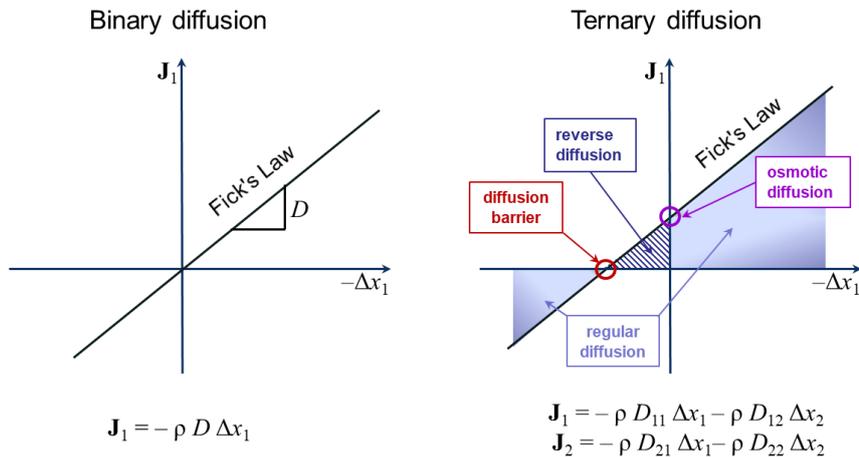


Prediction of transport diffusion coefficients of multicomponent mixtures in the liquid state

Transport diffusion plays a key role in many natural and technical processes. Basically all separation processes in chemical engineering, such as distillation, absorption, extraction or condensation, involve mass transport within a fluid mixture or across a phase boundary. Diffusion processes are often even the rate determining step in these unit operations, where chemical engineering applications usually deal with multicomponent mixtures. However, while there is extensive theoretical work on the development of phenomenological approaches for the description of mass transfer, in practice, strongly simplified transport approaches are still being used in many areas in which mass transfer models are required. This is in part because of the poor availability of experimental data on transport diffusion coefficients, which are essential to apply the phenomenological approaches to practical problems. In fact, diffusion coefficients have experimentally been measured only for a few ternary mixtures because of challenges related to the description of multicomponent diffusion processes.



In recent years, molecular modelling and simulation has become an alternative route not only to accurately predict dynamic properties of liquid mixtures, but also to interpret experimental data because it offers access to microscopic details which are often inaccessible with experimental techniques. In this project, a molecular simulation based methodology to predict transport diffusion coefficients of multicomponent liquid mixtures is targeted. This methodology should lead to accurate and trustworthy predictions of the Maxwell-Stefan diffusion coefficient, the thermodynamic factor and, hence, of the Fick diffusion coefficient of ternary and quaternary liquid mixtures of real fluids, including hydrogen-bonding components.

The employed approach is to determine the Maxwell-Stefan diffusion coefficients from simulations under equilibrium following the Kubo theory. It states that there is no difference between dynamical processes due to spontaneous fluctuations from equilibrium and those due to external perturbations, provided that the perturbations are sufficiently weak to ensure a linear response. Based on this, the Green-Kubo formalism provides the exact relation between a transport coefficient and the time integral of the autocorrelation function of the corresponding microscopic flux in a system under equilibrium. The big advantage of the equilibrium method is that during a single simulation run not only self- and mutual diffusion coefficients, but also other transport properties, like shear viscosity or thermal conductivity, can be obtained simultaneously without significant additional computational effort.

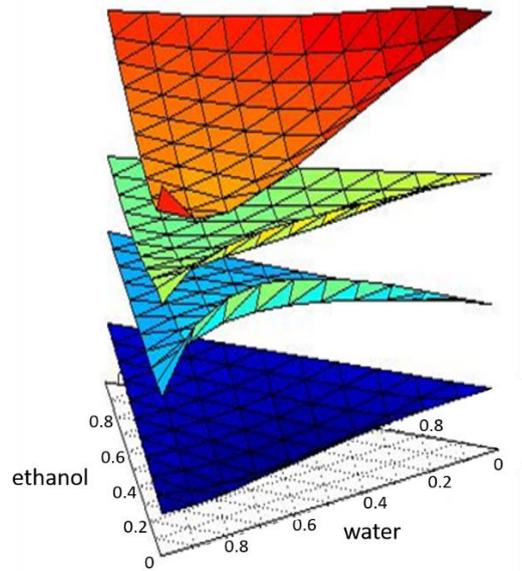
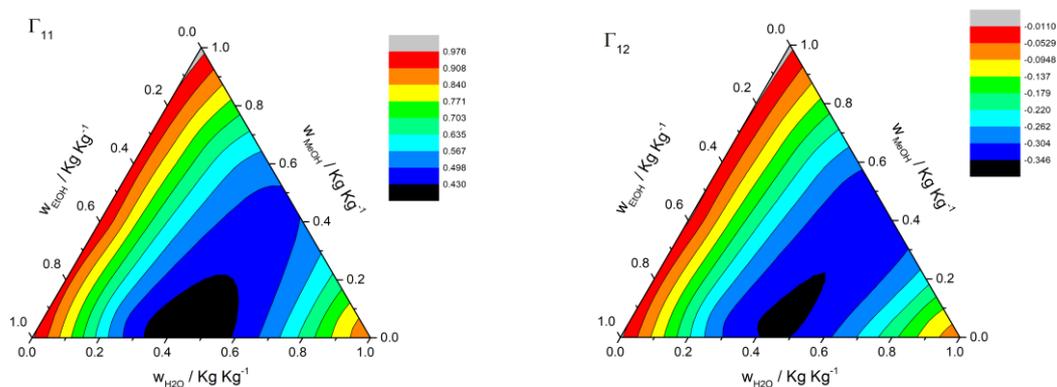


Fig. 1 Qualitative composition dependence of the components of the Fick diffusion coefficient matrix D_{11} (red), D_{22} (green), D_{12} (dark blue) and D_{21} (light blue) predicted by molecular simulation for the mixture water + methanol + ethanol

In this project, funded by Deutsche Forschungsgemeinschaft, the prediction of the Maxwell-Stefan diffusion coefficient as well as its conversion to the Fick diffusion coefficient are of interest. The Maxwell-Stefan diffusion coefficient can be transformed to the Fick diffusion coefficient and vice versa, if the derivative of the chemical potential at the composition of interest in form of the thermodynamic factor is known. Because the chemical potential cannot be experimentally, this factor is usually estimated from vapor-liquid equilibrium or excess enthalpy data employing an equation of state or an excess Gibbs energy G^E model. However, it can also be directly sampled by molecular simulations. E.g., the thermodynamic factor can be estimated from free energy perturbation methods like Widom's particle insertion or from the integral of the radial distribution function with respect to the distance using the Kirkwood-Buff theory.



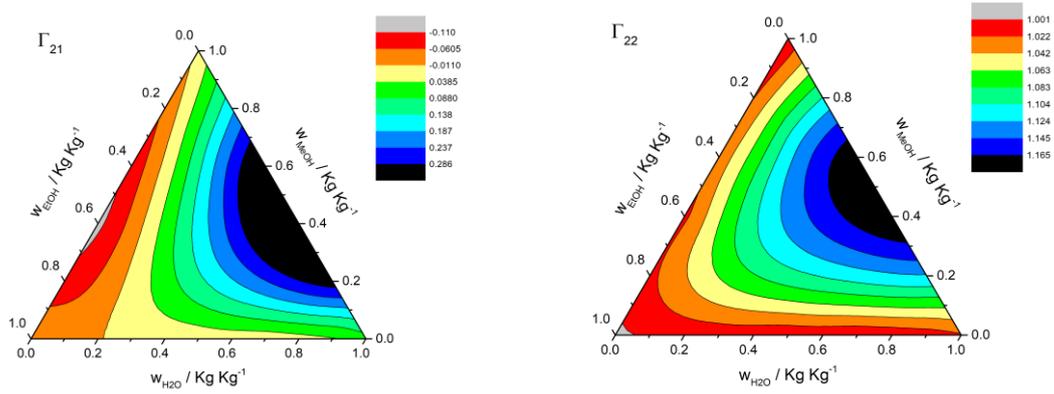


Fig. 2 Composition dependence of the components of the thermodynamic factor matrix of the ternary mixture water + methanol + ethanol obtained from molecular dynamic simulation methods

Furthermore, other estimation techniques and inter- and extrapolation methods predictive approaches are assessed on the basis of the available experimental and simulative extended data sets for a broad range of liquid systems and thermodynamic conditions. The anomalies in the proximity of the liquid-liquid binodal curve are also be investigated. From that analysis, it is expected to obtain new insights into the relationships between the different diffusion coefficients, thermodynamic conditions and the molecular interactions of multicomponent liquids.