

Towards Predictive Models for Fick- and Maxwell-Stefan Diffusivities Using Molecular Dynamics Simulation

Thijs Vlugt^{C, S}

Delft University of Technology, Process & Energy Department, Delft, Netherlands

t.j.h.vlugt@tudelft.nl

Understanding mass transport in liquids by mutual diffusion is an important topic for many applications in chemistry and chemical engineering. The reason for this is that diffusion is often the rate limiting step in chemical reactors and separators. To describe diffusive mass transport in liquid mixtures, generalized Fick's law and the Maxwell-Stefan theory are often used. It is often difficult to predict the concentration dependence of Fick- and Maxwell-Stefan diffusivities, especially for multicomponent systems. In the present work, equilibrium Molecular Dynamics (MD) simulations are used to analyze the concentration dependence of diffusion coefficients in multicomponent systems. Maxwell-Stefan diffusivities can be directly calculated from equilibrium MD simulations, while calculating Fick diffusivities requires knowledge on the matrix of thermodynamic factors. An efficient method is presented to compute the latter from MD simulations. By neglecting velocity cross-correlations between different molecules, a multicomponent Darken equation was derived and this predictive equation was tested against data generated from MD simulations. The results show that MD simulations are a useful tool for constructing models for the prediction of the concentration dependence of diffusivities.

Relevant literature:

- [1] Maxwell-Stefan diffusivities and velocity cross-correlations in dilute ternary systems, X. Liu, A. Bardow, T.J.H. Vlugt, *diffusion-fundamentals.org*, 2011, 16, 81.
- [2] Fick Diffusion Coefficients of Liquid Mixtures Directly Obtained From Equilibrium Molecular Dynamics, X. Liu, S.K. Schnell, J-M Simon, D. Bedeaux, S. Kjelstrup, A. Bardow, T.J.H. Vlugt, *J. Phys. Chem. B*, 2011, 115, 12921-12929.
- [3] Calculating Thermodynamic Properties from Fluctuations at Small Scales, S.K. Schnell, X. Liu, J-M Simon, A. Bardow, D. Bedeaux, T.J.H. Vlugt, S. Kjelstrup, *J. Phys. Chem. B*, 2011, 115, 10911-10918.
- [4] Predictive Darken Equation for Maxwell-Stefan Diffusivities in Multicomponent Mixtures, X. Liu, T.J.H. Vlugt, A. Bardow, *Ind. Eng. Chem. Res.*, 2011, 50, 10350-10358.
- [5] Multicomponent Maxwell-Stefan Diffusivities at Infinite Dilution, X. Liu, A. Bardow, T.J.H. Vlugt, *Ind. Eng. Chem. Res.*, 2011, 50, 4776-4782.