

CPP 12 POSTER Colloids, Nanoparticles and Self-Organizing Systems

Time: Tuesday 17:00–19:00

Room: P3

CPP 12.1 Tue 17:00 P3

Water density reduction at hydrophobic interfaces: a neutron reflectometry study — ●MARCO MACCARINI¹, MICHAEL HIMMELHAUS¹, ROLAND STEITZ², MAXIMILIAN WOLFF³, and MICHAEL GRUNZE¹ — ¹Institut für Angewandte Physikalische Chemie, Universität Heidelberg, Germany — ²Hahn-Meitner-Institut, Berlin, Germany — ³Institut Laue-Langevin, Grenoble, France

A close relationship exists between the structure of a liquid in the vicinity of a surface and the solvation force appearing between two surfaces immersed in the liquid. This relationship has important implications in the case of hydrophobic surfaces and water since the resulting force, the hydrophobic interaction, is responsible for key biological phenomena such as protein folding, self-assembling, colloids stability and membrane fusion. The origin of this interaction has still a number of unexplained features because the structure and the conformation of water molecules in the vicinity of hydrophobic surfaces are not fully understood. Theoretical studies (Lum 1999, Mamatkulov 2004) predicted a depletion layer, i.e. a reduced water density, near the hydrophobic surface/water interface. This extends to a thickness in the order of nm into the bulk water and is thermodynamically less stable than the vapor phase. In order to clarify the extension of the depletion layer and its dependence on some parameters like temperature, pH and electrolyte concentration, we performed neutron reflectometry on hydrophobic surfaces formed by the adsorption of alkanethiols self assembling monolayers (SAM) on gold surfaces in contact with water and non polar solvents.

CPP 12.2 Tue 17:00 P3

Interaction of a spherical particle with linear chains — ●JAROSLAW KLOS — Faculty of Physics, A. Mickiewicz Univ., Umultowska 85, 61-614 Poznan, Poland

Linear polymers surrounding a hard sphere are simulated using the Cooperative Motion Algorithm on the face centered cubic lattice. The excluded volume condition is taken into account, and the properties of the chains are examined in two situations of: (i) free polymers, (ii) chains end-grafted onto the spherical surface ("hairy spheres"). In case (i) the size ratio $q=R/R_g$ of the sphere radius to the mean radius of gyration of the chains is considered the main parameter. The simulations indicate (1) a depletion layer in the neighborhood of the sphere, (2) an enhancement of the chain ends concentration at the particle surface, (3) an enhancement of the chain centers of mass concentration at some distance from the surface for large q , (4) a penetration of the centers of mass into the sphere for small q , (5) an orientation ordering of the chains in the region of interest. In case (ii) the simulations are performed in two extremes of the surrounding matrix: (a) the hairy spheres immersed in a pure solvent of single beads and (b) the hairy spheres in a melt of chains. The simulations indicate that (1) the concentration profiles of the end-grafted chains under good solvent conditions are noticeably different from those calculated for the chains in a melt, (2) as the sphere radius increases, the monomer concentration profile changes from concave to convex (3) both the free ends and the centers of mass profiles are Gaussian-like, (4) depending on the position of the center of mass, both tangential and radial ordering of the polymers relative to the sphere are present.

CPP 12.3 Tue 17:00 P3

Surface Properties of Carbon Black Modified by Atmospheric Plasma — ●GERALD J. SCHNEIDER¹, JOHANN VANCEA¹, ROBERT C. WEISS¹, ANDREAS WEIGERT¹, NURIA TRICÁS², and DIETMAR GÖRITZ¹ — ¹Institut für Physik, Universität Regensburg, 93040 Regensburg — ²Institut Quimic de Sarrià, Universitat de Barcelona, España

To study the interaction between polymer and carbon black the filler surface chemistry was modified by means of atmospheric plasma. The treated carbon black was characterized by small angle x-ray scattering. The scattered intensity was analyzed with regard to the fractal dimensions of surface and mass. X-ray photoelectron spectroscopy was used to analyze changes of the surface chemistry and scanning tunneling microscopy to detect changes of active sites on the surface.

CPP 12.4 Tue 17:00 P3

A fundamental measure free-energy functional for nonspherical particles — ●HENDRIK HANSEN-GOOS^{1,2} and KLAUS MECKE³ — ¹Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, 70569 Stuttgart — ²ITAP, Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart — ³Institut für Theoretische Physik, Universität Erlangen-Nürnberg, Staudtstr. 7, 91058 Erlangen

In 1989, Y. Rosenfeld established his fundamental measure theory (FMT) free-energy functional for the hard-sphere fluid. The starting point for his derivation is an exact decomposition of the Mayer- f -bond in terms of convolutions of scalar and vectorial weight functions leading him to an excess free-energy function of scalar and vectorial weighted densities. Rosenfeld's free-energy has proved to describe very accurately inhomogeneous hard-sphere fluids and it is conveniently tractable computationally as only one-center convolutions are involved. Later on, a generalisation of his original FMT to nonspherical particles was given by Rosenfeld himself. Unfortunately, the theory does not show an isotropic-nematic transition as observed, e.g., for hard spherocylinders or ellipsoids. Other free-energy functionals that do predict an isotropic-nematic transition generally involve two-center convolutions and therefore demand more computational efforts. Starting from the exact expression for the Mayer- f -bond for convex particles we introduce an approximate decomposition leading us to a new free-energy functional for non-spherical particles. The functional is still based on one-center convolutions and can be shown to yield an isotropic-nematic transition for spherocylinders. Strategies to enhance the agreement with simulation data are presented.

CPP 12.5 Tue 17:00 P3

Vibrational properties of ZnO and Zn_{1-x}Mn_xO nanoparticles and ligand-nanoparticle interactions studied by Raman spectroscopy — ●M. SCHUMM¹, M. LENTZE¹, C. BARGLIK-CHORY², and J. GEURTS¹ — ¹Physikalisches Institut der Universität Würzburg, Am Hubland, 97074 Würzburg — ²Lehrstuhl für Silicatchemie, Universität Würzburg, Röntgenring 11, 97070 Würzburg

Nanostructured systems of the large bandgap semiconductor ZnO have attracted a great deal of attention in the recent past due to its special optical properties and various potential applications. Theoretical predictions of ferromagnetic behaviour at room temperature focused the interest among the group of diluted magnetic semiconductors on (Zn,Mn)O nanostructures.

We report on a study of wet chemically synthesised ZnO and (Zn,Mn)O nanoparticles (diameters 3-12 nm) by VIS micro- and Fourier Transform NIR Raman spectroscopy. Special attention was paid to properties of the binding between the ligands and the nanoparticle surface and to interactions between molecular vibrations of the ligands and the phonons of the nanocrystallites. Besides the verification of ligand binding to the particles' surface, ligand-induced strengthening of nanoparticle phonon modes and the formation of coupled modes between nanoparticle phonons and ligand vibrations were observed. Furthermore, the Raman spectra show confinement induced phonon peak shifting and broadening compared to the corresponding bulk material. Finally, for the Zn_{1-x}Mn_xO nanoparticles the successful substitutional incorporation of Mn in the Zn sublattice was proven by its specific vibration modes in the Raman spectrum.

CPP 12.6 Tue 17:00 P3

Monitoring enzymatic degradation of polymeric nanoparticles with scattering methods — ●THOMAS SIEGEMUND^{1,2}, BERND-REINER PAULKE³, HERBERT SCHMIEDEL¹, NATALIE BORDAG², STEFFEN LINDERT¹, and WOLFGANG HÄRTIG² — ¹Universität Leipzig, Institut für Experimentalphysik I, Physik der weichen Materie, Linnéstraße 5, 04103 Leipzig — ²Universität Leipzig, Paul-Flechsig-Institut für Hirnforschung, Jahnallee 59, 04109 Leipzig — ³Fraunhofer Institut für angewandte Polymerforschung, Geiselbergstraße 69, 14476 Potsdam

Nanoparticles can be used as carriers for the delivery of drugs. We prepared nanoparticles as carriers for the model drug thioflavin T that binds Alzheimer's disease related fibrillar amyloid β -peptides in the brain. These polymer colloids are composed of a polystyrene core and a degradable poly(butyl-2-cyanoacrylate) shell with diameters from 60 to 170 nm. The enzymatic degradation of core-shell nanoparticles, as required

in vivo, was observed after their treatment with porcine liver esterase, a non-specific esterase, and basic/acidic hydrolysis in vitro. Shells of nanoparticles were dose-dependently degraded while their polystyrene cores remained intact. We applied light scattering and neutron scattering as useful tools to monitor the particle diameters and to evaluate details of the degradation process, especially the degradation-dependent changes in the neutron scattering-length density profile. The degradation speed was studied at different temperatures as function of nanoparticle, enzyme and salt concentration at fixed pH. Deviations from Michaelis-Menten behavior are discussed within a simple model.

CPP 12.7 Tue 17:00 P3

Novel Metal Cages from Bionanoparticle Templates — ●GÜNTHER JUTZ, ANNE HORN, NATHALIE MOUGIN, and ALEXANDER BÖKER — Lehrstuhl für Physikalische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany

In the presented project we make use of the well-defined composition and structure of the cowpea mosaic virus (CPMV). We use this plant virus as a template for the production of monodisperse, well defined nanoparticles and nanocapsules. We followed this aim with different approaches. After the incubation of the aqueous virus solution with a metal salt under reductive conditions either a homogenous coating or the deposition of distinct nanoparticles onto the capsid has been observed by TEM, SEM and AFM. Another approach uses the well defined surface chemistry of the virus for the site specific decoration of the capsid with nanoparticles. To achieve this, preformed, monofunctionalized nanoparticles can be covalently bound to the capsid. To broaden the range of nanoparticles that can be attached to the virus, it was modified with different chelating ligands that promote binding of metal cations and serve as heterogeneous nucleation sites for the site specific in-situ growth of nanoparticles. Characterization of the ligand modified virus and the composite particles has been performed using FPLC, SPR, TEM, SEM and AFM.

CPP 12.8 Tue 17:00 P3

Modeling of anisotropic silica clusters — ●GERALD J. SCHNEIDER and DIETMAR GÖRITZ — Institut für Physik, Universität Regensburg, 93040 Regensburg

The mechanical properties of elastomers can be improved by adding precipitated silica. The hierarchical structure of this colloidal filler consists of primary particles, having typical diameters of about 20 nm. During an agglomeration process clusters are formed, which are build up from these primary particles. Regarding the mechanical properties of elastomers, structural changes of silica clusters due to external forces are of interest. These rearrangement during deformation can be studied by means of small-angle scattering experiments. To describe quantitatively the experimental results we introduce a new model, based only on the mathematics of fractals, which is able to predict experimental scattering patterns. With the help of experimental data the usability of the theory will be demonstrated.

CPP 12.9 Tue 17:00 P3

The scattering from thin, lamellar diblock copolymer films in the distorted-wave Born approximation — ●CHRISTINE M. PAPANAKIS¹, P. BUSCH², M. RAUSCHER³, D.-M. SMILGIES², and D. POSSELT⁴ — ¹Physikdepartment E13, TU München, James-Frank-Str. 1, D-85747 Garching — ²Cornell University, Ithaca NY, USA — ³MPI für Metallforschung und Universität Stuttgart — ⁴Roskilde University, Denmark

Grazing-incidence small-angle X-ray scattering (GISAXS) of thin films of diblock copolymers reveals information about the ordering and preferential orientations of the phase-separated microdomains within the films. The grazing-incidence geometry enhances the surface sensitivity; however, the scattering cannot be described any more with a simple kinematic theory, as in transmission small-angle scattering.

We have calculated the scattering cross-section in the framework of the distorted-wave Born approximation, a dynamical scattering theory. We treat the case of thin films of lamellar diblock copolymers, where the orientation of the lamellae is either perpendicular or parallel to the film interfaces and compare the predictions to experimental results from thin films of poly(styrene-*b*-butadiene) diblock copolymers. For perpendicular lamellae, Bragg rods are found, which are extended along the film normal, whereas for parallel lamellae, intensity maxima appear along the film normal. The positions of these maxima can be explained by accounting for refraction at the film surface and reflection at the film-substrate interface.

CPP 12.10 Tue 17:00 P3

pH-Responsive mixed Blockcopolymer/Surfactant Aggregates — ●THOMAS HELLWEG¹, GUILLERMO ORTOS GIL¹, and HELMUT SCHLAAD² — ¹TU Berlin, Stranski-Lab. (ER1), Strasse des 17. Juni 112, 10623 — ²MPI-KGF, 14424 Potsdam

Amphiphilic block copolymers can self-assemble into various ordered mesophases. The symmetry and stability of the microstructure depends intimately on chain size and chemistry as well as physical variables such as temperature. The present work is related to the study of three Poly(styrene)-Poly(L-lysine) diblock copolymers in aqueous surfactant and organic solvents, by Dynamic Light Scattering and Atomic Force Microscopy. The study is focussing on the following points: the characterization of the structures in solution, their stabilization using surfactants, the random coil- α -Helix transition in the polypeptide block and the influence of added substances on the system. The results show: the affinity of each polymer to the solvent depends strongly on the block length ratio. The pH induced transition from the random coil to α -helix seems to be between 10-11 and induces a significant decrease in the translational diffusion coefficient. The addition of water or benzoic acid to the organic solutions induces structural changes.

CPP 12.11 Tue 17:00 P3

Control of forces in aqueous wetting nanofilms — ●KATARZYNA CIUNEL¹ and REGINE V. KLITZING² — ¹Stranski-Laboratorium, TU Berlin, Str. d, 17. Juni 112, D-10623 Berlin — ²Institut für Physikalische Chemie, CAU Kiel, Ludewig-Meyn-Strasse 8, D-24118 Kiel

The (de)stability and functionality of thin liquid films plays an important role for processes in technical applications, like foaming, emulsification and flotation. The forces between the opposing interfaces depend on the composition of the film interfaces and of the film fluid. In the present paper the sum of interactions between the film surfaces is determined quantitatively by the disjoining pressure isotherm (disjoining pressure vs. film thickness) and it is measured by varying the outer pressure in a so-called thin film pressure balance. The approach of a solid substrate to one film interface (wetting film: air/water/solid) changes the drainage behaviour with respect to a free-standing film (foam film). In order to modify the interactions between the fluid and the interface in a wetting film the solid surface is pre-coated with polyelectrolytes of different charge and viscoelasticity. The air/water interface is varied by the adsorption of different amphiphiles. The results give a clear evidence for negative charges at the free air/water interface.

CPP 12.12 Tue 17:00 P3

Is the radial breathing mode really radial? — ●M. MOHR, M. MACHÓN, and C. THOMSEN — Institut für Festkörperphysik, TU Berlin, Hardenbergstr. 36, 10623 Berlin

The diameter-dependent radial breathing mode (RBM) plays a key role in the characterization of single-walled nanotubes. This mode is often assumed to be purely radial. *Ab initio* calculations of the phonons have shown the existence of a non-radial component which is small but has important effects, e.g. in the electron-phonon coupling.¹ A simple geometrical model based on symmetry considerations shows similar results.² We demonstrate with an independent variational approach that the RBM is not radial and study the dependence of the non-radial component on diameter and chirality.

[1] M. Machón *et al.* Phys. Rev. B **16** 035416 (2005)

[2] M. Damnjanović *et al.*, J. Phys.: Condens. Matter **16** (2004) L505

CPP 12.13 Tue 17:00 P3

Electric fields effects in thin films of symmetric diblock copolymers — ●XIULI JIANG¹, THOMAS GUTBERLET², MUKUL GUPTA², THOMAS GEUE², and THOMAS THURN-ALBRECHT¹ — ¹Department of Physics, Martin-Luther-University, Halle, Germany — ²Laboratory for Neutron Scattering, ETH Zürich & PSI, Villigen, Switzerland

Due to their potential use as nanostructure templates, it is of significant interest to control the orientation and order of the microstructure of block copolymers by means of external fields. Using neutron reflectivity, diffuse scattering and small angle scattering we analysed the microstructure of a lamellar diblock copolymer under competing influences of interfacial interactions and an electric field standing perpendicular to the surface of the film. While the electric field tends to align the lamellar normal to the substrate, interfacial interactions favour an alignment parallel to the film. In this situation a field, too weak to overcome the interfacial interactions which is typically limited to a range of about lamellar periods, leads to a reduction of the defects at the boundaries between domains

of different orientations, and in consequence to a complete alignment of the microphase structure parallel to the substrate. Otherwise, due to the confinement the torque exerted by the electric field leads only to a small increase of the mosaicity of the sample, which is reflected by a considerable increase in the diffuse scattering signal. Finally a field of several ten kV/mm is necessary to align the central part of the film with boundary layers parallel to the interfaces remaining even at these high fields.

CPP 12.14 Tue 17:00 P3

Electric Field induced Effects on the Microdomains in Concentrated Block Copolymer Solutions — ●KRISTIN SCHMIDT¹, HEIKO SCHOBERTH¹, THOMAS M. WEISS², VOLKER URBAN³, PETER LINDNER⁴, ALEXANDER BÖKER¹, and GEORG KRAUSCH¹ — ¹Lehrstuhl für Physikalische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany — ²European Synchrotron Radiation Facility (ESRF), F-38043 Grenoble, France — ³Oak Ridge National Laboratory (ORNL), Oak Ridge, TN-37831, USA — ⁴Institut Laue Langevin (ILL), F-38043 Grenoble, France

We investigate the microscopic mechanism of reorientation of concentrated block copolymer solutions exposed to an electric field by time-resolved synchrotron small-angle X-ray scattering (SAXS). As a model system, we use a lamellar polystyrene-*b*-polyisoprene block copolymer dissolved in toluene. The underlying mechanism at the level of individual macromolecules is studied by small-angle neutron scattering (SANS). Depending on the electric field strength we observe a decrease of the lamellar distance of lamellae orientated parallel to the E-field. Through the parallel orientation of the lamellar plane, the polymer backbones orient perpendicular to the E-field lines. We therefore expect that the diblock chains exhibit a certain degree of stretching. Hence, we study the single-chain form factor of the copolymer exposed to an electric field.

In addition, we observe an influence of the electric field on the order disorder temperature and phase separation in our block copolymer solutions. We found a significant shift in T_{ODT} at moderate field strengths. For further investigations we study this effect by birefringence.

CPP 12.15 Tue 17:00 P3

Analysis of Self Assembled Monolayers (SAMs) on metallic substrates by — ●P. ANGELOVA¹, M. GENSCHE², K. HINRICHS², K. KOSTOVA¹, and D. TSANKOV¹ — ¹Institute of Organic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str. Bl. 9, 1113 Sofia, Bulgaria — ²ISAS-Institute for Analytical Sciences, Department Berlin, Albert Einstein Str. 9, 12489 Berlin, Germany

Long-chain alkanethiols and disulfides tend to adsorb onto metallic surfaces and to form closely packed and well ordered monomolecular films. Besides adsorption, the self-assembly also includes spontaneous self-organization of the molecules constituting the film, mostly by means of van der Waals interactions. Essential role in forming highly ordered films has the type of the molecules which affects the intermolecular distance and the degree of orientation. Newly synthesized para-substituted benzyl esters of 16-mercaptohexadecanoic acid, containing NO₂, CN, OCH₃ and Cl as substituents were prepared as SAMs on different metallic substrates (Au, Ag, Pd) and investigated by IR ellipsometry. The specific stretching vibrations of the indicator groups were used for identifying of the film orientation. Particularly useful were the stretching vibrations of the NO₂ group and the respective optical simulations are presented. As input data for the simulations served vibrational parameter derived from previously investigated Langmuir-Blodgett films. The determination of thickness and dependence of the ellipsometric spectra on the average orientation of the vibrational transition moments of the NO₂ groups in the films with aligned molecules is addressed.

CPP 12.16 Tue 17:00 P3

Essential Parameters of PS-*b*-P4VP Nanotemplates Development for Applications — ●YIMING SUN¹, RADIM KRENEK¹, GANNA GORODYSKA¹, ALEXANDER SIDORENKO², and MANFRED STAMM¹ — ¹Leibniz-Institut für Polymerforschung e.V., Dresden, Germany — ²Bell Labs, Lucent Technologies, Murray Hill, USA

Block copolymer nanotemplates demonstrate a cheap and prospective way for nanodevices requiring regular patterns of closely packed asymmetric nanodomains (nanowires) of various materials on various substrates. Many application based on electrodeposition or PVD of metals and their alloys, electrochemical polymerization and other kinds of loading can be taken into account. Here we deal with essential parameters for the nanotemplate deposition improving ordering and varying periodicity of the nanotemplates. The nanotemplates are based on self-

assembly of poly(styrene-*block*-4-vinylpyridine) (PS-*b*-P4VP) with low molar mass additive 2-(4-hydroxyphenylazo)benzoic acid (HABA). Various morphologies may be formed, depending on ratio of molecular weights of the blocks, with a characteristic scale of nanodomains of about 10 nm. We show that ordering of patterns may be improved by a combination of slow vapour annealing and low roughness of substrates (ITO glass, Si and mica). Variation of periodicity was studied in respect to stoichiometric ratio of HABA in the assembly.

CPP 12.17 Tue 17:00 P3

Controlled Surface Design of Nanoparticles via Switchable Polymer Brushes — ●NIKOLAY HOUBENOV¹, SERGIY MINKO², ALEXANDER SIDORENKO³, PETRA UHLMANN¹, and MANFRED STAMM¹ — ¹Leibniz-Institut fuer Polymerforschung Dresden e.V., Germany — ²Clarkson University Potsdam, New York — ³Bell Labs, Lucent Technologies, Murray Hill, USA

Switchable multicomponent grafted polymer films (polymer brushes) can be successfully used to control the spatial position of nanoparticles of various size and nature. We applied different methods for creating surface patterns, as adsorption via dynamic wetting (by settling the substrates at different angles) of 10-100 nm charged latex particles, or plasma deposition of golden clusters (2-5 nm total film thickness), on stimuli responsive polymer brushes. It was shown, that via controlled surface arrangement, one is able to create long-ranged arrays of nanoparticles, with a characteristic lateral distance, which is a function of the physical-chemical properties of the particles and the polymer brushes. Changing the chain conformation of the grafted PAA-P2VP, PI-P2VP or PS-P2VP brush-like layers by external stimuli, we observed a disarrangement at the particles stripes location from a range of few nanometers to sub-microscopic scale. Such an altering of the quality of the surrounding medium creates a memory effect on the material surface by continuous revealing or concealing (replacing) the particles (clusters).

CPP 12.18 Tue 17:00 P3

Importance of boundary conditions for fluctuation forces between colloids — ●HARTWIG LEHLE^{1,2} and MARTIN OETTEL^{1,2} — ¹Max Planck Institut für Metallforschung, Heisenbergstraße 3, 70569 Stuttgart — ²ITAP, Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart

We consider rotationally symmetric colloids trapped at a fluid interface and subjected to thermal movement. Due to the constraints the colloids impose on the spectrum of the capillary waves the free energy becomes dependent on colloid-colloid separation leading to a thermal Casimir force. The free energy is calculated in a functional integral approach. We present two distinct schemes to calculate the partition function elucidating the importance of the various boundary-type dependent contributions to the Casimir force. The long-range behaviour of the Casimir force can be expressed in terms of multipole interactions of auxiliary "charge fields" on the colloids. The resulting force is shown to be long-range, $F \sim -1/(d \log(d))$ in the case of fixed colloids and a pinned contact line. If the colloid position or the contact line are also fluctuating, additional competing terms induce a cancellation of the leading terms. For a pinned contact line and fluctuating colloid heights the leading contribution to the interaction is of dipole-dipole ($\sim -1/d^4$), for a fluctuating contact line of quadrupole-quadrupole ($\sim -1/d^8$) character.

CPP 12.19 Tue 17:00 P3

Effects of the bead-surface interaction on the restricted rotational dynamics of nonrigid immobilized macromolecules. — ●ALEXANDER UVAROV and STEPHAN FRITZSCHE — Universität Kassel, D-34132 Kassel, Germany

Many problems in biophysics involve the rotational motion of macromolecules which immersed in solution. Well-known examples refer to dielectric relaxation, nuclear magnetic relaxation as well as to the depolarization of the fluorescence light. During the past decade, therefore, a large number of experiments and dynamic simulations (DS) have been carried out in order to describe the rotational properties of biomolecules. Apart from free macromolecules in solution, some experiments also concerned the restricted mobility of macromolecules which are immobilized on a surface and which are interpreted in terms of their molecular subsystems, the so-called *beads* of the macromolecule [1].

In the present contribution, we explore the question of how the bead-bead as well as bead-surface interaction affects the (restricted) rotational diffusion of molecules immobilized at a surface. Making use a recently derived Diffusion equation [1], we performed detailed computations for the

orientational correlation functions and the rotational diffusion coefficient of the macromolecule for several types of the bead-bead and bead-surface interaction potentials. Results from our theory will be compared with other computations including the Brownian DS of the macromolecule [2].

- [1] A. Uvarov and S. Fritzsche, *J. Chem. Phys.* **121**, 6561, (2004)
 [2] B. Carrasco, G. de la Torre, *Biophys. Journal* **75**, 3044, (1999).

CPP 12.20 Tue 17:00 P3

Experimental and theoretical investigation of vibrational modes in ringing gels — ●ERIK JÄRMSTORP, BARBARA DROSSEL, and RUDOLF FEILE — Institut für Festkörperphysik, Technische Universität Darmstadt, Hochschulstr., 64289 Darmstadt

Ringing gels exhibit a strong acoustic emission of sound waves when they are excited by knocking onto the containers they were prepared in. This distinguishes them from other gels, which do not show this ringing sound. To start a detailed investigation of the physical basis of the phenomenon we have investigated the vibrational modes of silica gels which show this ringing behaviour. Experimentally, we have developed a non-contact method using the reflection of a laser beam to study the oscillatory motion of the gel surface within a cylindrical container. This method allows a clear separation of gel modes from other acoustic emissions caused by the specific excitation process (knocking) and the experimental set-up which was not possible in former experiments [1]. We were also able to study the time development of the gelation process. Theoretically, we solved the wave equation of motion for vector displacements of volume elements according to the boundary conditions for the experimental set-up in cylindrical symmetry. The results are compared with a scalar ansatz presented in [1], and are discussed in respect to the experimental results. The results from the gelation experiments are compared with different models for the microscopic processes involved in the gelation.

- [1] C. Sinn, *J. Non-Cryst. Solids* **347**, 11-17 (2004)

CPP 12.21 Tue 17:00 P3

Brillouin and ultrasonic study of the gelation of ringing silica gels — ●BENJAMIN DÖNIGUS, ANDREAS KÖHLER, OLIVER MESETH, and RUDOLF FEILE — Institut für Festkörperphysik, Technische Universität Darmstadt, Hochschulstr. 8, 64289 Darmstadt

Ringing gels are distinguished from other gels by a strong acoustic emission of sound waves excited by knocking onto the containers they were prepared in [1]. Brillouin and ultrasonic experiments were performed on the influence of the microscopic network formation on the elastic properties of the bulk gel during the gelation and further aging process. We find a reduction of the speed of sound when the gelation proceeds. The decrease of the sound velocity is compared with existing theoretical predictions [2,3]. Additionally, both experimental methods indicate a two-step process in the gelation.

- [1] C. Sinn, *J. Non-Cryst. Solids* **347**, 11-17 (2004), and references therein
 [2] M.A. Biot, *J. Acoust. Soc. Am.* **28**, 168 (1956); **28**, 179 (1956); *J. Appl. Phys.* **33**, 1482 (1962)
 [3] D. L. Johnson, *J. Chem. Phys.* **77**, 1531-1539 (1982)

CPP 12.22 Tue 17:00 P3

Structure and dynamics of confined charged colloids — ●MADELEINE KITTNER¹ and PD DR. RER. NAT. SABINE KLAPP^{1,2} — ¹TU Berlin, Theoretische Chemie - Stranski-Lab, Strasse des 17. Juni 135, 10623 Berlin — ²TU Berlin, Theoretische Physik, Hardenbergstr. 36, 10623 Berlin

We investigate the structure and dynamics of charged colloids confined by two plane-parallel repulsive walls (slit pore), using Molecular Dynamics Simulations (MD) in a canonical ensemble. The colloidal system is described by a purely repulsive soft-sphere-Yukawa potential, that involves only the screened spherical macromolecules. The range of repulsion is controlled by the Yukawa parameter κ which, in real systems, is determined by the ionic strength or the charge density.

Our MD results show that an increase of the repulsion range (i.e., decrease of κ) yields an increase of the components of the pressure tensor, particularly in the direction normal to the walls. This is consistent with the behavior of the density profiles, which are highly structured for small κ especially in narrow pores. On the other hand, considering the translational dynamics parallel to the walls, we observe that decrease of the range of repulsion leads to decreasing pore-averaged diffusion constants. We also investigate the inhomogeneity of the dynamics induced by the layer formation.

CPP 12.23 Tue 17:00 P3

Self-Assembly of Inorganic and Biological Nanoparticles at Fluid Interfaces: Kinetics and Structure Formation — ●SERGEJ KOUTOUZOV, GÜNTHER JUTZ, MICHAELA HOFFMANN, and ALEXANDER BÖKER — Lehrstuhl für Physikalische Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany

We report on the self-assembly processes of photoluminescent CdSe nanoparticles and fluorescently labeled CPMV bionanoparticles at oil/water liquid interfaces and their ability to stabilize so-called Pickering emulsions. The adsorption kinetics and particle density at the interface were followed by the changes in interfacial tension during the particle segregation to the interface using a pendant drop tensiometer. In addition, we monitored the increase in luminescence or fluorescence light emission from the interface via 2-dimensional spectroscopy, which allows for a time resolved direct determination of the particle concentration gradient at the interface. Concentration as well as size dependence of the nanoparticle diffusion to the interface was investigated using the above mentioned methods. Finally, the morphology of the resulting aggregates was investigated using TEM.

CPP 12.24 Tue 17:00 P3

Capillary-induced interactions between colloids at an interface — ●MARTIN OETTEL^{1,2}, ALVARO DOMINGUEZ³, and SIEGFRIED DIETRICH^{1,2} — ¹MPI für Metallforschung, Heisenbergstr. 3, 70569 Stuttgart, Germany — ²ITAP, Universität Stuttgart, Pfaffenwaldring 57, 70569 Stuttgart — ³Física Teórica, Universidad de Sevilla, Apartado 1065, 41080 Sevilla, Spain

Within a general framework we study the effective, deformation-induced interaction between two colloids trapped at a fluid interface. For mechanically non-isolated systems, the effective interaction is logarithmic in the separation d , for isolated systems it follows a shorter-ranged power-law. As an application, we consider the interface deformation owing to the electrostatic field of charged colloids. Both the attractive, effective interaction and the direct electrostatic repulsion decay as d^{-3} . An attractive minimum in the total potential at intermediate separations is possible only for large enough colloidal charges.

CPP 12.25 Tue 17:00 P3

Luminescence of $ZnMnP_2O_7$ clusters in powders of KBr — ●OLGA GOMENYUK¹, SERGIY NEDILKO¹, IRYNA NEDEYLKO¹, OLEXANDER SLEPTYSOV¹, VASIL SCHERBATSII¹, NADIJA ANTRAPTSEVA², VOLODYMYR BOJKO², and NADIJA TKACHOVA² — ¹Taras Shevchenko Kyiv National University, Department of Physics, 2, block 1, Acad. Glushkova ave., Kyiv 03680, Ukraine — ²National Agriculture University, Geroiv Oborony st., 8, Kyiv 03041, Ukraine

Diphosphates of divalent metals (zinc, manganese) are the object of interest as multifunctional materials. The contents of cations in solid solutions, their physical, e.g. optical and luminescent properties are determined by the composition of initial reagents. Mentioned compounds were synthesized by precipitation of the suitable cations. Luminescence properties were investigated in the spectral region from 50 to 1100 nm at 4.2, 10, 77 and 300 K temperatures using visible, ultraviolet and vacuum ultraviolet (synchrotron) radiation for excitation of luminescence. Structure and peak positions of the luminescence bands depend on the samples temperature and excitation wavelength. The bands were considered as caused by both inner transitions in manganese ions, recombination of the self trapped excitons and emission of defects. Dependences of the luminescence intensity on the composition of the mentioned phosphates and their content in KBr are analyzed. Experiments with of synchrotron radiation use were done at SUPERLUMI, HASYLAB, Germany.

CPP 12.26 Tue 17:00 P3

The x-ray small angle scattering setup at beamline 9 at the synchrotron source DELTA, University of Dortmund: Measurements on Lysozyme solutions — ●CHRISTOF KRYWKA¹, CHRISTIAN STERNEMANN¹, NADEEM JAVID², ROLAND WINTER², and METIN TOLAN¹ — ¹Institute of Physics / DELTA, University of Dortmund, D-44221 Germany — ²Institute of Chemistry, University of Dortmund, D-44221 Germany

The physical and chemical properties of proteins are influenced by their aqueous microenvironment. Dynamics of folding and aggregation processes play an important role in conformational diseases (e.g. Alzheimer, Parkinson). It was shown that the latter processes are in fact influenced by the type and concentration of cosolvents. As a part of our immune system Lysozyme breaks carbohydrate chains, destroying the structural

integrity of bacteria cell wall. Small-angle X-ray scattering (SAXS) measurements on aqueous solutions of Lysozyme were performed in a wide range of concentrations and in presence of different types of cosolvents, typical for conditions where unfolding sets in within cells. We determined the effects of cosolvents on the unfolded state structures and aggregated structures. From the measured structure factors information about the structure of the hydration shell and, for the higher concentrated samples, information about the intermolecular interaction potential can be obtained.

CPP 12.27 Tue 17:00 P3

Absorption spectra for light-harvesting systems using non-Markovian as well as modified Redfield master equations — ●M. SCHRÖDER, M. SCHREIBER, and U. KLEINEKATHÖFER — Institut für Physik, Technische Universität Chemnitz, 09107 Chemnitz

Circular aggregates are studied to model the B850 ring of bacteriochlorophylls within the LH2 complex of purple bacteria. The spectral density which describes the coupling strength and frequency dependence of the interaction between the ring system and the environment has recently been determined by ab initio calculations [1]. Starting with a quantum master equation one can develop a formula for the frequency-domain absorption spectra [2]. Often one decouples the population dynamics from that of the coherences (secular approximation) and neglects memory effects (Markov approximation) in this procedure. Here we will investigate these approximations in some more detail as well as the influence of the form of the spectral density and static disorder using Monte Carlo methods. The calculations will be made using a numerical decomposition of the spectral density and different formalisms to treat the memory effects: time-local and time-nonlocal approaches as well as the modified Redfield method [3].

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[2] F. Neugebauer, D. Malzahn, and V. May, *Chem. Phys.* **201**, 151 (1995).

[3] W.M. Zhang, T. Meier, V. Chernyak, S. Mukamel, *J. Chem. Phys.* **108**, 7763 (1998)

CPP 12.28 Tue 17:00 P3

Characterization of Short-lived Radicals of Purine Bases in Aqueous Solution by Magnetic Resonance — ●ALEXEY KIRYUTIN^{1,2}, KONSTANTIN IVANOV², and HANS-MARTIN VIETH¹ — ¹Department of Physics, Free University of Berlin, Arnimallee 14, D-14195 Berlin, Germany — ²International Tomography Center of SB RAS, 630090, Institutskaya 3a, Novosibirsk, Russia

The structure of nucleotide radicals and their properties can be examined by the effects of chemically induced dynamic nuclear polarization (CIDNP) created in reversible photoreactions between nucleotides and suitable organic dye molecules. The CIDNP spectra with microsecond time resolution were obtained in photoreactions between purine bases and several dyes. Usually radical reactions such as protonation, deprotonation and termination occur on the microsecond time scale. The intensity and sign of the CIDNP at the aromatic protons of adenosine 5'-monophosphate and guanosine 5'-monophosphate (AMP, GMP) was studied depending on the dye and pH value of aqueous solution. From the shape of CIDNP spectra different nucleotide radicals were identified. For GMP and AMP the CIDNP was measured at variable magnetic field (0-7 T). From simulation of these field dependencies g-factors of the short-lived neutral, anionic and cationic forms of the nucleotide radicals were determined. These results contribute to the understanding of radical formation of nucleotides. In addition, the use of CIDNP effects for studying the structure of nucleic acids and the mobility of their bases will be discussed.

CPP 12.29 Tue 17:00 P3

Electron and Hydrogen Transfer Reactions in the Photolysis of Aromatic Amino Acids Studied by CIDNP — ●KARSTEN MIESEL and HANS-MARTIN VIETH — Department of Physics, Free University of Berlin, Arnimallee 14, D-14195 Berlin, Germany

The near UV photolysis of N-acetyl tyrosine (NATyrOH) and N-acetyl tryptophan (NATrph) in aqueous solutions was investigated by field dependent chemically induced dynamic nuclear polarisation (FD-CIDNP) and its time dependence in high magnetic field (TR-CIDNP). For both amino acids, ionisation is most efficient in basic solutions yielding a solvated electron (e^-_{aq}) and the amino acid radicals NATyrO• and NATrph•+. As the primary event, monophotonic ionisation occurring

from singlet excited precursors is identified, leading to a characteristic maximum in their CIDNP field dependencies. Simulations of the field dependencies allowed the determination of g-factors of the amino acid radicals. Concomitantly, some side reactions were investigated, such as decarboxylation and the formation of L-DOPA in the photolysis of tyrosine. The radical precursors are identified and a reaction scheme is presented. The observation of strong ¹H-CIDNP on the solvent peak (HDO) in the photolysis of NATyrO⁻ is attributed to H-transfer between the o-benzosemiquinone radical and NATyrO•, and subsequent deprotonation of NATyrOH. An equivalent mechanism is proposed to occur in the photolysis of NATrph.

CPP 12.30 Tue 17:00 P3

Secondary Structure Analysis of Synthetic Spider Silk Proteins by Fourier Transform Infrared Spectroscopy — ●MICHAEL TAMMER¹, PATRICK KÖLSCH¹, UTE SLOTTA², THOMAS SCHEIBEL², and FRIEDRICH KREMER¹ — ¹Universität Leipzig, Institut für Experimentelle Physik I, Linnestr. 5, 04103 Leipzig — ²Lehrstuhl für Biotechnologie, Technische Universität München, Lichtenbergstr. 4, 85747 Garching

Silk fibers produced by spiders for their web are extremely thin, lightweight, extendible and very strong. The combination of strength and stretchiness of this material gives a toughness comparable to that of high-tensile steel. Therefore several attempts has been done so far to produce artificial fibres spun from dope solutions composed of genetically modified natural proteins, designer proteins or protein-plastic blends.

In the contribution synthetic silk constructs based on the primary structure elements of the garden spider's (*Araneus diadematus*) major dragline silk proteins ADF-3 and ADF-4 are investigated by polarized FTIR spectroscopy. Thin films were prepared by spincoating a protein solution with one or more components forming a silk dope. IR spectra of these films and after solvent treatment with methanol or potassium phosphate were recorded. By analyzing the amide I absorbance band the secondary structure for the proteins of all samples are deduced. The treatment was found to emphasize beta-sheet conformations at the expense of alpha-helix and turn structures.

CPP 12.31 Tue 17:00 P3

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The near UV photolysis of N-acetyl tyrosine (NATyrOH) and N-acetyl tryptophan (NATrph) in aqueous solutions was investigated by field dependent chemically induced dynamic nuclear polarisation (FD-CIDNP) and its time dependence in high magnetic field (TR-CIDNP). For both amino acids, ionisation is most efficient in basic solutions yielding a solvated electron (e^-_{aq}) and the amino acid radicals NATyrO• and NATrph•+. As the primary event, monophotonic ionisation occurring from singlet excited precursors is identified, leading to a characteristic maximum in their CIDNP field dependencies. Simulations of the field dependencies allowed the determination of g-factors of the amino acid radicals. Concomitantly, some side reactions were investigated, such as decarboxylation and the formation of L-DOPA in the photolysis of tyrosine. The radical precursors are identified and a reaction scheme is presented. The observation of strong ¹H-CIDNP on the solvent peak (HDO) in the photolysis of NATyrO⁻ is attributed to H-transfer between the o-benzosemiquinone radical and NATyrO•, and subsequent deprotonation of NATyrOH. An equivalent mechanism is proposed to occur in the photolysis of NATrph.