

## CPP 68: Crystallization, Nucleation and Self-Assembly I

Time: Thursday 11:45–13:00

Location: C 230

CPP 68.1 Thu 11:45 C 230

**Molecular self-assembly and dynamics on supramolecular polymers: impact of polarity and interactions strength**

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The design of supramolecular polymers with novel or improved characteristics is an important segment on synthetic materials research. The present work focus on the self-assembly of low molecular weight polypropylene oxide (PPO) and polyethylene oxide (PEO) supramolecular polymers via H-bonding in the bulk. The pair diaminotriazine (Dat) and thymine-1-acetic acid (Thy), as well as 2-ureido-4[1H]-pyrimidinone (Upy) were the H-bonding groups of choice. Particularly SAXS and rheology were combined to study the correlation between the backbone polarity and the different groups interaction strength. Results on the structure show that PEO and PPO functionalized with Thy/Dat self-assemble as linear chains while functionalized with Upy show a sphere particle morphology corresponding to a Upy rich-phase, indicating phase separation. The corresponding Upy cluster radius is larger on PPO than on PEO due to the higher chain hydrophobicity. Moreover, the dynamical behavior indicates a dramatic change from predominantly viscous behavior as observed for Thy/Dat groups.

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CPP 68.2 Thu 12:00 C 230

**Structure Formation in Drying Colloidal Droplets**

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The stratification dynamics of a polydisperse colloidal dispersion in a spherical droplet is investigated during its evaporation via molecular dynamics simulation. Here, our primary focus lies on the structure formation of the dispersed particles during the evaporation process. As the solvent evaporates, the particle concentration inside the droplet increases. Depending on the evaporation rate and the particle size ratios (characterized through the Peclet number), we observe the formation of a dense layer of smaller particles at the receding vapor-liquid interface, whereas the core of the droplet contains a mixture of both small and large particles. When the solvent is completely evaporated from the droplet a colloidal superparticle is formed, which can be porous, amorphous or crystalline, depending on material properties and evaporation rate.

CPP 68.3 Thu 12:15 C 230

**Evaporation-induced assembly of colloidal crystals**

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Colloidal crystals have promising applications for technologies such as photonics, catalysis, and sensing. One convenient method to create such crystals is to disperse the colloids in solution and evaporate out the solvent, leaving behind a close-packed structure. In most situations, the crystal structures that form after evaporation are polycrystalline and highly sensitive to the processing conditions. For example, computer simulations have shown that in-plane crystalline order at the air-solvent interface undergoes a maximum with respect to evaporation

rate. The influence of evaporation on crystal structure at larger scales, e.g. across multiple crystal layers, is not fully understood.

We performed massive-scale, explicit-solvent molecular dynamics simulations to study the evaporation-induced assembly of a colloidal crystal. We classified the structure of the crystallizing colloids using a machine-learning approach, and showed how the crystal nucleates and grows from the drying air-solvent interface. Complementary implicit-solvent simulations were performed to demonstrate the nontrivial role that solvent plays in controlling the crystallization process. Our work has important implications for the processing of colloidal crystals from solution and nonequilibrium molecular modeling.

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**Salt-induced temperature-dependent protein cluster formation: access to binding entropies and enthalpies**

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With increasing Yttrium Chloride (YCl<sub>3</sub>) salt concentration  $c_s$ , aqueous Bovine Serum Albumin (BSA) protein solutions subsequently change from a visually transparent (regime I) to a turbid phase (regime II) and back to a transparent phase (regime III: reentrant dissolution). Within regime II, a lower critical solution temperature (LCST) associated with a liquid-liquid phase separation (LLPS) can be observed. Quasi-elastic neutron scattering (QENS) data as a function of  $c_s$  and the protein concentration  $c_p$  lend support to the formation of protein clusters when approaching regime II [1]. By applying the Wertheim theory for patchy particles [2] and the Flory-Stockmayer cluster size distribution function, it is possible to describe the temperature dependent cluster formation quantitatively. The ion-binding and protein-protein bridging entropies and enthalpies associated with the clusters can be determined directly from a simultaneous fit of the model to a large set of QENS spectra for different  $c_p$ ,  $c_s$ , and  $T$ . The results are compared with calorimetry measurements [3]. [1]Grimaldo, M. *et al*, JPCL 6 (2015) 2577; [2]Wertheim, M., J. Stat. Phys. 1984, 35, 19-34; [3]Matsarskaia, O. *et al*, J. Phys. Chem. B 120 (2016) 7731

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**On the colloidal behavior of hybrid inorganic-organic lead halide perovskite precursor solutions and its impact on thin film microstructure**

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Thin films based on crystalline hybrid organic-inorganic lead halide perovskites are processed by spincoating from precursor solutions of the organic and inorganic counterparts within suitably polar solvent systems (DMSO, DMF, GBL). The conditions of film formation follow non-equilibrium dynamics and resultant films display a range of microstructures including grain sizes, crystal strains, preferential orientations and remarkably, vivid hierarchical surface morphologies. By compositional engineering of the precursor, it is possible to tune the final film composition, as well as alter film morphology.

Colloidal nature of perovskite precursor solutions used for film fabrication is suggested, and phenomena such as glass-transitions, crystal twinning, and growth instabilities are explored in order to explain diffusion-limited self-organization of thin films. Microstructures are further demonstrated to be tunable by control of the colloidal chemistry of the precursor solution.