CPP 18: Crystallization, Nucleation and Self-Assembly II (joint session CPP/BP)

Time: Tuesday 9:30–10:30 Location: H14

CPP 18.1 Tue 9:30 H14

Investigation of the Short-Time Diffusive Dynamics During Salt-Induced Protein Crystallization Using Neutron Spectroscopy — •Christian Beck[1,2], Marco Grimaldo[1], Felix Roosen-Runge[3], Fajun Zhang[2], Frank Schreiber[2], and Tilo Seydel[1] — [1]Institut Laue Langevin, Grenoble, France — [2]University of Tübingen, Germany — [3]Lund University, Lund, Sweden

Protein crystals are needed to obtain high-resolution protein structures, and therefore understanding different processes/pathways leading to their formation is of fundamental biophysical and medical interest. Previous studies investigating the kinetics of crystallization *in situ* using static methods (SAXS and microscopy) provided evidence for non-classical crystallization pathways in the presence of multivalent salts [1,2]. Using dissolved β-lactoglobulin proteins as a model system, we studied the $ZnCl_2$-induced crystallization. Here, we employ quasi-elastic neutron backscattering (NBS) and neutron spin-echo (NSE) spectroscopy to access the kinetics of the nanosecond diffusive dynamics of proteins during crystallization on a nanometer length scale. NBS provides information on the changes of the center-of-mass diffusion, internal diffusive dynamics and on the fraction of immobile proteins associated with the crystals. Accessing coherent scattering with NSE, we probe different scattering vectors q to disentangle the different diffusive contributions of proteins in crystals or aggregates, and in the liquid phase, respectively.

[1] A. Sauter *et al.* ACS Cryst. Growth Des. 14 (2014) 6357
[2] A. Sauter *et al.* Faraday Discuss. 179 (2015) 41

CPP 18.2 Tue 9:45 H14

Protein crystallization near liquid-liquid phase separation — Klim Petrov, Jan Hansen, •Florian Platten, and Stefan U. Egelhaaf — Heinrich Heine University Duesseldorf

The crystallization of protein (lysozyme) solutions is studied as a function of protein and salt concentration at ambient conditions. In addition to tetragonal crystals at low salt concentrations (far away from phase separation), needle-like and kinetically roughened crystals occur in the vicinity of the binodal. The crystallization induction time and the growth rate are inferred from optical microscopy and linked to the solubility and protein-protein interactions. Based on these data, the different states of the protein solution are linked to different driving forces for crystallization.

CPP 18.3 Tue 10:00 H14

Does liquid-liquid phase separation enhance protein crystallization? — •Ralph Maier[1], Andrea Sauter[1], Georg Zocher[1], Stefano Da Vela[1], Olga Matsarskaia[1], Ralf Schweins[3], Michael Sztucki[4], Fajun Zhang[1], Thilo Stehle[1,2], and Frank Schreiber[1] — [1]Universität Tübingen, Germany — [2]Vanderbilt University School of Medicine, Nashville, USA — [3]ILL, Grenoble, France — [4]ESRF, Grenoble, France

Solutions of the protein human serum albumin (HSA) exhibiting a reentrant phase behavior with a metastable liquid-liquid phase separation (LLPS) inside the condensed regime in the presence of trivalent salts [1] were studied, focussing on the effects of the metastable dense liquid phase on the crystallization pathways. Optical microscopy and small angle X-ray and neutron scattering were used to follow protein crystallization and to explore the role of metastable LLPS. No evidence of nucleation inside the dense liquid phase was observed. On the contrary, heterogeneous nucleation at the walls of the glass container dominates. This suggests that the existence of a metastable LLPS is not a sufficient condition for a two-step nucleation. The unstable or metastable dense liquid phases serve as a reservoir for crystal growth. Furthermore, the crystallographic analysis of the resulting crystals shows that crystals with different morphology grown under different conditions share the same structure and the metal ions create two bridging contacts within the unit cell which stabilize the unit cell.
[1] Matsarskaia *et al.*, *J. Phys. Chem. B*, **120**, 7731 (2016)

CPP 18.4 Tue 10:15 H14

Using x-ray scattering to understand the formation of unexpected structures in organic thin films — Jenny Lebert[1], Eva M. Kratzer[1,2], Axel Bourdick[3], Mihael Coric[1], Stephan Gekle[3], and •Eva M. Herzig[1,2] — [1]Herzig Group, MSE Technische Universität München, Lichtenbergstr. 2a, 85748 Garching, Germany — [2]Dynamik und Strukturbildung - Herzig Group, Universität Bayreuth, Universitätsstr. 30, 95447 Bayreuth, Germany — [3]Biofluid Simulation and Modeling, Universität Bayreuth, Universitätsstr. 30, 95447 Bayreuth, Germany

The morphology plays an important role for the performance of organic, semi-conducting thin films. Understanding the self-assembly processes that occur during the drying of the photoactive films, will allow us to make progress in controlled nanomorphology tuning. We have therefore developed tools to investigate thin film formation processes using synchrotron radiation to resolve structure and structural developments [1,2]. We have now investigated an in-situ polymerization method for polythiophene to examine how much we can influence the morphology during film formation with such an approach. GI-WAXS measurements, molecular dynamics simulations, and spectroscopic analysis suggest the presence of polythiophene in a novel and stable crystal structure with an enhanced intermolecular interaction [3].
[1] S. Pröller et al. Rev. Sci. Instrum. 2017, 88(6): 066101. [2] S. Pröller et al. Adv. Energy Mater. 2016, 6(1): 1501580. [3] J. Lebert et al. ACS Omega 2018, 6: 6388-6394.