

8th Minisymposium of the SFB TRR 102

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Program

- 2:30 pm *A β fibrillation - a non-nucleation process?*
Jana Wägele, Martin Luther University Halle-Wittenberg
- 2:50 pm *Super-resolution imaging of functional, responsive microgels*
Dominik Wöll, Aachen University
- 3:25 pm Break and discussions in breakout rooms
- 3:45 pm *Thermodynamics of Interface-Induced Crystallization via Prefreezing*
Muhammad Tariq, Martin Luther University Halle-Wittenberg
- 4:05 pm *Growth and Dissolution of Crystal Nuclei in PLLA*
Christoph Schick, Rostock University
- 4:40 pm Discussions with speakers in breakout rooms
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A β fibrillation - a non-nucleation process?

Jana Wägele, Maria Ott

Small globular aggregates, so-called oligomers, of the Alzheimer's peptide Amyloid- β (A β) are believed to play an important role both for development of Alzheimer's disease and the formation of A β fibrils. [1] The latter is often considered as a nucleation and growth process. [2,3] Here we demonstrate that experimental conditions, which reduce competing aggregation processes such as heterogeneous nucleation or fragmentation, reveal a non-nucleated aggregation process

for A β (1-40) and potentially A β (1-42). We use single-molecule fluorescence spectroscopy to show the dependence of the presence of significant oligomer fractions on environmental conditions, and Thioflavin T assays to characterize the underlying kinetic process for three different A β (1-40) variants. Our results strongly support the recent hypothesis [4] that oligomer formation is not part of A β fibril formation, but rather a competing process.

[1] Chiti, F. & Dobson, C.M. *Annu. Rev. Biochem.* (2017) **86** 27-68

[2] Cohen et al. *PNAS* (2013) **110** 24, 9758-9763

[3] Meisl et al. *PNAS* (2014) **111** 26, 9384-9389

[4] Finkelstein, A.V. et al. *Mol. Biol.* (2018) **52** 1, 62-68

Super-resolution imaging of functional, responsive microgels

Dominik Wöll, Silvia P. Centeno Benigno, Laura Hoppe Alvarez, Ashvini Purohit, Oleksii Nevskyi, Eric Siemes, Alex Oppermann, Sarah K. Turnhoff, Walter Richtering.

Super-resolution fluorescence imaging has been frequently used for biological and biomedical applications.[1] Applying these methods to material science, and in particular to polymer systems, bears high potential to unravel details on the nanoscopic scale and to learn about local environments in polymers.

Our work on the nanoscopic imaging of functional microgels that can swell and collapse in response to stimuli, such as changes in temperature, ionic strength or pH, will be presented. We could show that compartmentalized microgels can be specifically labelled in the core or in the shell and, this way, visualize these compartments via localization-based super-resolution fluorescence imaging methods.[2] Applying

switchable fluorescent diarylethene cross-linkers during the synthesis of microgels by precipitation polymerization, we could determine the positions of single cross-linkers within the microgels.[3] Cross-linking has direct influence on the mechanical properties of microgels and determines their deformation at solid-liquid and liquid-liquid interfaces. Also, these deformations can be readily visualized with super-resolved fluorescence imaging. Finally, it is of paramount importance to understand which local environment molecules “feel” in microgels. This question can be addressed by a super-resolution method call PAINT (Point Accumulation In Nanoscale Topography) with the solvatochromic dye Nile Red. We found the existence of surprisingly apolar environments in PNIPAM microgels.[4]

[1] S. W. Hell, ***Nature Methods* 2009**, 6, 24.

[2] A. Gelissen, A. Oppermann, T. Caumanns, P. Hebbeker, S. Turnhoff, R. Tiwari, S. Eisold, U. Simon, Y. Lu, J. Mayer, W. Richtering, A. Walther, D. Wöll, ***Nano Lett.* 2016**, 16, 7295.

[3] E. Siemes, O. Nevskyi, D. Sysoiev, S. K. Turnhoff, A. Oppermann, T. Huhn, W. Richtering, D. Wöll, ***Angew. Chem. Int. Ed.* 2018**, 57, 12280.

[4] A. Purohit, S. P. Centeno, S. K. Wypysek, W. Richtering, D. Wöll, ***Chem. Sci.* 2019**, 10, 10336.

Thermodynamics of Interface-Induced Crystallization via Prefreezing

Muhammad Tariq, Oleksandr Dolynchuk, Ann-Kristin Flieger, and Thomas Thurn-Albrecht
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A solid substrate can induce crystallization of a liquid either by heterogeneous nucleation or by preefreezing. Prefreezing refers to an abrupt formation of a thin crystalline layer at the melt-solid interface at a temperature T_{max} above the melting point, and is an equilibrium phenomenon [1, 2]. A recently developed phenomenological theory of preefreezing [3] predicts that thermodynamic properties of the preefrozen phase are controlled by the substrate-material interactions. According to the theory, while the preefreezing transition temperature T_{max} depends primarily on the difference of the interfacial free energies $\gamma_{sub,melt} - (\gamma_{sub,cry} + \gamma_{cry,melt})$, the minimum jump of thickness l_{min} at T_{max} depends on the ratio $\frac{\gamma_{sub,cry} + \gamma_{cry,melt}}{\gamma_{sub,melt}}$. To test these predictions, we performed a series of in situ AFM experiments on different polymer-substrate systems [1, 2, 4] and made a direct comparison of four relevant cases of

prefreezing, namely two polymers polyethylene (PE) and poly(ϵ -caprolactone) (PCL) on two different substrates. Experiments on PE films on a MoS₂ substrate evidenced a significantly higher T_{max} than on graphite [4]. In case of PCL, where direct measurements of the preefrozen layer thickness were possible, T_{max} of the preefrozen PCL on MoS₂ remained nearly the same as on graphite, whereas l_{min} clearly decreased, thereby, indicating that T_{max} and l_{min} are indeed independent. Therefore, these experimental findings are consistent with the predictions of the phenomenological theory and explicitly demonstrate the effects of substrate interactions on thermodynamics of preefreezing. With these results, we conclude a first series of experiments aimed at an experimental exploration of the theoretically predicted variations of the preefreezing phenomenon.

References:

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- [2] A.-K. Flieger, M. Schulz, T. Thurn-Albrecht, Macromolecules, 51, 189 (2018).
- [3] O. Dolynchuk, M. Tariq, T. Thurn-Albrecht, J Phys Chem Lett, 10, 1942 (2019).
- [4] M. Tariq, O. Dolynchuk, T. Thurn-Albrecht, Macromolecules, 52, 9140 (2019).

Growth and Dissolution of Crystal Nuclei in PLLA

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Properties of many crystalline and semicrystalline materials strongly depend on crystal morphology. Crystal nucleation, as the primary step, is of particular importance [1,2]. Tamman's nuclei development method allows for a detailed study of crystal nucleation by letting the nuclei formed at some nucleation temperature grow to measurable sizes at a higher development temperature. In this method, however, the problem occurs to what extent the crystal nuclei formed in nucleation retain their stability in the course of transfer to the development temperature [3]. By fast scanning calorimetry (FSC) [4], the influence of the transfer of nuclei from the nucleation stage at low temperature to the growth stage at higher temperature was systematically studied. Poly(L-lactic acid) (PLLA), a slowly crystallizing polymer, was chosen for the experiments performed in a wide transfer-heating-rate range. At heating rates between

1 K s⁻¹ and 20,000 K s⁻¹, there occurs stabilization/growth of crystal nuclei at low heating rates and their dissolution/melting at high heating rates. Heating rates above 1000 K s⁻¹ are sufficient to prevent growth of crystal nuclei at the transfer from 60 °C to 125 °C and to higher temperatures. The critical heating rate for preventing nuclei growth is about 1000 times higher than the critical heating rate to prevent crystal growth in a nucleated sample on heating. In a second experiment, from the remaining fraction of crystal nuclei after a short (1 ms) exposure to a temperature above the development temperature, the cluster size distribution after isothermal nucleation of PLLA at 60 °C for 1000 s was estimated. In the temperature interval from 125 °C to 145 °C, the density of critical nuclei decreases from the initial value $\sim 4 \times 10^{24} \text{ m}^{-3}$ to zero, as nuclei with $R > 2 \text{ nm}$, the critical radius for 145 °C, were not formed at the nucleation temperature [5].

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