17th Zsigmondy Colloquium 2022

of the German Colloid Society

From interactions to structures in colloids

Aachen, April 6, 11:30 am – April 8, 01:30 pm, 2022

Topics: • chemistry and physics of functional colloids • phase behavior and dense systems • formulations • theory and simulations	Abstract Deadline: *February 27th* Registration Deadline: *March 3rd* More Information on our website: **zsigmondy22.pc.rwth-aachen.de**
Registration fee: PostDoc/Professor: 160.00 € Students/PhD Students: 100.00 €	The registration fee includes one lunch, coffee breaks, the conference dinner and one guided tour through Aachen.

Confirmed Speakers

- Prof. Mathias Karg - *Chair of Colloids and Nanooptics at the Heinrich-Heine-University, Düsseldorf*
- Prof. Janne-Mieke Meijer - *Assistant Professor in the Theory of Polymers and Soft Matter group in the Applied Physics department of Eindhoven University of Technology (TU/e)*
- Dr. Yuri Gerelli - *Tenure track researcher at the Department of Life and Environmental Sciences of the Polytechnic University of Marche (Ancona, Italy)*
- Dr. Thomas Mosciatti - *Polyurethanes Product R&D PU Global Development Center, Correggio DOW Italia*

Location: RWTH Aachen University, Templergraben 57, 52062 Aachen, Germany

Thermoresponsive core-shell microgels: Properties and dense packings

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Responsive microgels are polymeric objects with an internal gel-like structure that react on external stimuli like temperature, pH or ionic strength.[1] For poly-N-isopropylacrylamide (PNIPAM) based microgels the degree of swelling can be conveniently adjusted by temperature. Typical PNIPAM microgels possess a fuzzy sphere like structure in the swollen state because of the gradient like distribution of cross-links with higher cross-link densities in the interior and a loose outer periphery. During the volume phase transition (VPT) a significant reduction in microgel volume is observed and the internal mass distribution becomes more homogeneous. The VPT is accompanied by a significant increase in light scattering (turbidity) as the microgels collapse. Surprisingly, these changes in optical properties in relation to the microgel structure have not been investigated so far.

We utilize core-shell microgels with small gold nanoparticle cores and much larger PNIPAM shells as an ideal model system to study the structure-property relation of microgels. Importantly, the cores are small enough to not influence the basic physical properties of the microgels and mostly serve as high contrast markers.[2] Using absolute intensity SAXS and SANS measurements, we were able to determine quantitative, radial polymer density profiles that could be converted into refractive index profiles. Supported by theoretical simulations, we show that the increase in light scattering during the collapse is related to the structural transition from fuzzy spheres to rather homogeneous but still relatively low contrast spheres that behave more like Rayleigh-Debye-Gans scatterers.[3]

Our experimental results reveal a direct correlation between changes in microgel size and changes in turbidity. This correlation was used to study the kinetics of the VPT of microgels of different sizes and cross-linker densities using temperature-jump spectroscopy.[4]

In dense packings, the VPT can be used to melt and recrystallize microgel samples in the crystalline phase regime. We studied this transition by SAXS in the ultra-small-angle regime (USAXS) and used detailed Bragg peak analysis to monitor melting and recrystallization events.[5]

Our findings deepen the understanding of structural transitions in microgels and underline the potential of core-shell microgels as ideal model system for soft and deformable objects.

[1] M. Karg, et al., Langmuir, 2019, 35, 6231.
[2] M. Hildebrandt, et al., Macromolecules, 2022, 55, 2959
[3] E. Ponomareva, B. Tadgell, M. Hildebrandt, M. Krüsmann, S. Prévost, P. Mulvaney and M. Karg, Soft Matter, 2022, 18, 807.
[4] B. Tadgell, E. Ponomareva, M. Karg and P. Mulvaney, J. Phys. Chem. C, 2022, 126, 4118.
[5] D. Lapkin, et al., Soft Matter, 2021, 18, 1591.

Tailoring thermal conductivity in polyurethanes foams: challenges and perspectives

Thomas Mosciatti[1]

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Polyurethane foams are the leading insulation material in many applications: from appliances to buildings, from refrigerated transport to pipelines, they play a pivotal role in reducing energy dissipation in different environments, saving millions of eq. MT of CO_2 each year. Albeit their wide diffusion, fundamentals of polyurethane foams, such as nucleation, growth, expansion, curing and their effect on the final foam morphology, are still not completely understood. Moreover, polyurethanes foams are produced by mixing two components, one of which is usually a formulation of different chemicals, with a blowing agent. The intricate interactions among components during the reaction, which occurs while the mixture is expanding and changing viscosity, are difficult to be disentangled and accounted singularly for their contribution.

Tailoring the final foam morphology is the main way to impart desired characteristics, such as the foam thermal conductivity, a parameter of great importance in insulation science, and strictly correlated to the foam cell size.[1]

On this regard, in collaboration with University of Naples, we have developed a new optical setup to observe the foam during the different stages. In particular we have focused on the effect of different chemical and physical blowing agents, and on the outcome of adding nucleation air, a common industrial technique.[2] For the first time we have shown how the bubbles collapse by different mechanisms depending on the introduced external air in the system. One of this mechanism is the Ostwald Ripening (OR) and is the main process that reduces bubble density during foam expansion. We have proposed different formulations, where, dedicated fluorinated additives, can be used to reduce the OR.[3] The final result of the use of such OR inhibitors are foams with reduced average cell size and improved insulation properties.[4]

The approach we have implemented, however, can only bring small improvements in the insulation properties. In order to achieve larger enhancements, new paradigms need to be pursued. Dow has proposed in collaboration with University of Naples and CANNON AFROS SPA a novel process to obtain microcellular foams at macroscopic scales.[5] This process is based on the innovative concept of “chasing the synthesis reaction with the pressure”.[6] Such extreme foam morphology can reduce the thermal conductivity of more than 30% with respect to the current state of the art materials. This proof of concept is the first step towards a new journey, yet to be explored.

References

1. Smits, G. F., Effect of Cellsize Reduction on Polyurethane Foam Physical Properties. *Journal of Thermal Insulation and Building Envelopes* **1994,** *17* (4), 309-329.
2. Brondi, C.; Di Maio, E.; Bertucelli, L.; Parenti, V.; Mosciatti, T., Competing bubble formation mechanisms in rigid polyurethane foaming. *Polymer* **2021,** *228*, 123877.
3. Brondi, C.; Maio, E. D.; Bertucelli, L.; Parenti, V.; Mosciatti, T., The effect of organofluorine additives on the morphology, thermal conductivity and mechanical properties of rigid polyurethane and polyisocyanurate foams. *Journal of Cellular Plastics* **2022,** *58* (1), 59-102.
4. Kramer, T. M. H. Rigid polyurethane foam made with a hydrocarbon blowing agent and 1,1,1,4,4,4-hexafluorobut-2-ene. WO2021045887A1, 2020.
5. Parenti, V., Cavalca, Sara , Mosciatti, Thomas , Di Maio, Ernesto, Di Caprio, Maria Rosaria , Brondi, Cosimo , Iannace, Salvatore Methods for Producing Polyurethane Foams. US20200109249A1, 2020.

6. Brondi, C.; Di Caprio, M. R.; Scherillo, G.; Di Maio, E.; Mosciatti, T.; Cavalca, S.; Parenti, V.; Corti, M.; Iannace, S., Thermosetting polyurethane foams by physical blowing agents: Chasing the synthesis reaction with the pressure. *The Journal of Supercritical Fluids* **2019,** *154*, 104630.

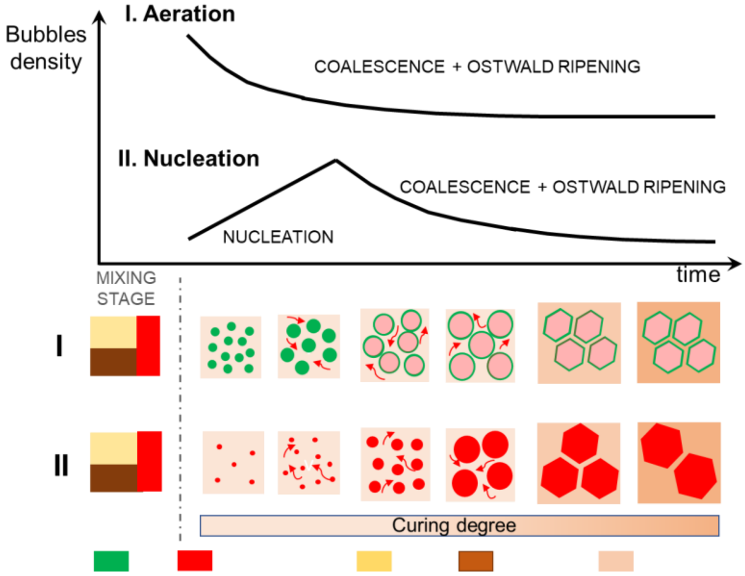

Figure 1. Bubble density in a polyurethane foam in formation: I. with external nucleation air, II. Without nucleation air. On the bottom a visual representation of the different stages is reported. Adapted from [2]

Shape Matters: Visualizing the Self-Assembly of Anisotropic Colloids

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The recent availability of rationally designed colloidal building blocks opens up new ways to study complex materials. At the same time, these colloids are of interest as the building blocks for the preparation of the next generation of functional materials with specific mechanical, optical or magnetic properties.

However, a main challenge in colloid physics remains understanding the relationship between the colloidal building block properties and the order/disorder in self-assembled structures.

In this talk I will show how studying colloidal crystal materials with both x-ray scattering techniques and quantitative microscopy is uniquely powerful for visualizing structural defects on a single-particle level. I will show how small shape changes from a sphere to a cube or a bowl, leads to marked differences in phase behaviour, such as the appearance of plastic crystals, in which particles rotate on their lattice sites, and other unique dense packings. I will further address the influence of directed self-assembly methods such as solvent evaporation, critical Casimir forces and electric fields on the crystal and defect structures of these anisotropic colloids.

Phase transition behaviour in single solid-supported lipid bilayer

Yuri Gerelli

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Concepts derived from the physics and chemistry of colloids can be applied to complex systems as biological membranes to understand lipid supramolecular structure, self-assembly, interactions and phase behaviour.

Solid-supported lipid bilayers (SLBs) are widely used tools in biological- and technological-oriented studies, for the investigation of interactions and molecular processes involved in cell functioning, diseases and for sensing applications. Coexistence of ordered and disordered domains, structural and dynamical coupling between leaflets and the structural responses to changes in the environmental parameters such as temperature, are of fundamental interests in all these scientific fields. Moreover, SLBs are one of the prototypes of natural self- assembling systems.

We applied time- and temperature-resolved neutron reflectometry for the real-time characterization of the structural changes taking place across phase transitions in SLBs. This new method allowed to determine the presence of an isothermal phase transition, characterized by a symmetrical rearrangement of lipids molecules in both bilayer leaflets, followed by a thermotropic phase transition characterized by an independent melting of the two leaflets. Contrary to recent results on similar samples by atomic-force microscopy we demonstrate that the presence of a substrate equally increases the enthalpy of melting for both SLB leaflets with respect to that reported for free standing bilayers. These results are of extreme importance for the further understanding of cooperative structural dynamics in SLBs and for their use in biophysical and biological studies, as for example, for the investigation of thermally activated processes as the lipid flip-flop.

Further readings

Y. Gerelli, ***PRL*** 122, 248101, **2019**