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Transport properties of hydrogen bonding fluids: molecular simulation and Taylor dispersion measurements

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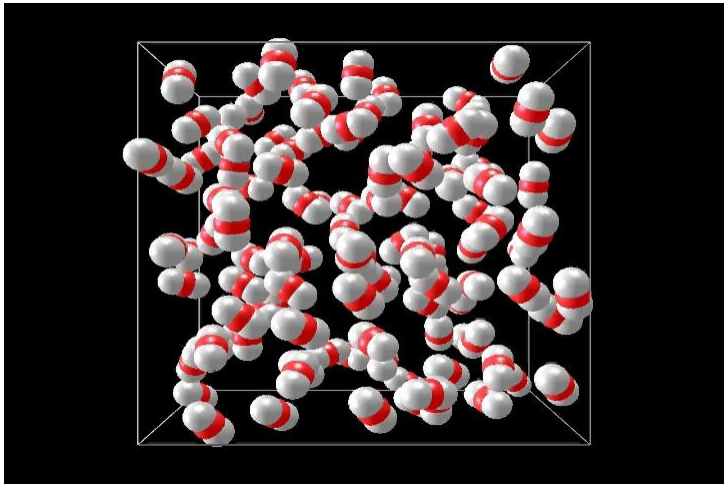
Molecular simulation

- **Goal**

  Macroscopic behaviour from intermolecular interactions



- **Molecular Dynamics (MD)**

  Solve Newton's equation of motion

  ✓ Static properties

  ✓ Dynamic properties

- **Transport properties prediction**

  ✓ Equilibrium MD (EMD)

  → Green-Kubo method

  → D_i, D_{ij}, η

  ✓ Non-Equilibrium MD (NEMD)

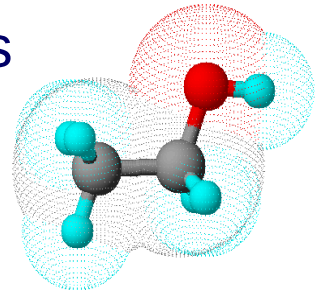
  → Reverse BD - NEMD

  → λ

Molecular models

Rigid United-Atom multicenter Lennard-Jones (LJ) models

Hydrogen bond modelling through point charges



Mixtures: unlike LJ parameters

→ Lorentz-Berthelot

$$\sigma_{AB} = \left(\frac{\sigma_A + \sigma_B}{2} \right) \qquad \varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B}$$

• **Parameters**	**methanol**	**ethanol**	**water**
✓ Geometric parameters	3	5	SPC/E Berendsen et al.,1987
✓ Lennard-Jones parameters	4	6	TIP4P Jorgensen et al.,1983
✓ Point charge parameters	2	2	TIP4P_2005 Abascal & Vega, 2005

Parameters adjusted to:
- ✓ vapour pressure
- ✓ sat. vapour density
- ✓ critical temperature

No transport properties !

EMD: Green-Kubo formalism

equilibrium fluctuations ➡ $F_i = \sum_j L_{ij} Y_j$ microscopic flux ➡ microscopic equilibrium

transport coefficients ⟺ autocorrelation functions

- self-diffusion

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

- binary Maxwell-Stefan mutual diffusion

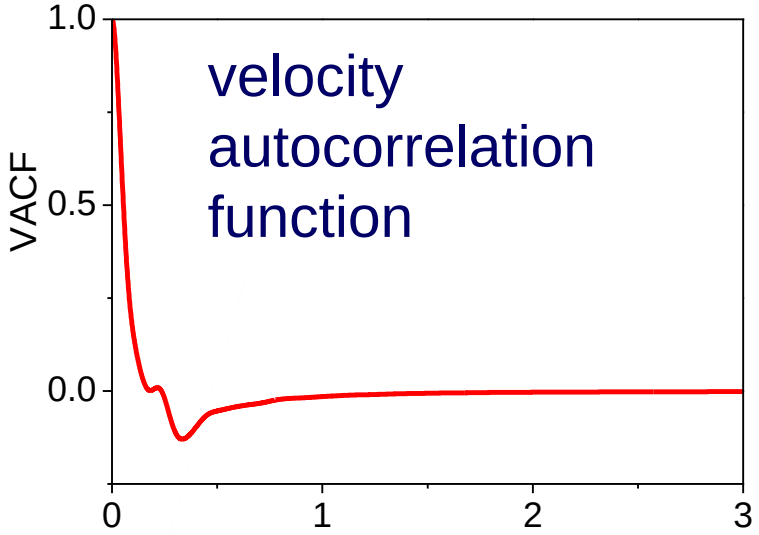
$$D_{12} = \frac{x_2}{3N_1} \left(\frac{M_1 x_1 + M_2 x_2}{M_2 x_2} \right)^2 \int_0^\infty dt \left\langle \sum_{i=1}^{N_1} v_i(0) \cdot \sum_{j=1}^{N_1} v_j(t) \right\rangle$$

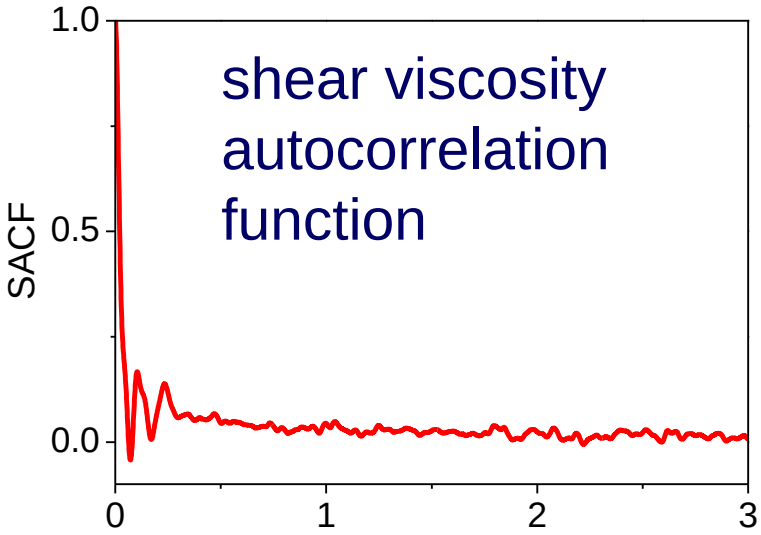
- shear viscosity

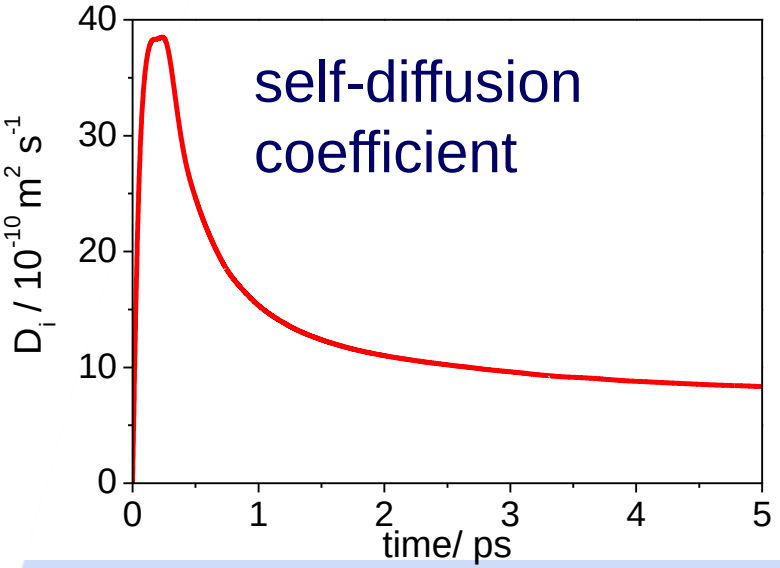
$$\eta_s = \frac{1}{V k_B T} \int_0^\infty dt \left\langle J_P^{xy}(t) \cdot J_P^{xy}(0) \right\rangle$$

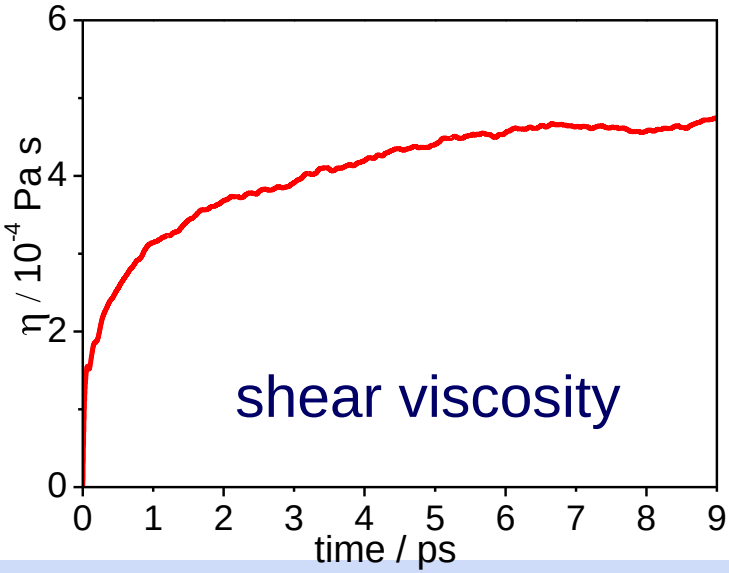
$$J_p^{xy} = \sum_{i=1}^N m_i \cdot v_i^x \cdot v_i^y - \sum_{i=1}^N \sum_{j>i}^N r_{ij}^x \frac{\partial \phi(r_{ij})}{\partial r_{ij}^y}$$

Autocorrelation functions

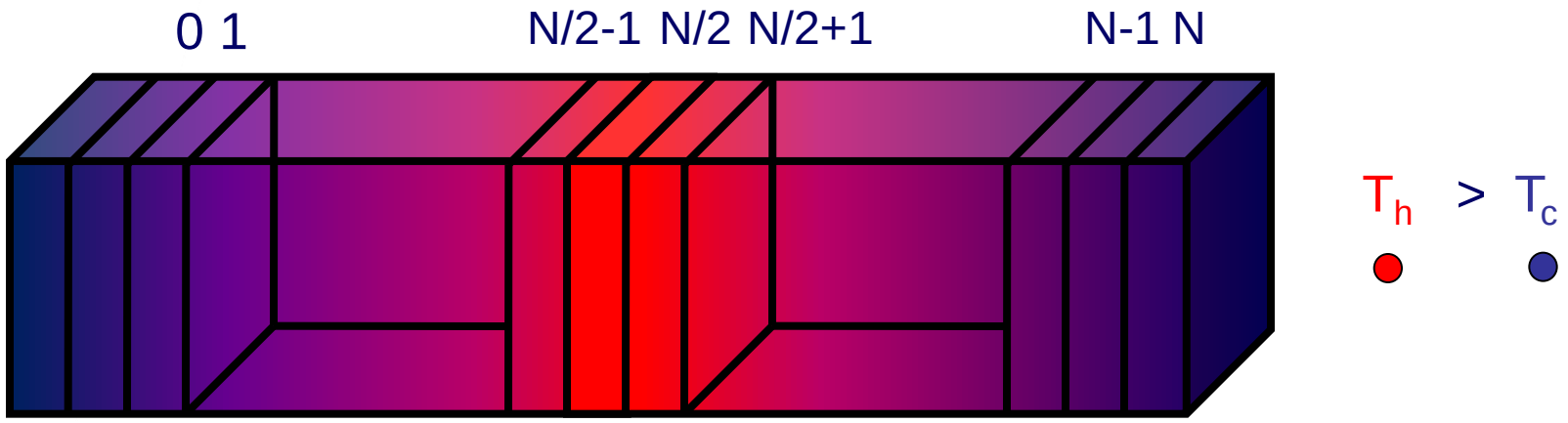








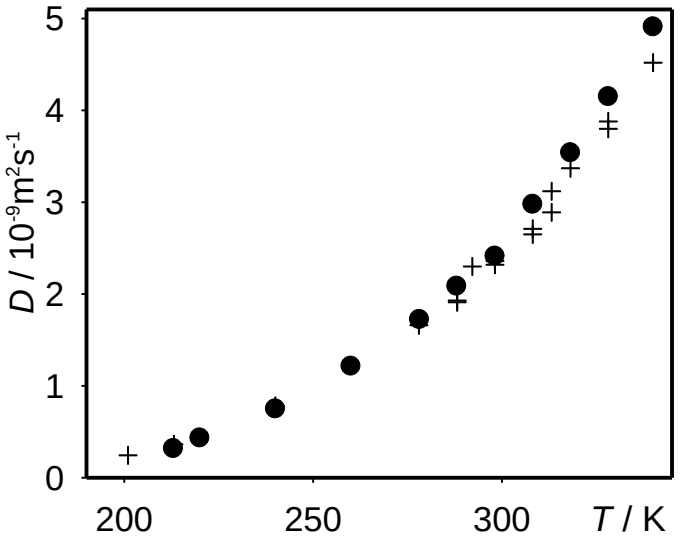
Non-equilibrium method (NEMD)

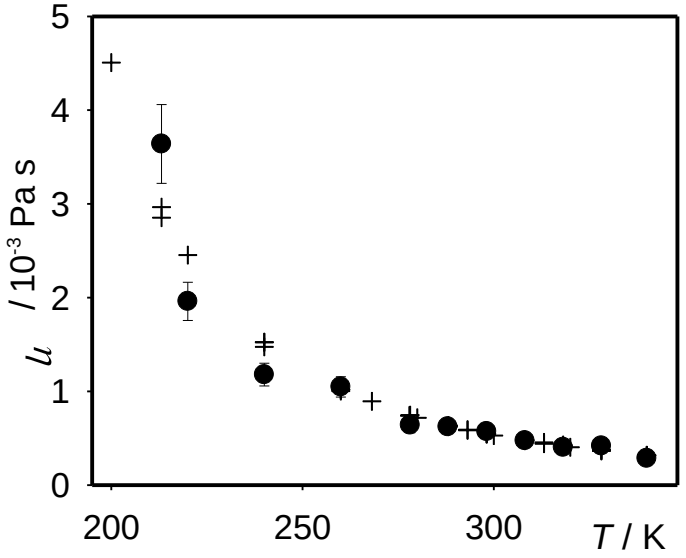


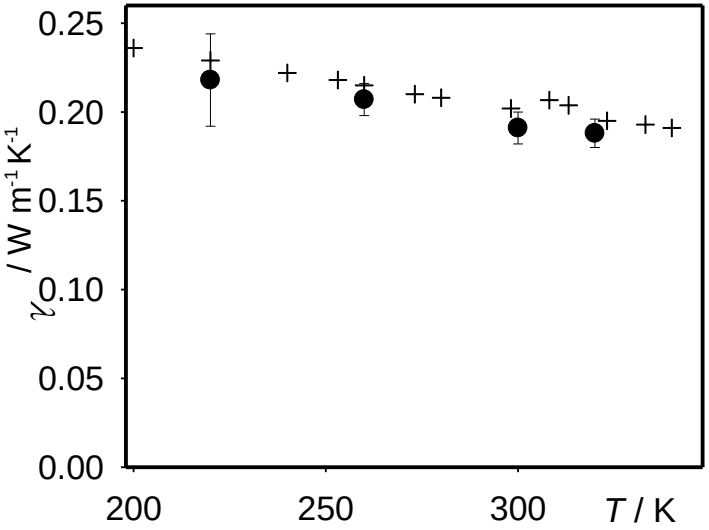
“Standard” NEMD Input: $\Delta T \rightarrow$ heat flow

“Reverse” NEMD Input: heat flow $\rightarrow \Delta T$

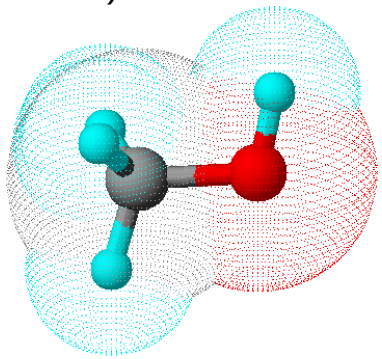
Prediction transport coefficients: methanol



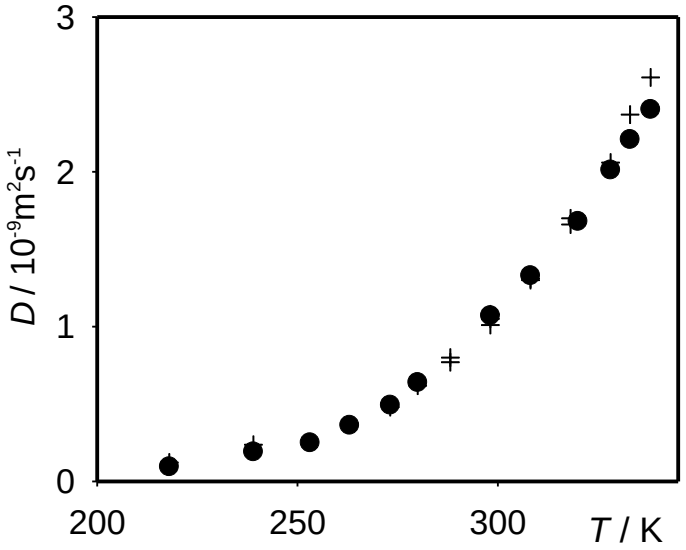


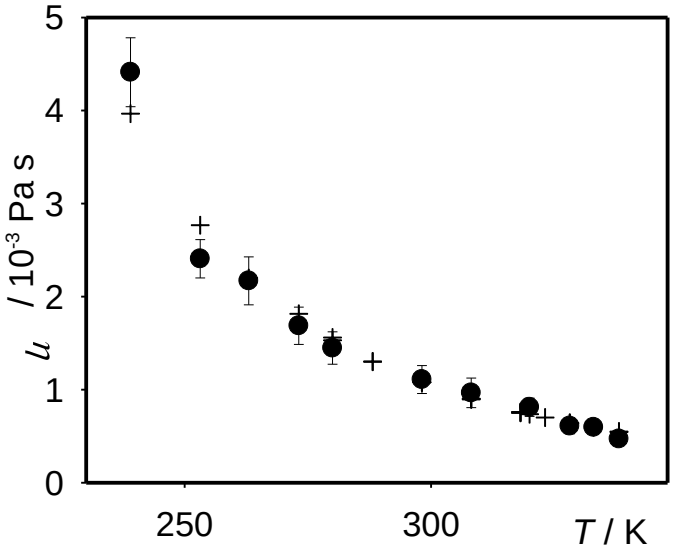


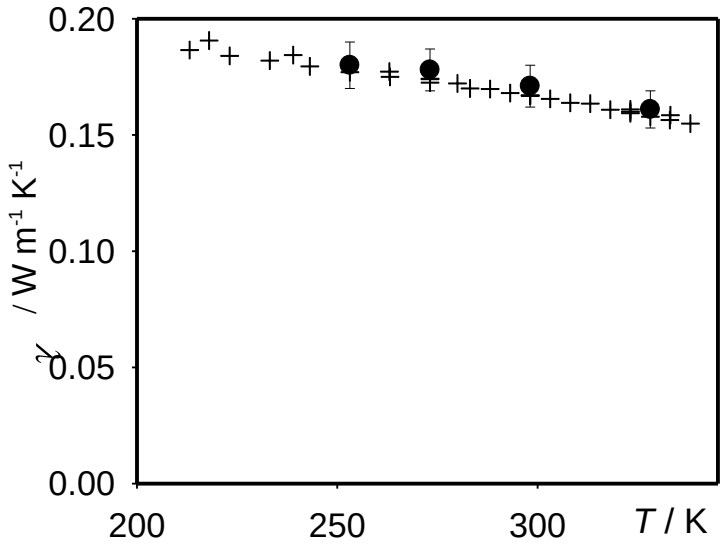
● Prediction MD simulation
+ Experiments (literature)



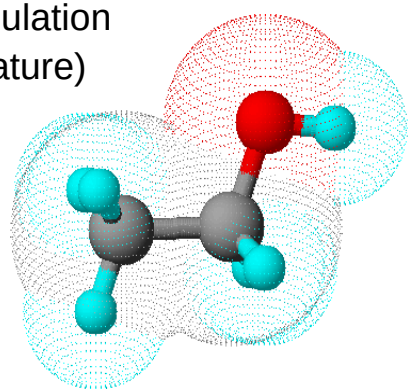
Prediction transport coefficients: ethanol



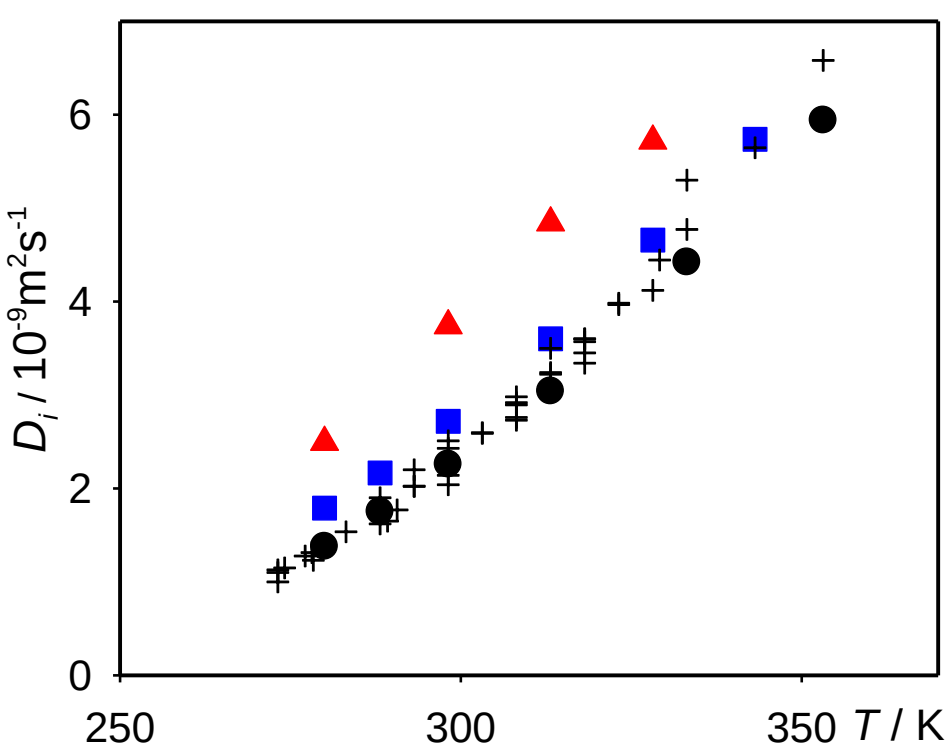


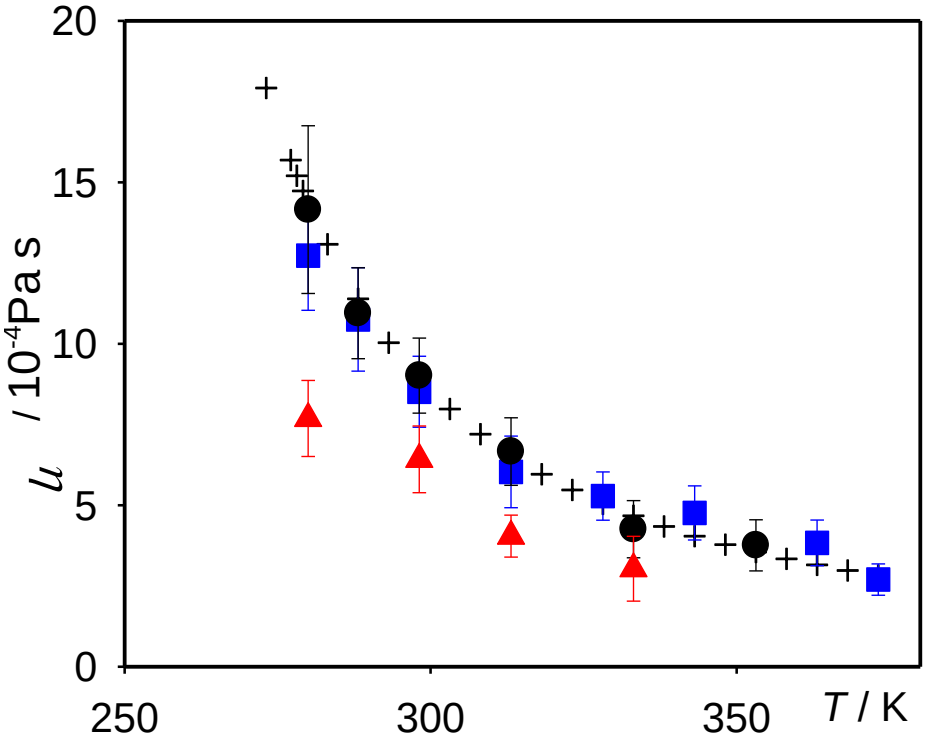


● Prediction MD simulation
+ Experiments (literature)



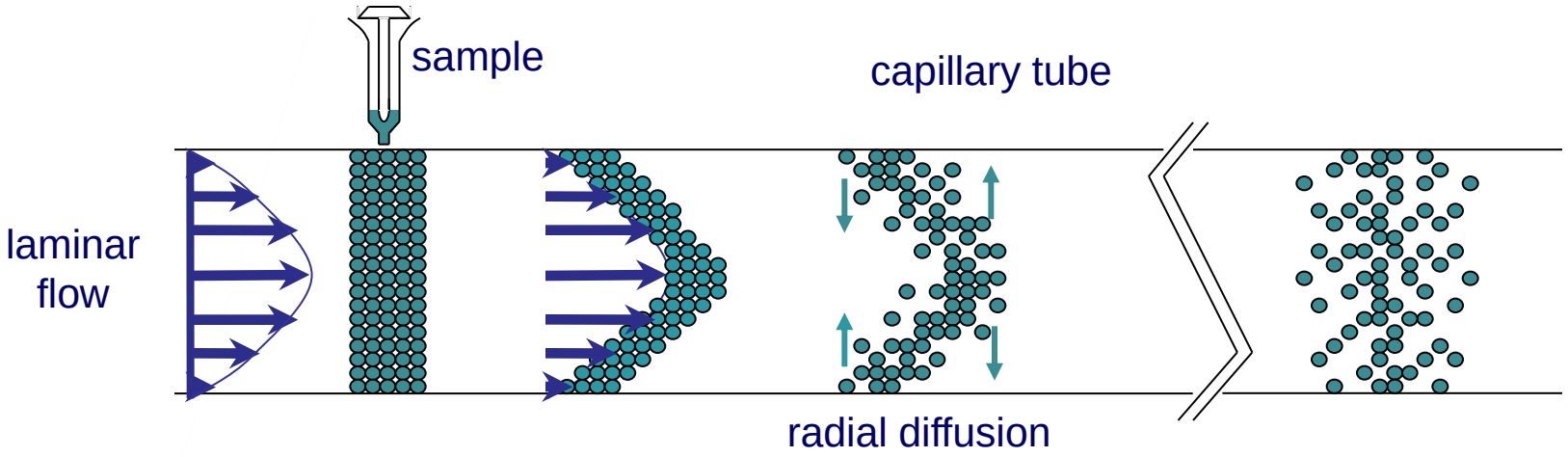
Prediction transport coefficients: water





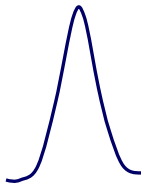
Prediction simulation SPC/E model
Prediction simulation TIP4P model
Prediction simulation TIP4P_2005 model
Experiments (literature)

Taylor dispersion fundamentals



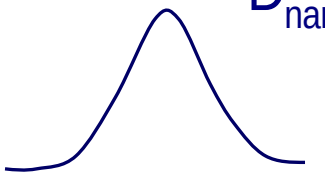
Concentration distribution

fast diffusion



$D_{narrow} > D_{broad}$

slow diffusion

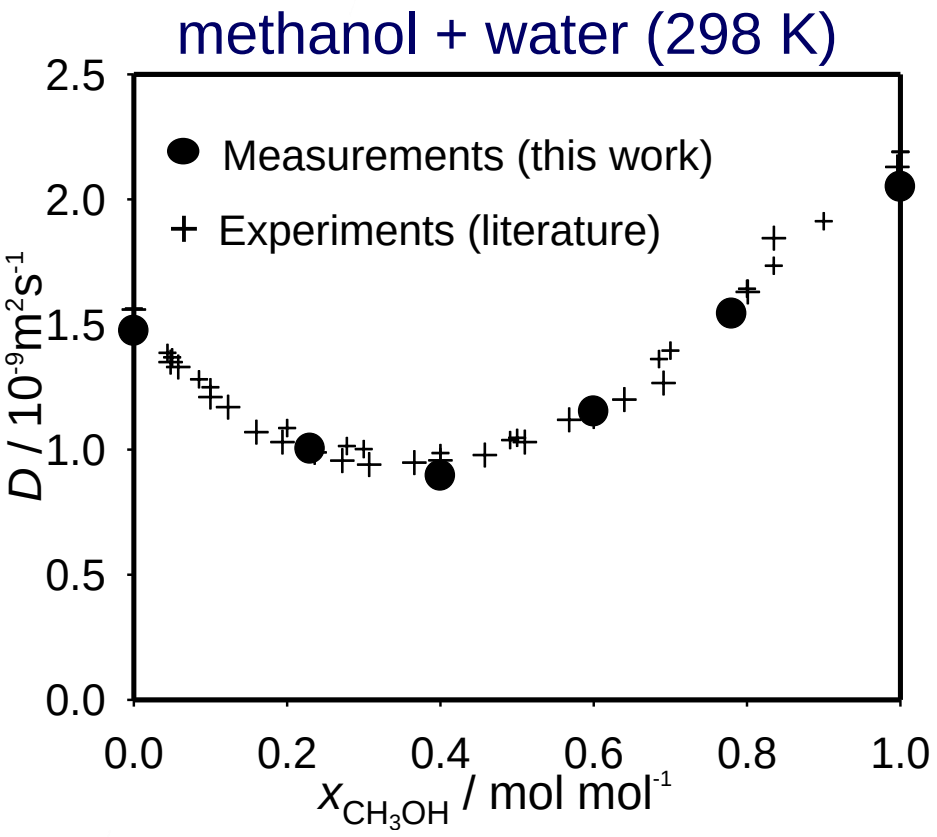


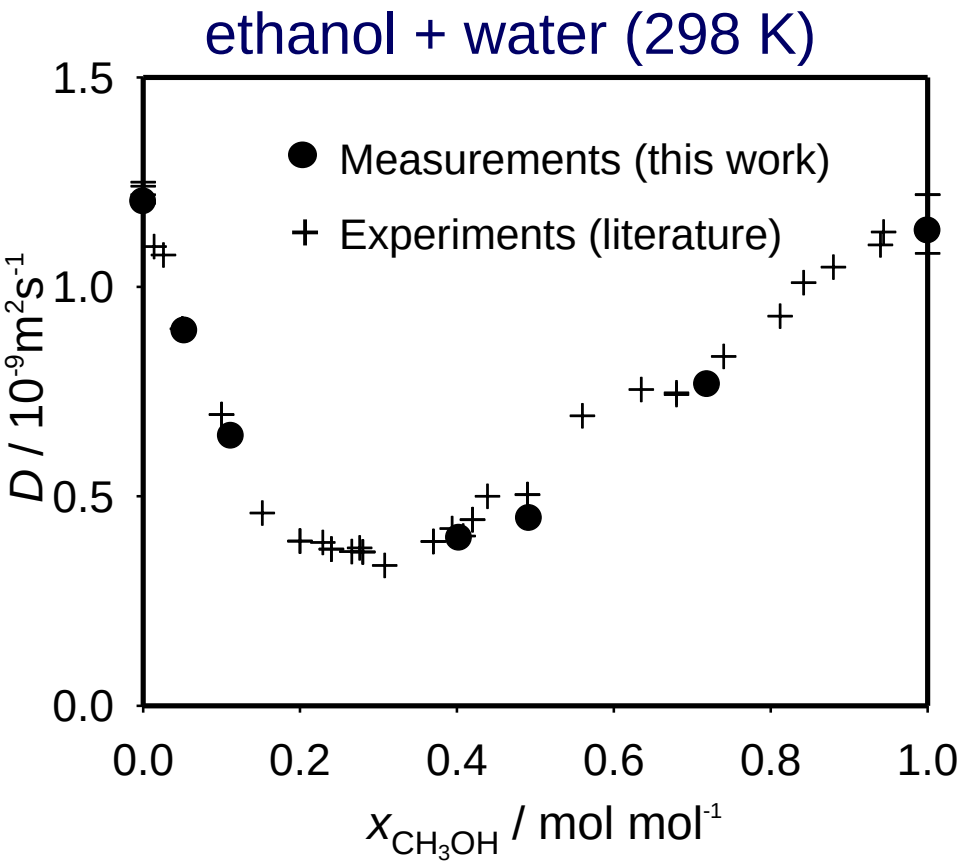
Taylor's solution

$$\bar{c}_i(t) = \frac{V_i c_i}{2\pi R^2} \frac{1}{\sqrt{(\pi kt)}} \exp\left(\frac{-L^2 \left(1 - \frac{t}{\tau}\right)^2}{4kt} \right)$$

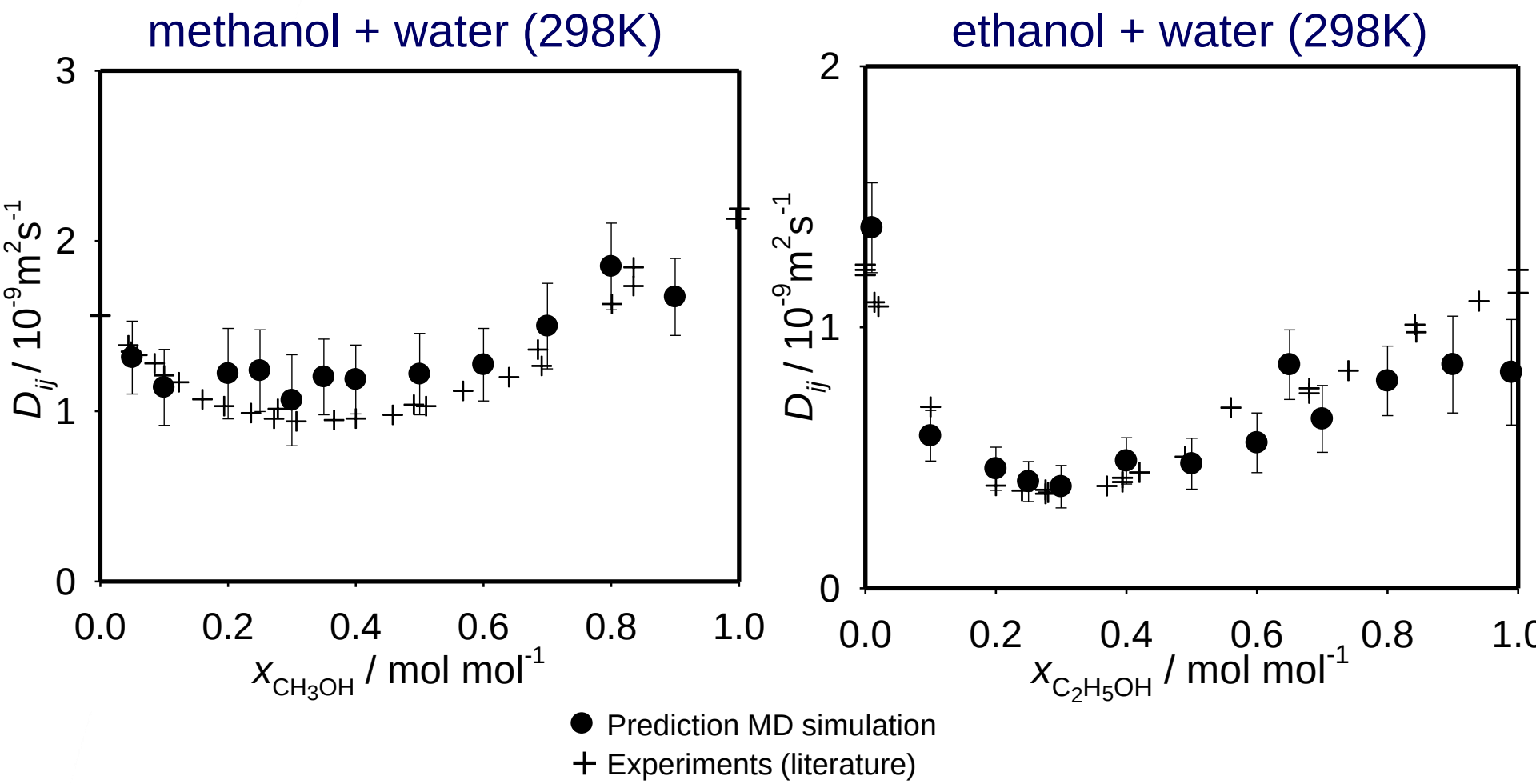
$$k = \frac{R^2 L^2}{48 \tau^2 D_F}$$

Fickian diffusion coefficients from Taylor dispersion measurements (I)

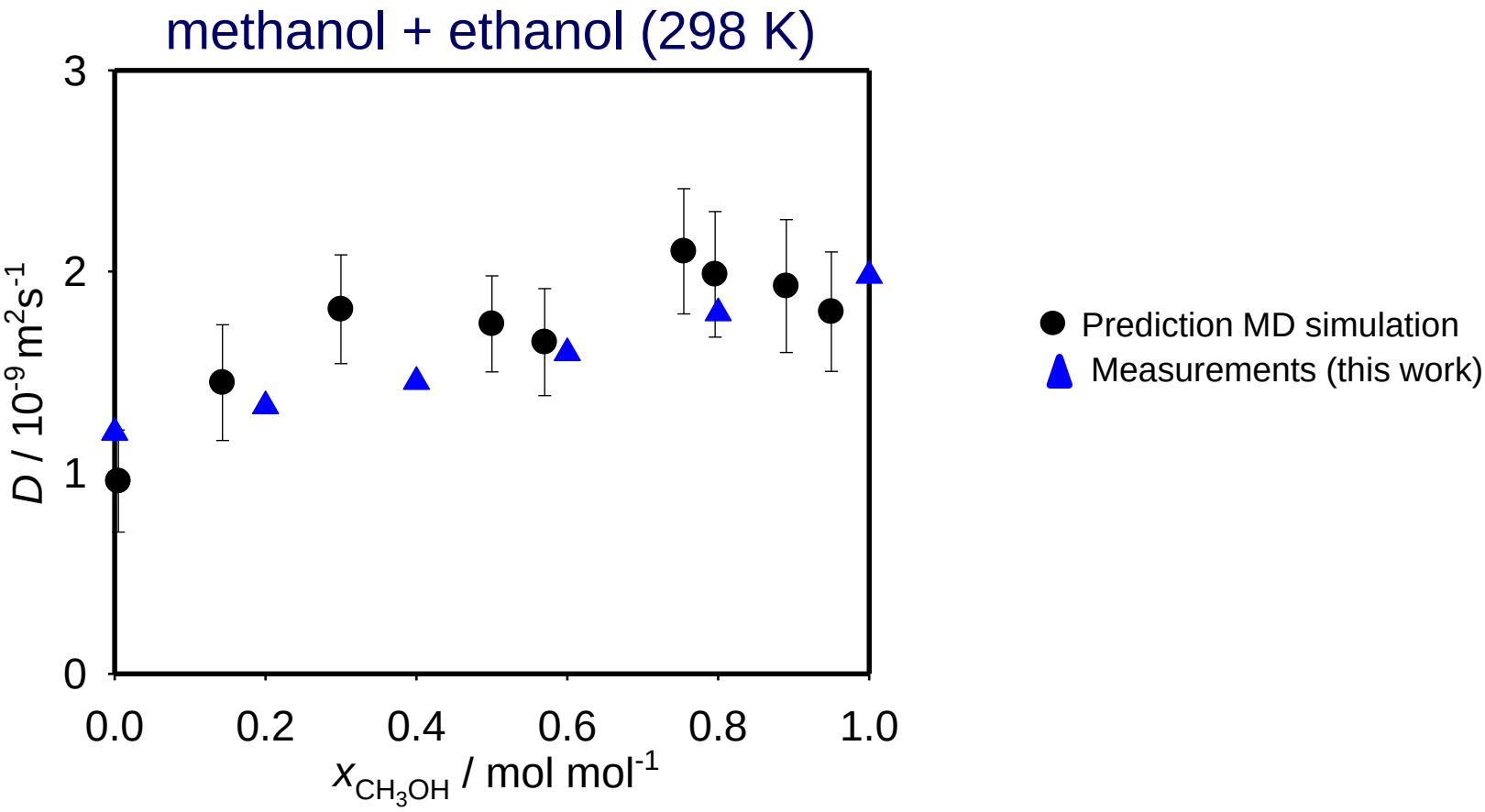




Fickian diffusion coefficient prediction vs. experiment

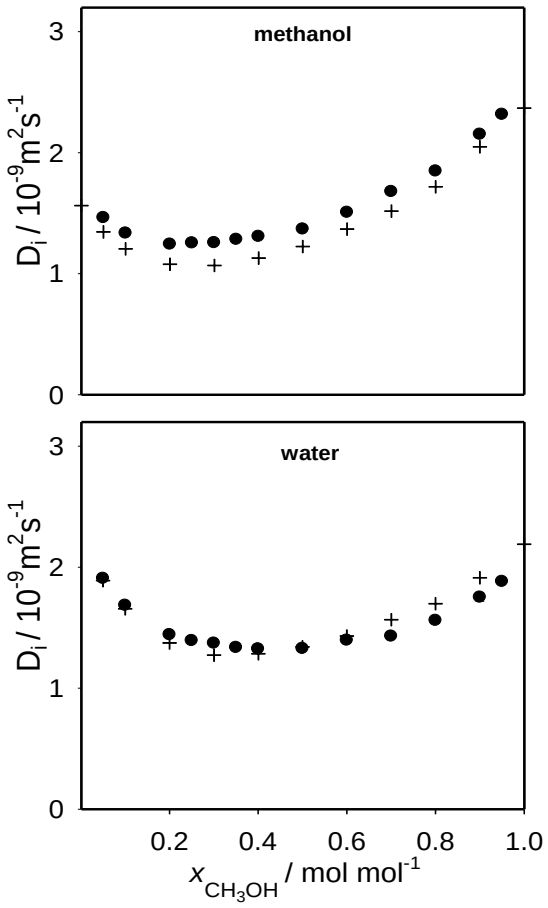


Fickian diffusion coefficient from Taylor dispersion measurements (II)

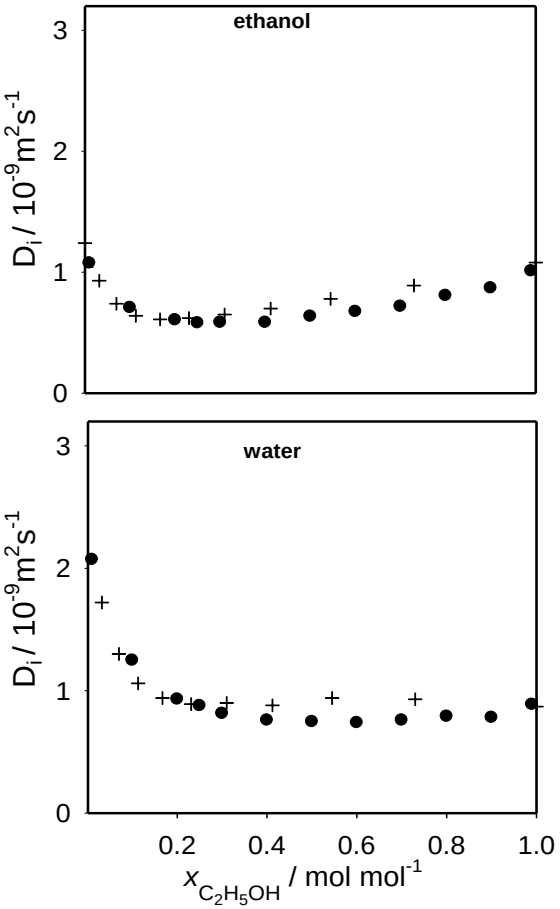


Self-diffusion coefficients in mixtures

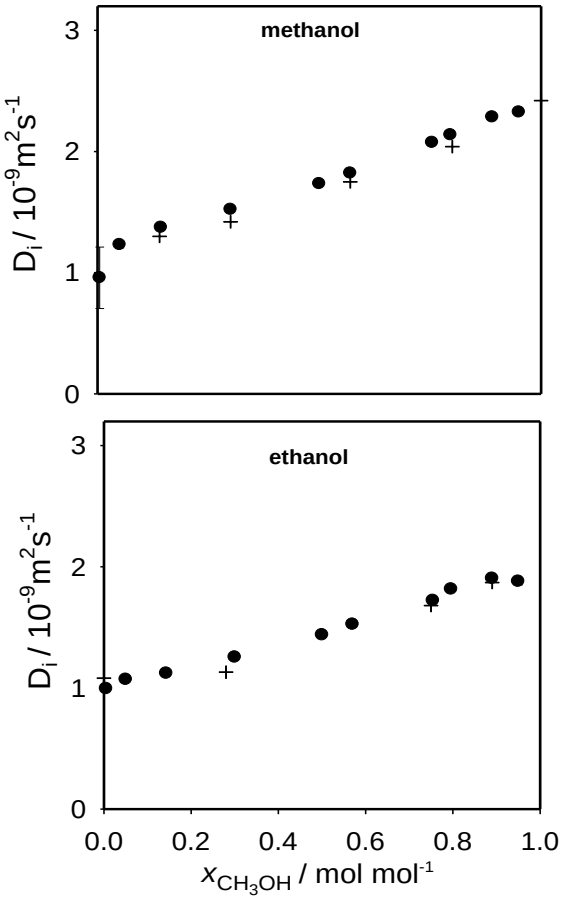
methanol + water



ethanol + water



methanol + ethanol

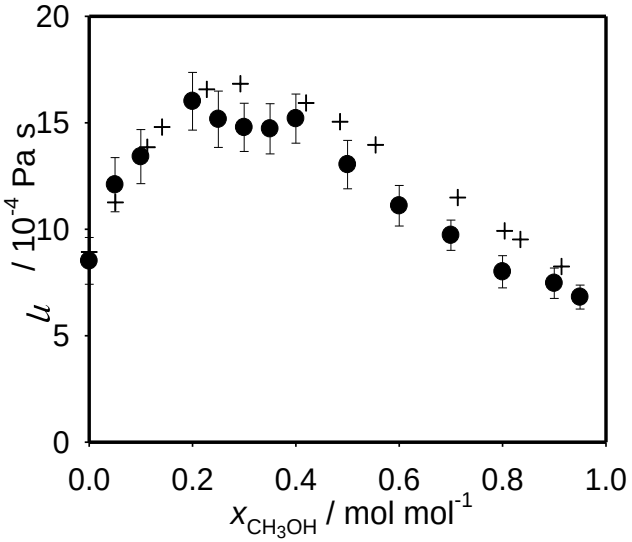


● Prediction MD simulation
\+ Experiments (literature)

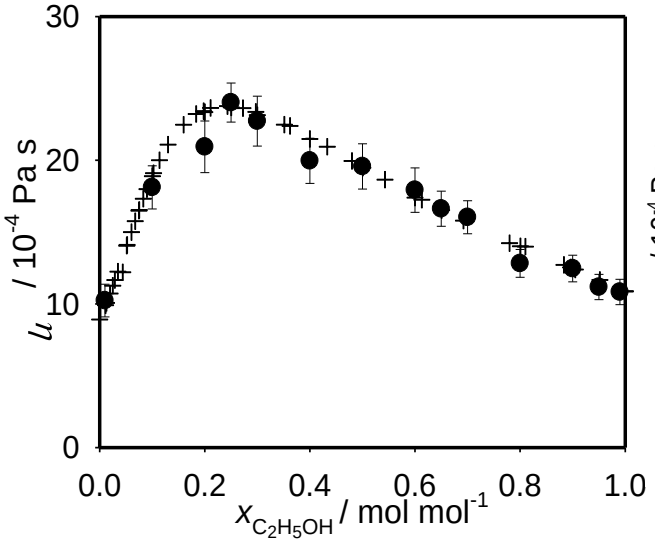
all data at 298 K

Shear viscosity of mixtures

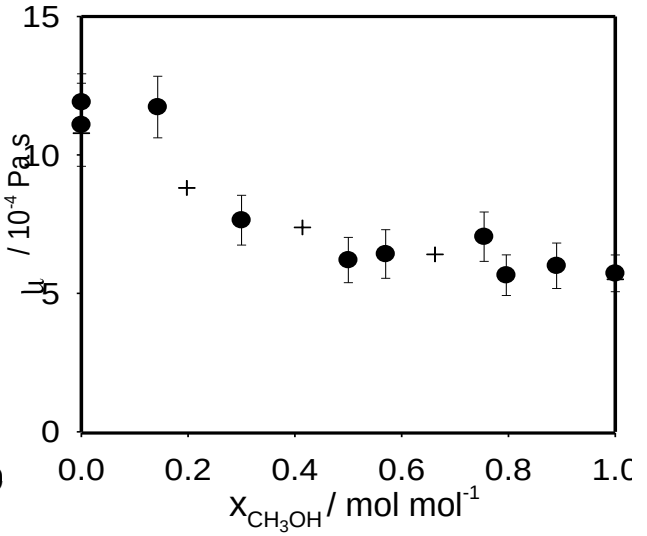
methanol + water



ethanol + water



ethanol + methanol



● Prediction MD simulation
\+ Experiments (literature)

all data at 298 K

Summary

- Prediction of transport properties of hydrogen-bonding liquids using rigid UA molecular models
- Self-diffusion, mutual diffusion, shear viscosity, thermal conductivity
- Green-Kubo MD und reverse-NEMD methods
- Pure substances and mixtures
- Very good agreement using models that were adjusted just to VLE data
- Best water model tested from the literature: TIP4P_2005
- Experimental determination of transport diffusion coefficients using the Taylor dispersion method