

DY 17: Complex Fluids - organized by Christine M. Papadakis (Technical University of Munich, Garching) (joint session CPP/DY)

Time: Tuesday 9:00–16:30

Location: CPPb

Invited Talk

DY 17.1 Tue 9:00 CPPb

Polymer Micelles with Crystalline Cores: confinement effects, molecular exchange kinetics and mechanical response

— NICO KOENIG¹, LUTZ WILLNER², and •REIDAR LUND¹ —
¹Department of Chemistry, University of Oslo, Postboks 1033 Blindern, 0315 Oslo, Norway. — ²Jülich Centre for Neutron Science JCNS and Institute for Complex Systems ICS,

Partially crystalline, self-assembling systems with multiple components are omnipresent in nature with living cells as a prominent example. Here we study micelles formed by self-assembly of a series of well-defined n-alkyl-(polyethylene oxide) (C_n-PEO) polymers in aqueous solutions [1]. Using small-angle X-ray/neutron scattering (SAXS/SANS), densimetry and differential scanning calorimetry (DSC), we show that the n-alkane exhibit a first-order phase transition in the micellar cores, but with reduced melting points accurately described by the Gibbs-Thomson equation [2]. The effect of core crystallinity on the molecular exchange kinetics is investigated using time-resolved SANS (TR-SANS) [3-9]. We show that the melting transition is cooperative in the confined micellar core, whereas the exchange process is decoupled and unimeric in nature. [9] Telechelic polymers based on C_n-PEO-C_n forms clustered micelles and hydrogels composed of interconnected micelles at higher concentrations.[10] The results show that, contrary to regular micelles, the kinetics occurs in a multistep process involving a novel collision-induced single-molecule exchange mechanism.[11] Moreover exchange kinetics directly controls the mechanical response of hydrogels through the bond life time [12]

DY 17.2 Tue 9:40 CPPb

Foams stabilized by PNIPAM microgels — •MATTHIAS KÜHNHAMMER, CHRISTIAN APPEL, and REGINE VON KLITZING — Technical University of Darmstadt, Department of Physics, Soft Matter at Interfaces, 64287 Darmstadt, Germany

Cross-linked, short-chained poly-N-isopropylacrylamide (NIPAM) polymers have been in the focus of numerous studies in the past years and are still being discussed very actively in the context of multiple possible applications, because of their ability to respond to external stimuli. Because of their amphiphilic character, PNIPAM microgels can be used to stabilize dispersions like emulsions or foams.

In this contribution microgel stabilized foams are investigated. These foams are very stable at temperatures below the volume phase transition temperature (VPTT) of NIPAM and can be destabilized by increasing the temperature above the VPTT. The structure of the microgels inside the foam lamellae is investigated with neutron scattering. These results are compared to the organization of microgels at a single gas / water interface, which is studied with Langmuir isotherms and X-ray reflectivity.

Finally, these findings are related to macroscopic properties of the foams, namely foamability and foam stability.

DY 17.3 Tue 10:00 CPPb

Functional, responsive microgels enlightened with super-resolution fluorescence microscopy — •DOMINIK WÖLL, LAURA HOPPE ALVAREZ, ERIC SIEMES, ASHVINI PUROHIT, and SILVIA CENTENO BENIGNO — Institut für Physikalische Chemie, RWTH Aachen University, Landoltweg 2, 52074 Aachen

The elucidation of the structure and functionalization of materials in the sub-micron range is a key to their further development and application. Microgels are a class of such soft materials with high potential for multiple fields. Several groups have learnt to functionalize and structure microgels in sophisticated ways, but the evaluation of a successful functionalization or the envisioned properties are often limited by the ways of analysis and visualization. The development of modern super-resolved fluorescence microscopy methods opened up new ways of nanoscopic visualization that had not been possible previously due to the diffraction limit of light prohibiting spatial resolution beyond approx. 200 nm. In my contribution, the possibilities to elucidate shape and functionalization, to visualize single cross-linker positions and to address local polarity in microgels with 3D super-resolution fluorescence imaging will be discussed, and ways presented to address and answer scientific questions in soft matter science.

40 min. meet the speakers - break**Invited Talk**

DY 17.4 Tue 11:00 CPPb

Dynamic behaviour of anisotropic magnetic particles in suspensions — •SOFIA KANTOROVICH — University of Vienna — Ural Federal University

Stable dispersions of magnetic colloidal particles with sizes ranging from nanometers to couple of microns have been actively studied for several decades and the interest to them seems to keep growing. Such an attention to these systems is paid because of several reasons: they are biocompatible, can be remotely controlled by external magnetic fields and new synthesis techniques enable a rich variety of particle morphologies. In classical magnetic fluids with spherical poly-disperse nanoparticles, dominating dipolar interactions typically limit the structural complexity of their aggregates to linear arrangements, namely chains, rings and branched structures. In this contribution I will show, how to either alter the shape of magnetic particles or their internal structure in order to extend dramatically the topology and properties of their suspensions. In particular I will focus on magnetic cubes, magnetic Janus particles, soft magnetic colloids and magnetically anisotropic nanoparticles. I will show how lattices, branched clusters of staggered chains, compact clusters, linear chains, and non aggregated configurations can be formed and interconverted reversibly in a controlled way. I will also discuss how adding an active component to magnetically anisotropic particles leads to unique properties. The results gathered in this presentation demonstrate that fundamentally new possibilities for responsive magnetic materials can arise when we step away from conventional dipolar hard spheres.

DY 17.5 Tue 11:40 CPPb

Graphical Magnetogranulometry — •INGO REHBERG, REINHARD RICHTER, and STEFAN HARTUNG — Bayreuth University

The dipole strength of magnetic particles in a colloidal suspension can be obtained by a graphical rectification of the magnetization curves based on the inverse Langevin function. The method [1] yields the arithmetic and the harmonic mean of the particle distribution. It has an advantage compared to the fitting of magnetization curves to some appropriate mathematical model: It does not rely on assuming a particular distribution function of the particles.

[1] Measuring magnetic moments of polydisperse ferrofluids utilizing the inverse Langevin function, Ingo Rehberg, Reinhard Richter, Stefan Hartung, and Niklas Lucht, Birgit Hankiewicz, and Thomas Friedrich, Phys. Rev. B 100, 134425 (2019).

DY 17.6 Tue 12:00 CPPb

Phase Behavior of Charged Magnetic Nanoplatelets

— •MARGARET ROSENBERG¹ and SOFIA KANTOROVICH^{1,2} —
¹Department of Physics, University of Vienna, Austria —
²Department of Mathematical Physics, Ural Federal University, Russia

Recent decades have seen the emergence of a new branch of science, magnetic soft matter, fueled by the advances in synthesis techniques, which have also made a wide variety of anisotropic magnetic colloidal nanoparticles available. Colloidal anisotropy can be used as an effective control parameter to tune both self-assembly scenarios and thermodynamic, rheological and phase behavior of dipolar (magnetic) soft matter. For instance, magnetic nanoplatelets can form macroscopic ferromagnetic phases at room temperature. Although the phase behavior of a system hard-core platelets is well known, the influence of the magnetic dipole moment and electrostatic repulsion on suspensions of magnetic platelets is not yet fully understood. We use MD simulations to recreate such a system. The colloidal particles are modelled by charged soft spheres, with a central dipole possessing a magnetic moment of a constant length, permanently oriented perpendicular to the platelet surface. In order to investigate the self-assembly and structural properties of the platelets, we vary the amplitude of an applied magnetic field and the magnetic dipole. We analyze at which electrostatic conditions the system exhibits self-assembly or/and field alignment, based on RDFs, structure factors parallel and perpendicular to the field and extensive cluster analysis.

DY 17.7 Tue 12:20 CPPb

Magnetically Functionalized Star Polymers in Equilibrium and under Shear — ●GERHARD KAHL¹, DAVID TONEIAN¹, and CHRISTOS N. LIKOS² — ¹Institut für Theoretische Physik, TU Wien — ²Fakultät für Physik, Universität Wien

Star polymers are macromolecules consisting of a central site, attached to which are a number f of linear polymer chains, called arms. Depending on the chemical composition of the arms, the polymer stars exhibit intriguing features, both in isolation and in concentrated solution.

We present star polymers with magnetically functionalized end groups as a novel polymeric system whose morphology, self-aggregation and orientation can easily be tuned by exposing these macromolecules simultaneously to an external magnetic field and to shear forces within a channel. Our investigations are based on a specialized simulation technique which faithfully takes into account the hydrodynamic interactions of the surrounding, Newtonian solvent. We find that the combination of magnetic field (including both strength and direction) and shear rate controls the mean number of magnetic clusters, which in turn is largely responsible for the static and dynamic behavior. While some properties are similar to comparable non-magnetic star polymers, others exhibit novel phenomena; examples of the latter include the breakup and reorganization of the clusters beyond a critical shear rate and a strong dependence of the efficiency with which shear rate is translated into whole-body rotations on the direction of the magnetic field.

DY 17.8 Tue 12:40 CPPb

Structural details of polymer grafted nanoparticles: Insights from coarse-grained molecular dynamics simulations — ●JIARUL MIDYA¹, MICHAEL RUBINSTEIN², SANAT K. KUMAR³, and ARASH NIKOUBASHMAN¹ — ¹Johannes Gutenberg University of Mainz, Mainz, Germany — ²Duke University, Durham, United States — ³Columbia University, New York, United States

Polymer grafted nanoparticles (GNPs) are promising materials with a wide range of applications in drug delivery, gas separation, photonic and electric materials. In this work, the structural properties of GNPs are studied via coarse-grained molecular dynamics simulations. We systematically vary the degree of polymerization at fixed grafting density, and study in detail the shape and size of the GNPs, the interpenetration between the grafted polymers and their conformations. We then compare these properties to the ones of pure polymer melts to assess the effect of confinement. We observe that the amount of chain-sections in the interpenetration zone is proportional to the length of the grafted chains, N_g , whereas, the brush height follows a power-law like behavior $h \sim N_g^\alpha$, where exponent α decreases from a value close to one to the limiting value of 1/3 with the increase of N_g . To understand the scaling behavior of h we provide an empirical form, involving the length of the grafted polymers and the core size of the GNPs, which explains our simulation results.

60 min. meet the speakers - break

DY 17.9 Tue 14:00 CPPb

Charge regulation radically modifies electrostatics in membrane stacks — ●ARGHYA MAJEE¹, MARKUS BIER^{1,2}, RALF BLOSSEY³, and RUDOLF PODGORNİK⁴ — ¹MPI for Intelligent Systems, Stuttgart & University of Stuttgart, Germany — ²University of Applied Sciences, Würzburg-Schweinfurt, Germany — ³University of Lille, CNRS, UMR8576 UGSF, France — ⁴CAS & KAVLI Institute of Theoretical Sciences, Beijing

Motivated by biological membrane-containing organelles in plants and photosynthetic bacteria, we study charge regulation in a model membrane stack [1]. Considering (de)protonation as the simplest mechanism of charge equilibration between the membranes and with the bathing environment [2], we uncover a symmetry-broken charge state in the stack with a quasiperiodic effective charge sequence. In the case of a monovalent bathing salt solution, our model predicts complex, inhomogeneous charge equilibria depending on the strength of the (de)protonation reaction, salt concentration, and membrane size. Our results shed light on the basic reorganization mechanism of thylakoid membrane stacks.

References:

- [1] A. Majee, M. Bier, R. Blossey, and R. Podgornik, *Phys. Rev. E* **100**, 050601(R) (2019).
[2] A. Majee, M. Bier, and R. Podgornik, *Soft Matter* **14**, 985 (2018).

DY 17.10 Tue 14:20 CPPb

Emulsion destabilisation by squeeze flow — ●RIANDE DEKKER, ANTOINE DEBLAIS, and DANIEL BONN — Van der Waals-Zeeman Institute, Institute of Physics, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, The Netherlands

There is a large debate on the destabilisation mechanism of emulsions. We present a simple technique using mechanical compression to destabilise oil-in-water emulsions while at the same time confocal microscopy allows to visualise the mechanism directly. Upon compression of the emulsion, the continuous aqueous phase is squeezed out, while the dispersed oil phase progressively deforms from spherical to honeycomb-like shapes. The liquid films that separate the oil droplets are observed to thin and break at a critical oil/water ratio, leading to coalescence events that destabilise the emulsion. The destabilisation occurs like an avalanche propagating through the system. Local rearrangements occur after the first destabilisation due to the first coalescence event. The films participating in the cascade are the finest ones.

DY 17.11 Tue 14:40 CPPb

Impact of hydrogen bonding strength on the structure and dynamics of supramolecular PEO — ●ANA BRÁS¹, ANA ARIZAGA¹, UXUE AGIRRE¹, MARIE DORAU¹, PATRICIA BACH¹, JUDITH E. HOUSTON^{2,3}, AUREL RADULESCU³, MARGARITA KRUTEVA⁴, and ANNETTE M. SCHMIDT¹ — ¹UzK, Cologne, Germany — ²ESS, Lund, Sweden — ³FZJ, Garching, Germany — ⁴FZJ, Jülich, Germany

In this work we investigate supramolecular poly(ethylene oxide) (PEO) oligomers at the entanglement molar mass (Me) with different hydrogen bonding end groups, such as diaminotriazine (Dat) and thymine-1-acetic acid (Thy), as well as 2-ureido-4[1H]-pyrimidinone (Upy). Small angle scattering and rheology were combined to study the influence of different end-groups association strength as Upy is highly self-associative in comparison to the heterocomplementary pair Thy/Dat. Results on the structure provide insight into the underlying molecular mechanisms and reveal that while Upy-terminated chains phase segregate, forming network-like systems, the Thy/Dat pair-terminated system self-assemble to linear chains, thereby increasing the effective chain length. Moreover, rheological measurements also reveal differences in the viscoelastic response as Upy-terminated chains exhibit an extended rubbery plateau, typical of networks, and the pair Thy/Dat presents a Newtonian fluid behaviour. Remarkably, albeit both systems show end-group association, different hydrogen bonding species influence the type of associates. Acknowledgements: DFG for a research grant (BR5303) and Prof. Dr. D. Richter, Prof. Dr. R. Strey and Dr. Wim Pyckhout-Hintzen for fruitful discussions.

DY 17.12 Tue 15:00 CPPb

Structural characterization and rheology of biocompatible wormlike micelles - comparing experiment and theory — ●BENJAMIN VON LOSPICHL^{1,2}, SABINE H. L. KLAPP², and MICHAEL GRADZIELSKI¹ — ¹Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 124, D-10623 Berlin — ²Institut für Theoretische Physik, Technische Universität Berlin, Hardenbergstraße 36, D-10623 Berlin

Wormlike micelles exhibit a unique viscoelastic behaviour, which has been investigated intensely in the past decades by experimentalists and theoreticians [1,2]. Within our studies we explore the self-assembled structures and the flow behaviour of biocompatible wormlike micelles, which are a mixture of a short-chained C₈ cationic surfactant and the salts of long-chained C₁₈ to C₂₂ omega-9 fatty acids. The variation of the omega-9 fatty acids yields a change in thickness of the micelles, which strongly influences the flowing properties of the system. To characterize the size distribution and the relaxation time of the micellar solutions we use neutron scattering, rheology and electric birefringence. The obtained experimental results are then quantitatively compared to an established theoretical model describing the dynamics of micelles under shear. The model links mechanical properties such as stress to structural quantities like alignment or micellar length [3].

[1] C. Dreiss, *Soft Matter* **3**, 956, (2007)[2] P. D. Olmsted, *Rheo. Acta* **47**, 283, (2008)[3] B. v. Lospichl, S. H. L. Klapp, *Phys. Rev. E* **98**, 042605, (2018)

DY 17.13 Tue 15:20 CPPb

Light driven passive and active motion of colloidal particles — ●POOJA ARYA, DAVID FELDMANN, and SVETLANA SANTER — University of Potsdam, Potsdam, Germany

We report on how one can manipulate an ensemble of colloidal particles trapped at a solid/liquid interface during irradiation with light of different wavelengths. The colloids are dispersed in an aqueous solution of photosensitive azobenzene containing cationic surfactant, which can photo-isomerize from trans to cis state under irradiation with light of appropriate wavelength. When focused light is applied, light-driven diffusioosmotic (LDDO) flow¹ is generated at the solid/liquid interface resulting in a passive motion of particles within this flow. Utilizing the same LDDO mechanism one can also induce active motion of porous particles. Here the radially directed flow is generated by and around a

single porous colloid when it is irradiated with either UV or blue light. This results in either mutual long-range diffusioosmotic repulsion of the particles or in even self-propelled motion when the colloids are turned into a Janus-like shape. Here, we discuss how to extend of passive and active motion of colloidal particles depends on the irradiation conditions such as wavelengths and intensities of light.

1.*Feldmann, D.; Maduar S.R.; Santer, M.; Lomadze, N.; Vinogradova, O.I.; Santer, S., Scientific Reports 6 (2016) 36443

50 min. meet the speakers - break