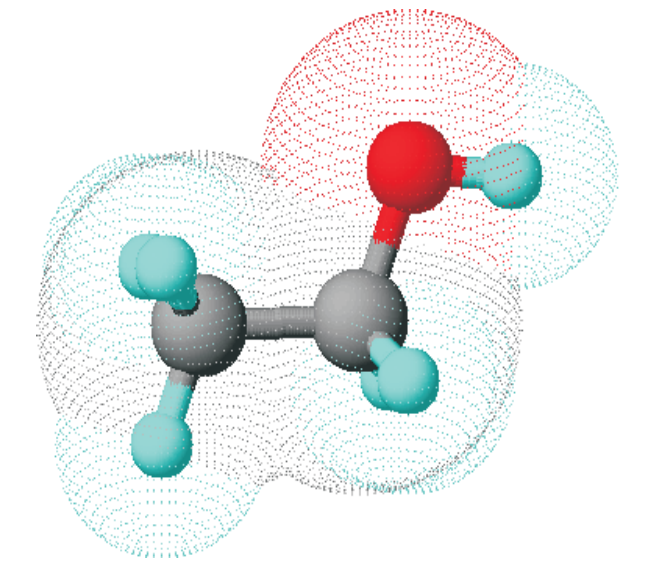
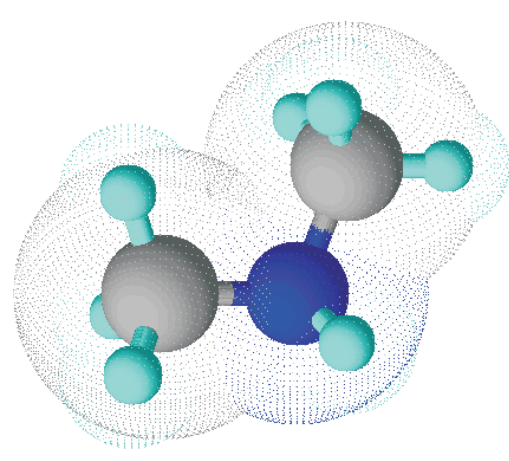


Prediction of Transport Properties of Hydrogen Bonding Liquids by Molecular Simulation

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Introduction

The prediction of transport properties of liquids is of high interest in process design since experimental data is often lacking, especially for non-ambient conditions. Moreover, due to the complexity of the involved physical mechanisms, the presently available theoretical approaches often fail. In recent years molecular modeling and simulation has become a powerful tool to accurately predict the dynamic properties of model and real fluids. The present work intends to demonstrate the capabilities of molecular simulation in this sense. Transport properties of highly polar and hydrogen bonding real fluids are predicted for a wide range of temperatures and pressures. Furthermore, some transport properties of the binary mixtures containing short monohydric alcohols and water are also predicted in this work. The transport properties self-diffusion coefficients as well as the shear viscosity are determined using equilibrium molecular dynamics and the Green-Kubo formalism. The thermal conductivity is obtained using reverse boundary driven non-equilibrium molecular dynamics.

Molecular Models

The simulations were performed using rigid united-atom multicenter Lennard-Jones models. Hydrogen bonding is modeled through superimposed point charges.

$$u = \sum_{a=1}^N \sum_{b=1}^N 4\epsilon_{ab} \left(\frac{\sigma_{ab}^{12}}{r_{ab}} - \frac{\sigma_{ab}^6}{r_{ab}} \right) + \frac{q_a q_b}{4\pi\epsilon_0 r_{ab}}$$

Lennard-Jones Coulomb

The molecular models for ammonia [1], ethanol [2], methanol [3] and methylamine [4] were developed in our group. The parameters of these models were adjusted exclusively to experimental data on vapour-liquid equilibrium. No information on transport properties was used. The TIP4P/2005 model from Abascal and Vega [5] was used for simulations with water.

Pure Fluids

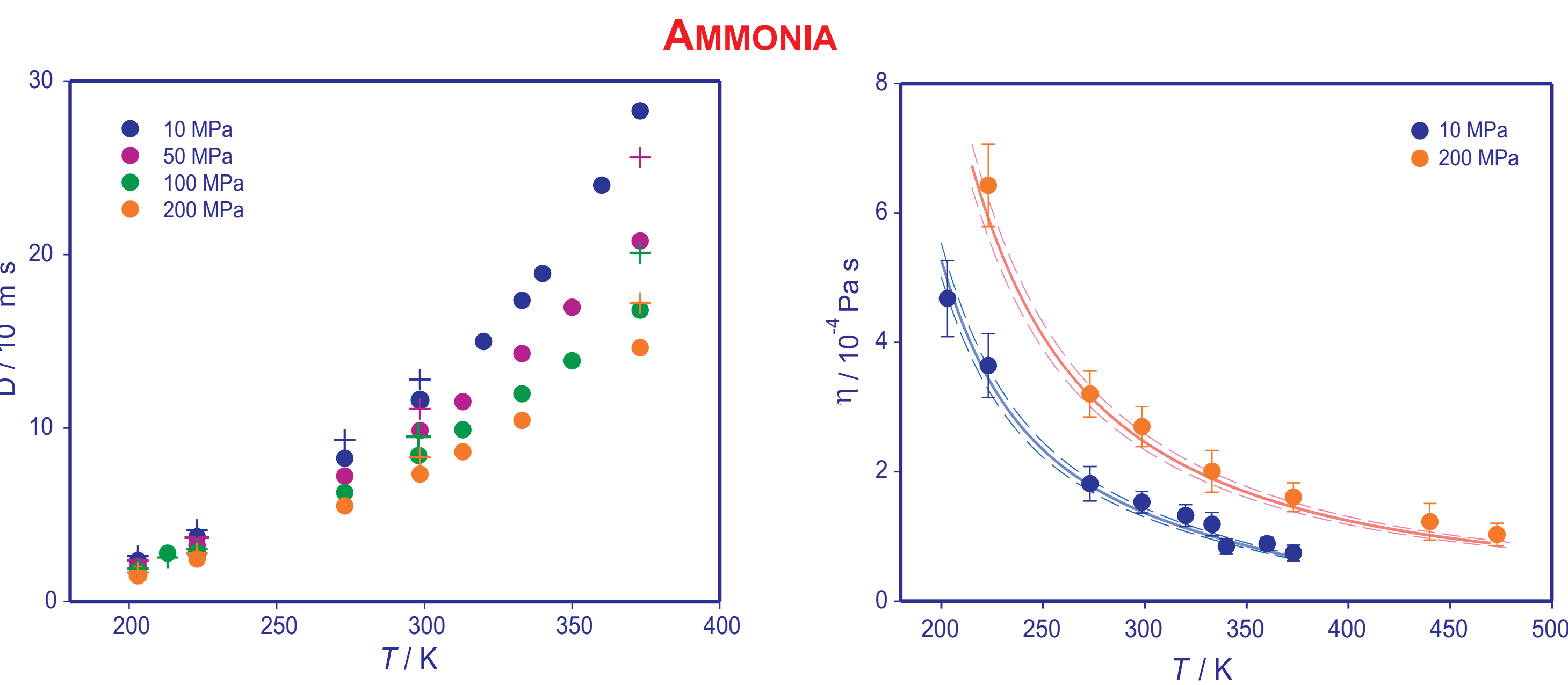


Figure 1: Ammonia: temperature dependence of the self-diffusion coefficient (upper left) and the shear viscosity (upper right) at different pressures; temperature dependence of the thermal conductivity at $p = 50 \text{ MPa}$ (lower left). The bullets represent the simulation results, the crosses are experimental data [6], the solid lines show the correlations from REFPROP and the dashed lines are their uncertainties.

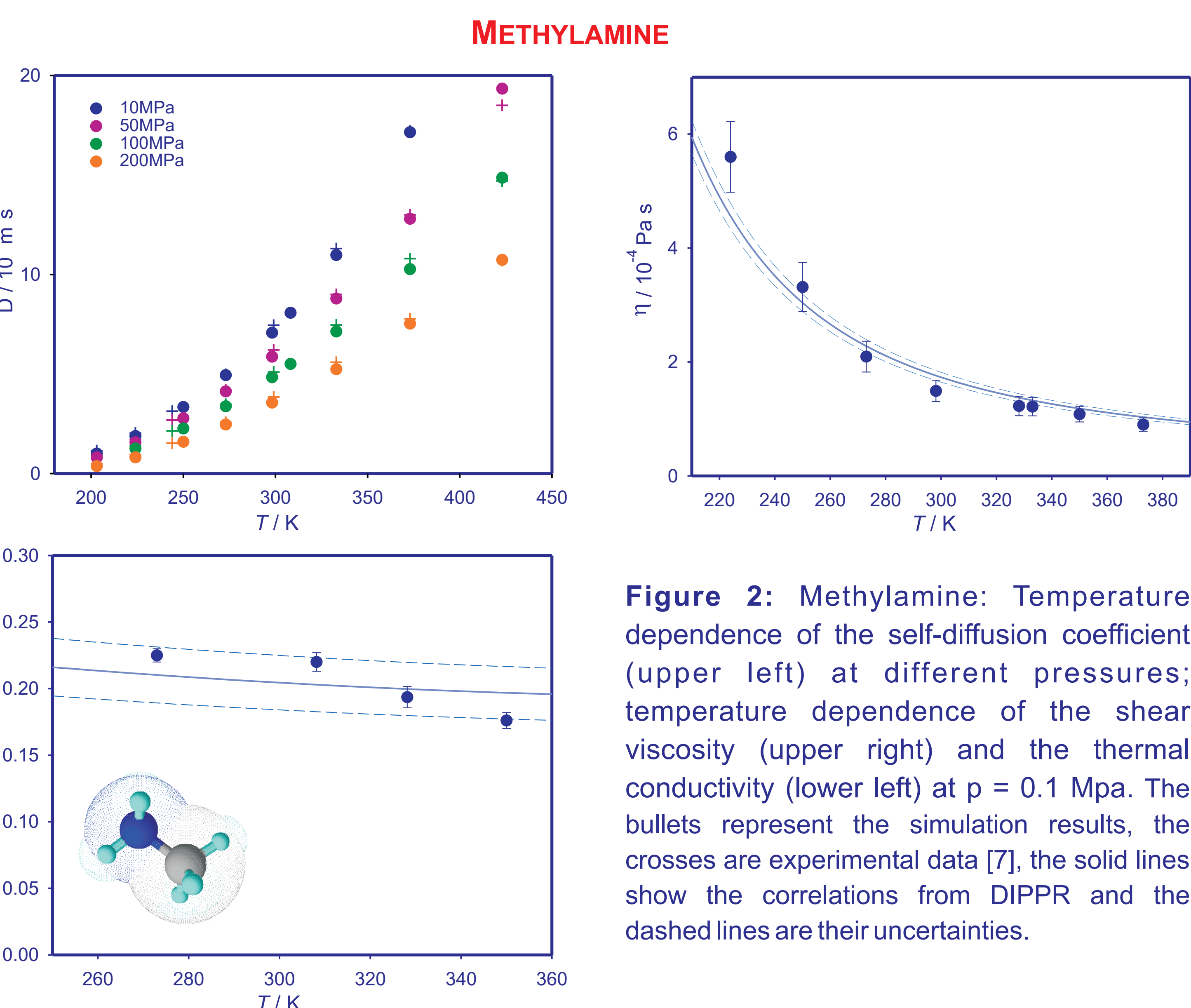


Figure 2: Methylamine: Temperature dependence of the self-diffusion coefficient (upper left) at different pressures; temperature dependence of the shear viscosity (upper right) and the thermal conductivity (lower left) at $p = 0.1 \text{ MPa}$. The bullets represent the simulation results, the crosses are experimental data [7], the solid lines show the correlations from DIPPR and the dashed lines are their uncertainties.

Mixtures

WATER + METHANOL

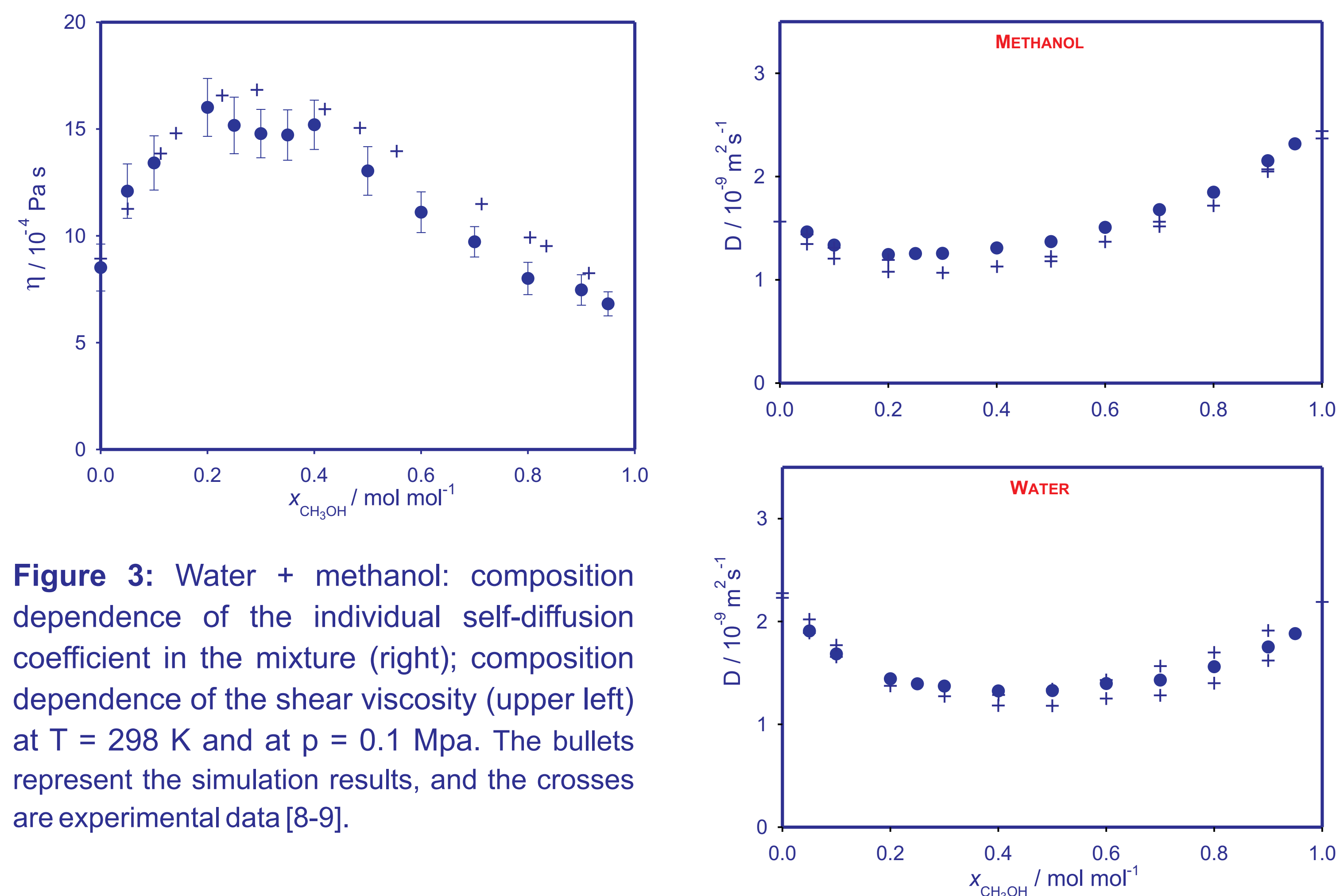


Figure 3: Water + methanol: composition dependence of the individual self-diffusion coefficient in the mixture (right); composition dependence of the shear viscosity (upper left) at $T = 298 \text{ K}$ and at $p = 0.1 \text{ MPa}$. The bullets represent the simulation results, and the crosses are experimental data [8-9].

WATER + ETHANOL

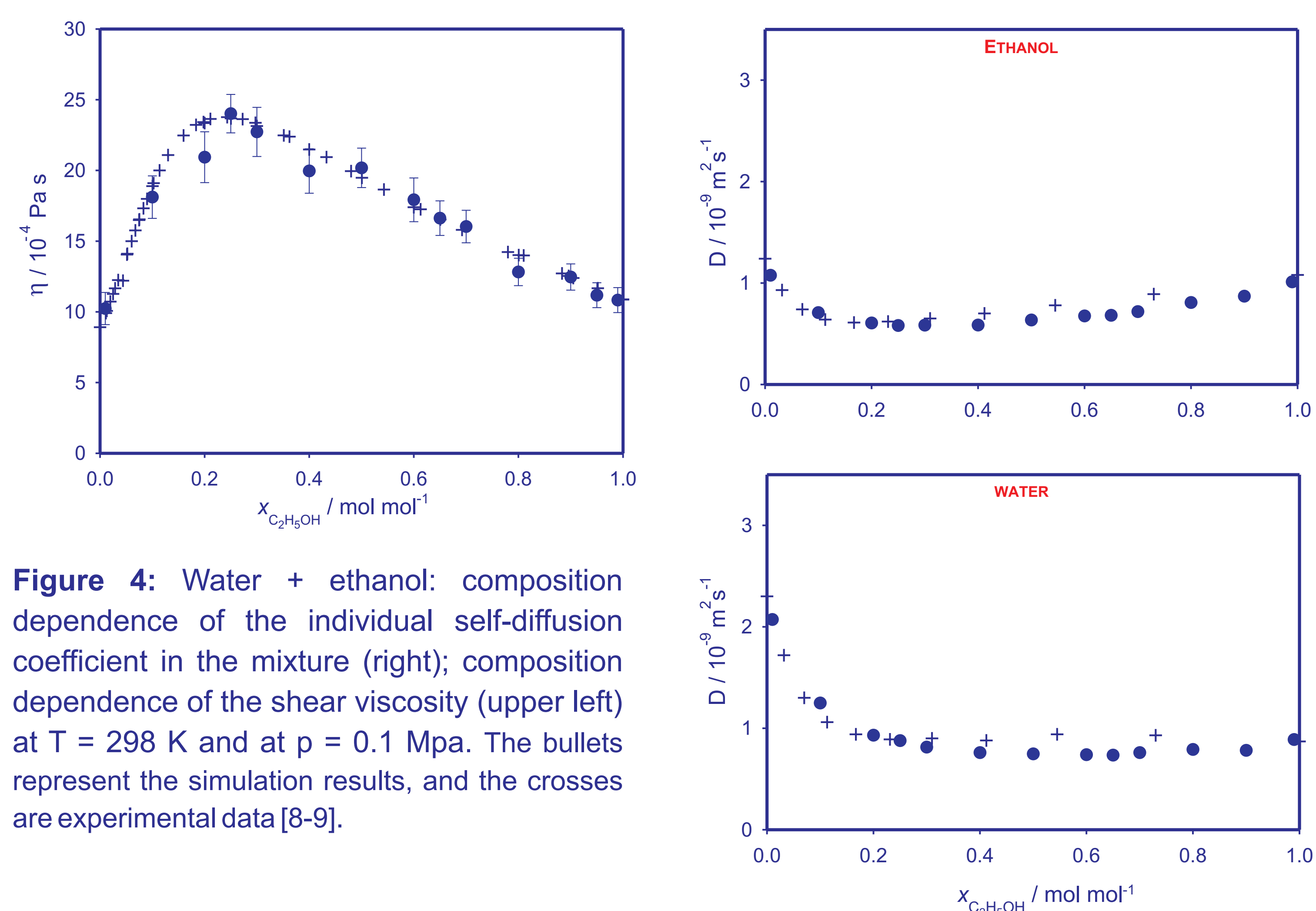


Figure 4: Water + ethanol: composition dependence of the individual self-diffusion coefficient in the mixture (right); composition dependence of the shear viscosity (upper left) at $T = 298 \text{ K}$ and at $p = 0.1 \text{ MPa}$. The bullets represent the simulation results, and the crosses are experimental data [8-9].

Summary

- Prediction of transport coefficients of hydrogen-bonding fluids by EMD and NEMD using molecular models adjusted just to VLE data.
- The pure predictions from molecular simulation have in general a very good agreement with experimental data at a wide range of temperatures and pressures.
- The viscosity anomaly of the mixtures of water and short alcohols could be well reproduced.

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