10 MPa, with varying CH₄ mole fraction x_{CH_4} from 5% to 95%. MD simulations were performed using VLE-based FFs [18], which are expected to have sound predictive capabilities in the large system densities, have been used to calculate concentration-dependent mass diffusivity in near the critical point of CH₄-CO₂ mixtures. The results were compared with the few available experimental data [7], [10] and simulated data generated by GROMACS [11] simulation engine [17].

2. Molecular Dynamic Simulations

This section discusses the molecular FFs used for modelling the binary mixtures, simulation details, and data evaluation procedures of the calculated structural and dynamical properties.

2.1. Molecular Force Fields

Equilibrium MD simulations were performed, using rigid non-polarizable VLE-based FFs [18] characterized by site-site pairwise-additive potential energy functions. All-atom (AA) model for CO₂ [24] and united atom model for CH₄ [25] was used to model interactions of the CH₄ - CO₂ binary mixtures. The dispersive and repulsive interactions were modelled

via the Lennard-Jones (LJ) 12 - 6 potential [26] while electrostatic interactions for CO₂ were considered by placing a superimposed point quadrupole moment [24]. The LJ interactions between unlike atoms i and j of pure components are described with Lorentz-Berthelot (LB) mixing rules [27], [28] using an arithmetic average for the size parameter, σ_{ij} and a geometric average for the energy parameter ϵ_{ij} . The modified LB mixing rule [29] with two additional parameters κ and ζ was used for mixtures according to equation (1-2) to describe the interaction between LJ sites. For all MD simulations, $\kappa = 1.000$ and $\zeta = 0.962$ [18] was used.

$$\sigma_{ij} = \kappa(\sigma_i + \sigma_j) \quad (1)$$

$$\epsilon_{ij} = \zeta \cdot \epsilon_i \epsilon_j \quad (2)$$

2.2 Simulation details

Equilibrium MD simulations were performed using the *ms2* simulation program [23]. A cubic simulation box with periodic boundary conditions was employed in all directions. To reduce the computational effort, a cut-off radius of 45% from the simulation box length was introduced. For the long-range corrections of LJ interactions, a homogeneous fluid beyond the cut-off radius is assumed while the reaction field method [30] was used for the corrections of electrostatic models. Newton's equations of motion were solved with a fifth-order Gear predictor-corrector numerical integrator [30]. All EMD simulations were performed with an integration time step of 1.16 fs. The statistical uncertainties of the predicted values were estimated with a block averaging method [31] while Gaussian error propagation considering the uncertainties of the simulated data was used for the derived quantities.

The densities of the binary gas mixtures were obtained from EMD simulations in the isobaric-isothermal (NpT) ensemble, in which N, p and T are defined as number of molecules in the simulation box, pressure, and Temperature, respectively. These simulations included 1000 molecules and were equilibrated over 7.5×10^5 time steps, followed by a production run of 2×10^6 time steps. The transport properties for each composition at 295 K and 10 MPa were predicted in the canonical (NVT) ensemble, in which V defines the volume of the simulation box. The NVT simulations were equilibrated over 5×10^5 time steps, followed by a production run of 1×10^7 time steps.

2.3 Thermophysical Properties

The Fick diffusion coefficient D_{11} is used to characterize mass transfer in fluid mixtures. For a binary mixture of species 1 and 2, D_{11} can be related to Maxwell-Stefan (MS) diffusion coefficient D_{12} and thermodynamic factor Γ_{11} which demonstrates the kinetic contribution and thermodynamic contribution of the mass transport phenomena, respectively. The relation between these three parameters is given using [32]

$$D_{11} = \Gamma_{11} D_{12} \quad (3)$$

In order to sample D_{12} , simulations employing Green-Kubo Formalism [33] which functionalizes the time-dependent microscopic fluctuations of a system around its equilibrium state with the transport properties is employed. D_{12} is obtained from the phenomenological Onsager coefficients in the form of [34],

$$D_{12} = \frac{x_2}{x_1} A_{11} + \frac{x_1}{x_2} A_{22} - A_{12} - A_{21}, \quad (4)$$

x_1 and x_2 represent the molecule fractions of species 1 and 2. Coefficients A_{11} and A_{22} include self and cross-correlations between molecules of the same species, 1 and 2, while the distinct cross-correlations between molecules of different species are denoted by A_{12} and A_{21} . Next, the thermodynamic contribution to the Fickian diffusion can be characterized via thermodynamic factor Γ_{11} . The more common methods used to extract Γ_{11} are excess Gibbs energy models and Equation of States. However, in this study Kirkwood-Buff (KB) Integrals [35] are combined with molecular simulations to sample Γ_{11} [36] which is defined by [37],

$$\Gamma_{11} = 1 - \frac{x_1 x_2 \rho (G_{11} + G_{22} - 2G_{12})}{1 + x_1 x_2 \rho (G_{11} + G_{22} - 2G_{12})}, \quad (5)$$

where x_1 and x_2 are mole fractions of species 1 and 2 while ρ is the mixture density. The KB coefficient G_{ij} is accessible by the integral of the respective radial distribution functions (RDF) $g_{ij}(r)$ which quantifies the centre-of-mass positions as a function of the distance r [38]. Since the infinite integration limit in RDF is not possible to reach in the simulation environment, the correction proposed by Ganguly and van der Vegt [39], also referred to as vdV, is used to extrapolate to the thermodynamic limit. The method used in the present study for calculating Γ_{11} depends on the FF parameters. Thus, the results can be used to determine the predictive capabilities of the FFs employed in the study. To further investigate the effect of the FFs on calculated dynamical properties the self-diffusion coefficient D_1 (species 1), D_2 (species 2) and the shear viscosity η were calculated. The latter characterises the momentum transport within the binary fluid mixture and is defined using the time autocorrelation function of the off-diagonal elements of the stress tensor [33]. The equations used for calculating these properties and data evaluation procedures are highlighted elsewhere [12], [33].

3. Results and Discussion

The first part of this section summarizes the simulated concentration-dependent D_{11} of CH₄ and CO₂ binary fluid mixtures obtained in this study by employing VLE-based FFs [18] in the supercritical and compressed liquid states, as a function of x_{CH_4} . These simulated D_{11} data are compared with the simulations performed using AI-based FFs [17] and experimental data to investigate the predictive performance of the employed VLE-based FFs implemented via the *ms2* simulation engine. Next, the kinetic and thermodynamic contributions of the Fick diffusivity are further analysed by considering D_{12} and Γ_{11} , respectively. For obtaining additional insights, simulated self-diffusion coefficient of each species in the binary mixtures are also discussed. Finally, the shear viscosity of the CH₄-CO₂ binary mixtures are studied to further validate the predictive performance of the VLE-based FFs [18].

Fig. 1-a shows the variation of simulated D_{11} results obtained using VLE-based FFs [18] compared with the AI-based FFs predictions [17], experimental data [7], [10] and a theoretical prediction obtained using the Fuller correlation [40] (see fig. 1-b) and GERG EoS [41] (see fig. 1-c). The simulated VLE-based FFs predicted D_{11} data using the *ms2* engine, in this study, follows a similar trend to the D_{11} data calculated via AI-based FFs using GROMACS [11] engine in a previous study [17]. The AI-based FFs predicted data [17] are within the statistical uncertainties of simulated VLE-based FFs predictions in the present study, except at the $x_{\text{CH}_4} = 0.25$ presenting 62% deviation. The predicted D_{11} data obtained via VLE-based FFs depict 48%, 70% and 43% deviations from the experimental data of Jeffries and Drickamer [7] at $x_{\text{CH}_4} = 0.25$, $x_{\text{CH}_4} = 0.5$, and Piszko et. al [10] at $x_{\text{CH}_4} = 0.5$ respectively. For further understanding of the observed concentration dependent simulated Fick diffusion coefficient variation, its kinetic and thermodynamic contributions were analysed separately. The MS diffusion coefficient calculated via VLE-based FFs in this study is compared with results obtained from AI-based FFs [17] and the ones obtained via Fuller correlation [40] in fig. 1-b. The VLE-based FFs predicted D_{12} data underpredicts in comparison to the ones obtained via AI-based FFs predictions, however, both datasets follow a similar concentration-dependent trend. The AI-based FFs predictions of D_{12} [17] are within the statistical uncertainties of VLE-based FFs predicted D_{12} data, except at $x_{\text{CH}_4} = 0.1$ and $x_{\text{CH}_4} = 0.25$ where the difference is beyond the simulated statistical uncertainties. It should be noted that the Fuller correlation [40] provides D_{12} data accurately in the gaseous states, thus, deviates significantly from simulated data in the compressed liquid state at low CH₄ mole fractions.

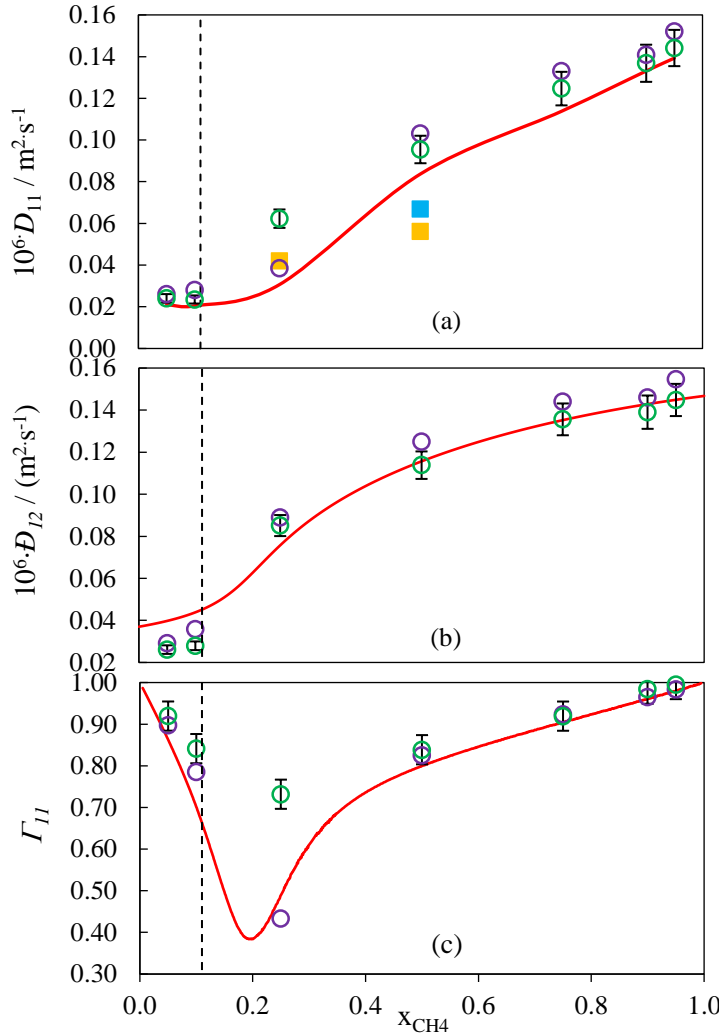


Fig. 1- Fick diffusion coefficients D_{11} (a), MS diffusion coefficient D_{12} (b), and thermodynamic factor Γ_{11} (c) as a function of mole fraction of CH_4 , x_{CH_4} , for binary mixtures of CH_4 and CO_2 at 10 MPa and 295 K. Simulation data (open circles) for D_{11} , D_{12} and Γ_{11} : VLE-based FFs (green) and AI-based FFs (purple) [17]. Experimental D_{11} data (filled squares): Piszko et al. [10] at $T = 293.15$ K and $p = 10$ MPa (blue); Jeffries and Drickamer [7] at $T = 298.15$ K and $p = 10.1$ MPa (yellow). Theoretical calculations (red line): D_{11} obtained (a) using Fuller correlation (b) [40] and GERG EoS (c) [41], D_{12} using Fuller correlation [40] (b), Γ_{11} using GERG EoS [41] (c). The vertical dashed line shows x_{CH_4} where the thermodynamic state changes from compressed liquid to supercritical conditions with increasing x_{CH_4} .

The thermodynamic contribution to the Fick diffusivity can be characterized through the thermodynamic factor Γ_{11} . The VLE-based FFs [18] and AI-based FFs [17] simulated Γ_{11} , and theoretical predictions from the GERG-2008 EoS [41] are shown in fig. 1-c. The simulation results obtained from the VLE-based FFs show agreement to AI-based FFs predictions [17] and the theoretical calculations from GERG-2008 [41] except at few state points. In detail, it is evident that the VLE-based FFs employed in this study, has over-predicted the thermodynamic factor around the $x_{\text{CH}_4} = 0.2$ and has unable to follow the minima of Γ_{11} variation with concentration which is accurately predicted by AI-based FFs [17]. This limitation to predict Γ_{11} accurately via VLE-based FFs is reported previously as well [17], [42]. The effect of the prediction limitation of Γ_{11} around $x_{\text{CH}_4} = 0.2$ in turn affect D_{11} predictions, where 61% deviation can be observed in reference to the AI-based FFs predictions [17]. Considering experimental reference data [7], [10], both VLE-based FFs and AI-based FFs predictions

present significant deviations at $x_{\text{CH}_4} = 0.5$. This may be due to the fact that the challenging nature of the employed experimental technique for obtaining mass diffusivities at $x_{\text{CH}_4} = 0.5$ [10]. In this regard, more accurate mass diffusivity data, at these thermodynamic states, are preferred by means of other experimental techniques [43] for validating the FFs predictions.

Fig. 2 presents self-diffusion coefficient of CH_4 and CO_2 species of the binary mixtures against x_{CH_4} . As expected, CO_2 shows lower self-diffusivity in comparison to CH_4 due to its higher molar mass. Compared to the self-diffusion coefficient values predicted via AI-based FFs [17], results from this study follow the same trend but underpredict the ones for both CH_4 and CO_2 . The reason for the underprediction of self-diffusivities could be mainly due to the UA nature of the molecular model of CH_4 in VLE-based FFs employed simulations. The statistical uncertainties are within the symbol size of the data points, thus, the predicted self-diffusivities from AI-based FFs [17] are given beyond the statistical uncertainties of this study considering CH_4 rich mixtures.

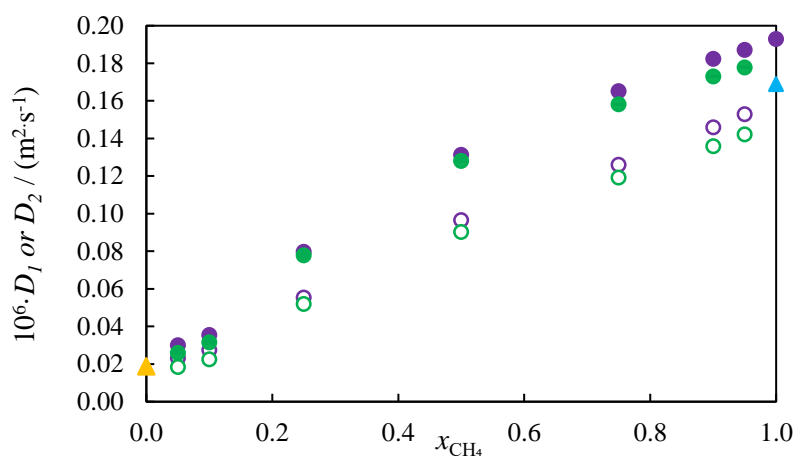


Fig. 2 - Self diffusivities of CO_2 (open circles) and CH_4 (filled circles) as a function of mole fraction of CH_4 , x_{CH_4} , for binary mixtures of CH_4 and CO_2 at 10 MPa and 295 K. MD simulation data via VLE-based FFs (green) and AI-based FFs (purple) [17]. Experimental self-diffusivity data (filled triangles): Groß et al. [44] at $T = 298$ K and $p = 10$ MPa (yellow), Harris [45] at $T = 298$ K and $p = 10.49$ MPa (blue).

Finally, the momentum transfer effect of the binary fluid mixtures is analysed using shear viscosity η calculations. Fig. 3 shows η predictions using different FFs and reference data (REFPROP database) [46], [47] with x_{CH_4} . Furthermore, Fig. 3 includes experimental η data of pure CO_2 at 293.15 K and 10.17 MPa [48], and CH_4 at 298.15 K and 10.13 MPa [49]. The simulated η via VLE-based FFs [18] display a better agreement at lower system densities with the previously reported η via AI-based FFs [17], TraPPE FFs [50] and REFPROP database [46], [47]. However, deviations beyond the statistical uncertainties can be seen at $x_{\text{CH}_4} = 0.05$ and $x_{\text{CH}_4} = 0.10$ where, 40% and 36% over prediction with the AI-based results [17] and 30% and 29% overprediction with REFPROP data [46], [47] are observed. Moreover, this overprediction is confirmed by the experimental η of pure CO_2 [48] as well. The general trend of overprediction of shear viscosity alongside with underprediction of Fick diffusivity, is observed with the VLE-based FFs predictions in this study.

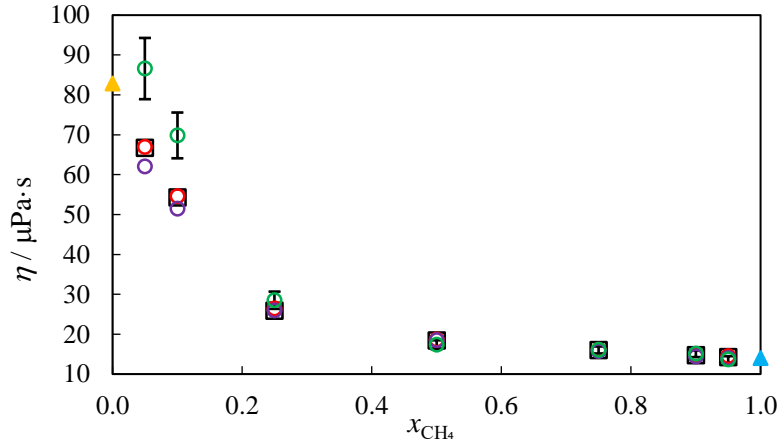


Fig. 3 - Shear viscosities η (open circles) as a function of mole fraction of CH_4 , x_{CH_4} , for binary mixtures of CH_4 and CO_2 at 10 MPa and 295 K. MD simulation data via VLE-based FFs (green), AI-based FFs (purple) [50] and TrAPPE FFs (red) [50]. Calculated shear viscosities (open squares) from REFPROP database (black) [46], [47]. Experimental shear viscosity data (filled triangles): Amar et al. [48] at $T = 293.15$ K and $p = 10.17$ MPa (yellow), Golubev [49] at $T = 298.15$ K and $p = 10.13$ MPa (blue).

4. Conclusion

In the present work, previously reported anomaly of the Fick diffusivity in the near-critical region around the Widom line for CH_4 and CO_2 fluid mixtures was investigated using a vapour-liquid equilibrium (VLE) data-based calibrated force fields (FFs) and compared with scarce simulated and experimental data in the literature. The equilibrium molecular dynamic simulations were carried out using the *ms2* release 4.0 molecular simulation engine at the temperature and pressure of 295 K and 10 MPa, respectively. The Fick diffusivity D_{11} of the binary fluid mixtures are analysed in terms of the kinetic and thermodynamic contributions via the Maxwell-Stefan (MS) diffusivity D_{12} and thermodynamic factor Γ_{11} , respectively. Further, the self-diffusivity of the two species and the shear viscosity η of the binary mixtures were calculated to analyse the predictive capabilities of the selected VLE-based FFs and the *ms2* molecular simulation engine.

The Fick diffusivity which was obtained using MS diffusion coefficient and thermodynamic factor, depicts similar trend in both VLE-based and *ab initio*-based FFs predictions. Both FFs show a large deviation from the experimental results at equimolar concentrations where the possible causes have been discussed in section 3. The predictions given by the Fuller correlation [40] for the MS diffusion coefficient showed better agreement with VLE-based FFs simulated data where the predictions obtained via the GERG-EoS [41] for the thermodynamic factor was found to be in better agreement with *ab initio*-based FFs predictions. Overall, the D_{11} , D_{12} and Γ_{11} results from the equilibrium molecular dynamic simulations obtained using VLE-based FFs in this study presents the correct trends in comparison to reference data. In conclusion, the mass transfer phenomena of binary fluid mixtures, characterized by the Fick diffusion coefficient, seems to be significantly affected by variation of the FF parameters. In fact, the nature of the FFs, characterized by the underlying sources used for calibrating them, mainly affects the predictive power in connection with structural properties. However, the predictive capabilities for dynamical properties such as MS diffusivity, self-diffusivity, and shear viscosity of the investigated binary fluid systems seems to be less sensitive to FF parameter variation or the underlying sources employed for FFs calibration.

In conclusion, the VLE-based FFs investigated via *ms2* simulation engine in this study can be used to obtain reliable predictions for mass diffusivities of investigated binary fluid mixtures in the near critical region while GERG-EoS [41] is more appropriate for thermodynamic factor calculations.

References

- [1] E. Reverchon and I. De Marco, "Supercritical fluid extraction and fractionation of natural matter," *J. Supercritical Fluids*, vol. 38, no. 2, pp. 146–166, 2006.
- [2] D. M. D'alessandro, B. Smit, and J. R. Long, "Carbon Dioxide Capture: Prospects for New Materials," *J. Angewandte Chemie International Edition*, vol. 49, no. 35, pp. 6058–6082, 2010.
- [3] L. Peters, A. Hussain, M. Follmann, T. Melin, and M.-B. Hägg, "CO₂ removal from natural gas by employing amine absorption and membrane technology—A technical and economical analysis," *J. Chemical Engineering*, vol. 172, no. 2–3, pp. 952–960, 2011.
- [4] T. Rufford, S. Smart, G. Watson, B. Graham, J. Boxall, J. C. Diniz Da Costa, E. F. May, "The removal of CO₂ and N₂ from natural gas: A review of conventional and emerging process technologies," *J. Petroleum Science & Engineering*, vol. 94–95, pp. 123–154, 2012.
- [5] E. Hendriks, G. Kontogeorgis, R. Dohrn, J-C. de Hemptinne, I. G. Economou, L. Žilnik and V. Vesovic "Industrial Requirements for Thermodynamics and Transport Properties," *J. Industrial & Engineering Chemistry Research*, vol. 49, no. 22, pp. 11131–11141, 2010.
- [6] G. Kontogeorgis, R. Dohrn, I. Economou, J-C. De Hemptinne, A. Ten Kate, S. Kuitunen, M. Mooijer, L. Žilnik and V. Vesovic, "Industrial Requirements for Thermodynamic and Transport Properties: 2020," *J. Industrial & Engineering Chemistry Research*, vol. 60, no. 13, pp. 4987–5013, 2021.
- [7] Q. R. Jeffries and H. G. Drickamer, "Diffusion in CO₂ –CH₄ Mixtures to 225 Atmospheres Pressure," *J. Chemical Physics*, vol. 22, no. 3, pp. 436–437, 1954.
- [8] T. Kugler, M. H. Rausch, and A. P. Fröba, "Binary Diffusion Coefficient Data of Various Gas Systems Determined Using a Loschmidt Cell and Holographic Interferometry," *Int. J. Thermophysics*, vol. 36, no. 10–11, pp. 3169–3185, 2015.
- [9] P. Zangi, M. H. Rausch, and A. P. Fröba, "Binary Diffusion Coefficients for Gas Mixtures of Propane with Methane and Carbon Dioxide Measured in a Loschmidt Cell Combined with Holographic Interferometry," *Int. J. Thermophysics*, vol. 40, no. 2, p. 18, 2019.
- [10] M. Piszko, K. Batz, M. H. Rausch, C. Giraudet, and A. P. Fröba, "Diffusivities of Binary Mixtures Consisting of Carbon Dioxide, Methane, and Propane by Dynamic Light Scattering," *J. Chemical & Engineering Data*, vol. 65, no. 3, pp. 1068–1082, 2020.
- [11] B. Hess, C. Kutzner, D. Van Der Spoel, and E. Lindahl, "GROMACS 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation," *J. Chemical Theory & Computation*, vol. 4, no. 3, pp. 435–447, 2008.
- [12] S. Deublein, B. Eckl, J. Stoll, S. Lishchuk, G. Guevara-Carrion, C. Glass, T. Merker, M. Bernreuther, H. Hasse and J. Vrabec, "*ms2*: A Molecular Simulation Tool for Thermodynamic Properties," *J. Computer Physics Communications*, vol. 182, no. 11, pp. 2350–2367, 2011.
- [13] J. R. Vella, "Fick Diffusion Coefficients of The Gaseous CH₄ –CO₂ System from Molecular Dynamics Simulations Using TraPPE Force Fields at 101.325, 506.625, 1013.25, 2533.12, And 5066.25 kPa," *J. Chemical & Engineering Data*, vol. 64, no. 9, pp. 3672–3681, 2019.
- [14] M. G. Martin and J. I. Siepmann, "Transferable Potentials for Phase Equilibria. 1. United-Atom Description of N-Alkanes," *J. Physical Chemistry B*, vol. 102, no. 14, pp. 2569–2577, 1998.
- [15] J. J. Potoff and J. I. Siepmann, "Vapor–Liquid Equilibria of Mixtures Containing Alkanes, Carbon Dioxide, and Nitrogen," *AIChE Journal*, vol. 47, no. 7, pp. 1676–1682, 2001.
- [16] G. Guevara-Carrion, S. Ancherbak, A. Mialdun, J. Vrabec, and V. Shevtsova, "Diffusion of methane in supercritical carbon dioxide across the Widom line," *J. Scientific Reports*, vol. 9, no. 1, p. 8466, 2019.
- [17] U. A. Higgoda, C. J. Kankanamge, R. Hellmann, T. M. Koller, and A. P. Fröba, "Fick diffusion coefficients of binary fluid mixtures consisting of methane, carbon dioxide, and propane via molecular dynamics simulations based on simplified pair-specific *ab initio*-derived force fields," *J. Fluid Phase Equilibria*, vol. 502, p. 112257, 2019.
- [18] J. Vrabec, Y. Huang and H. Hasse, "Molecular models for 267 binary mixtures validated by vapor–liquid equilibria: A systematic approach," *J. Fluid Phase Equilibria*, vol. 279, no. 2, pp.120–135, 2009.

- [19] J. Vrabec, G. K. Kedia, G. Fuchs, and H. Hasse, “Comprehensive study of the vapour–liquid coexistence of the truncated and shifted Lennard–Jones fluid including planar and spherical interface properties,” *J. Molecular Physics*, vol. 104, no. 9, pp. 1509–1527, 2006.
- [20] R. A. Messerly, M. C. Anderson, S. M. Razavi, and J. R. Elliott, “Improvements and limitations of Mie λ -6 potential for prediction of saturated and compressed liquid viscosity,” *J. Fluid Phase Equilibria*, vol. 483, pp. 101–115, 2019.
- [21] D. K. Dysthe, A. H. Fuchs, and B. Rousseau, “Fluid transport properties by equilibrium molecular dynamics. iii. evaluation of united atom interaction potential models for pure alkanes,” *J. Chemical Physics*, vol. 112, no. 17, pp. 7581–7590, 2000.
- [22] A. W. S. Hamani, J.-P. Bazile, H. Hoang, H. T. Luc, J.-L. Daridon, and G. Galliero, “Thermophysical properties of simple molecular liquid mixtures: On the limitations of some force fields,” *J. Molecular Liquids*, vol. 303, p. 112663, 2020.
- [23] R. Fingerhut, G. Guevara-Carrion, I. Nitzke, D. Saric, J. Marx, K. Langenbach, S. Prokopev, D. Celný, M. Bernreuther, S. Stephan, M. Kohns, H. Hasse and J. Vrabec, “ms2: A molecular simulation tool for thermodynamic properties, release 4.0,” *J. Computer Physics Communications*, vol. 262, p. 107860, 2021.
- [24] T. Merker, C. Engin, J. Vrabec, and H. Hasse, “Molecular model for carbon dioxide optimized to vapor-liquid equilibria,” *J. Chemical Physics*, vol. 132, no. 23, p. 234512, 2010.
- [25] J. Vrabec, J. Stoll, and H. Hasse, “A Set of Molecular Models for Symmetric Quadrupolar Fluids,” *J. Physical Chemistry B*, vol. 105, no. 48, pp. 12126–12133, 2001.
- [26] J. E. Lennard-Jones, “Cohesion,” *Proceedings of The Physical Society*, vol. 43, no. 5, pp. 461–482, 1931.
- [27] H. A. Lorentz, “Ueber die Anwendung des Satzes vom Virial in der kinetischen Theorie der Gase,” *Annalen der Physik*, vol. 248, no. 1, pp. 127–136, 1881.
- [28] D. Berthelot, “Sur le Mélange Des Gaz,” *Compt. Rendus*, vol. 126, no. 3, 1898.
- [29] J. Fischer, D. Möller, A. Chialvo and J. M. Haile, “The Influence of Unlike Molecule Interaction Parameters on Liquid Mixture Excess Properties,” *J. Fluid Phase Equilibria*, vol. 48, pp 161 – 176, 1989.
- [30] M. Allen and D. Tildesley, “Computer Simulation of Liquids”, Clarendon Press, Oxford, 1987.
- [31] H. Flyvbjerg and H. G. Petersen, “Error estimates on averages of correlated data,” *J. Chemical Physics*, vol. 91, no. 1, pp. 461–466, 1989.
- [32] X. Liu, S. K. Schnell, J.-M. Simon, D. Bedeaux, S. Kjelstrup, A. Bardow, and T. J. H. Vlugt, “Fick Diffusion Coefficients of Liquid Mixtures Directly Obtained from Equilibrium Molecular Dynamics,” *J. Physical Chemistry B*, vol. 115, no. 44, pp. 12921–12929, 2011.
- [33] K. Singer, Ed., *Statistical Mechanics*, vol. 1. Cambridge: Royal Society of Chemistry, 1973.
- [34] R. Krishna and J. M. Van Baten, “The Darken Relation for Multicomponent Diffusion in Liquid Mixtures of Linear Alkanes: An Investigation Using Molecular Dynamics (MD) Simulations,” *J. Industrial & Engineering Chemistry Research*, vol. 44, no. 17, pp. 6939–6947, 2005.
- [35] J. G. Kirkwood and F. P. Buff, “The Statistical Mechanical Theory of Solutions. I,” *J. Chemical Physics*, vol. 19, no. 6, pp. 774–777, 1951.
- [36] R. Fingerhut and J. Vrabec, “Kirkwood-Buff Integration: A promising route to entropic properties,” *J. Fluid Phase Equilibria*, vol. 485, pp. 270–281, 2019.
- [37] J. C. Rasaiah, “Molecular Theory of Solutions. By Arie Ben-Naim,” *J. American Chemical Society*, vol. 129, no. 28, pp. 8922–8922, 2007.
- [38] P. Krüger, S. K. Schnell, D. Bedeaux, S. Kjelstrup, T. J. H. Vlugt, and J.-M. Simon, “Kirkwood–Buff Integrals for Finite Volumes,” *J. Physical Chemistry Letters*, vol. 4, no. 2, pp. 235–238, 2013.
- [39] P. Ganguly and N. F. A. van der Vegt, “Convergence of Sampling Kirkwood–Buff Integrals of Aqueous Solutions with Molecular Dynamics Simulations,” *J. Chemical Theory & Computation*, vol. 9, no. 3, pp. 1347–1355, 2013.
- [40] E. N. Fuller, P. D. Schettler, and J. C. Giddings, “New Method for Prediction of Binary Gas-Phase Diffusion Coefficients,” *J. Industrial & Engineering Chemistry*, vol. 58, no. 5, pp. 18–27, 1966.

- [41] O. Kunz and W. Wagner, “The Gerg-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of Gerg-2004,” *J. Chemical & Engineering Data*, vol. 57, no. 11, pp. 3032–3091, 2012.
- [42] X. Liu, A. Martín-Calvo, E. McGarrity, S. K. Schnell, S. Calero, J-M. Simon, D. Bedeaux, S. Kjelstrup, A. Bardow, and T. J. H. Vlucht, “Fick Diffusion Coefficients in Ternary Liquid Systems from Equilibrium Molecular Dynamics Simulations,” *J. Industrial & Engineering Chemistry Research*, vol. 51, no. 30, pp. 10247–10258, 2012.
- [43] E. L. Cussler and E. L. Cussler, *Diffusion: Mass Transfer in Fluid Systems*. Cambridge University Press, 2009.
- [44] T. Groß, J. Buchhauser, and H.-D. Lüdemann, “Self-diffusion in fluid carbon dioxide at high pressures,” *J. Chemical Physics*, vol. 109, no. 11, pp. 4518–4522, 1998.
- [45] K. R. Harris, “The Density Dependence of The Self-Diffusion Coefficient of Methane at -50° , 25° and 50°C ,” *Physica A: Statistical Mechanics and Its Applications*, vol. 94, no. 3–4, pp. 448–464, 1978.
- [46] E. Lemmon, M. Huber, and M. McLinden, “Nist Standard Reference Database 23: Reference Fluid Thermodynamic and Transport Properties-REFPROP, Version 9.1.” Natl Std. Ref. Data Series (Nist Nsrds), National Institute of Standards and Technology, Gaithersburg, Md, Feb. 2013.
- [47] A. Fenghour, W. A. Wakeham, and V. Vesovic, “The Viscosity of Carbon Dioxide,” *J. Physical & Chemical Reference Data*, vol. 27, no. 1, pp. 31–44, 1998.
- [48] M. N. Amar, M. A. Ghriga, H. Ouaer, M. El Amine Ben Seghier, B. T. Pham, and P. Ø. Andersen, “Modeling viscosity of CO_2 at high temperature and pressure conditions,” *J. Natural Gas Science & Engineering*, vol. 77, p. 103271, 2020.
- [49] I. F. Golubev, *Viscosity of gases and gas mixtures: A handbook*, Israel Program for Scientific Translations, 1970.
- [50] U.A. Higgoda, “Improvement of the predictive power of molecular dynamics simulations for the determination of transport properties demonstrated for selected fluid systems”, Ph.D. dissertation, ESYTEC Energie- und Systemtechnik GmbH, Erlangen, Germany.