

Transport Properties of Liquids by Molecular Simulation: from Model Systems to Hydrogen Bonding Fluids

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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. A comprehensive study of the transport properties for the truncated and shifted Lennard-Jones potential is presented. This fluid model is attractive since it is well suited for molecular simulation studies in which large particle numbers are needed. Furthermore, transport properties of highly polar and hydrogen bonding real fluids are predicted for a wide range of temperatures and pressures.

Molecular Models

Molecular models of real fluids studied here are rigid, non-polarizable and based on united-atom Lennard-Jones potentials with superimposed point charges or point dipoles.

Model	LJ sites	Electrostatics	Ref.
Ammonia	1	3 point charges	[1]
Dimethylamine	3	4 point charges	[2]
Monomethylamine	2	4 point charges	[2]
Dimethylether	3	1 point dipole	[3]

The parameters of the models were adjusted exclusively to experimental vapor-liquid equilibrium data. No information on transport properties was used.

Simulation Techniques

Transport properties of the studied fluids were calculated mostly by equilibrium molecular dynamics simulation and the Green-Kubo formalism.

Self-diffusion coefficient

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

Shear viscosity

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

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

Thermal conductivity

$$\lambda = \frac{1}{V k_B T^2} \int_0^\infty dt \langle J_q^x(t) J_q^x(0) \rangle$$

$$J_q = \frac{1}{2} \sum_{i=1}^N (m v_i^2 + \sum_{j \neq i} \phi_{ij}) v_i - \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i} \sum_{k=1}^3 \sum_{l=1}^3 r_{ij}^k (v_i \frac{\partial \phi_{ij}}{\partial r_{kl}})$$

Truncated and Shifted Lennard-Jones fluids (2.5 σ)

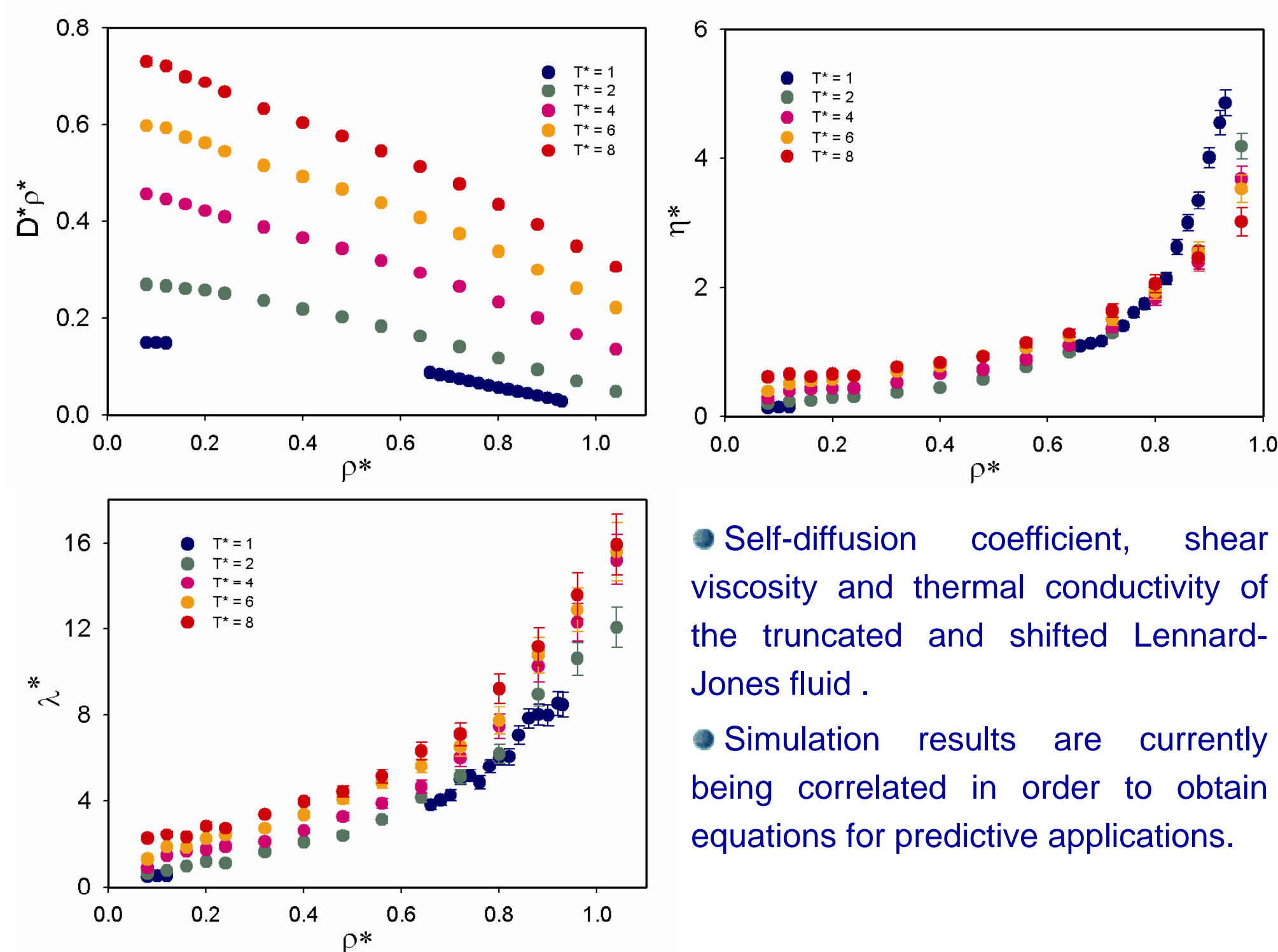


Figure 1: Reduced self-diffusion coefficient - density product (top left); reduced shear viscosity (top right); and reduced thermal conductivity (bottom) as function of the reduced density for selected reduced temperatures.

Summary

- Study of the transport properties of truncated and shifted Lennard-Jones fluids for a large number of state points covering a substantial part of the fluid region.
- Prediction of transport coefficients of real fluids by EMD using molecular models adjusted exclusively to VLE data.
- The strictly predictive data from molecular simulation shows a very good agreement with experimental data for the studied fluids for a wide range of temperatures and pressures.

References

- [1] B. Eckl, J. Vrabec, H. Hasse, Mol. Phys. 106 (2008) 1039-1046.
- [2] T. Schnabel, J. Vrabec, H. Hasse, Fluid Phase Equil. 263 (2008) 787-793.
- [3] B. Eckl, J. Vrabec, H. Hasse, J. Phys. Chem. B 112 (2008) 12710-12721.
- [4] C. Liuping, T. Gross, H. Lüdemann, PCCP 1 (1999) 3503-3508.
- [5] A. Heinrichschramm, A. Price, H. Lüdemann, J. Phys. Sciences 50 (1995) 145-148.
- [6] T. Gross, J. Buchhauser, A. Price, I. Tarassov, H. Lüdemann, PCCP 3 (2001) 3701-3706.

Real Fluids

Monomethylamine

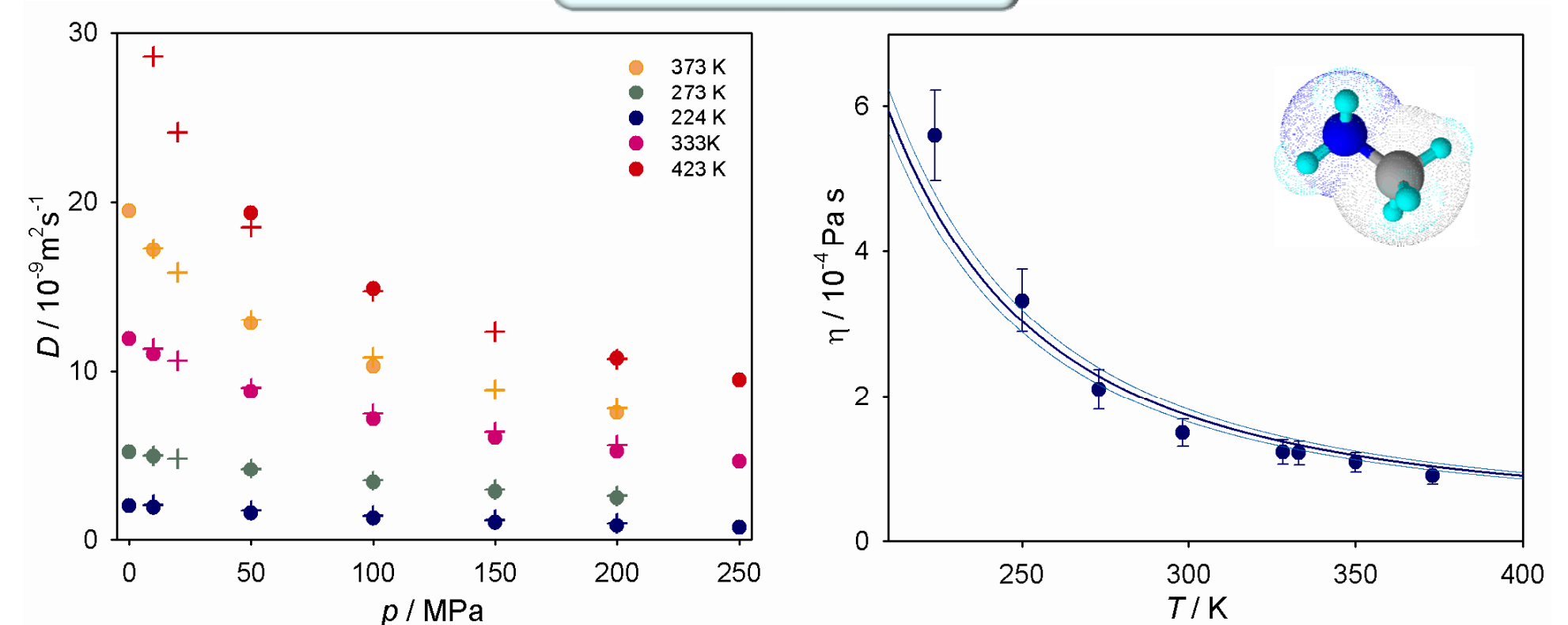


Figure 2: Liquid monomethylamine: pressure dependence of the self-diffusion coefficient at different temperatures (left); temperature dependence of the shear viscosity at $p = 0.1$ MPa (right). The bullets represent the simulation results, the crosses are experimental data [4], the dark blue line is the DIPPR correlation and the light blue lines are the estimated uncertainties.

Dimethylamine

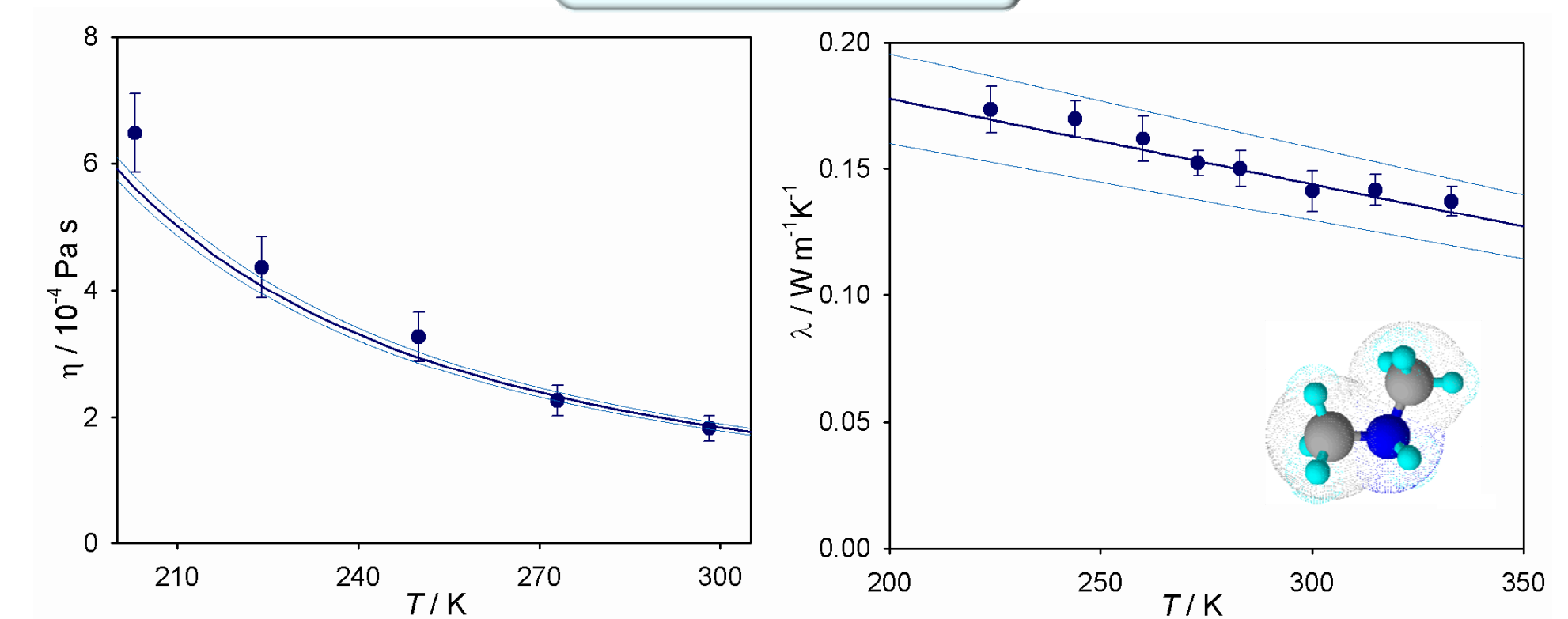


Figure 3: Temperature dependence of the shear viscosity (left) and the thermal conductivity (right) of liquid dimethylamine at $p = 0.1$ MPa. Simulation results (bullets) are compared with the DIPPR correlations (dark blue lines) and their estimated uncertainties (light blue lines). The thermal conductivity was predicted using reverse NEMD simulations.

Dimethylether

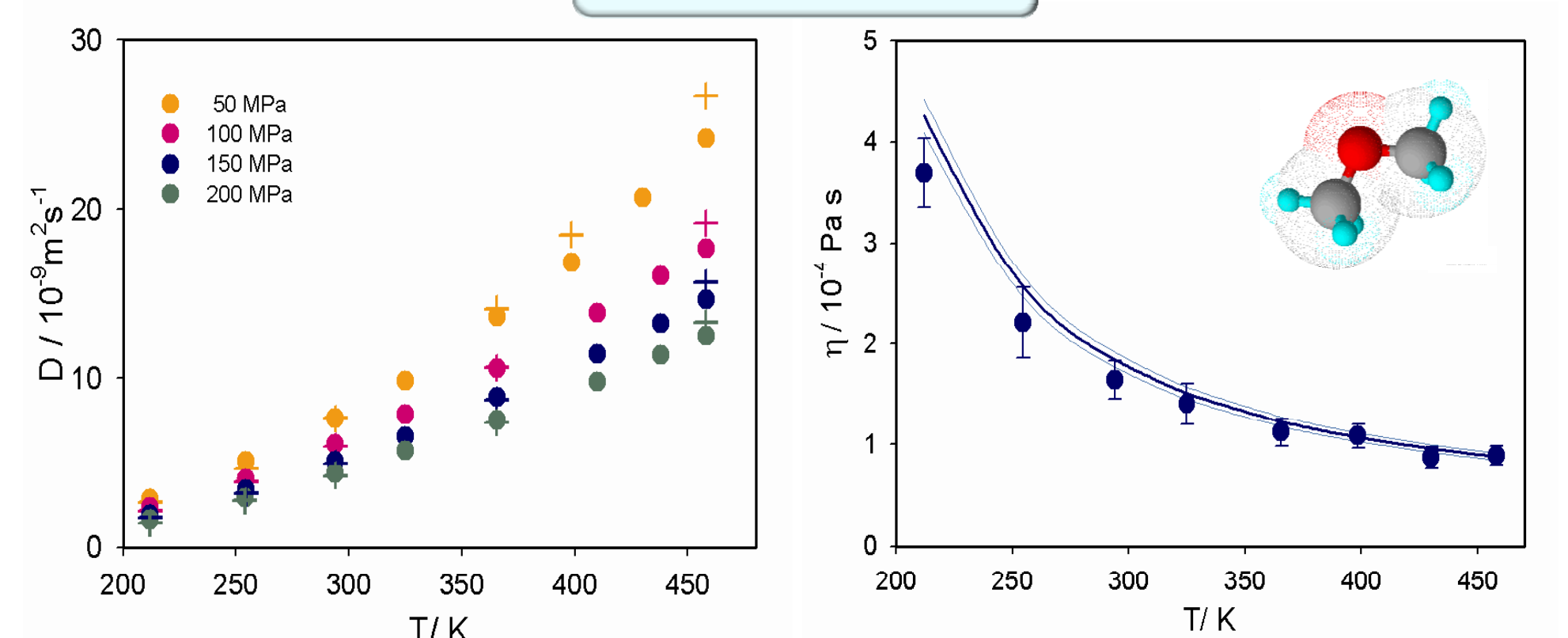


Figure 4: Liquid dimethylether: temperature dependence of the self-diffusion coefficient at different pressures (left); temperature dependence of the shear viscosity at $p = 50$ MPa (right). The bullets represent the simulation results, the crosses are experimental data [5], the dark blue line is the correlation from REFPROP, and the light blue lines are the estimated uncertainties.

Ammonia

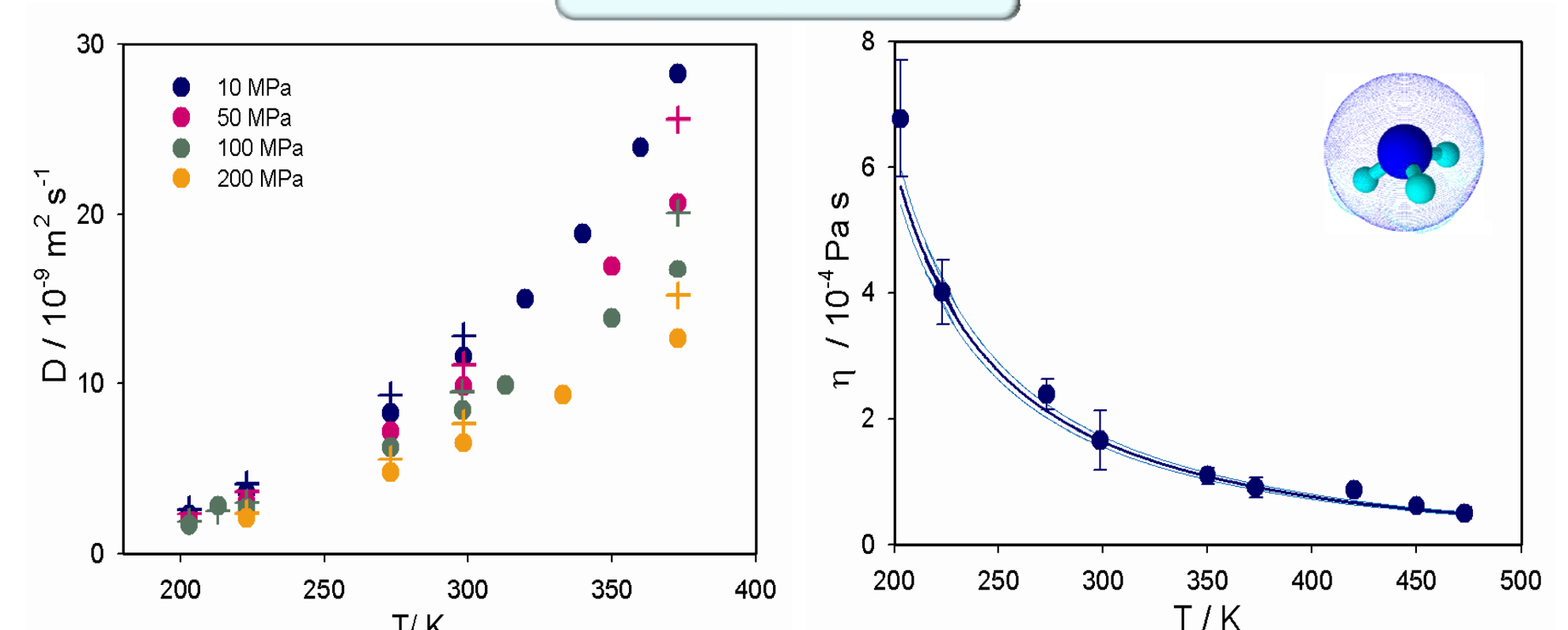


Figure 5: Liquid ammonia: (left) temperature dependence of the self-diffusion coefficient at different pressures; (right) temperature dependence of the shear viscosity at $p = 50$ MPa. The bullets represent the simulation results, the crosses are experimental data [6], the dark blue line is the correlation from REFPROP and the light blue lines are the uncertainties.