

## CPP 21: Crystallization, Nucleation and Self-Assembly

Time: Monday 15:00–17:00

Location: ZEU 255

CPP 21.1 Mon 15:00 ZEU 255

**The thermodynamics and kinetics of protein crystallization probed by isothermal microcalorimetry** — LORENA HENTSCHEL, JAN HANSEN, •FLORIAN PLATTEN, and STEFAN U. EGELHAAF — Condensed Matter Physics Laboratory, Heinrich Heine University, Düsseldorf, Germany

The formation of tetragonal lysozyme crystals from supersaturated solutions has been monitored by isothermal microcalorimetry. The weak dependence of the crystallization enthalpy  $\Delta H$  on salt concentration and pH value can be explained by a linearized Poisson-Boltzmann theory. The calorimetric signal is related to the concentration change during nucleation and growth, from which the induction time  $t_{\text{ind}}$  and, using a finite difference model, the growth rate  $G$  are determined. The dependences of  $t_{\text{ind}}$  and  $G$  on the chemical potential are in line with previous findings and can be modelled by classical nucleation theory and the growth of 2D clusters, respectively.

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**Specific ion selection of protein crystal structures and growth** — •RALPH MAIER<sup>1</sup>, CHRISTIAN SIMO<sup>1</sup>, AAFIYA IDREES<sup>1</sup>, GEORG ZOCHER<sup>1</sup>, FAJUN ZHANG<sup>1</sup>, THILO STEHLE<sup>1,2</sup>, and FRANK SCHREIBER<sup>1</sup> — <sup>1</sup>Universität Tübingen, Germany — <sup>2</sup>Vanderbilt University School of Medicine, Nashville, USA

We study protein crystallization in aqueous solutions of  $\beta$ -lactoglobulin (BLG) with  $\text{ZnCl}_2$  by microscopy and small angle X-ray scattering (SAXS). This system is compared to a previously investigated system of BLG with another divalent salt ( $\text{CdCl}_2$ ). Both systems exhibit a reentrant condensation phase behavior with phase transitions at the salt concentration ( $c_s$ )  $c^*$  and *pseudo*- $c^{**}$  and a morphology change of the resulting crystals by increasing  $c_s$  [1]. Importantly, in contrast to BLG with Cd where all crystals share the same structure [2], the morphology change with Zn is accompanied by a change of the crystal structure as verified by SAXS measurements. While the needle-like crystals nucleate in a  $P3_21$  structure, the structure of the more compact crystals, which is similar as for Cd, could not yet be resolved due to twin crystals for Cd. Interestingly, for BLG-Cd, a two-step crystallization mechanism has been proposed and an intermediate phase between the initial solution and the final crystal was identified by a specific SAXS correlation peak, which, however, has not yet been observed for Zn [2] despite forming the similar structure. This provides a model system to investigate different crystallization pathways leading to different structures. [1] Sauter *et al.*, *J. Am. Chem. Soc.*, 2015, 137, 1485-1491. [2] Sauter *et al.*, *Cryst. Growth Des.*, 2014, 14, 6357-6366.

CPP 21.3 Mon 15:30 ZEU 255

**Crystal structure prediction for benzene using basin-hopping global optimisation** — •ATREYEE BANERJEE<sup>1</sup> and DAVID WALES<sup>2</sup> — <sup>1</sup>MPIP — <sup>2</sup>Cambridge University

Organic molecules can be stable in distinct crystalline forms known as polymorphs, which are important for industrial application. Here we use basin-hopping global optimization [1] to predict different low energy structures for crystalline benzene. An anisotropic pair potential is employed using rigid benzene molecules and periodic boundary conditions [2]. We find that basin-hopping can rapidly locate most of the stable crystal structures even for a small cell, validating the methodology as well as the accuracy of the potential. We adopted a recently developed methodology where the supercell is adjusted dynamically to contain the cutoff radius for the real space interaction. During the basin-hopping run, we find a number of unphysical structures that are eliminated by choosing a larger system size. A critical size of the cell is proposed in order to eliminate the system-size effects. Our results suggest that the basin-hopping framework is effective for structure prediction of crystalline systems, in addition to clusters and biomolecules, without additional information from experimental data or symmetry constraints.

References:

- [1] D.J. Wales and J. P. K Doye, *J. Phys. Chem. A*, 101, 5111, 1997.  
[2] T. S. Totton, A. J. Misquitta, and M. Kraft, *J. Chem. Theory Comput.*, 6, 683, 2010.

CPP 21.4 Mon 15:45 ZEU 255

**Ordering of small polymer systems through the prism of par-**

**titition function zeros.** — •TIMUR SHAKIROV and WOLFGANG PAUL — Institute of Physics, University of Halle, Halle, Germany

Typical low temperature conformations of small alkane systems (single chains and few chain aggregates) differ frequently from the melt ones: even relatively short chains are folded in non-trivial structures at low temperatures [1]. The ordering of a system is related to change of thermodynamic and conformational characteristics of chains. In the case of big systems, the changes occur at one the same transition temperature, whereas for small systems the typical temperatures of the changes can be shifted relative to each other. The sensitivity of thermodynamic functions to the shift differs and can be hidden because of a widening of the transition region of the small system. We present here the results of an analysis of the partition function zeros, which helps to identify a two stage conformational reorganization of small alkane systems. Our calculations are based on Wang-Landau-type Monte Carlo simulations [2,3] of a chemically realistic united atom model [4].

[1] T. Shakirov, and W. Paul, *J. Chem. Phys.* 2019, 150, 084903.[2] F. Liang, C. Liu, R. J Carroll, *J. Am. Stat. Assoc.* 2007, 102, 305-320.[3] T. Shakirov, *Comp. Phys. Commun.* 228 (2018), 38-43.[4] W. Paul, D. Y. Yoon, and G. D. Smith, *J. Chem. Phys.* 103 (1995) 1702-1709.

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**Independent Variation of Transition Temperature and Order Parameter at Prefreezing Transition** — •MUHAMMAD TARIQ, OLEKSANDR DOLYNCHUK, ANN-KRISTIN FLIEGER, and THOMAS THURN-ALBRECHT — Institute of Physics, Martin Luther University Halle-Wittenberg, Germany

A solid substrate can induce crystallization of a liquid by either heterogeneous nucleation or prefreezing. Prefreezing refers to the formation of a crystalline layer of thickness  $l_{\text{min}}$  at the melt-solid interface at a temperature  $T_{\text{max}}$  above the melting point  $T_m$ , and is an equilibrium phenomenon. Recently developed phenomenological theory of first-order prefreezing predicts that the transition temperature  $T_{\text{max}}$  depends mainly on the difference of interfacial free energies  $\gamma_{\text{sm}} - (\gamma_{\text{sc}} + \gamma_{\text{cm}})$ , whereas the order parameter  $l_{\text{min}}$  depends on the ratio  $\frac{\gamma_{\text{sc}} + \gamma_{\text{cm}}}{\gamma_{\text{sm}}}$ . To test these predictions, we performed series of in situ AFM experiments on different polymer-substrate systems. Experiments on polyethylene PE films on a molybdenum disulfide  $\text{MoS}_2$  substrate evidence a significantly higher  $T_{\text{max}}$  than on highly oriented pyrolytic graphite HOPG. In case of poly( $\epsilon$ -caprolactone) PCL, where direct experimental measurements of the preformed layer thickness are possible,  $T_{\text{max}}$  of the preformed PCL on  $\text{MoS}_2$  remains nearly same as on HOPG, whereas  $l_{\text{min}}$  decreases to a smaller value and, thereby, indicates that  $T_{\text{max}}$  and  $l_{\text{min}}$  are independent. As such, these experimental findings are consistent with the above-mentioned predictions of the phenomenological theory.

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**Intramolecular inhomogeneities during glassy densification as studied for polyalcohols by FTIR-spectroscopy** — •FRIEDRICH KREMER, WILHELM KOSSACK, and JAN GABRIEL — Peter Debye Institute for Soft Matter Physics, University of Leipzig, Linnéstr. 5, 04103 Leipzig, Germany

The intra-molecular potentials of a series of short polyalcohols (glycerol, threitol, xylitol, sorbitol) are studied by Fourier-Transform InfraRed (FTIR) Spectroscopy far above and below the calorimetric glass transition temperature. Analyzing the temperature dependencies of specific IR absorption bands reflecting dedicated molecular moieties, enables one to unravel on an intra-molecular scale the process of glass formation. For the  $\nu(\text{O}-\text{H})$  stretching vibration with increasing temperature a pronounced red shift is observed which enables one to deduce quantitatively the change in the extension of the inter-molecular N-H\*O bonds. The intra-molecular vibrations being not involved in H-bonding show in contrast an albeit weak blue shift. The relative variation of the width of their respective potentials can be extracted from fits based on the Morse-function. By that the characteristic signature of the intra-molecular inhomogeneities in the glassy systems far above and below the calorimetric glass transition temperature is obtained.

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**Simultaneous SAXS-SANS to study direct influence of surfactant on anisotropic gold nanorod growth** — •TOBIAS ZECH<sup>1</sup>, EZZELDIN METWALLI<sup>1</sup>, KLAUS GÖTZ<sup>1</sup>, LIONEL PORCAR<sup>2</sup>, ANNE MARTEL<sup>2</sup>, and TOBIAS UNRUH<sup>1</sup> — <sup>1</sup>Friedrich-Alexander-University Erlangen-Nuremberg, Institute for Crystallography and Structural Physics, Erlangen, Germany — <sup>2</sup>Institut Laue-Langevin, Grenoble, France

Despite many years of research on understanding the anisotropic growth of gold nanorods (AuNR), some questions remain. One is the influence of the ligand CTAB on shape, size and purity of synthesized gold nanorod solutions. However, in-situ studies, typically done with UV-Vis spectroscopy or SAXS, are only sensitive to the scattering volume of the inorganic gold nanoparticle. The influence of the organic parts, which make up most of the non-aqueous constituents in the solution are often treated as constant during the synthesis. We performed in-situ experiments to observe both inorganic and organic parts during AuNR synthesis via the unique SAXS/SANS instrument developed at our institute. This device is readily positioned at the D22 beamline at ILL. We not only observed, that the micelle structure is changing over time during the synthesis of AuNR but could also link those changes to the stages of growth of the nanoparticles. Furthermore, the influence of modified micelle structures via addition of n-alcohols can be directly correlated to differences in shape and size of the synthesized AuNR. This study shows a new perspective on how ligands can control anisotropic growth of noble metals on a nanoscale.

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**Vertically aligned silica in the hard X-ray spotlight: an in situ GISAXS study of EASA** — •GILLES E. MOEHL<sup>1</sup>, LI SHAO<sup>1</sup>, SAMUEL S. FITCH<sup>1</sup>, CHRIS NICKLIN<sup>2</sup>, JONATHAN RAWLE<sup>2</sup>, PHILIP N. BARTLETT<sup>1</sup>, and ANDREW L. HECTOR<sup>1</sup> — <sup>1</sup>Chemistry, University of Southampton, Southampton, SO17 1BJ, UK — <sup>2</sup>Diamond Light Source, Didcot, OX11 0DE, UK

Under the Advanced Devices by Electroplating EPSRC programme grant (EP/N035437/1) we are working on the integration of nanowire semiconductor structures into electronics, by electrodepositing high quality chalcogenide semiconductors into aligned mesoporous templates. Mesoporous silica films are typically produced by evaporation-induced self assembly (EISA), but vertical alignment of the pores to the substrate is very difficult to achieve. Hexagonal arrays of vertically aligned mesopores can be achieved by electrochemically assisted surfactant assembly (EASA). The application of a negative potential to an electronically conductive substrate results in the self-assembly of a cationic surfactant (typically cetyltrimethylammonium bromide) close to the substrate surface, but also the formation of spheroidal surface aggregates, limiting the obtainable film thickness to a few hundreds of nm. The resulting pore spacing and diameter of only a few nanometres make the characterisation of such structures very challenging and time consuming. In this work, we show the results obtained from in situ GISAXS experiments done during the EASA of silica, following the evolution of the structure formation in real time with sub-second time resolution.