

Mass spectroscopy in molecular resolution:

Atom probe tomography of polymers and complex fluids

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Atom probe tomography is a method of microscopic analysis well-established in the study of hard materials. It is based on the controlled field desorption of individual atoms or small molecular fragments from nanometric specimens and stands out by combining single-atom sensitivity with a 3D volume reconstruction in sub-nanometer resolution. A particular stronghold of the method is the accurate measurement of chemical segregation at grain boundaries and interfaces in complex nanostructured matter.

Our current efforts concern advanced volume reconstruction schemes, the simulation by first-principles methods of the evaporation process [1] and a full statistical understanding of chemical fluctuations in the data sets [2]. Most recently, we desire to break the materials limitations towards the analysis of soft matter and polymeric materials with this method [3].

In order to investigate the structure of complex fluids and soft materials, micro-droplets of liquids are quench-frozen in tiny metallic beakers cut into tungsten tips and then after freezing, the liquids are shaped with focused ion beams into nano-needles. These needles are transferred into the atom probe measurement chamber without melting. Meanwhile, we investigated with this method, aqueous solutions, alkanes and organic solvents as well as complex molecular liquids such as liquid crystals.

Usually, the time-of-flight mass spectra of organic liquids are quite complex containing a variety of small to large fragments. Nevertheless, by accurate fitting procedures, a peak assignment and correct quantitative interpretation becomes often possible. The talk focuses on the issue of volume reconstruction. We present an advanced scheme of reconstruction, that takes into account frequent deviations from the required ideal hemispherical sample shape. In order to clarify whether the obtained reconstructions of polymeric materials and disordered liquids may contain reliable spatial information, we apply next-neighbor statistical methods and fluctuation analysis. i) By evaluating fluctuations of the local chemical environment, order/disorder tendencies are identified and even the Gibbs energies of mixture can be quantified. ii) Similarly, fluctuation analysis is a helpful tool to check the accuracy of positioning atomic species in the volume reconstructions. Statistical next-neighbor analysis is proposed to reveal structural aspects of amorphous polymers or mixtures of amino acids. As examples, measurements of carnosine in aqueous solution as well as of polyvinylpyrrolidone (PVP) will be presented.

References

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