

Mesoscopic Structures in Complex Electrolytes

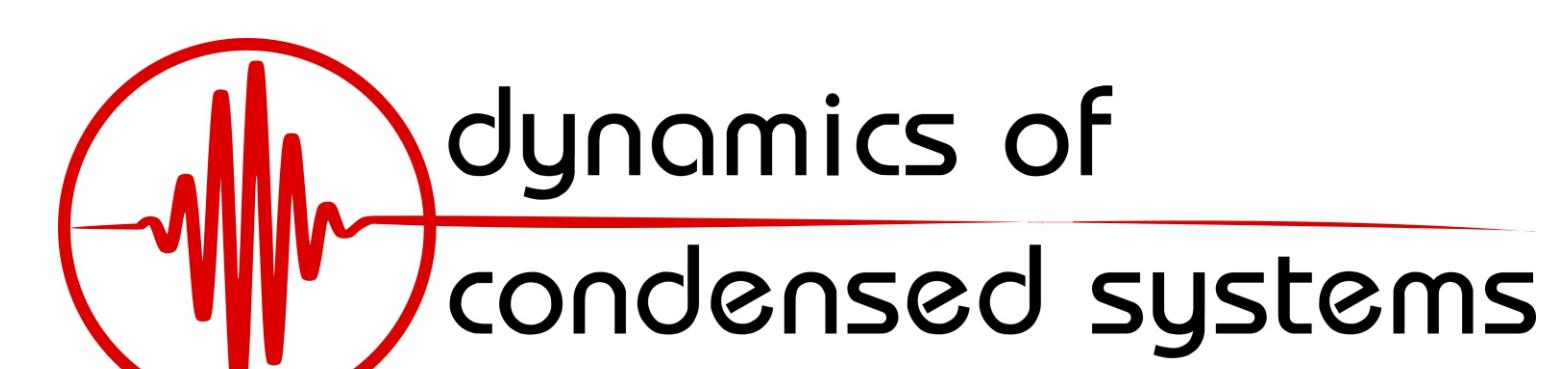
Small Angle X-Ray and Neutron Scattering



universität
wien

Markus Mezger, Kim Hao Ng, Michelle Tesar, Susanna Wolf, Markus Batzer, Timon Tausendpfund

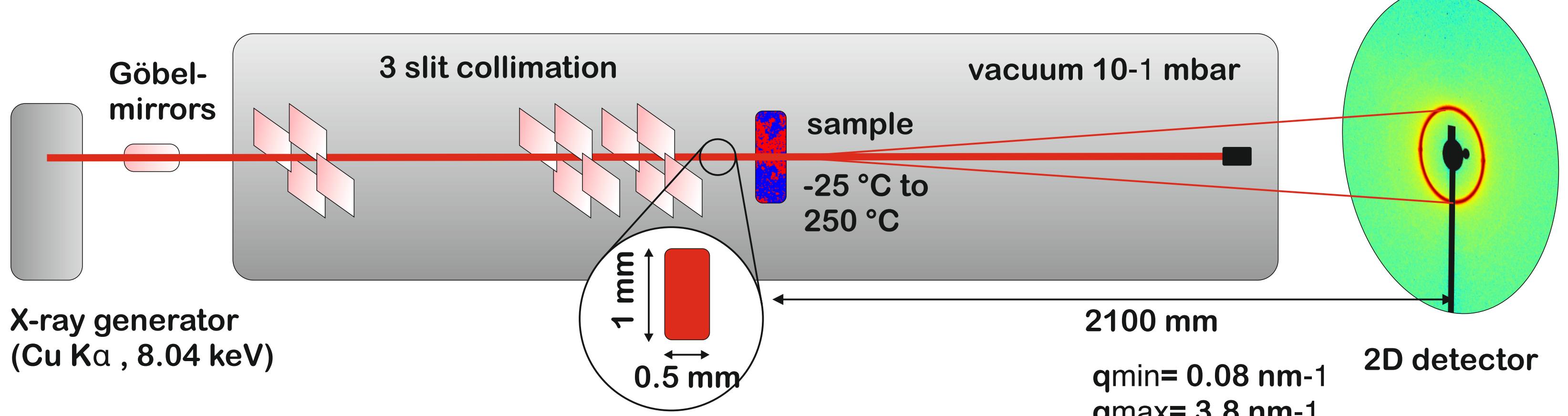
University of Vienna, Faculty of Physics, Vienna, Austria



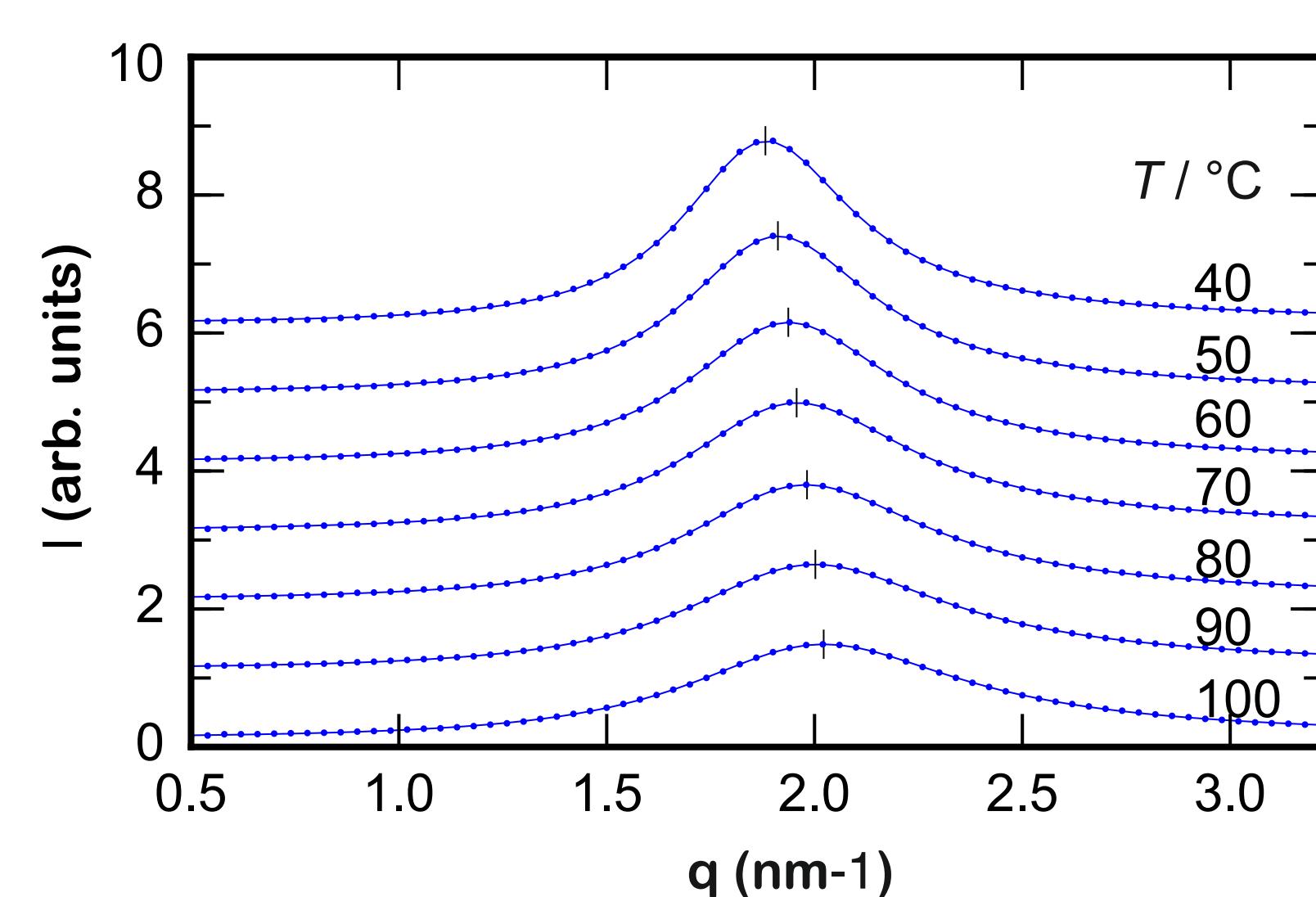
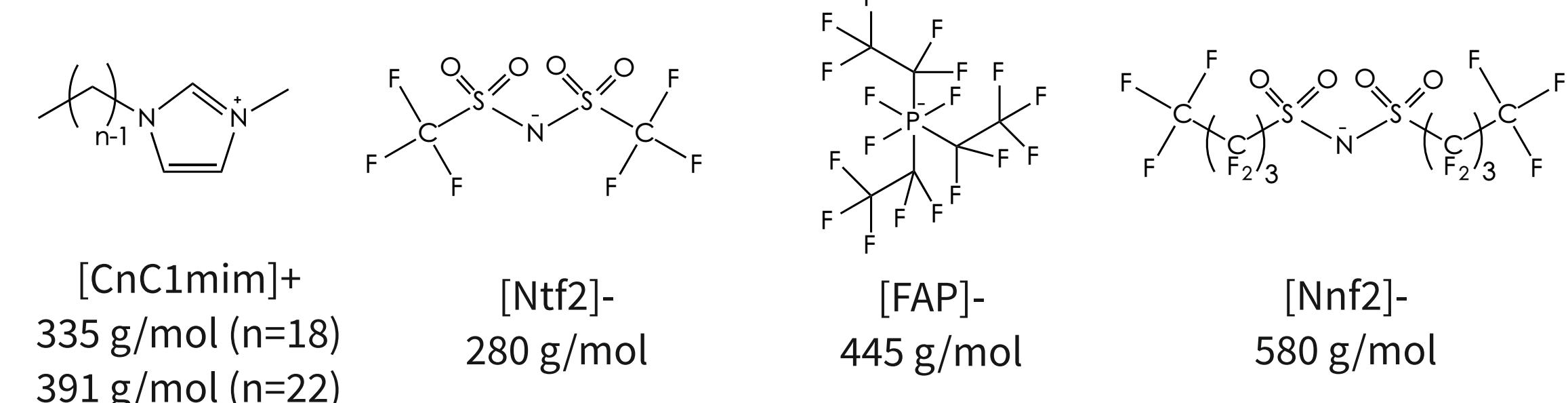
Abstract

Structure formation in complex fluids is a well known phenomenon. Commonly, the different components of the system or molecular groups are classified by their hydrophilic/hydrophobic or polar/apolar character. In most cases, the structural length scales of the systems are governed by the molecular dimensions of these molecular moieties. Classical salt solutions are characterized by their Debye length. For diluted aqueous solutions the Debye length and the molecular size of ions and water molecules have different length scales. In contrast, structural length scales in complex electrolytes can be comparable to the Debye length. Therefore, the competing underlying interactions may lead to novel properties such as oscillatory charge correlations. Here, we present a small-angle X-ray scattering (SAXS) studies on the mesoscopic structure in ionic liquids, near-critical binary electrolyte solutions with anticoagulant salts, and fluoroalcohol mixtures.

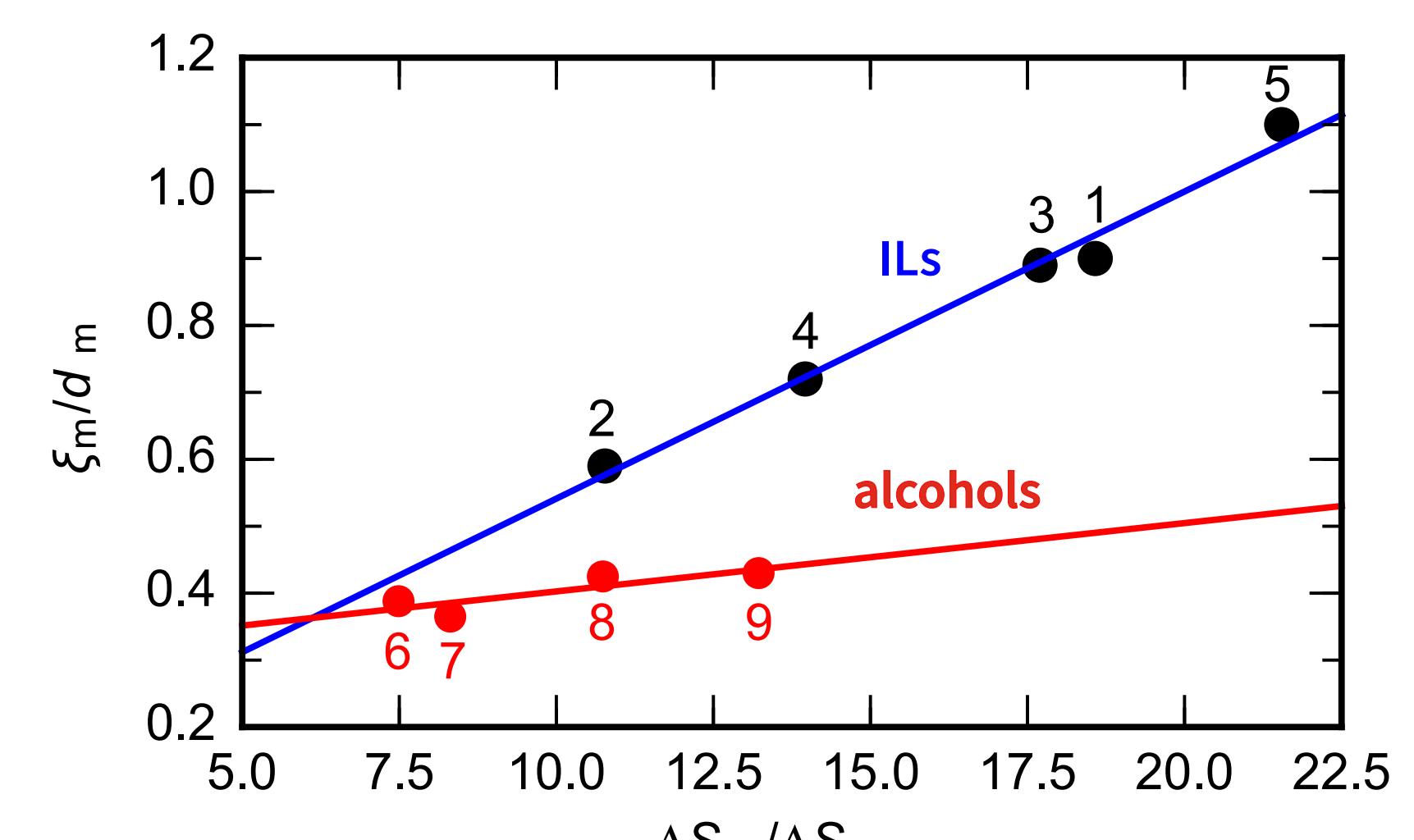
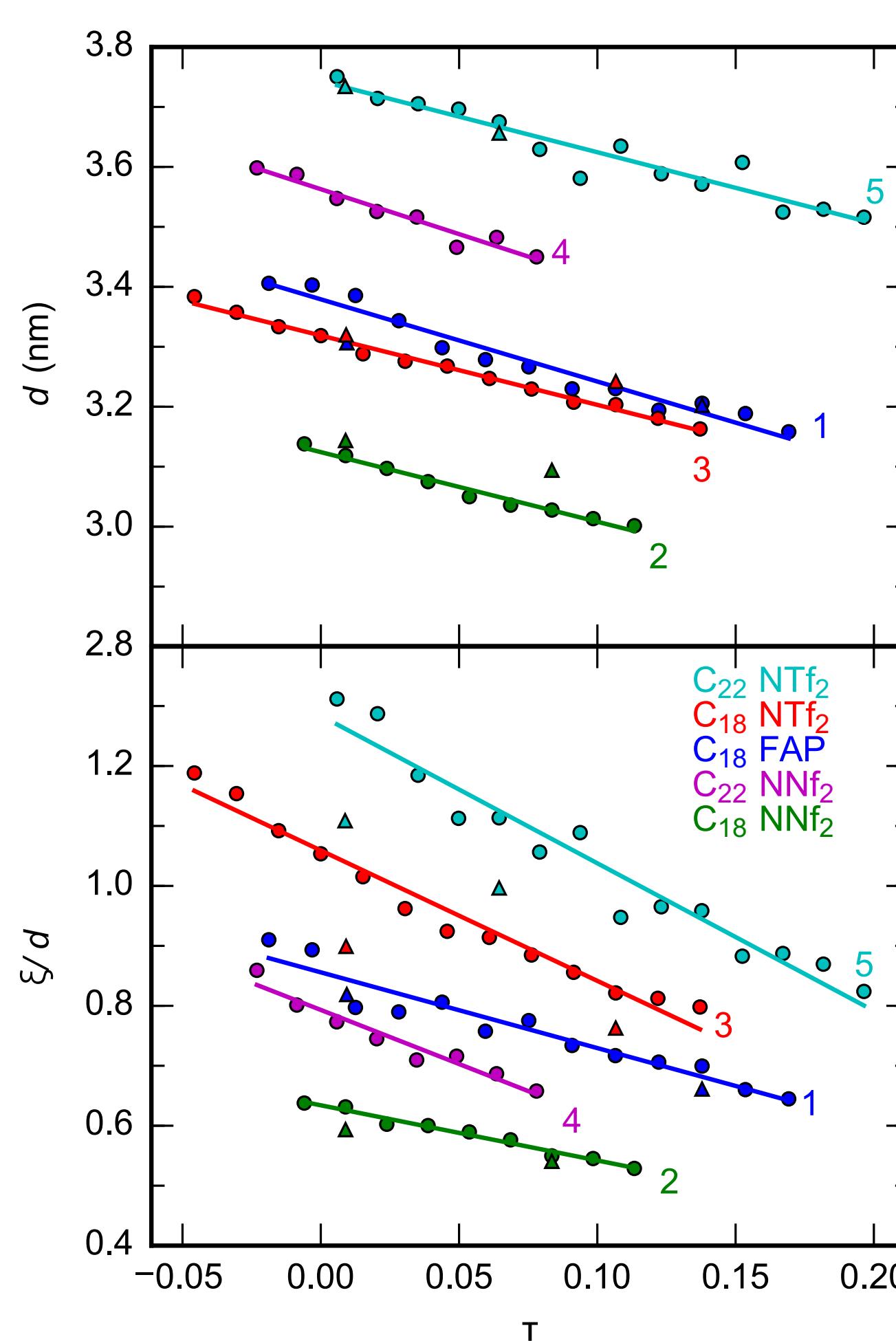
Small Angle X-Ray Scattering (SAXS)



Ionic Liquids



- ILs with long alkyl side-chains exhibit micro-phase separation
- Quantitative analysis using generalized Teubner-Strey model
- Periodicity $d \rightarrow$ peak position
- Correlation length $\xi \rightarrow$ peak width
- Periodicity d primarily determined by alkyl chain length
- Correlation length ξ strongly affected by temperature and anion/cation size ratio



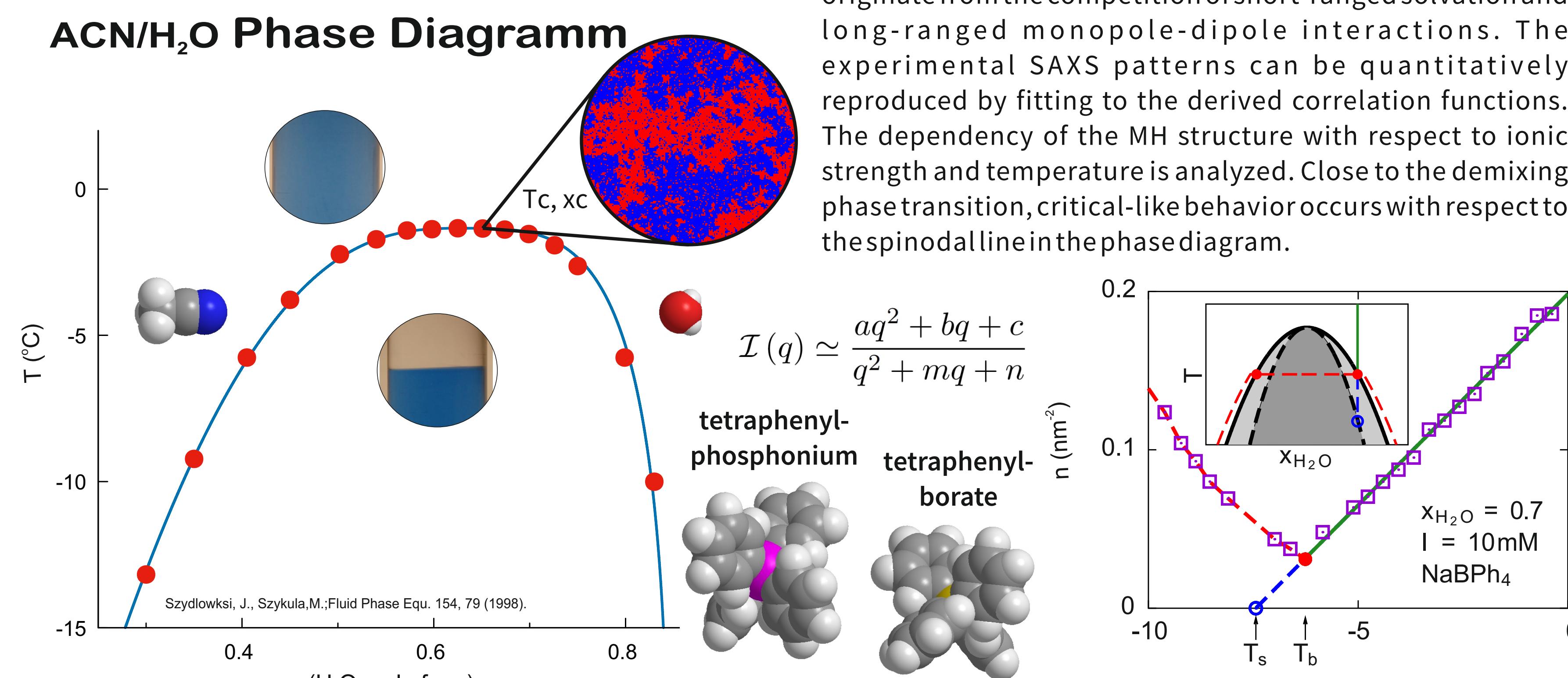
Linear dependency of normalized correlation length $d\xi/d_m$ with entropy of fusion $\Delta S_f / \Delta S_{cc}$

Molecular Scale Structure \longleftrightarrow Thermodynamic Quantities

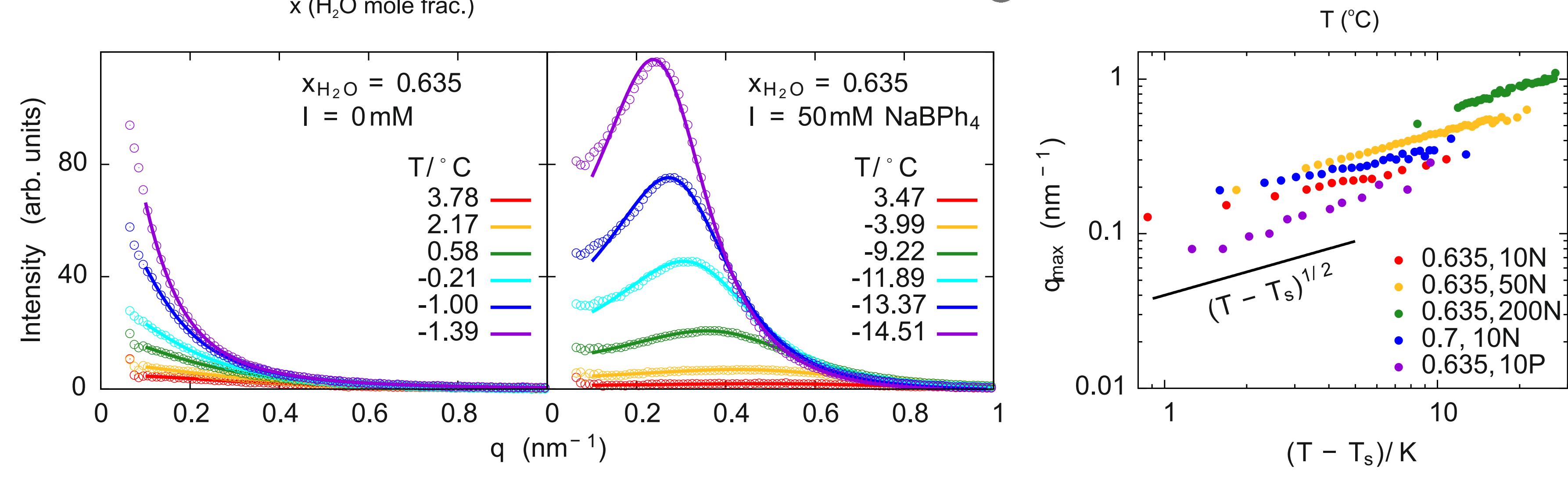
low T, small anions
high T, small anions
large anions

Salt-Induced Heterogeneities in Binary Liquids

ACN/H₂O Phase Diagram



Microheterogeneities (MHs) in binary solvent mixtures originate from the competition of short-ranged solvation and long-ranged monopole-dipole interactions. The experimental SAXS patterns can be quantitatively reproduced by fitting to the derived correlation functions. The dependency of the MH structure with respect to ionic strength and temperature is analyzed. Close to the demixing phase transition, critical-like behavior occurs with respect to the spinodal line in the phase diagram.

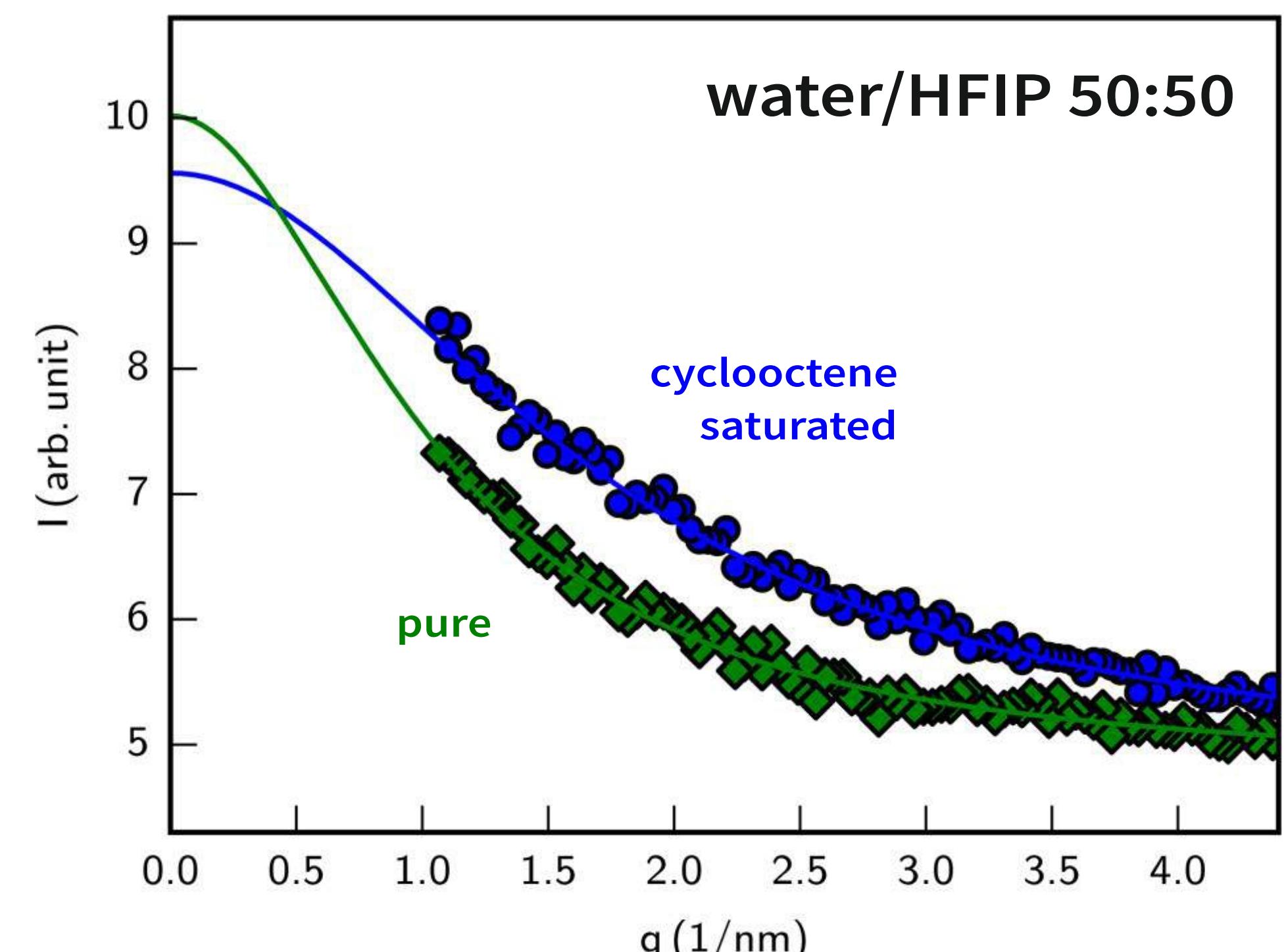


Collaboration with M. Bier (MPI Intelligent Systems, Stuttgart)

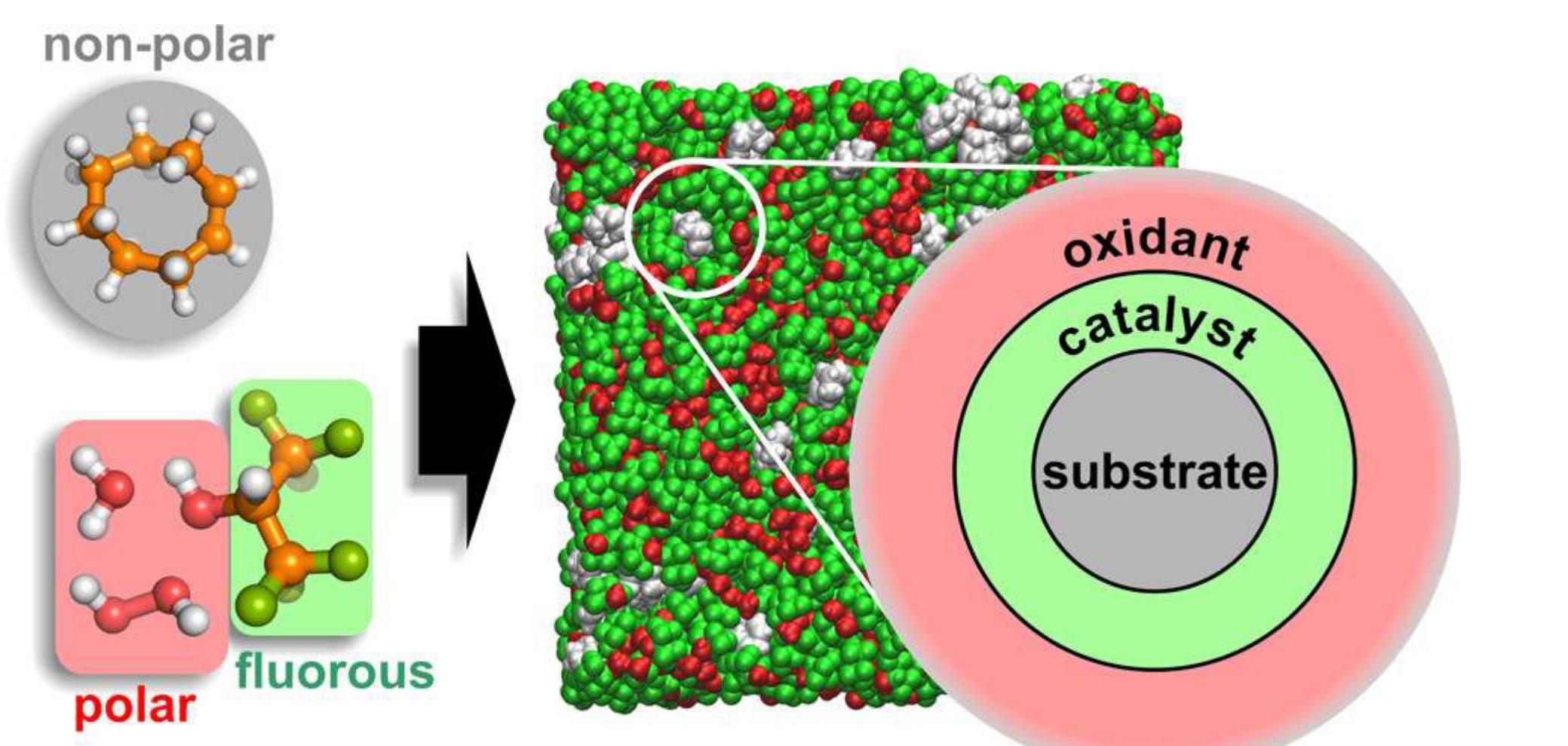
References

- [1] H. Weiss, J. Mars, H. Li, G. Kircher, O. Ivanova, A. Feoktystov, O. Soltwedel, M. Bier, M. Mezger, *J. Phys. Chem. B*, 121, 620, (2017).
- [2] O. Hollóczki, A. Berkessel, J. Mars, M. Mezger, A. Wiebe, S. Waldvogel, and B. Kirchner, *ACS Catal.* 7, 1846 (2017).
- [3] M. Mezger, R. Roth, H. Schröder, P. Reichert, D. Pontoni, and H. Reichert, *J. Chem. Phys.* 152, 164707 (2015).
- [4] M. Bier, J. Mars, H. Li, and M. Mezger, *Pys. Rev. E* 96, 022603 (2017).
- [5] H.W. Cheng, H. Weiss, P. Stock, Y.-J. Chen, C.R. Reinecke J.-N. Dienemann, M. Mezger, and M. Valtiner, *Langmuir* 34, 2637 (2018).

Fluoroalcohol Mixtures



Catalytic Effect of Domain Formation



Collaboration with S. Waldvogel (Organic Chemistry, JGU Mainz)
B. Kirchner (Theoretical Chemistry, Univ. Bonn)

Collaborations

