Mutual diffusion of binary liquid mixtures
containing methanol, ethanol, acetone, benzene, cyclohexane, toluene and carbon tetrachloride

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Computational Molecular Engineering

Thermodynamics and Energy Technology **ThEt**

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Motivation

The knowledge of diffusion coefficients and other transport properties of fluids is essential for the modeling of complex systems and processes in science and engineering. Since the experimental estimation of diffusion coefficients can be very challenging and time consuming there is a growing need for accurate predictive methods. Due to the rapid development of computing power, molecular modelling and simulation has emerged as an alternative for empirical correlations, especially when dealing with complex and strongly non-ideal liquid mixtures.

Description of mutual diffusion

Fick: $\boldsymbol{J}_i = -\rho_m \sum_{j=1}^{n-1} D_{ij} \nabla x_j$ → coefficients from experiment

Maxwell-Stefan: $-\frac{1}{RT}\nabla\mu_i = \sum_{j\neq i=1}^{n} \frac{x_j(\boldsymbol{u}_i - \boldsymbol{u}_j)}{Đ_{ij}}$ →coefficients from molecular simulation

$x_i \boldsymbol{u}_i = -\frac{1}{RT}\sum_{j=1}^{n} \Lambda_{ij}\nabla\mu_j$ In binary mixture: $Đ_{ij} = \frac{x_j}{x_i}\Lambda_{ii} + \frac{x_i}{x_j}\Lambda_{jj} - \Lambda_{ij} - \Lambda_{ji}$

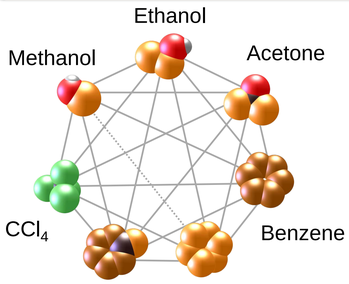
Onsager reciprocal relation: $\Lambda_{ij} = \Lambda_{ji}$ $\sum_i M_i \Lambda_{ij} = 0$

Fick ⟺ **Maxwell-Stefan**

Thermodynamic factor Γ: Binary mixture: $D = Đ\Gamma$ $\Gamma = 1 + x_1 \frac{d\ln\gamma_1}{dx_1}$

- Factor describes thermodynamic non-ideality of a mixture
  - Ideal mixture: $\Gamma = 1$
  - Thermodynamic instability (phase separation): $\Gamma < 0$
- Can be calculated by G^E models (e.g. Wilson, NRTL, UNIQUAC)
- Fitting of model parameters to experimental VLE data or simulation data

Studied mixtures



Molecular models:
- Rigid molecules (united atom)
- Lennard-Jones sites, point charges, point dipole, point quadrupole
- Non-polarizable
- LJ parameters optimized to saturated liquid density and vapor pressure, (self diffusion)
- Mixing behavior: predicted

20 binary mixtures at T = 298.15 K, p = 0.1 MPa

Three groups according to deviation of thermodynamic factor from ideal behavior.

References

[1] Guevara-Carrión, Janzen, Muñoz-Muñoz, Vrabec, *J. Chem. Phys*. 144 (2016) 124501: Mutual diffusion of binary liquid mixtures containing methanol, ethanol, acetone, benzene, cyclohexane, toluene and carbon tetrachloride

[2] Glass et al., *Comp. Phys. Commun.* 185 (2014) 3302: ms2: A Molecular Simulation Tool for Thermodynamic Properties, New Version Release

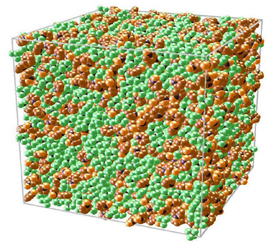
Method

Molecular simulation

Molecular simulation of thermodynamic properties:
Macroscopic behavior of fluids results directly from intermolecular interactions.
Prediction of transport properties
- Equilibrium molecular dynamics: numerical solution of Newton's equations of motion to obtain molecular trajectories
- Autocorrelation functions according to the Green-Kubo formalism

Tool: *ms2*

Molecular models defined by force fields
Molecular dynamics (MD) / Monte Carlo (MC)
Several classical ensembles
All static properties (thermal, caloric, entropic)
Code: FORTRAN90
Parallelization: MPI / OpenMP



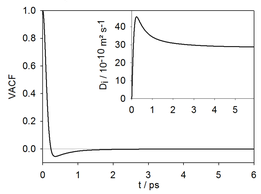
Green Kubo formalism

Microscopic fluctuations around equilibrium
→ Description of non-equilibrium phenomena
→ Transport coefficients from time dependent autocorrelation functions of corresponding fluxes

Self diffusion $D_i = \frac{1}{3N_i}\int_0^\infty dt \left\langle \sum_i^N \boldsymbol{v}_i(0)\cdot\boldsymbol{v}_i(t)\right\rangle$

Onsager coefficients $\Lambda_{ij} = \frac{1}{3N}\int_0^\infty dt \left\langle \sum_{k=1}^{N_i}\boldsymbol{v}_{i,k}(0)\cdot\sum_{l=1}^{N_j}\boldsymbol{v}_{j,l}(t)\right\rangle$

Example: Velocity autocorrelation functions

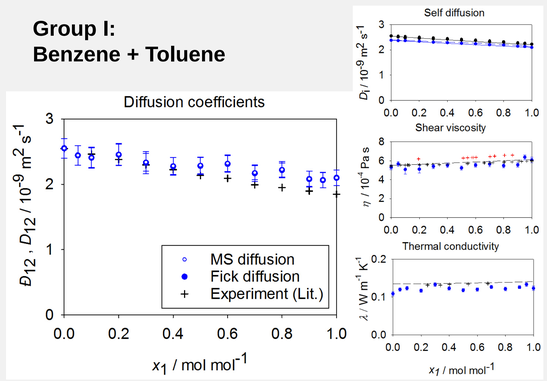


Shear viscosity $\eta = \frac{1}{Vk_BT}\int_0^\infty dt\langle \boldsymbol{J}_p^{xy}(0)\cdot\boldsymbol{J}_p^{xy}(t)\rangle$

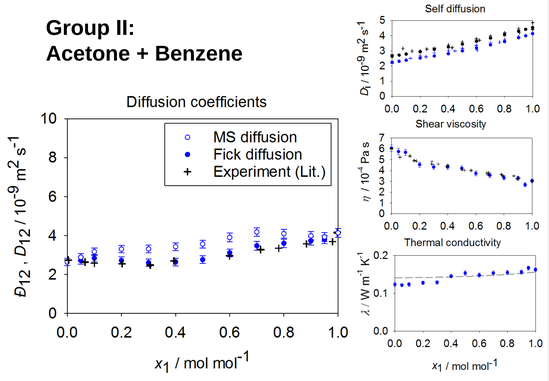
Thermal conductivity $\lambda = \frac{1}{Vk_BT^2}\int_0^\infty dt\langle \boldsymbol{J}_q^{x}(0)\cdot\boldsymbol{J}_q^{x}(t)\rangle$

Simulation results

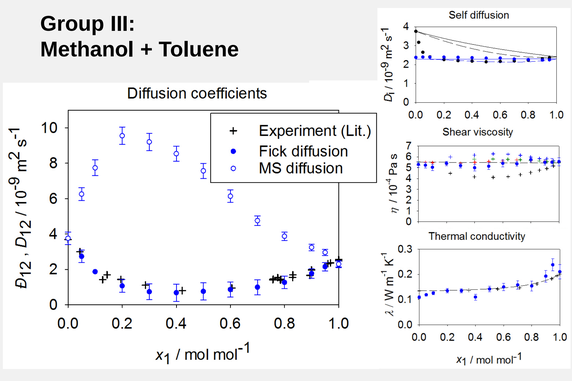
Group I: Benzene + Toluene



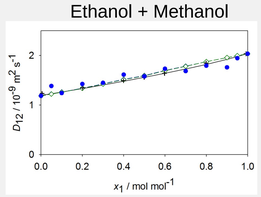
Group II: Acetone + Benzene



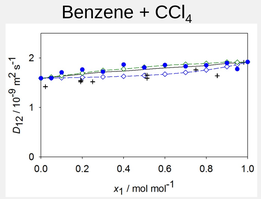
Group III: Methanol + Toluene



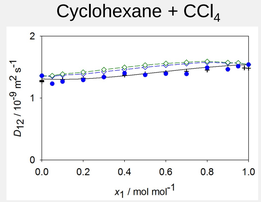
Ethanol + Methanol



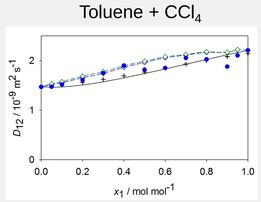
Benzene + CCl_4



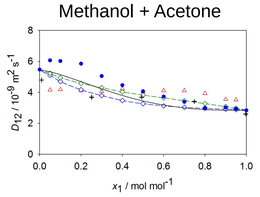
Cyclohexane + CCl_4



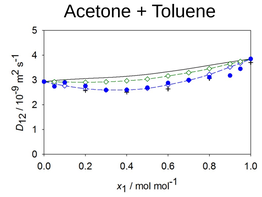
Toluene + CCl_4



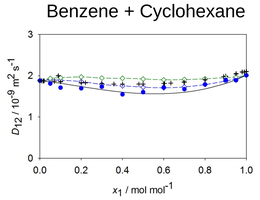
Methanol + Acetone



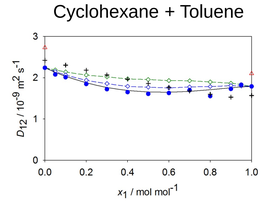
Acetone + Toluene



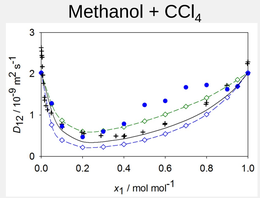
Benzene + Cyclohexane



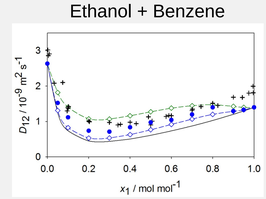
Cyclohexane + Toluene



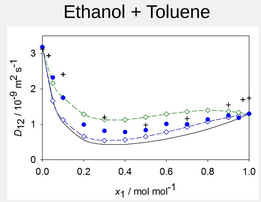
Methanol + CCl_4



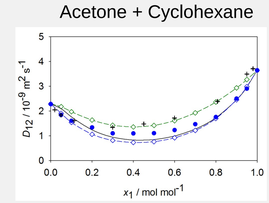
Ethanol + Benzene



Ethanol + Toluene



Acetone + Cyclohexane



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