Wigner 121
Scientific Symposium

Wigner Research Centre for Physics
Institute for Solid State Physics and Optics
Department of Complex Fluids
Liquid Structure Research Group

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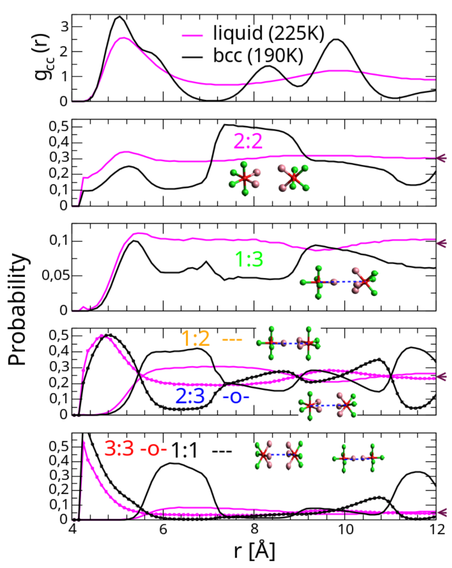
Order in disorder and disorder in order

Physical properties of technologically relevant materials cannot be understood without detailed knowledge of their microscopic structure. For several decades this goal was achieved by determining the unit cell parameters of crystals. With the advent of nanotechnology atomic level disorder became relevant and new tools of structure description had to be found. Our group combines **experimental methods** (X-ray and neutron diffraction, X-ray absorption spectroscopy) and **simulation techniques** (molecular dynamics and reverse Monte Carlo) to obtain a realistic microscopic description of liquids, glasses and disordered crystals.

High-symmetry molecules



To describe the mutual orientational correlations of pairs of tetrahedral molecules a classification scheme is presented earlier [1]. It is based on, how many ligand atoms are from each molecule within 2 parallel planes, containing the molecular centres and perpendicular to their connecting line. This way any arrangement is classified into one of the 6 groups (1:1, 1:2, 1:3, 2:2, 2:3 and 3:3).

For high-symmetry molecules, the classification is extended by taking cones instead of planes, whose apex angle is chosen to be found 2 ligand atoms on average on random orientation.

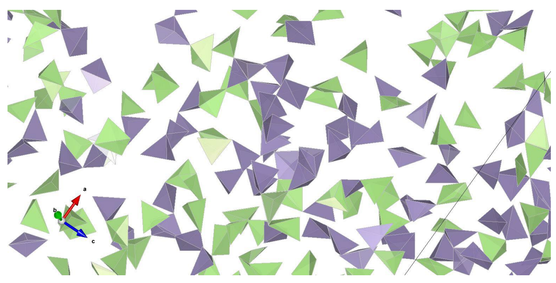
Molecular dynamics simulations are conducted on disordered (gaseous, liquid) and plastic crystalline phases of the octahedral-shaped SF_6 molecule and RT phase of C_{60}. For SF_6, the close contact regions and medium-range orientational correlations (for dense liquid states) are identified. In the plastic crystalline state, fluorine atoms are oriented along the lattice directions with higher probability.

Fig. 1 Arrangements in liquid and plastic crystal phases of SF_6

[1] *Quantitative characterization of orientational order in liquid carbon tetrachloride*, R. Rey, J. Chem. Phys. 126 (2007) 164506.
[2] *A generalized scheme for characterizing orientational correlations in condensed phases of high symmetry molecules: SF_6 and C_{60}*, L. Temleitner, J. Mol. Liq. 341 (2021) 116916

Glasses

Short range order and topology of $Ge_xGa_xTe_{100-2x}$ glasses was investigated by neutron- and x-ray diffraction as well as extended x-ray absorption fine structure measurements. Large scale structural models were obtained by fitting experimental datasets simultaneously with the reverse Monte Carlo simulation technique.

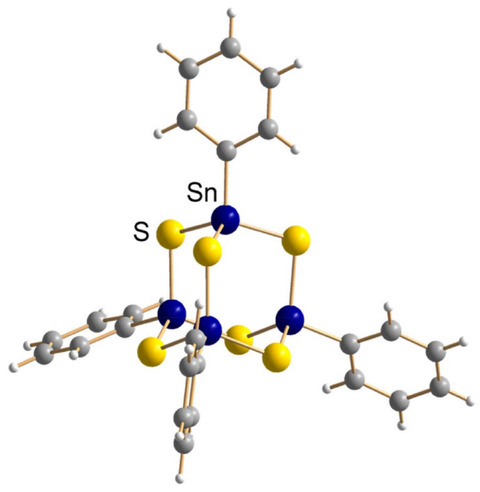


Models, relying only on experimental data and basic physical information without constraining the average coordination numbers, give **3.9–4.1** for the number of the atoms in the first coordination sphere of Ge atoms, while the average number of first neighbors of Ga atoms scatters around **3.8**. It is found that the vast majority of $GeTe_4$ and $GaTe_4$ tetrahedra have at least one corner sharing tetrahedron neighbor.

Fig. 2 Interconnected network of $GeTe_4$ and $GaTe_4$ tetrahedra

[3] *Short Range Order and Topology of $Ge_xGa_xTe_{100-2x}$ glasses*, I. Pethes et al, J. Alloys Compd. 834 (2020) 155097.

Molecular white-light emitters



In recent years a group of materials has been found to emit a continuous spectrum covering the visible region when irradiated with a simple infrared laser diode.[4] The emitted light is perceived by the human eye as white and interestingly keeps the low divergence and direction of travel from the incoming laser beam. The mechanism of the effect is still unclear but a structural origin is likely since non-crystalline materials are exclusively reported to show this effect while most crystalline samples of the same and similar compositions show second-harmonics generation (SHG) instead.

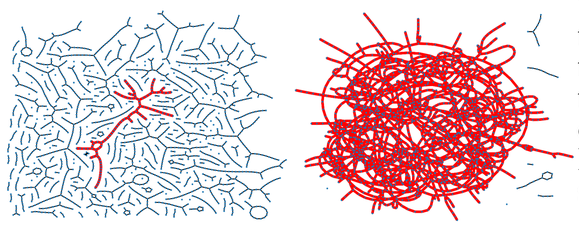
Using Reverse Monte-Carlo modeling adapted to molecular systems in tandem with experimental methods like x-ray diffraction we aim to identify the structural origin of the white-light emission effect.[5-7]

Fig. 3 The molecular structure of one of the materials that shows the white light generation effect: $[(PhSn)_4S_6]$, Ph = phenyl = C_6H_5.[7]

[4] *A highly efficient directional molecular white-light emitter driven by a continuous-wave laser diode*, N.W. Rosemann et al., Science 352 (2016) 1301.
[5] *Local Cluster Distortions in Amorphous Organotin Sulfide Compounds and Their Influence on the Nonlinear Optical Properties*, J. R. Stellhorn et al., Advanced Optical Materials 11 (2023) 2201932.
[6] *Local Structure of Amorphous Organotin Sulfide Clusters by Low-Energy X-Ray Absorption Fine Structure*, J.R. Stellhorn et al., Physica Status Solidi b 259 (2022) 2200088.
[7] *Origin of crystallization suppression in a new amorphous molecular white-light-generating material*, B.D. Klee et al., Scripta Materialia 219 (2022) 114851.

Alcohol-water mixtures

Aqueous mixtures of methanol, ethanol, 1-propanol and 2-propanol have been investigated over the entire concentration range, from room temperature to the freezing point, by diffraction experiments and molecular dynamics simulations. The main objective was to monitor changes in the hydrogen bonding network.
The average number of H-bonds in all mixtures increases with decreasing temperature. H-bonds between unlike molecules are more frequent at lower temperatures, while the number of H-bonds between like molecules remains constant, or even decreases in some mixtures, on cooling.



The H-bond network percolates even at the highest alcohol concentrations close to the freezing point, whereas at room temperature this occurs only at alcohol concentrations below a threshold value. In water-rich mixtures, the water subsystem also percolates.

Fig. 4 Typical H-bond topology of (left) pure methanol at T=300K and (right) 90 mol% methanol-water mixture at T=193K.

The formation of small cyclic units (primitive rings) is preferable at lower temperatures. Rings of 5 molecules are most common in most mixtures, but 6-membered rings are more likely in water-rich methanol-water mixtures, and in ethanol-water and 1-propanol-water mixtures below 10% alcohol concentration.

[8] *Evolution of the hydrogen-bonded network in methanol-water mixtures upon cooling,* I. Pethes, L. Pusztai, L. Temleitner, J. Mol. Liq. 386 (2023) 122494
[9] *Properties of hydrogen-bonded networks in ethanol-water liquid mixtures as a function of temperature: diffraction experiments and computer simulations*, Sz. Pothoczki et al., J. Phys. Chem. B 125 (2021) 6272
[10] *Hydrogen bonding and percolation in propan-2-ol – water liquid mixtures: X-ray diffraction experiments and computer simulations*, Sz. Pothoczki et al. J. Mol. Liq. 329 (2021) 115592
[11] *Temperature-dependent structure of 1-propanol/water mixtures: X-ray diffraction experiments and computer simulations at low and high alcohol contents*, Pethes et al., J. Mol. Liq. 340 (2021) 117188

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