Mass Diffusivities of Binary Mixtures of Normal Alkanes with Dissolved Gases

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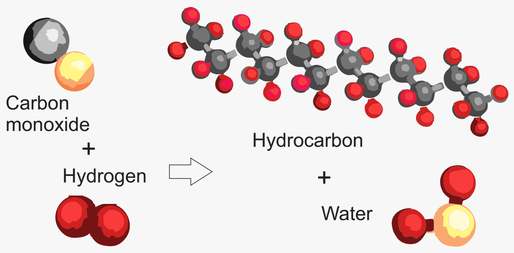
Motivation

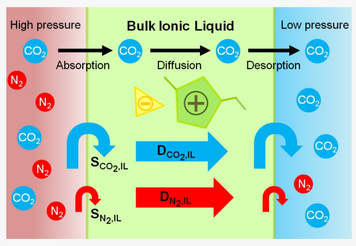
For which applications is the investigation of mass diffusion coefficients for liquids with dissolved gases of interest?

Example systems relevant for ...

...Fischer-Tropsch Synthesis...



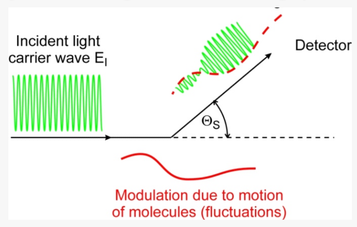
... and Supported Ionic Liquid Membranes



Which techniques are preferable for the investigation of mass diffusion coefficients?

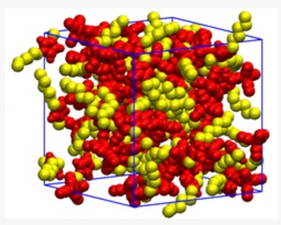
Methods studying microscopic fluctuations in macroscopic thermodynamic equilibrium

Dynamic light scattering (DLS)



validation ⇄ microscopic insight

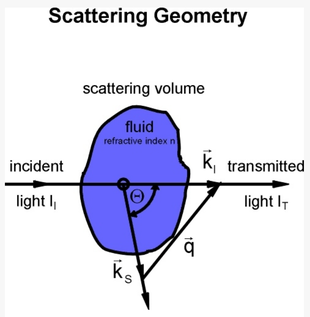
Molecular Dynamics (MD) simulations



Dynamic Light Scattering (DLS)

Principle

Scattering Geometry

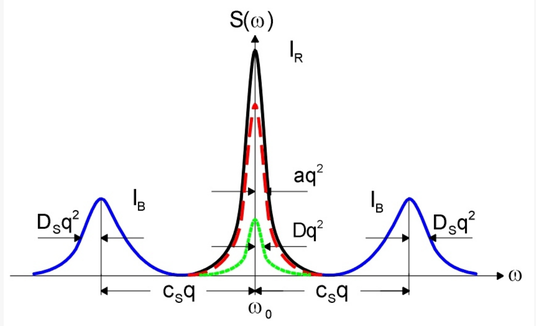


scattering vector $q = |\vec{k}_I - \vec{k}_S|$

$$q = \frac{4 \cdot \pi \cdot n}{\lambda_0} \sin\frac{\Theta}{2}$$

Spectrum of Scattered Light

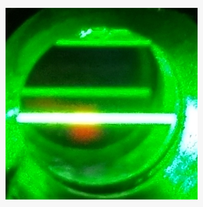
caused by local statistical fluctuations of temperature, concentration, and pressure in thermodynamic equilibrium



(a: thermal diffusivity; D: diffusion coefficient; c_S: sound velocity; D_S: sound attenuation; S: Landau-Placzek ratio)

Data evaluation

Visual observation during sample preparation



Pure *n*-alkane

10 min after adding CO

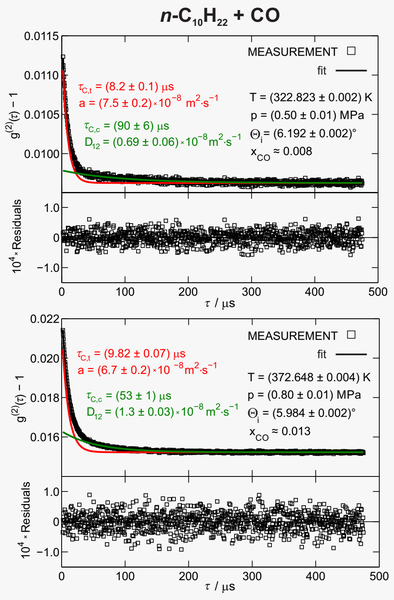
Lewis number

$$Le = \frac{a}{D_{12}}$$

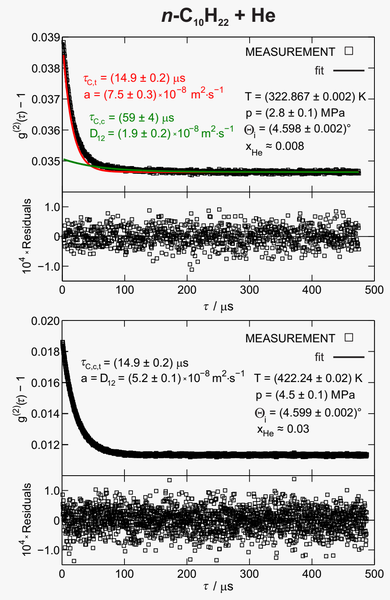
Representation of the correlation functions by a sum of two exponentials

$$g^{(2)}(\tau) = b_0 + b_t \exp(-\tau / \tau_{C,t}) + b_c \exp(-\tau / \tau_{C,c})$$

n-$C_{10}H_{22}$ + CO

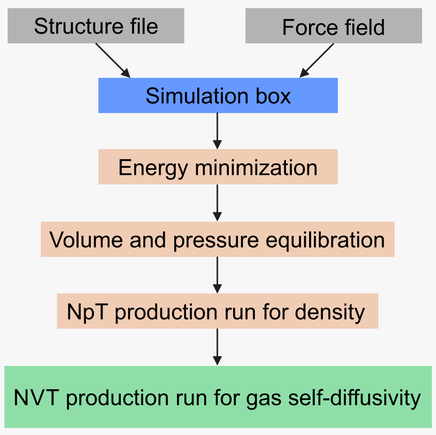


n-$C_{10}H_{22}$ + He



Molecular Dynamics (MD) Simulations

Principle



Force field

$$U = \sum_i^N U_i = \sum_i^{N-1} \sum_{j>i}^N \frac{1}{4\pi\varepsilon_0} \frac{q_i q_j}{r_{ij}}$$ Electrostatic potential

$$+ \sum_i^{N-1} \sum_{j>i}^N 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]$$ Lennard-Jones (LJ) potential

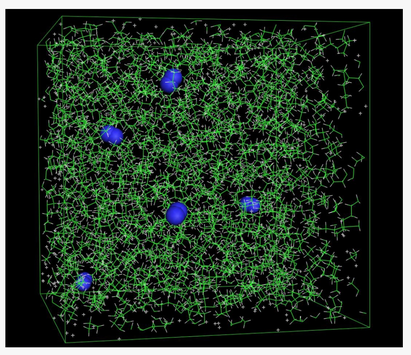
$$+ \sum_{bond} \frac{k_r}{2}(r - r_0)^2 + \sum_{angle} \frac{k_\theta}{2}(\theta - \theta_0)^2 + \sum_{torsion} k_\chi [1 + \cos(n\chi - \delta)]$$ Intramolecular potential

Simulation details

- Force fields for *n*-alkanes and gases from literature
- 70 ns production runs for gas self-diffusivities
- 5 independent simulation runs
- Mole fraction of dissolved gas 1%

Data evaluation

Simulation box containing 500 n-C_6H_{14} (1) and 5 N_2 (2) molecules (edge length of 4.83 nm)



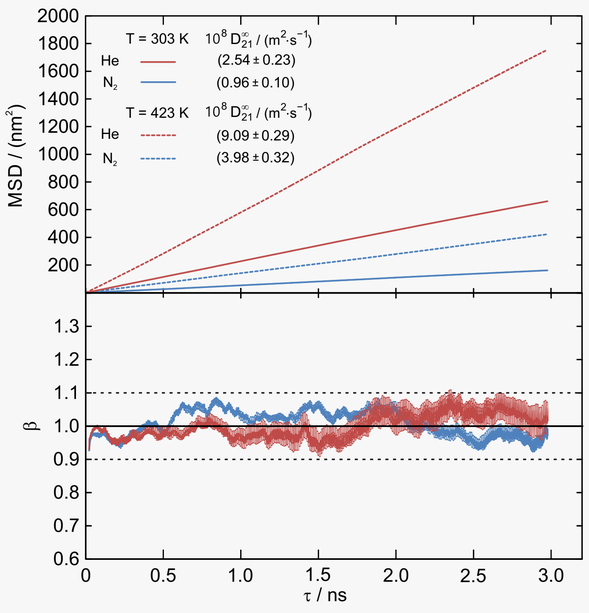
coefficient $\beta = \frac{d(\log(MSD_2))}{d(\log(\tau))}$

with β = 1 for Fickian diffusive regime

Gas self-diffusivity by fit in the linear part (β = 1) according to the Einstein equation

$$D_{21}^{\infty} = \frac{1}{6} \lim_{\tau \to \infty} \frac{d(MSD_2)}{d\tau}$$

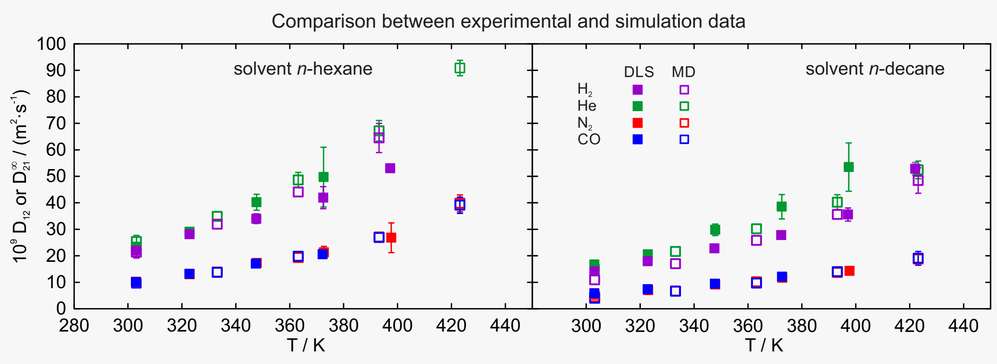
Mean square displacement (MSD) $\langle (r_2(\tau) - r_2(0))^2 \rangle$ of gases dissolved in *n*-hexane by 1 mole-%



Results and Discussion

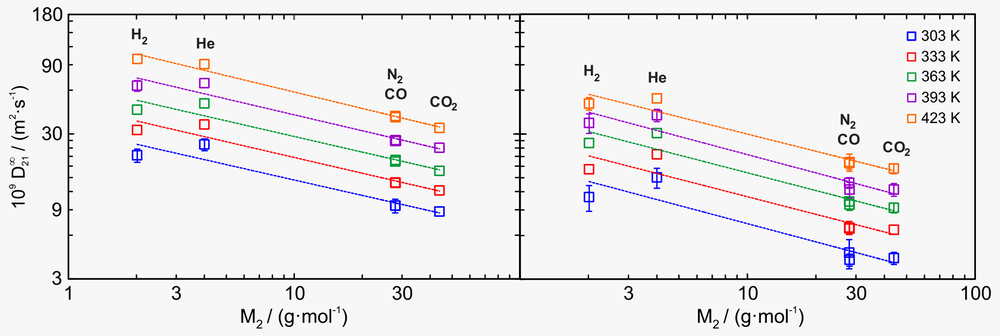
Mass diffusion coefficients for binary mixtures of *n*-alkanes with dissolved gases in dependence on temperature close to infinite dilution

Comparison between experimental and simulation data



In agreement with theory, similar values for the mutual diffusivity D_{12} and the self-diffusivity of the gas D_{21}^{∞}

Self-diffusion coefficients of gases for binary mixtures of *n*-alkanes with dissolved gases in dependence on molar mass of the gaseous solute



With exception of H_2 and He, decreasing mass diffusion coefficients with increasing molar mass of gaseous solute

Prospects

Study of two further classes of alkane-based solvents: normal alcohols and ionic liquids

Using DLS data to test the capabilities of MD simulations for the prediction of mutual diffusivities

Development of simple prediction scheme for mutual diffusivities of liquids with dissolved gases

Acknowledgements

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