

CPP 2: Nanoparticles and Composite Materials

Time: Monday 9:30–13:15

Location: C 243

CPP 2.1 Mon 9:30 C 243

Fabrication of metamaterials by colloidal mask templating and glancing angle deposition: An in situ grazing incidence X-ray scattering study — ●JAN PERLICH¹, ADELINE BUFFET¹, MATTHIAS SCHWARTZKOPF¹, MOTTAKIN M. ABUL KASHEM¹, GERD HERZOG¹, KAI SCHLAGE¹, EZZELDIN METWALLI², VOLKER KÖRSTGENS², RALF RÖHLSBERGER¹, PETER MÜLLER-BUSCHBAUM², STEPHAN V. ROTH¹, and RAINER GEHRKE¹ — ¹HASYLAB-DESY, Hamburg (Germany) — ²TU München, Physik Department, LS Funkt. Mat., Garching (Germany)

Metamaterials are artificially structured materials which attain their properties from the unit structure rather than the constituent materials using small inhomogeneities. Metamaterials have become a new subdiscipline in physics and their widespread areas of application include optics and optoelectronics, electromagnetics, microwave and antenna engineering, semiconductors, etc. We present the fabrication of such a metamaterial by sputter deposition of gold on colloidal polystyrene nanoparticles acting as shadowing mask. The gold is deposited under a glancing angle (GLAD) resulting in asymmetrically shaped gold-capped polystyrene nanospheres. The sputtering process is monitored in situ real-time by grazing incidence small angle X-ray scattering (GISAXS) performed at the synchrotron beamline P03 of PETRA III enabling millisecond time resolution. The characterization is complemented by scanning electron microscopy, yielding high-resolution images of the final morphology, and ellipsometry to determine the optical properties of the nanostructured material.

CPP 2.2 Mon 9:45 C 243

Molecular dynamics study of tracer diffusion in hairy nano-channel: normal vs anomalous — ●RAJARSHI CHAKRABARTI, STEFAN KESSELHEIM, PETER KOŠOVAN, and CHRISTIAN HOLM — Institute for Computational Physics, Universität Stuttgart, Pfaffenwaldring 27, 70569, Stuttgart, Germany

We carry out extensive molecular dynamics simulation to analyze the diffusion of tracer particles inside a cylindrical nano-channel randomly grafted inside with polymeric chains. We show that depending on the attraction between the tracer and the polymer an intermediate subdiffusive behavior along the cylindrical axis can be observed but the long time diffusion is always normal. We also analyze the dependence of diffusion coefficient on the volume fraction of the grafted polymeric chains. Although simple the model presented here has the features of nuclear pore complex in the context of biological transport.

CPP 2.3 Mon 10:00 C 243

Diblock Copolymer - Selective Nanoparticle Mixture in Lamellar Phase Confined between two Parallel Walls : A Mean Field Model — ●LENIN SINGH SHAGOLSEM^{1,2} and JENS-UWE SOMMER^{1,2} — ¹Leibniz Institute of Polymer Research Dresden, Dresden, Germany — ²Institute of Theoretical Physics, TU Dresden, Dresden, Germany

We present a mean field model for a mixture of AB diblock-copolymers and A-block selective nanoparticles confined between two identical non-selective walls. A horizontally symmetric lamellar structure of the nanocomposite is considered. For a given nanoparticle volume fraction, ϕ , and wall separation, L , we study the change in the free energy as a function of the number of lamellar layers, p , and the nanoparticle uptake of the polymer film, $y = \phi x$, where $0 \leq x \leq 1$. We observe that there exists a particular p which is commensurate with the given film thickness. At small values of y , the equilibrium-uptake is mainly controlled by the balance of stretching, and the interaction between monomers and nanoparticles. We find that the equilibrium value of y is independent of ϕ and increase sub-linearly with monomer-nanoparticle interaction strength. In addition, we also consider A-block selective walls. Here, we investigate the non-wetting/wetting transition and constructed a corresponding phase diagram.

CPP 2.4 Mon 10:15 C 243

Assembly of nanoparticles on diblock copolymer brushes: toward laterally nanostructured composites — ●OLGA GUSKOVA¹ and CHRISTIAN SEIDEL² — ¹Leibniz Institute of Polymer Research, Dresden, Germany — ²Max Planck Institute of Colloids and Interfaces, Potsdam, Germany

We study the self-assembly of polymer-insoluble nanoparticles (NPs) at the surface of microphase-separated AB diblock copolymer brushes in a selective solvent by means of dissipative particle dynamics (DPD) simulations. The structure of such nanocomposites depends both on the morphology of the underlying brush which is basically determined by chain composition f and solvent selectivity $t(B)$, and on specific parameters of the NPs added such as polymer compatibility $a(BP)$, solvophobicity $a(PS)$, and concentration c , where $a(ij)$ are the DPD interaction parameters. The immense parameter space is explored within a coarse grained model that contains polymer A and B beads, solvent (S), nanoparticle (P), and wall (W) beads. For composites with B-like nanoparticles, i.e., NPs that are covered by polymer B ligands, we construct the phase diagram in the f - c space. For B-unlike NPs, it is found that the solvophobicity of the particles set by $a(PS)$ is crucial for the spreading of the nanodroplets. We show that in principle microphase separated diblock copolymer brushes can be used to create ordered nanodots as well as nanowires and deduce some rules which should facilitate the design of such novel polymer nanocomposites.

CPP 2.5 Mon 10:30 C 243

Assembly of nanoparticles on hard surfaces and surface-grafted polyelectrolyte brushes — ●ZÜLEYHA YENICE and REGINE VON KLITZING — Technische Universität Berlin, Stranski-Laboratorium, Department of Chemistry, Strasse des 17. Juni 124 D-10623 Berlin, Germany

Self-assembly of nanoparticles using modified surfaces like polymer brushes, surface grafted molecular and macromolecular gradients attract great interest in recent years [1,2].

Here, we present our studies on self-assembly of nanoparticles on bare silicon wafer and wafers modified by PDMAEMA brushes. PDMAEMA is a weak polyelectrolyte with pH dependent properties which gives us space to do further modifications on this brushes. We also present our effort to get a better understanding of the particle interpenetration into the polyelectrolyte brushes by investigating the effect of different brush lengths and different sizes of nanoparticles using x-ray reflectivity, ellipsometry and atomic force microscopy.

[1] J. Genzer and R. R. Bhat, *Langmuir*, Vol. 24, No. 6, 2008

[2] R. R. Bhat et al. *Nanotechnology*, 14 (2003) 1145-1152

CPP 2.6 Mon 10:45 C 243

Block Copolymer - Nanoparticle Composites in Electric Fields — ●CLEMENS LIEDEL, KERSTIN SCHINDLER, CHRISTIAN WILHELM PESTER, and ALEXANDER BÖKER — Lehrstuhl für Makromolekulare Materialien und Oberflächen, DWI an der RWTH Aachen e.V., RWTH Aachen University, D-52056 Aachen, Germany

The creation of thin and densely-packed metallic wires is of key importance for creating new devices for electronic applications. Because of its size, block copolymers and metal nanoparticles are promising materials for this purpose. By creating composite materials from both, it is possible to combine the possibility of orienting block copolymer structures in electric fields with the conductivity of metal nanoparticles. Hence, ordered metallic structures are accessible.

We present a deeper understanding of nanoparticle - block copolymer composites in electric fields. Therefore, we show the influence of nanoparticles on the field strength that is necessary for aligning the morphologies. In addition, we describe the impact on the kinetics of orientation and the resulting order parameter.

Understanding composites from block copolymers and nanoparticles in electric fields may help to build new devices in the field of optical gratings, data storage or organic-inorganic solar cells.

CPP 2.7 Mon 11:00 C 243

Reactive epoxies with functional zeolite fillers: IR spectroscopy and PALS studies — ●KLAUS RÄTZKE¹, QASIM SHAIKH¹, JAN GAUKLER², WULFF POSSART², and FRANZ FAUPEL¹ — ¹Materials Science Univ. Kiel, Germany — ²Adhesion and Interphases, Materials Science, Saarbrücken, Germany

Epoxy-dicyandiamide (Dicy) formulations frequently contain a free accelerator for reducing the curing temperature and the time for network formation. However, an accelerator reduces the shelf life of these adhesives. This study compared the reaction kinetics during the storage at 60 °C for a pre-cured epoxy adhesive (EP = diglycidyl ether of

bisphenol A and Dicy, mass ratio 100 : 6.7, pre-cured at 150 °C for 1 h) mixed either with free accelerator or with the same concentration of accelerator immobilised in micro or nano-zeolite fillers [1]. During storage, the IR study probed the chemical modifications. They lead to increasing crosslinking density and a loss of free volume as detected by positron annihilation lifetime spectroscopy (PALS) [2]. Crosslinking proceeds to the chemical vitrification. Additionally, the glass transition and the free volume parameters were investigated for the three systems as a function of temperature by PALS after thermal curing.

[1] K. Rätzke, M. Q. Shaikh, F. Faupel, P. L. M. Noeske *International Journal of Adhesion & Adhesives*, 30 (2010) 105

[2] M. Q. Shaikh, K. Rätzke, J. Ch. Gaukler, W. Possart, F. Faupel, J. Mater. Res., 26, (2011) 2877

15 min break

Topical Talk

CPP 2.8 Mon 11:30 C 243

Gold nanoparticle assisted thermophoretic trapping of single nano-objects — MARCO BRAUN, ROMY SCHACHOFF, and FRANK CICHOS — Molecular Nanophotonics Group, University of Leipzig, Linéstraße 5, D - 04103 Leipzig

Optical tweezing is the most common technique for the trapping of individual particles in solution. It is based on the gradient force of focused electromagnetic radiation. Hence, a sufficient high polarizability contrast between the particle and the solution is required. While it is thus easy to trap single dielectric particles larger than 100 μm , a trapping of smaller objects such as single molecules by means of an optical tweezer is hardly possible. Molecular trapping can be achieved by a technique called Anti-Brownian Elektrokinetic trap (ABEL trap), which exploits the time-dependent electric field of four electrodes. Here, we present a new technique which replaces the electric field by local thermal fields generated by single Au nanoparticles. The so-called Thermophoretic trap exploits thermophoretic forces that act on a particle placed in a temperature gradient, which e.g. locally distorts the screening of the surface charges. Such forces are sufficient for the manipulation of small nanoparticles or proteins. In our approach, the thermal gradient around optically heated Au nanoparticles immobilized in an appropriate arrangement shall be used to trap single nanoobjects. The plasmonic heating of the separate Au nanoparticles hereby is achieved by a focused laser beam that is controlled by a suitable feedback loop. Numerical simulations as well as first experimental results will be presented.

CPP 2.9 Mon 12:00 C 243

Determination of the three-dimensional orientation of gold nanorods by in-situ measuring their elastic scattering and luminescence signal — FRANK WACKENHUT¹, ANTONIO VIRGILIO FAILLA², TINA ZÜCHNER¹, and ALFRED J. MEIXNER¹ — ¹Eberhard Karls University, Institute of Physical and Theoretical Chemistry, Tübingen, Germany — ²University Medical Center Hamburg-Eppendorf, Hamburg, Germany

We will demonstrate that it is possible to determine the three-dimensional orientation of a single gold nanorod (GNR) by simultaneously measuring the elastic scattering and luminescence pattern. For excitation we used radially and azimuthally polarized doughnut shaped modes (RPDM/APDM). In this work we will extend the results shown in [1] to a not index matched sample geometry. We will demonstrate that the combined acquisition of four patterns (luminescence and scattering patterns excited either by a RPDM or an APDM) allows us to determine the three-dimensional orientation of individual GNRs with high precision covering the full angular spectrum. In general the luminescence pattern is mainly used to determine the GNR orientation, while the acquisition of the scattering pattern in reflection mode permits us to gain additional information about the nano environment surrounding the GNR. This extends the results shown by Züchner et al. [2] to a 3D experimental system.

[1] F. Wackenhut, A.V. Failla, T. Züchner, A. J. Meixner, (2011). *Proc. SPIE* 8096 (1), 80962V. [2] T. Züchner, A. V. Failla, M. Steiner, A. J. Meixner, (2008). *Opt. Express*, 16; 14635-14644.

CPP 2.10 Mon 12:15 C 243

Cross-over in the power law statistics of the fluorescence of CdSe/CdS/ZnS nanocrystals — GERALD HINZE and THOMAS BASCHÉ — Institut für Physikalische Chemie, Johannes Gutenberg-Universität, 55099 Mainz

Semiconducting quantum dots (QD) are often characterized by bright

luminescence and high photo stability compared to usual aromatic molecular dyes. On a single particle level, however, their fluorescence typically shows intermittencies. That is, under continuous light illumination stochastic jumps between light (on) and dark states (off) occur. At the same time the fluorescence decay from single QDs often cannot be described by a single exponential. Recently, there have been attempts to explain both observations within a single model implementing an additional dark state. We have studied CdSe/CdS/ZnS colloidal quantum dot emission over 9 decades in time. By combining different experimental setups we were able to follow the temporal evolution of the fluorescence intensity of a bulk sample from ns to seconds. We observe three inverse power-laws differing in the exponent with cross over times at $\sim 100\mu\text{s}$ and $\sim 5\text{ms}$. From single molecule intensity time traces we calculated the off-time statistics related to the intermittency of the fluorescence. Within the accessible range of the off-time statistics, which was obtained for 3 decades of time, it nicely matches the time-dependent fluorescence intensity. Our results support the recent proposed model of diffusion-controlled electron transfer being the origin for the observed power law statistics.

CPP 2.11 Mon 12:30 C 243

Synthesis and characterization of selective sensor nanoparticles for magnetic resonance imaging — DANIEL NORDMEYER¹, PATRICK STUMPF¹, DOMINIC GRÖGER², FLORIAN PAULUS², RAINER HAAG², ANNETTA SEMISCH³, CONSTANZE RICHTER³, ANDREA HARTWIG³, JENS DERNEDDE⁴, RONNY MALZ⁵, URSULA RAUCH-KRÖHNERT⁵, JÖRG SCHNORR⁶, INES GEMEINHARDT⁶, MATTHIAS TAUPITZ⁶, CHRISTINA GRAF¹, and ECKART RÜHL¹ — ¹Physikalische Chemie, FU Berlin — ²Organische Chemie, FU Berlin — ³Institut für Angewandte Biowissenschaften, Karlsruhe Institut für Technologie — ⁴Institut für Laboratoriumsmedizin, Klinische Chemie und Pathobiologie, Charité — ⁵Centrum für Herz-, Kreislauf- und Gefäßmedizin, Charité — ⁶Institut für Radiologie, Charité

The aim of the present study is the synthesis of iron oxide nanoparticles (FeOx-NP) functionalized by hyperbranched sulfated polyglycerols (hPGS, a heparin analogue) on their surfaces. This leads to anti-inflammatory and antimetastatic effects in organism. Stability measurements with hPGS coordinated FeOx-NP are performed in different biological media. Human colon cancer cells are incubated with these hydrophilic nanoparticles, indicating that the viability of the cells is increased. Surface plasmon resonance (SPR) studies indicate that the hPGS coordinated FeOx-NP lead to an inhibition of L-selectin binding. Finally, the binding of hPGS functionalized FeOx-NP to myocarditis infected tissue is tested, using a mice-model. These results indicate that hPGS coordinated FeOx-NP may be suitable for being used as a contrast agent in magnetic resonance imaging.

CPP 2.12 Mon 12:45 C 243

Analysis of multivalent effects using single molecule force spectroscopy (SMFS) on pyridine coordination compounds — MANUEL GENSER¹, CHRISTIAN EIDAMSHAUS², ARTUR GALSTYAN², ERNST-WALTER KNAPP², HANS-ULRICH REISSIG², and JÜRGEN P. RABE¹ — ¹Institut für Physik, Humboldt-Universität zu Berlin — ²Institut für Chemie und Biochemie, Freie Universität Berlin

Multivalency is an important effect in biological processes and supramolecular assemblies. Multiple noncovalent interactions of two partners may occur with an affinity greater than the sum of the corresponding monovalent interactions. The mechanical stability of multivalent interactions is important for the understanding of numerous biological processes. However due to their complexity, the binding enhancement in such systems is not yet fully understood. [1]

We developed a simple model system using coordinative bonds between pyridine nanorods. SFM based single molecule force spectroscopy (SMFS) [2] in aqueous solutions of CuSO₄, combined with DFT calculations of bond dissociation under force, revealed details of the bond opening that are usually not accessible by ensemble methods. The bivalent system rather opens successively than simultaneously, which leads to lower rupture forces than for the monovalent system, over a broad range of loading rates. Our model system can be varied to study structural effects influencing the mechanical stability of multivalent interactions.

[1] J.D. Badjic et al. *Acc. Chem. Res.* 2005, 38, 723-732. [2] M.I. Gianotti and G.J. Vancso *ChemPhysChem* 2007, 8, 2290-2307.

CPP 2.13 Mon 13:00 C 243

Mechanical Stability Behavior of Fullerenes — MARKUS A. HARTMANN¹, MELANIE TODT², DAVID HOLEC³, PAUL H.

MAYRHOFER³, OSKAR PARIS¹, FRANZ D. FISCHER⁴, and FRANZ G. RAMMERSTORFER² — ¹Institute of Physics, Montanuniversitaet Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria — ²ILSB, Vienna University of Technology, Gusshausstrasse 27-29, 1040 Vienna, Austria — ³Department of Physical Metallurgy and Materials Testing, Montanuniversitaet Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria — ⁴Institute of Mechanics, Montanuniversitaet Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria

Carbon nanostructures are a fascinating class of materials combining high stiffness with low weight and exceptional toughness. Understanding the mechanical performance and stability of larger, hierarchical

structures like carbon onions and fibers demands to understand the fullerene behavior also on microscopic length scales making a multi-scale/multi-method approach inevitable. We used ab initio calculations to extract classical potentials that were used in subsequent Monte Carlo simulations and Finite Element studies on larger structures. The simulations were used to perform (computational) mechanical tests on single fullerenes of different sizes to characterize their mechanical behavior. Special attention was paid to the influence of pentagons inherent in any fullerene structure on the stability behavior. The simulation results were compared to the predictions of Finite Element methods to evaluate macroscopic parameters like elastic modulus or Poisson ratio of the investigated structures.