University of Konstanz
Physics Department

SOFT CONDENSED MATTER PHYSICS

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Cover Design: Carsten Ruß

Cover (from top):
membrane wrapping around charged colloidal particle (D3);
binary decoration of a penrose pattern (E1);
coarse grained lattice model for ionic diffusion (B2);
schematic figure of a colloidal dispersion in a shear flow (C9);
local density-optimised crystallite-clusters (C12).
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Preface

This is the third report on research activities in soft condensed matter at the Physics Department of the University of Konstanz, which comprises the years 2001 and 2002. As previous reports it is intended to inform experts in this research area by surveying the experimental and theoretical work at Konstanz. During the last two years two of our colleagues have left; Dr. Philipp Maass became a Professor of Theoretical Physics at the Technical University of Ilmenau in 2001, and Dr. Clemens Bechinger accepted a position as Professor of Experimental Physics at the University of Stuttgart in 2002. On the other hand, new people have joined our groups; Dr. Holger Stark (since 2001) and Dr. Matthias Fuchs (since 2002) have strengthened the theoretical activities. They are holders of Heisenberg Fellowships of the German Science Foundation (DFG). The group leaders express their gratitude to all scientific collaborators, the technical and administrative staff for their support. This report has been edited on behalf of the soft-condensed matter groups by

Hans-Hennig von Grünberg
Rudolf Klein.

Konstanz, June 2003.
A Liquids
A1 Frustration effects in antiferro-quantum spin fluids

K. Franzrahe, S. Sengupta (U. Calcutta), R. Stadelhofer, P. Nielaba

As a simplified model for adsorbates with internal degrees of freedom we have studied the phase diagram of a fluid with classical translational degrees of freedom and internal quantum mechanical degrees of freedom by path integral Monte Carlo simulations (PIMC), finite size scaling, Gibbs ensemble- and grand canonical simulation techniques [1-7]. The Hamiltonian of the fluids is:

\[ H = \frac{1}{2M} \sum_{i=1}^{N} \mathbf{p}_i^2 + \sum_{i<j} U(\mathbf{r}_i - \mathbf{r}_j) \]

\[ - \frac{\omega_0}{2} \sum_{i=1}^{N} \sigma_i^z - \sum_{i<j} J(\mathbf{r}_i - \mathbf{r}_j)\sigma_i^x\sigma_j^x \]

Here \( \mathbf{p}_i \) is the momentum and \( \mathbf{r}_i \) the position of the particles, whose masses \( M \) are assumed to be sufficiently large to justify the classical treatment of the translational degrees of freedom. The two internal quantum states of a molecule are modeled by the term \( -\frac{\omega_0}{2}\sigma_i^z \) (\( \sigma_i^\pm \) are the Pauli- matrices of a spin-\( \frac{1}{2} \)- degree of freedom, \( \omega_0/J \approx 4 \)). The particles interact via their internal quantum mechanical degrees of freedom in a “square well” potential range \( U(r) = \infty : r < R, U(r) = 0 : r > R \).

\( J(r) = |J| : R < r < 1.5R, J(r) = 0 : r > 1.5R \). Our model has the property that the internal degree of freedom gets lifted out of the ground state by the interaction into an hybrid state. Due to this interaction the system has a para- ferro- transition as well as a gas- liquid transition as a function of temperature \( T \) and density \( \rho \) beginning at the tricritical point of the para- ferro- transition.

If the constraint of a constant coupling \( J \) for all spin values in the Hamiltonian in Eq. (1) is relaxed and instead the Hamiltonian is generalized such that \( J \) has the same value for parallel spins, \( J_{++} = J_{--} \), and for antiparallel spins the value \( J_{+-} = -\delta J_{++} \), a simplified Hamiltonian results for a mixture of \( A-\) and \( B- \) particles with different \( A-B \) interactions. For the case \( \omega_0 = 0 \) we have obtained [8] the surprising result, that the demixing line does not end at the gas- liquid critical point anymore, but rather as a critical end point at a higher density on the liquid side of the phase diagram and the liquid coexistence region strongly gets deformed. In Ref. [8] the rich phase diagram could be obtained as a function of \( \delta \) by MC simulations. In these studies a triple point was found and studied, which resulted due to the coexistence of a gas phase and two liquids at different densities. The simulations were accompanied by analytical computations on the mean-field- and Landau-theory level.

In case of \( \omega_0 = 0 \) and an antiferromagnetic interaction \( J = -1 \) in Eq. (1) between the particles of our fluid up to an inter-particle distance of 1.4 \( R \) we obtain an “anti-ferro” fluid with interesting properties. Due to the frustration effect of such a system on a triangular lattice at high densities a competition results between the tendency towards formation of a triangular lattice with frustrated spins and a formation of a square lattice with non-frustrated spins.

Using a perturbative density functional approach [10] we obtained the interesting result that at high densities and low temperatures the triangular lattice structure as well as the square lattice structure gets destabilized. Interestingly, the calculated phase diagram suggests that at low temperatures, this transition is suppressed so that over a range of parameters, the system refuses to crystallize. The resulting phase diagram is shown in Figure 1.

Figure 1: Temperature (\( T^* \)) and density (\( \rho^* \)) phase diagram of the anti-ferromagnetic fluid as obtained from density functional theory [10]. The square lattice has a density \( \rho^* = 1 \) and is denoted by the square. The region where the triangular lattice is stable is denoted by \( \Delta \). The dotted lines represent the extrapolated coexistence boundary between the liquid and the triangular lattice. Our perturbative density functional theory breaks down for low temperatures and high densities so that we do not observe a freezing transition in this range of values for \( T^* \) and \( \rho^* \). Inset shows our calculated gas-liquid phase boundary together with Monte Carlo results from Ref. [9]. The Bethe-Peierls approximation overestimates the short-range AF ordering in the fluid, leading to a higher gas-liquid critical point temperature. The horizontal line is the triple line.

By Monte Carlo simulations [11] we found good qualitative agreement with the approximate results given above for the liquid-solid phase transition at high densities. Indeed at high densities and high temperatures the system is in the triangular lattice structure, at low temperatures and high densities however a disordered structure appears. The stability region of the square lattice at low temperatures has been quantified as well.
The system properties can be obtained as thermal averages with the canonical partition function of the $N$ times $P$ particles, \[ \exp[-\beta \sum_{i<j} U(r_i - r_j) - \beta \tilde{V}_P(\{S\})]. \]

Since in this case spin - "values" between -1 and +1 are possible (see averages along the direction of the Trotter-"axis" in Eq. (4)), the frustration is reduced and the triangular lattice is stabilized at low temperatures. As phase transition density we obtain approximately the value of the hard disk system without spin interaction, see Fig. 2.

At medium densities and low temperatures a square lattice is found without spin- frustration. PIMC - studies [12] show that the stability region of this phase is shifted to much lower temperatures compared to the classical case ($P = 1$), see Fig. 2.

In total the interesting picture emerges that in certain regions of the phase diagram at high densities the properties of the system with quantum spins can reasonably well be approximated as such of a system of hard disks without spin interaction. This result gives us confidence that the region of very high densities and low temperatures in the phase diagram is indeed accessible and can be characterized by PIMC- studies. We plan to investigate this topic in future studies in greater detail.

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A2  The liquid-solid transition of hard disks

S. Sengupta (U. Calcutta), K. Binder (U. Mainz), P. Nielaba

Although the system of hard disks in two dimensions is one of the simplest models of a fluid, it nevertheless exhibits a rich and complex behaviour: the problem that needs to be considered is that of phase transitions driven by the formation of topological defects and the possible occurrence of a hexatic phase.

For hard disks, the potential energy $U$ is infinite if two disks (of diameter $\sigma = 1$) overlap while otherwise $U = 0$. So temperature essentially plays no role here, since there is no finite energy scale, and the only nontrivial control parameter still left is the density $\rho$ in the system. Therefore it was a controversial discovery made by molecular dynamics simulation long ago that a transition from a fluid phase at low density to a high-density crystal (with triangular lattice structure) does indeed occur. While the early studies [1] concluded that this transition is a first order transition (like in the three-dimensional case), the validity of this conclusion is doubtful, since the early work relied on studies of a few hundred particles only, and with the computer resources at that time a serious study of finite size effects could not have been attempted. Also, no study of bond orientational order was carried out. More recent theories show [2] that a discussion of bond orientational order is crucial, however.

Note that in general the crystal is characterized both by positional long-range order and by bond orientational long-range order. In $d = 2$ dimensions, however, rigorous theorems [3] exclude positional long-range order (for $\rho < \rho_G = 2/\sqrt{3}$, where $\rho_G$ is the density of the close-packed structure; note that the hard-sphere diameter is our unit of length), while orientational long-range order can still occur.

In order to define the bond orientational order parameter, imagine a Voronoi construction carried out between the centres of mass of a disk and its neighbors. In this way, nearest neighbors can unambiguously be defined for each configuration, and the straight line connecting the centres of mass of two nearest neighbours is called a bond. Taking the direction of a bond between particle $k$ and one of its neighbours as a reference direction for a whole lattice, we define the angle between the bond connecting particle $k$ and one of its nearest neighbours $j$ and the reference direction as $\phi_{kj}$. For a perfect triangular structure, $\phi_{kj}$ will be $2\pi/6$ or a multiple thereof. Therefore it makes sense to define the order parameter $\psi$ as

$$\psi = \left| \sum_k \psi_k \right| / N, \quad \psi_k = \frac{1}{6} \sum_{j[n.n.of \, k]} \exp(6i\phi_{jk}), \quad (1)$$

$N$ being the particle number in the system. For a perfect triangular structure, $\psi_k = 1$ for all $k$ and $\psi = 1$, while in the disordered phase the $\psi_k$ become complex numbers and $\psi$ will average to zero for $N \to \infty$. But in the disordered phase it still makes sense to study the bond orientational correlation function $g_0 = \langle |\psi_k \psi_l| \rangle$, with $r = |r_k - r_l|$. According to RG theory proposed by Halperin, Nelson and Young [2], melting in $d = 2$ dimensions can occur via two continuous transitions (at densities $\rho_h$ and $\rho_p$) with corresponding pressures $p_h$ and $p_p > p_h$, rather than via a single first-order transition at pressure $p_h$ (where a fluid of density $\rho_h$ and a solid of density $\rho_p$ will coexist). Both in the fluid phase and in the hexatic phase, $\langle \psi \rangle = 0$, but the behaviours of $g_0(r)$ are different: in the fluid one finds an exponential decay, while there is a power-law decay in the hexatic phase, and the correlation length $\xi$ of the bond orientational order diverges according to a KT behaviour as $\rho_p$ is approached, as does the bond orientational susceptibility $\chi = \int d^2r g_0(r)$: $\ln \xi \propto \ln \chi \propto (\rho_h - \rho_p)^{-1/2}$. Conversely, if one has a first-order transition, both $\xi$ and $\chi$ stay finite at $\rho_p$, and a nonzero order parameter $\langle \psi \rangle$ has already started to increase (linearly in the density) at $\rho_h$ (according to the lever rule), while according to the Kosterlitz, Thouless, Halperin, Nelson and Young (KTHNY) scenario, $\langle \psi \rangle$ is nonzero for $\rho > \rho_p$ only.

The mechanism of these continuous phase transitions is the unbinding of topological defects. Just as in the two-dimensional XY ferromagnet or planar rotor model, where vortex-antivortex unbinding occurs, the transition from the solid to the hexatic phase is driven by the unbinding of dislocation pairs with oppositely oriented Burgers vectors. While a free dislocation would have an infinitely long extra half-row of atoms, such a dislocation pair at finite distance involves a finite number of atoms in the extra row only, and such an excitation hence costs only a finite energy and can occur in the crystal in thermal equilibrium. The hexatic phase then melts into the liquid via disclination pair unbinding.

In Refs. [4] we designed a new method for exploring KT transitions. The basic idea is to check the self-consistency of the RG flow equations that describe this problem using the appropriate MC ‘input’. The theory can be cast in the framework of a two-parameter renormalization flow for the Young’s modulus $K(l)$ and the fugacity of vortices $y(l)$, where $l$ is related to the length scale considered. The flow equations can be solved numerically, starting from states of the model on the smallest possible scale - that of the lattice spacing, for which there are no vortices, and the corresponding ‘bare’ $K(0)$ and vortex fugacity $y(0)$. These starting values were obtained from specially constrained MC simulations. Resulting flow lines on one side of the separatrix all flow to $y' = 0$, i.e. a state with no free vortices on large length scales, on the other side...
of the separatrix they flow to large $y'$; this means disordered phase. From the MC simulation we know which initial condition falls on the separatrix, which gives us an access to the transition density.

In our MC simulations we applied a constraint that forbids the creation of dislocation pairs, determined the rejection rate due to this constraint and estimated the dislocation core energy $E_c$ from this rate:

$$ p = p_{pair} = \exp(-2E_c/k_BT)/Z(K),$$

where $K$ is the dimensionless Young's modulus, and $Z(K)$ the 'internal partition function' of a dislocation pair which is (using $k_BT = 1$ again)

$$Z(K) = \left[2\pi\sqrt{3}/(K/8\pi - 1)\right] J_0(K/8\pi )\exp(K/8\pi),$$

where $J_0$ is a Bessel function. From $p$ we hence obtain $y = \exp[-E_c(K)]$, which is one input in the RG flow equation. The elastic constants of the defect-free solid were measured by a new subblock technique [5]. In this way, $K$ could be obtained with high precision over the whole density range of interest ($0.88 \leq \rho \leq 1.1$). The flow diagram is shown in Figure 1, the universal fixed-point value is $K = 16\pi$. Figure 2 plots both the starting value $K(0)/16\pi$ and the renormalized value $K_R/16\pi$, as obtained from the recursion relations: in this way one would obtain an estimate $\rho_s = 0.916$ and $\rho_c = 9.39$. Of course, the known recursion relations contain only the leading terms, and experience with the planar rotor model indicates that the neglect of the next-to-leading terms implies significant errors. Therefore it is likely that the true result for $K_R/16\pi$ in Figure 2 lies somewhere in between the first-order result and the unrenormalized value (which would imply a transition at $\rho = 0.904$ which also exceeds $\rho_c = 0.899$, but is not a reasonable estimate for $\rho_s$ because the corresponding pressure would be too low). In view of these considerations, we suggest $\rho_s = 0.914 \pm 0.002$ as a preliminary estimate for the location of the phase boundary between the solid and hexatic phases.

In summary, we have discussed the evidence for the applicability of the KTHNY theory to the melting/crystallization transition of the hard-disk fluid. It has been shown that the currently available simulation data are compatible with a continuous transition from the fluid to the hexatic phase (with divergent bond orientational susceptibility) at $\rho_h \approx 0.899$, and with a hexatic-to-crystal transition at $\rho_s \approx 0.914 \pm 0.002$. However, no simulations that reach full thermal equilibrium in the density range $0.90 \leq \rho \leq 0.915$ and show directly the existence of the hexatic phase are available so far. Without such direct evidence, the possibility of a (very weak) first-order transition from the fluid to the crystal cannot yet be firmly ruled out, although so far signals of two-phase coexistence are also lacking.

![Figure 1](image-url)  
**Figure 1:** Schematic flows of the dimensionless Young's modulus $K$ and the dislocation fugacity $y$ according to the KTHNY recursion relations. The dashed lines show the separatrix whose intersection with the line of initial states (the solid line connecting the full circles $y(l = 0)$ and $K^{-1}(l = 0)$ at different temperatures $T$ or densities $\rho$, respectively) determines the transition point ($T_c$ or $\rho_c$, respectively).

![Figure 2](image-url)  
**Figure 2:** Bare Young's modulus $K(0)/16\pi$ (upper curve) and renormalized modulus $K_R/16\pi$ (lower curve) plotted versus density. The dotted horizontal line $K/16\pi = 1$ highlights the value at which the solid-to-hexatic transition is predicted.

A3 Colloid–polymer mixtures as model complex fluids

Y. L. Chen,* M. Schmidt,† M. Kroutievá,‡ K. S. Schweizer,* and M. Fuchs

Mixtures of differently shaped mesoscopic particles, be it colloids, spherical or elongated proteins or viruses, polymer coils or (clay–) platelets, often demix solely because of the shape difference and the resulting steric hindrances. In the absence of enthalpic contributions, phase diagrams, thermodynamic free energies and structural correlations in these mixtures are determined by entropy considerations alone, which poses interesting questions to statistical physics. At the same time, the problem of the packing of differently shaped objects is present in various complex fluids and ‘soft matter’ systems, and e.g. in the context of biological environments leads to effects referred to as ‘macromolecular crowding’ [1]. Mixtures of spherical (colloidal) particles and flexible polymer chains can be considered as one model system, because two different kinds of entropies compete, the translational of both species and the conformational entropy of the polymeric macromolecules.

Since the work by Asakura and Oosawa (AO) in the 1950s, it is known that small polymers (with radius of gyration \( R_g \)) induce a ‘depletion attraction’ among a dilute suspension of colloids of much larger radius \( R \). Because polymer segments cannot penetrate the colloidal spheres, the center–of–mass of the polymer coils is restricted from a shell with width \( R_g \) around each colloid. If two colloids approach, their depletion shells overlap and one ‘overlap volume’ becomes accessible to the polymers, whose translational center–of–mass entropy increases.

To achieve this entropy gain, particles thus arrange as if interacting with an attraction. Note, that polymer conformational entropy is neglected in the AO–model!

Numerous systems exist where the restrictions of the Asakura–Oosawa study to \( R_g \ll R \) and low concentrations do not hold, e. g. mixtures containing proteins or other nanoparticles. It is not clear what one means by ‘depletion’ if \( R_g \gg R \) and polymers can ‘wrap around’ particles (see Fig. 1). Besides the obvious fact, that pair–decomposable effective colloidal potentials lose meaning, interpretation in terms of the center–of–mass of the polymer coils becomes inapplicable. However, the fundamental idea that the perturbation of polymer coils by hard particles can be reduced, and the polymer (in general conformational!) entropy enhanced, by the physical clustering of particles remains valid. The effect of increasing polymer concentration measured relative to the overlap–concentration where polymer coils start touching, \( c/e^* \), also is of interest because the polymer correlation length \( \xi \) (‘mesh size’) for \( c/e^* \gg 1 \) replaces \( R_g \) as relevant polymer length scale. Figure 1 shows the resulting distinct physical regions, with I addressed by AO.

Figure 1: A schematic illustration of the four distinct physical regimes in a colloid–polymer mixture. Dilute (\( c < c^* \)) and semidilute (\( c > c^* \)) polymer solution regimes are divided according to \( R_g \ll R \) (I) or \( R_g \gg R \) (II), and \( \xi \ll R \) (III) or \( \xi \gg R \) (IV), respectively; from [2].

From polymer field theory it had been known, that, irrespective of chain size, polymer segments are depleted close to isolated (spherical) particles because chain–connectivity enforces a smooth increase of the segment density outside the excluded particle volume. Figure 2 shows that a recent binary mixture Ornstein–Zernicke–type approach recovers this effect [2]. (In contrast to the older approaches, it can be extended to arbitrary particle densities.) Importantly, for large polymers the depletion layer is ruled by two different length scales. While the width at half height (\( g_{cp} = 1/2 \)) becomes independent on polymer parameters and is determined by the parti-

Figure 2: Polymer segment density exhibiting a depletion layer close to an isolated colloidal sphere for various polymer correlation lengths \( \xi \) (in units of \( 2R \)) and for dilute (replace \( \xi \) by \( R_g \)) and semidilute polymer concentrations. The inset shows the data replotted as \( r^2 h_{cp}(r) = r^2 (g_{cp}(r) - 1) \) which reveals the long–ranged tail of the depletion layer for large polymers.
particle radius $R$, there exists a long–ranged tail where the polymer profile increases with a power–law $\sim r^{1-\nu/d}$; $d = 3$ is the spatial dimension, and the Flory exponent connects coils size with degree of polymerization $N$, $R_g \sim N^{\nu}$. For the Gaussian chains considered in Fig. 2, $\nu = 1/2$. The power-law is cut–off at the polymer correlation length $\xi$ (the 2nd relevant length in the depletion layer for dilute colloids); see the inset of Fig. 2.

Overlap of the depletion layers around two particles removes constraints on the polymer conformational fluctuations, conformational entropy increases, and thus there exists a polymer induced attraction even between two colloids that are much smaller than the chain size. Because of the long–ranged tail in the depletion layer (see the inset of Fig. 2), the induced attraction has a weak long–ranged component extending out to the correlation length $\xi$. For simplicity, looking at two particles, a non–monotonous variation of the 2nd virial coefficient follows, because adding polymer increases the depth of the attraction but decreases the range set by the polymer correlation length. Figure 3 thus shows one example for the much richer variations of the polymer induced effects for large $R_g \gg R$ than in the AO–model for $R_g \ll R$, where $B_2^c$ decreases monotonously with $c/c^*$.

The induced change of the particle arrangements can be read off from the colloid pair distribution function [2]

$$g_{cc}(r) \rightarrow g^{HS}(r) + b \frac{R}{r} e^{-r/\xi} \quad \text{for} \quad R_g/R \gg 1 .$$

It gives the probability of finding nanoparticles at a distance $r$ if a particle is at the origin. Without polymer, $g^{HS}$ gives the packing of hard spheres. The long–ranged term ($\xi_c$ generalizes $\xi$ to finite colloid densities) is clearly attractive as it describes an increased probability of finding particles. Importantly, its magnitude — except for a coefficient $A^2$ measuring the void space between particles — is given by the insertion free energy for adding one particle to the polymer solution, $b \sim \frac{4\pi R^2 \rho^* b}{\xi_c}$. It is proportional to the displaced number of polymer strands, which follows from the number of segments $cNR_g^3$ in the sphere volume divided by number of segments $N(R/R_g)^2$ on a strand of length $R$. Recovering this one–particle parameter, shows that finite particle densities do not screen the polymer correlations. A van der Waals like picture emerges for the colloids in the limit of $R_g \gg R$, with local steric repulsion and a weak long–ranged attraction.

We aim at interpreting in this picture [3] the phase diagrams (see Fig. 4), where a finite density is predicted for phase separation even in the limit of $R_g/R \rightarrow \infty$.

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B  Polymers and Liquid Crystals
B1 Soft particle models for polymer systems

F. Eurich, P. Maass

The control of phase morphologies of inhomogeneous polymer systems is a problem of active current research and offers a wide spectrum of possible technological applications. These range from easy construction of lithographic masks to self-organized fabrication of microelectronic circuits consisting of organic semiconductors. By using spontaneous demixing processes in thin films cast on heterogeneous substrates, it is possible to tailor morphologies of technological interest. Optimization of these processes requires knowledge of the long-time kinetics of polymeric systems on surfaces. Due to the enormous difference between typical vibrational times ($\sim 1 \text{ ps}$) and the characteristic time scales for diffusion processes ($\sim 1 \text{ s}$) of the macromolecules, studies by molecular dynamics simulations are hardly feasible.

A promising approach to tackle this problem is based on the idea that on semi-macroscopic time and length scales, polymers can be described as soft ellipsoids [1]. Using Gaussian chains as a microscopic model, we set up a soft particle model that is in agreement with well-known scaling relations of polymer physics and can reproduce kinetic properties of polymeric bulk systems on large time and length scales [2].

In collaboration with the group of Prof. Baschnagel (Institute Carles Sadron, Strasbourg) we have extended this study to systems in confined geometries [3]. The interactions of the ellipsoids with the confining walls are modeled by a linear coupling of the monomer densities with an external wall potential. For homogeneous systems in thermal equilibrium the soft ellipsoidal particles near the wall show shape and orientation effects that are similar to those found in simulations of chain molecules.

Spinodal decomposition processes of binary mixtures confined between neutral walls show an increase of the lateral size of the emerging domains and a slowing down of the demixing kinetics, as the distance between the walls is reduced. This effect is illustrated in Fig. 1. The findings are in agreement with predictions from time-dependent Ginzburg–Landau theory. In the case of a patterned wall, which periodically favors one of the two mixture components, different equilibrium structures emerge. Either the surface–induced structure propagates through the whole film (“full structure”), or it remains confined to a narrow region near the patterned wall (“partial structure”). Consideration of surface energies suggests that this behavior depends on the ratio between pattern periodicity and film thickness, $L_\parallel/L_z$, as shown in Fig. 2. The different equilibrium structures lead to different kinetic pathways of spinodal decomposition processes in such systems. For example, the demixing process can be triggered by the patterned surface, leading to pattern-directed spinodal decomposition.

Recently, we generalized the soft particle model approach to allow for a more flexible choice of the internal degrees of freedom [4]. The polymers are described by soft spheres that are connected by an effective bond potential. These models will be applied to block copolymer systems in the future.

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B2 Polymer ion conductors

O. Dürre, W. Dieterich

Chain polymers carrying electro-negative atoms (e.g. oxygen or nitrogen) in their repeat unit can act as solvents for certain salts. Well-known examples are Li-salts dissolved in polyethylene-oxide (PEO). At temperatures sufficiently above the glass-transition temperature these polymer-salt solutions show a significant DC ionic (Li$^+$) conductivity. Such “polymer electrolytes” could in principle offer widespread applications in batteries, sensors and fuel cells. However, today’s conductivities at room temperatures are limited by $10^{-4}$ to $10^{-5}$ S/cm, while battery applications would require at least $10^{-3}$ S/cm. Therefore a deep physical insight into these materials is desirable in order to optimize their conduction. From the scientific point of view the interplay between ion diffusion and the polymer network dynamics is an interesting fundamental problem.

Numerical simulation on a microscopic level could in principle give insight into the complex dynamics of those materials. However, these simulations are extremely demanding through the fact that time scales for motion of the chain molecules and time scales for ionic motions normally differ by orders of magnitude. This necessitates the design of appropriate coarse-grained models based on stochastic moves of chain segments and ions. In this project we investigate stochastic models on different levels of coarse-graining:

i) Dynamic Monte Carlo studies of lattice chains interacting with ions.

From extensive simulations we obtained the diffusion constants of both chains and ions and their dependence on model parameters. In particular we were able to discuss important trends in the glass transition temperature as a function of the ion content. By combining simulations under constant volume with the quasichemical approximation for the equation of state we also deduced the diffusion constant for infinite dilution, respectively. Evidently the DP-approximation agrees very well with the full simulation for all chain lengths considered. Since the computation of the input quantities for the DPT is about five times less time consuming than a full simulation, DPT considerably speeds up the determination of the diffusion constant.

Our studies so far are limited to an athermal system but in principle our method has the potential of being used for realistic models, in which the determination of the ionic diffusion constant is extremely difficult. A first rough comparison with MD studies by Gusev et al. [6] for a frozen polymer matrix support the potential of applying DPT for more realistic models [7]. Since the determination of the distribution $\Psi(t)$ is more complicated than the determination of diffusion constant for ion diffusion within the frozen network, it is tempting to connect $\Psi(t)$ with an experimentally determined relaxation time of the polymer host. We hope to address these questions in future work.

Recent experiments, showed a new way to enhance the conductivity of polymer ion conductors by mechanically stretching them [8]. To describe this effect, we considered a phenomenological model consisting of a mixture of two phases each with different conductivity where the geometry of phase distribution is sensitive to the stretching [9]. Experimental observations suggest that fast ionic transport in polymer ion conductors takes place along directed structures such as the helices formed by the PEO chains. We model this systems by randomly placing highly conducting spheres into a poorly conducting medium. The deformation of the macroscopic sample is accounted for by changing the geometry of spheres to ellipsoids with the symmetry axis lying in the direction of the stretching. Both dc and ac-conductance properties
are worked out by applying differential effective medium theory, developed earlier for transport problems in porous media [10], showed similar behavior compared to the experiments [8]. All the above projects are pursued in collaboration with A. Nitzan, Tel Aviv.

A further question concerns the viscosity $\eta$ of polymer electrolytes and its dependence on the ion concentration. For pure polymer melts a Kramers relaxation time $\tau_K$ can be defined through the response of the radius of gyration to an external potential which mimics a shear acting on the beads of the polymer chain. For a single Rouse chain, $\tau_K$ is proportional to the relaxation time $\tau_1$ of the end–to–end vector [11]. We gave a new proof of this relation, providing strong evidence that this relation is also valid for unentangled melts [12]. Treating the Kramers potential as a perturbation, one can relate $\tau_K$ to averages of the fourth and sixth moments of chain coordinates at equilibrium and thus obtain a dynamic quantity from static properties. Using MC–simulations, we tested this concept in collaboration with H.L. Frisch (Albany) for a simple athermal lattice model [13]. In Fig. 2 we compare $\tau_K$ and $\tau_1$ for a monomer concentration of $c = 0.3$. Obviously, at intermediate chain lengths $N$ both times have the same $N$–dependence. Simulations for different concentrations showed that the range of agreement between $\tau_K$ and $\tau_1$ depends on the monomer concentration and is extended for lower concentrations. Since the Kramers method uses only static averages it can be applied to obtain the $N$–dependence of $\tau_1$ with modest computational effort and hence also yields the chain–length dependence of the viscosity. The breakdown of this concept for longer chains is attributed to entanglement effects.

Figure 1: Comparison of the tracer correlation factor $f(c)$ from DP-theory for chains of different length (data-points) with full simulations. The full lines represent fit functions for the simulation data.

Figure 2: Comparison of relaxation times using the Kramers approach ($\times$) with “conventional” MC– simulations ($\square$).

B3 Structural and conformational dynamics of polymer melts

S.–H. Chong,* M. Aichele,† J. Baschnagel,† and M. Fuchs

Polymeric materials often find application as amorphous solids. During the process of vitrifying a polymer melt, conventionally induced by cooling, the 'structural relaxation' (viz. particle rearrangements) slows down strongly (the longest relaxation time increases by orders in magnitude), and a glassy state is reached when the melt cannot flow anymore on the time scale of interest. A characteristic feature of macromolecular systems is the large number of internal ('conformational') degrees of freedom a single polymer possesses. Because of chain–connectivity, conformational rearrangements are slow already at high temperatures and cause characteristic anomalies in single chain transport or relaxation processes. Their role during vitrification is not yet well understood, where they may influence transport and viscoelastic properties, which change strongly close to the glass transition. We are developing a first–principles approach to the structural and conformational relaxations in chain polymer melts, building on and testing the theory by comparisons with molecular dynamics simulations, which have become possible for model systems [1].

In order to describe the slow dynamics in a polymer melt as sketched in Fig. 1, the choice of a set of slow variables is necessary. Building on the mode coupling theory for simple and low–molecular fluids [2], and on site–approaches to the equilibrium structure of polymer fluids [3], we use the monomer–density fluctuations for wavevector $q$, $\rho_q^m(t) = \sum_{a=1}^n \exp \{i \mathbf{q} \cdot \mathbf{r}_a(t)\}$, where $\mathbf{r}_a(t)$ denotes the position of the $a$th monomer in the $i$th chain at time $t$; considering $n$ chains of $N$ monomers. The most familiar quantity describing their time–dependence is the monomer averaged intermediate scattering function $F_q(t)$,

$$F_q(t) = \frac{1}{N} \sum_{a,b=1}^N F_q^{ab}(t), \quad (1)$$

$$F_q^{ab}(t) = \langle \rho_q^m(t) \rho_q^m(0) \rangle / n, \quad (2)$$

which also can be measured in scattering experiments.

Closed equations of motion for $F_q(t)$ can be obtained by concentrating only on the set of slow variables and using the so–called 'mode coupling approximation'. Importantly, parameter free results are obtained because the final equations of motion are uniquely specified by the static structure factor $S_q = F_q(t = 0)$, which can be obtained from simulations or liquid state theories like [3].

Vitrification at a (idealized) glass transition is signaled by the existence of arrested, non–decaying components in the density relaxation functions, $f_q = \lim_{t \to -\infty} F_q(t)/S_q$, where the $f_q$ are called glass form factors. The $f_q$, like the Debye–Waller factors of crystalline solids, give the amplitude of elastic scattering. Figure 2 compares results from simulations of a model polymeric melt with theoretical calculations without adjustable parameters [4,5]. The
'cage–effect' discussed in Fig. 1 can be held responsible for structural arrest, as can be seen by the peak in \( f_z \) at a wavevector \( q_{dp} \), characteristic for the average monomer separation. Here the local short ranged order dominates. It is measured by \( S_{dp} \), which grows smoothly upon lowering the temperature. Yet, the glass structure develops discontinuously, \( f_z = 0 \) for \( T > T_c \) and \( f_z > 0 \) for \( T < T_c \), where \( T_c \) defines an idealized glass transition temperature. It corresponds to a bifurcation in the nonlinear dynamical equations which aim at mathematically capturing the feed–back mechanism of the cage–effect.

In agreement with previous phenomenological models [1], the structural arrest in the collective density fluctuations of polymer melts in the present approach thus is dominated by a local monomeric caging. Consequently it becomes asymptotically independent on degree of polymerization. It follows the scenario of mode coupling theory previously worked out for simple liquids.

Because of the polymer specific slow dynamics in the motion of a tagged chain, which originates in chain connectivity, the question arises whether the same theoretical approach can rationalize the conformational dynamics. The classical 'Rouse model', which often is applied, considers a single polymer chain immersed in a low–molecular solvent, treating the latter as a Markovian heat bath. It thus postulates a separation of time scales, which a priori is not justified as the tagged chain in a polymer melt is surrounded by chains of identical degree of polymerization \( N \). To study the conformational dynamics, the set of collective slow variables (density fluctuations with correlators given in E's. (1,2)) shall be kept, and the tagged chain (with label \( s \)) shall be described by its density fluctuations, \( g_{q,sa}(t) = \exp \{ i \mathbf{q} \cdot \mathbf{r}_s(t) \} \). Again the dynamics is characterized by the matrix of scattering functions, \( F_{q,sa}(t) = \langle j_{q,sa}(t) j_{q,sa}^*(0) \rangle \), which are easily connected to the familiar mean–squared displacements, like the monomer averaged one:

\[
g_M(t) = \frac{1}{N} \sum_{a=1}^{N} |(\mathbf{r}_a^z(t) - \mathbf{r}_a^z(0))^2|.
\]

For simple liquids at \( T > T_c \), classical diffusion would be expected, \( g_M(t) \to 6Dt \), for times long after the decorrelation of the constraining collective cage. Denoting the time scale for the collective cage decay by \( \tau \) (it could be measured from \( F_{q,sa}(t = \tau)/S_{dp} = f_{dp}/e \), this behavior would be expected for \( t \gg \tau \). Yet, chain connectivity hinders the monomers because motion over larger distances requires successively more segments of the same chain to be pulled along. The Rouse model postulates that the number of monomers from other chains that are pulled along remains small (finite in the limit \( N \to \infty \)).

Extending the approach to the tagged particle dynamics, the question of a time scale separation between structural and conformational dynamics can be addressed, and the validity of the Rouse model studied. There opens a window in time where the mean–squared displacement grows subdiffusively, \( g_M(t) \sim t^x \), for \( \tau \ll t \ll \tau_R \); with \( \tau \approx 10^{-2}/D \) and \( \tau_R \approx 10^0/D \) in Fig. 3. In this window conformational correlations dominate \( g_M(t) \) and in the limit \( N \to \infty \) the Rouse model exponent \( x = \frac{1}{2} \) can be derived [5]. Large finite \( N \) corrections are observed numerically and in the simulations, which lead to an 'apparent' exponent \( x = 0.63 \) for \( N = 10 \) [1,5]. Thus the assumptions of the Rouse model are verified asymptotically, as the intermolecular friction decays much faster (\( \tau \sim N^0 \)) than the slowest conformational fluctuations, whose relaxation time grows with \( N, \tau_R \sim N^2 \).

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B4 Rotational diffusion of frozen liquid-crystalline particles in external fields

Kirill Sandomirski, Alenka Mertelj, José Luis Arauz-Lara, Georg Maret, Holger Stark, Thomas Gisler

Colloidal particles in a solvent do not only experience random forces due to the collisions with the surrounding molecules, but are also imparted random torques that lead to fluctuating particle orientations described by the orientation vector \( \mathbf{u}(t) \). If the colloids possess optical anisotropy, e.g., due to intrinsic birefringence or shape birefringence, these orientational fluctuations can be probed by depolarized quasielastic light scattering. For isolated, freely rotating spherical particles in the limit of high solvent viscosity \( \eta \), the rotational part of the measured field auto-correlation function \( \mathcal{g}^{(1)}(t) \) of the scattered depolarized electric field decays exponentially with time \( t \); the corresponding decay rate is proportional to the rotational diffusion constant \( D_\theta = k_B T/(8\pi\eta R^3) \), where \( k_B T \) is the thermal energy and \( R \) is the particle radius.

Permanent or induced dipoles localized on the particles can be subject to a torque via external electric or magnetic fields, leading to a distribution of orientations which is no longer isotropic but exhibits a peak along the direction of the external field. As a consequence, the amplitudes of the orientational fluctuations are reduced, leading to reduced fluctuations of the depolarized scattering. The dynamics of the orientational relaxation towards the equilibrium distribution of orientations, on the other hand, is known to depend critically on the detailed shape of the external potential \( V(\mathbf{u}) \).

Unlike the Debye relaxation in polar fluids, the orientational relaxation of induced dipoles in an external field has been much less studied. For particles possessing an intrinsic uniaxial symmetry in their dielectric or magnetic properties the potential energy of the induced dipole is equal for both parallel and antiparallel alignment of the particle axis along the field. The two energy minima of such a bistable potential are separated by a barrier which increases with increasing field strength, equivalent to the situation in Néel relaxation in single-domain ferromagnetic particles and the dielectric relaxation of electric dipoles in nematic liquid crystals.

Using depolarized quasielastic light scattering from optically anisotropic colloids which are aligned either with a magnetic or an electric field we have been able to provide detailed tests of theoretical models for the relaxation of induced dipoles in an external field. Different characteristic relaxation rates are probed by choosing different orientations of the aligning field with respect to the scattering plane. Our data provide experimental evidence for an unexpected non-monotonic dependence of one relaxation rate on field strength, consistent with a theoretical description on the basis of the orientational Smoluchowski equation which we solve both by a perturbation approach and by a numerical treatment.

Optically anisotropic colloidal particles were prepared by ultraviolet curing of an emulsion of polymerizable liquid crystal droplets. This procedure freezes the nematic order in the droplet whose anisotropy axis defines the particle director \( \mathbf{u}(t) \). Polydispersity in particle radius within a single batch could be kept as low as 10\%. Light scattering experiments were performed in a superconducting 7 T magnet. The particles at low volume fractions \( \phi \approx 10^{-3} \) were oriented in the magnetic field due to the anisotropy of their diamagnetic susceptibility; in these experiments, the magnetic field \( B_0 \) was aligned parallel to the wave vector \( \mathbf{k}_0 \) of the excitation beam; its polarization was parallel to the scattering plane, while the outgoing polarization was perpendicular to it. Scattered light at a scattering angle \( \theta = 4^\circ \) was collected with a single-mode fiber, detected by two photomultipliers, and the intensity-intensity cross-correlation function \( \mathcal{g}^{(2)}(t) \) was measured by a digital correlator. At small scattering angles the decay of \( \mathcal{g}^{(2)}(t) \) due to translation is slow enough that the faster rotational correlation function which is, in this specific geometry, given by \( F_{22}(t) = \langle Y_{22}[^{\mathbf{u}}(0)]Y_{22}[^{\mathbf{u}}(t)] \rangle \), can be resolved. \( Y_{22}[^{\mathbf{u}}(t)] \) denotes the \( (l = 2, m = 2) \) spherical harmonics for the particle director \( \mathbf{u}(t) = (\varphi(t), \theta(t)) \) (see Fig. 1).

![Figure 1: Rotational correlation functions](image)

Figure 1: Rotational correlation functions \( F_{22}(t) = \langle Y_{22}[^{\mathbf{u}}(0)]Y_{22}[^{\mathbf{u}}(t)] \rangle \) for particles with mean radius \( R = 304 \text{ nm} \) measured at \( B_0 = (0.0 \ldots 1.5) \text{ T.} \)

The strong acceleration of the orientational relaxation even at the shortest correlation times measurable is described by the solution of the Smoluchowski equation for an isolated particle in an external field

\[
\frac{\partial W(\mathbf{u}, t)}{\partial t} = \mathcal{L}W(\mathbf{u}, t),
\]

where

\[
\mathcal{L}W(\mathbf{u}, t) = \sum_{\mathbf{a}} \mathbf{a} \cdot \nabla W(\mathbf{u}, t) + \frac{1}{2} \nabla^2 W(\mathbf{u}, t).
\]

The Laplacian \( \mathcal{L} \) acts on the angle distribution \( W(\mathbf{u}, t) \) with respect to the external field direction, and the sum is taken over all \( \mathbf{a} \) with \( \mathbf{a} \cdot \mathbf{u} \neq 0 \).

[^1]: Kirill Sandomirski, Alenka Mertelj, José Luis Arauz-Lara, Georg Maret, Holger Stark, Thomas Gisler

[^2]: The Laplacian \( \mathcal{L} \) acts on the angle distribution \( W(\mathbf{u}, t) \) with respect to the external field direction.
where \( W(\mathbf{u}, t) \) denotes the probability of finding the particle oriented along the unit vector \( \mathbf{u} \) at time \( t \). In the Smoluchowski operator

\[
\mathcal{L} = D_r \left[ \nabla^2 + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial V(\theta)}{\partial \theta} \ldots \right) \right]
\]

(2)

the angular part of the Laplacian, \( \nabla^2 \), i.e., the square of the angular momentum operator of quantum mechanics, describes free rotational diffusion whereas the drift term reflects the fact that the particle experiences a torque \( -\partial V(\theta)/\partial \theta \) due to the uniaxial potential \( V(\theta) = -\sigma \cos^2 \theta \) with \( \sigma = C\Delta \chi^\nu B_0^2/(2k_B T) \) where \( \Delta \chi = \chi_\parallel - \chi_\perp \) is the diamagnetic anisotropy of the nematic phase, and \( v = \frac{4}{3} R^3 \) is the volume of the particle. The geometrical factor \( C \) is unity for a uniform director field in the droplet.

For weak field strengths the Smoluchowski equation has been solved by perturbation analysis, yielding analytical expressions for the relaxation rates of the measured correlation functions as a function of the external field strength now first decreases from \( 6D_r \) to a shallow minimum at an incident laser power of about 40 mW after which the relaxation rate increases again as illustrated in Fig. 3. This unexpected decrease is indeed predicted by the second-order perturbation theory for \( |m| = 1 \).

A critical test of the applied theory is the comparison of the prediction for \( F_{21}(t) \) with experiment. The correlation function \( F_{21}(t) \) can be observed by choosing the scattering plane perpendicular to the aligning field. We have realized this geometry by illuminating the sample with a V-polarized laser beam having an \( 1/e \) width at the focus of about 50 \( \mu \)m which produces a much higher electric field strength \( E_0 \) than in our first experiment. As a result, the particles experience a torque originating from the anisotropy of their dielectric constant. The magnitude of the torque is completely equivalent to the magnetic field case, i.e., \( \sigma \sin 2\theta \) with \( \sigma = C \Delta \varepsilon |E_0|^2/(8\pi k_B T) \), where \( \Delta \varepsilon = \varepsilon_\parallel - \varepsilon_\perp \) is the dielectric anisotropy of the nematic phase. Quite unlike the situation for \( |m| = 2 \), \( m = 2 \) observed above, the average relaxation rate \( \overline{\lambda}_{21}(\sigma) \) as a function of the external field strength now first decreases from \( 6D_r \) to a shallow minimum at an incident laser power of about 40 mW after which the relaxation rate increases again as illustrated in Fig. 3. This unexpected decrease is indeed predicted by the second-order perturbation theory for \( |m| = 1 \).

As in the case of magnetic alignment, the average relaxation rate \( \overline{\lambda}_{21}(\sigma) \) computed numerically closely follows the result from perturbation theory up to a coupling strength \( \sigma \approx 2 \) (see Fig. 3.) The plateau of the measured relaxation rates at about 8.5 \( \delta D \), might be due to depolarization fields within the particle and is subject of further investigation. The peculiar minimum in the relaxation rate at \( \sigma \approx 1 \) indicates the competition of the enhanced restoring torque tending to accelerate the relaxation of \( \mathbf{u}(t) \) back to the equilibrium direction and the increasingly slow exchange between parallel and anti-parallel particle orientations over the potential barrier.

Colloids
C1 Computer simulations of phase transitions in nano-pore condensates

J. Hoffmann, P. Nielaba

Many of the interesting effects in pore condensates take place at low temperatures so that the consideration of quantum mechanics is important. We studied [1-5] structures, phase transitions and quantum effects in pore condensates, by a combination of finite-size-scaling methods and path integral Monte Carlo (PIMC [6-9]) simulations. Canonical averages $\langle A \rangle = Z^{-1} \text{tr} \left[ \exp(-\beta H) \right]$ are given by:

$$\langle A \rangle = Z^{-1} \text{tr} \left[ \exp(-\beta H) \right]. \tag{1}$$

Here $Z = \text{tr} \left[ \exp(-\beta H) \right]$ is the partition function and $\beta = 1/k_B T$ is the inverse temperature. Utilizing the Trotter–product formula,

$$\exp(\beta H) = \lim_{P \to \infty} \left( \exp(-\beta E_{kin}/P) \exp(-\beta V_{pot}/P) \right)^P, \tag{2}$$

we obtain the path integral expression for the partition function:

$$Z(N,V,T) = \lim_{P \to \infty} \left( \frac{m P}{2 \pi \hbar^2} \right)^{3 N P/2} \prod_{s=1}^P \int d\{r^{(s)}\} \exp \left\{ -\frac{\beta P}{2} \sum_{k=1}^N \frac{m P^2}{2 \hbar^2 \beta^2} \left( \mathbf{r}^{(s)}_k - \mathbf{r}^{(s+1)}_k \right)^2 + V_{pot}(\{ \mathbf{r}^{(s)} \}) \right\}. \tag{3}$$

Here, $m$ is the particle mass, integer $P$ is the Trotter number and $\mathbf{r}^{(s)}_k$ denotes the coordinate of particle $k$ at Trotter-index $s$, and periodic boundary conditions apply, $P + 1 = 1$. This formulation of the partition function allows us to perform Monte Carlo simulations [10] for increasing values of $P$ approaching the true quantum limit for $P \to \infty$. Thermal averages in the ensemble with constant pressure $p$ are given via the corresponding partition function $\Delta(N, V, T) = \int_{0}^{\infty} dV \exp[-\beta p V] Z(N, V, T)$. In Eq. (3) we see that in the path integral formalism each quantum particle $k$ can (for finite $P$-values) be represented by closed quantum chains of length $P$ in position space where the classical coordinate of the point $\mathbf{r}^{(s)}_k$ on this chain at the Trotter index $s$ has a harmonic interaction to its nearest neighbors at $\mathbf{r}^{(s+1)}_k$ and $\mathbf{r}^{(s-1)}_k$. An interaction between different quantum particles takes place only between particles $\{ \mathbf{r}^{(s)} \}$ with the same Trotter index $s$. Due to this property the entire system with Trotter index $s$ can be placed efficiently in one processor of a parallel computer with $P$ processors, where the potential energy of all $N$ particles can be computed for this Trotter index $s$ (with an effort $\propto N(N - 1)/2$).

With computer simulations we have analyzed [1,2] many interesting properties of “Ar”- and “Ne”- pore condensates recently modeled as Lennard-Jones systems with particle diameter $a$ and interaction energy $\epsilon$, in our computations we use particle masses $m^\text{Ar}=100$ and $m^\text{Ne}=1000$ for simplicity well approximating the particle masses of Ne and Ar ($m^\text{Ar}=112$ and $m^\text{Ne}=1160$)).

The effective wall potential has been computed by integration over the matrix, modeled as a Lennard-Jones-continuum. These systems have - like the gas-liquid-transition in “bulk” systems - an adsorbate-condensate phase transition at low temperatures, the precise shape of the phase diagram is strongly influenced by the system geometry (pore radius). In turns out that with increasing attractive wall interaction the critical density increases, the adsorbate density increases strongly, and the condensate density increases weakly.

Figure 1: Typical condensate configuration ($T^* = 0.31$) showing the meniscus structure.

A meniscus is formed with increasing curvature, the configurations become less stable and the critical temperature decreases. The critical temperature is reduced with decreasing pore diameter. Beginning from the wall a formation of layered shell structures is found which may favor or disfavor the occupancy of sites at the pore axis due to packing effects. The density at the pore axis thus is an oscillatory function of the pore radius with density maxima for pore radii of $\sigma a$ and minima for pore radii of $(n + 1/2)\sigma$. For large pore diameters the density oscillations decay from the wall towards the pore axis and the system approaches the “bulk”. At lower temperatures we obtain [1,2] a phase transition into a solid phase with long ranged positional order. In this solid phase cylindrical shells are formed with triangular lattice structures in azimuthal direction. In Fig. 1 a meniscus shaped interface in the solid phase is shown for a pore with radius $5\sigma$ in a NVT-ensemble simulation.

The meniscus curvature decreases with the temperature...
in the solid as well as in the fluid phase. The triple point temperature is influenced by the geometrical finite size effects (pore radius) as well as by the wall-particle interaction. Increasing interaction strength results in an increasing freezing temperature. Only a small radius effect on the triple point temperature was detected. The geometrical finite size effect of the pore radius results in a packing effect with preferential occupancy of sites at the pore axis for pores with diameters $3.75\,\sigma$ and $4.75\,\sigma$, whereas for diameters of $3.25\,\sigma$ and $4.25\,\sigma$ the density at the axis is reduced. Beyond these results a two step phase transition from the fluid to the solid phase was found in agreement with results obtained in experimental studies of specific heat capacities at the freezing of Ar in Vycor [11].

By path integral Monte Carlo simulations [6-9] the effect of the quantum mechanics on the potential energy as a function of the temperature has been quantified [1,2]. In contrast to classical simulations we obtain by PIMC simulations for Ar- and Ne-condensates an horizontal temperature dependency of the energy resulting in a decrease of the specific heat to zero at small temperatures in agreement with the third law of thermodynamics. The resulting phase diagram for Ar- and Ne-condensates and a comparison with classical computations is shown in Fig. 2. In the Ne-system (containing the lighter particles) a significant reduction (by about 5-10\%) of the critical temperature is found due to quantum delocalizations as well as a strong reduction of the solid density and a crystal structure modification in comparison with the classical case.

Corresponding PIMC studies for N$_2$- and CO-pore condensates [1,2] reveal an interesting and rich phase behavior resulting from the interplay of rotational and translational degrees of freedom. Besides structural transitions the systems show phase transitions where the orientational degrees of freedom “freeze”. First studies show that at low temperatures interesting solid structures appear, in which particles locally have FCC- or HCP-neighborhood. Dark: HCP-type neighborhood. Particles, which cannot assigned be to any symmetry, are not shown (border particles). Top: a FCC-cell taken from the CO-pore condensate.

Figure 2: Phase diagrams of (classical) Ar and Ne in cylindrical pores (radius $3.5\,\sigma$, length $60\,\sigma$, $N=650$). Comparison of PIMC and classical MC. Lines: quadratical fits through the data ($T^* > 0.6$) for $m^*=100$, $P=64$ and the classical case.

Figure 3: Solid CO- (left) and N$_2$- pore condensate in a hard $R = 14$ Å-pore at 2 K. Light: Particles with FCC-type neighborhood. Dark: HCP-type neighborhood. Particles, which cannot assigned be to any symmetry, are not shown (border particles). Top: a FCC-cell taken from the CO-pore condensate.

References:
C2 Phase transitions of colloidal systems in the presence of square pinning arrays

K. Mangold, P. Leiderer, C. Bechinger

Properties of two-dimensional (2D) systems are well known to be crucially affected by the presence of periodic substrate pinning sites. One intriguing example are type II superconductors in the mixed state where vortices are arranged in a flux-line lattice. In the case of regularly ordered substrate pinning sites, strong anomalies in the temperature and magnetic-field dependencies of the magnetization, electrical resistance, and critical current are observed [1,2]. Several groups investigated recently the melting behavior of such vortex lattices in square, triangular and kagomé pinning lattices by means of molecular dynamics and Langevin dynamics simulations [3] [4]. For weak pinning and matching field conditions, on square lattices, an order-order transition from a commensurate square vortex array to a triangular floating solid phase was observed. In contrast, for strong pinning, only a single transition from the square pinned lattice to the liquid state was found.

Here we investigate the phase behavior of a colloidal monolayer of super paramagnetic particles on a square patterned substrate potential, the latter being produced by a holographic optical tweezer technique [5]. We used aqueous suspensions of superparamagnetic colloidal particles with 4.55 μm diameter which were filled into cell which have been divided into several compartments with an area of about 0.14 mm² each. In the presence of an external magnetic field B, which was applied perpendicular to the sample plane, a magnetic moment M(B) was induced in the particles, which lead to a repulsive magnetic dipole interaction V_{ij} = \mu_i (M(B) \cdot \vec{r}_{ij}) / 4\pi r_{ij}^3, where r_{ij} denotes the distance between particle i and j [6,7] and M(B) is described by the Langevin function. For convenience we introduce a dimensionless plasma parameter \( \Gamma = V_{\text{mag}} / k_B T = (\mu_i M^2(\pi p)^2)/(4\pi k_B T) \), where p is the particle number density and k_B T the thermal energy of the suspension (T=295 K).

The holographic image consisted of a square array of 9 x 9 about Gaussian light dots which differed in intensity only by a few percent (Fig. 1a). The colloidal spheres were imaged with an inverted video microscope onto a CCD-camera, and the particle positions were determined online with a rate of 0.1 Hz and a lateral accuracy of 100 nm. From these data we obtained particle trajectories, averaged particle densities and pair correlation functions.

First, we investigated the effect of decreasing interparticle potential (i.e. plasma parameter \( \Gamma \)) at constant pinning strength \( V_0 = 4.9 k_B T \). The particle density in the sample cell was kept constant and corresponded to about 4 particles per pinning site, i.e. a filling factor \( m \approx 4 \). We measured the particle trajectories over about 3 hours and determined the averaged local particle density around a pinning site. Both quantities are plotted in Figs.2a-f as the left and right column, respectively.

At the highest magnetic fields (\( \Gamma = 65.3 \)) used in this work, the colloidal interaction energy considerably exceeded the influence of the substrate pinning sites. Therefore, the structure of the 2D colloidal system should be dominated by inter colloidal forces, i.e. a triangular lattice (in the absence of pinning sites crystallization takes place above \( \Gamma = 56.5 \) [8]). This is in good agreement with Fig.2a where a triangular pattern is observed. A closer analysis, however, yields small deviations from an ideal triangular lattice by about 6% (regarding the length of the lattice vectors) which are due to the influence of the substrate pinning sites. While the colloidal pair potential favors a triangular lattice, as many as possible substrate pinning sites have to be occupied with a particle in order to minimize the free energy of the whole system. As shown in Figs.2ab the system responds by the alignment of a lattice vector of the colloidal crystal along one of the lattice vectors of the pinning array. While the periodicity of the substrate lattice is commensurate with the particle spacing in horizontal direction in Fig.2a, there is a lattice mismatch in vertical direction. On average only each second row of pinning sites is occupied with particles. Obviously, the interaction energy between the colloidal particles is too high, to allow the system to lock to the periodicity of the substrate potential and a floating or incommensurate solid is formed [9].

At \( \Gamma = 37.6 \), the elasticity of the colloidal system increases and allows its geometry to accommodate to that of the substrate lattice. As shown in Figs.2c,d all the pinning sites are now occupied with a particle, i.e. the monolayer partially adopts the square symmetry of the substrate. The interstitial particles in this registered commensurate solid phase are arranged in a lattice with rhombic symmetry. This phase is in perfect agreement with numerical calculations of the trajectories of a vortex lattice in the mixed state of type II superconductors in square periodic pinning arrays as found by Reichhardt et al. [3].

Further decrease of the particle interaction (\( \Gamma = 362 \)) leads to melting of the interstitial particles while the particles at the pinning sites are still highly localized (Figs. 2e, f). The trajectories of the interstitial particles are constrained to a square-like grid which exclude the region around the pinning sites. This is due to the repul-
sive dipole-interaction of the particles. Similar to the commensurate solid, this coexistence of a solid and a liquid phase has also been reported for vortex melting in periodic pinning arrays [3]. When both the strength of the particle interaction and the substrate pinning were further decreased ($\Gamma=23.5$, $V_0=1.5$), the particles at the pinning sites also become mobile and the entire lattice is in a liquid state as shown in Figs. 2g,h.

Finally, we also investigated the colloidal structure for different filling factors $m$. Fig. 4a shows the averaged local density of the commensurate crystalline phase for $m \approx 2$, $V_0=9.5$ kBT, and $\Gamma=35$. The interstitial colloidal particles are localized in the center regions between the lattice sites, and the colloids form a centered (1 x 1) super lattice on the substrate. For $m=5.5$ the averaged local particle density of the interstitial particles is plotted for $V_0=6.4$ kBT and $\Gamma=44.4$ in Fig. 4b. In contrast to Fig. 4a, the particle density is almost zero at those positions where the interstitial particles were localized in Fig. 4a. Now, the colloids are arranged in a square-like geometry around these depletion zones. Because $m=5.5$ deviates slightly from perfect matching conditions, i.e. $m=5$, the localization of the interstitial particles is less pronounced and defect particles can diffuse along a square-like network across the sample.

Due to competing interplay of interparticle forces which favor a triangular symmetry of the colloids and the square substrate geometry, a rich phase behavior with incommensurate, commensurate and liquid structures is observed. Our results are in excellent agreement with recent numerical studies on vortex melting in periodic pinning arrays and thus underline the validity of colloidal suspensions as versatile model systems.

![Fig. 2: Contour-plots of averaged particle densities of crystalline structures for filling factors (a) $m=2$ and (b) $m=5.5$. The pinning sites are marked with open circles. The axis tics correspond to 10$\mu$m [5].](image)

Fig. 1: Particle trajectories and contour-plots for averaged local particle densities for $m \approx 4$ at different $\Gamma$ and $V_0$ (in units of kBT), respectively. (ab) $\Gamma=65.3$, $V_0=4.9$, (cd) $\Gamma=37.6$, $V_0=4.9$, (ef) $\Gamma=36.2$, $V_0=4.9$, (gh) $\Gamma=23.5$, $V_0=1.5$. The pinning sites are marked with open circles. The axis tics correspond to 10$\mu$m [5].

To summarize, we have experimentally investigated the phase behavior of 2D colloidal suspensions in the presence of periodic pinning arrays with square symmetry.

C3 Phase transitions and quantum effects of two-dimensional model colloids in external fields

W. Strepp, M. Lohrer, S. Sengupta, P. Nielaba

Hard and soft disks in external periodic potentials show rich phase diagrams with freezing and melting phase transitions when the density of the system is varied [1]. In a NIC/HLRS project large scale Monte Carlo simulations have been done in order to determine the phase diagram by detailed finite-size-scaling analyses of different thermodynamic quantities like the order parameter, its cumulants and other quantities for various values of the density and amplitude of the external potential [2-7].

We have investigated [2,4] the phase behavior of a two-dimensional hard disk system in an external potential. In addition to the pair interaction a particle with coordinates $(x, y)$ is exposed to an external periodic potential of the form: $V(x, y) = V_0 \sin(2\pi x/d_0)$. The constant $d_0$ is chosen such that, for a density $\rho = N/S_x S_y$, the modulation is commensurate to a triangular lattice of hard disks with nearest neighbor distance $a_x$: $d_0 = a_x \sqrt{3}/2$. The only parameters which define our system are the reduced density $\rho^* = \rho^* / V_0^{*}$ and the reduced potential strength $V_0^{*}/k_B T = V_0^{*}$, where $k_B$ is the Boltzmann constant and $T$ is the temperature. Within our range of densities, one has a clear signature of a re-entrant liquid phase showing that this phenomenon is indeed a general one as indicated in Ref. [8]. We have determined phase transition points by the order parameter cumulant intersection method [9] applied to the order parameter $\psi_{G_1} := \left| \sum_{j=1}^{N} \exp(-i\mathbf{G}_1 \cdot \mathbf{r}_j) \right|$, where $\mathbf{r}_j$ is the position vector of the $j$th particle, $\mathbf{G}_1$ is the vector pointing to the next nearest neighbor (at an angle of $\pi/3$ to the $x$-axis), $|\mathbf{G}_1| = 2\pi / d_0$.

In order to analyze the influence of the pair potential range on the reentrance additional MC-studies [6,7] have been performed for the $1/r^{12}$, $1/r^6$- and the DLVO-potential [5]. For the short ranged $1/r^{12}$- potential [3] and the DLVO- potential [2] good evidence for a reentrance has been found, the phase diagram for an $1/r^{12}$- pair potential is shown in Fig. 1. With increasing interaction range the effect of “one-dimensional” reentrant melting is less pronounced since more and more neighbors have to be passed by a particle in order to leave its lattice site. This results in a stabilization of the solid relative to the modulated liquid at large $V_0^{*}$- values and in a much less pronounced increase of the transition density for large $V_0^{*}$- values in case of the $1/r^6$- potential [3], the data however are still compatible with a reentrance scenario.

The phase diagram for the DLVO-system [2] is shown in Fig. 2, a pronounced reentrance region can be identified again.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Phase diagram for the system with an $1/r^{12}$- pair interaction (cutoff at $r = 2$) in the $\rho^*/V_0^{*}$- plane. Transition points for transitions from the solid to the modulated liquid have been obtained by the order parameter cumulant intersection method. The system size is $N = 1024$ (except for $V_0^{*} = 2.5, 5$ and 7, for which $N = 400$).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{Phase diagram in the DLVO- system in an external periodic potential with amplitude $V^* = V_0 / k_B T$. Symbols: MC-data of the $\psi_{G_1}$ order parameter cumulant intersection points at the transition from the solid to the fluid phase, $\kappa$: inverse Debye-screening length.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{Schematic picture of the effect of an external periodic potential of the form $V(x, y) = V_0 \sin(\pi / a)$ on the “effective” diameter of quantum hard disks.}
\end{figure}

Our simulation thus have shown, that systems with DLVO- or “soft disk” interaction behave similar to charge stabilized colloids [1].
We have analyzed the scaling behavior of the order parameter cumulant and the susceptibility, assuming both, critical and KTHNY- behavior. At high $V^*$ the scaling plots apparently are slightly more consistent with the KTHNY-scenario [8].

Besides these classical studies we explore the validity of our results on atomic length scales. In this context we were able to investigate [2] the properties of quantum hard disks with a finite particle mass $m$ and interaction diameter $\sigma$ in an external periodic potential by path integral Monte Carlo simulations (PIMC [11-14]). Due to the quantum delocalization effect a larger effective particle diameter results, and in the external potential this delocalization is asymmetrical: in the direction perpendicular to the potential valleys we obtain a stronger particle localization than parallel to the valleys, s. Fig. 3. As a result the reentrance region in the phase diagram is significantly modified in comparison to the classical case, s. Fig. 4.

Due to the larger quantum “diameter” the transition densities at small potential amplitudes are reduced in comparison to the classical values. At large amplitudes the classical and quantum transition densities merge. This effect is due to the approach of the effective quantum disk size to the classical value in the direction perpendicular to the potential valleys and leads to the surprising prediction, that the quantum crystal in a certain density region has a direct transition to the phase of the modulated liquid by an increase of the potential amplitude. This scenario is not known in the classical case. We plan to explore this interesting topic for systems with different particle masses by PIMC studies and finite-size-scaling methods.

Besides this we plan to analyze the order of the phase transition at high potential amplitudes by an application of our new method for the computation of elastic constants. The influence of a potential with higher symmetry shall be explored as well as the effect of the potential amplitude on the Bose condensation in case of systems with Bose statistics.

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**Figure 4:** Phase diagram in the density ($\rho^* = \rho \sigma^2$)-potential amplitude ($V_0/k_B T$)-plane for a system with $N=400$ particles, $m^* = m T \sigma^2 = 10.000$ (“qm”) and $m^* = \infty$ (classical) and Trotter order $P = 64$.

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C4 Many-body forces between charged colloids

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Suspensions of charge-stabilized colloidal particles have long been understood in terms of the DLVO theory. This theory predicts that the effective interactions between a pair of charged colloids immersed in a simple electrolyte consists of the sum of (i) hard-core repulsions (ii) van-der-Waals attractions and (iii) screened-Coulomb (Yukawa) repulsions with the screening length given by the Debye length $\kappa^{-1}$ of the electrolyte. For relatively high charges and low salt concentrations the hard-core repulsion and the van der Waals attraction become unimportant. The remaining electrostatic interaction can be obtained by solving the Poisson Boltzmann equation

$$\nabla^2 \Phi(r) = \kappa^2 \sinh \Phi(r),$$

for the electrostatic potential $\Phi(r)$ with the appropriate boundary conditions on the charged surfaces of the colloidal particles and at infinity. Using $\Phi(r)$ one can calculate the grand potential $\Omega_N$ of the overall configuration of $N$ colloidal particles. One can decompose this uniquely into the so-called effective $n$-body potentials $\Omega^{(n)}$:

$$\Omega_N = N\Omega^{(1)} + \sum_{i<j} N\Omega^{(2)}(ij) + \sum_{i<j<k} \Omega^{(3)}(ijk) + \cdots.$$ 

These can be recursively determined since $\Omega^{(1)} = \Omega_4$ and $\Omega^{(2)} = \Omega_2 - 2\Omega^{(1)}$ and so on. While DLVO theory predicts only pair potentials, we were especially interested in higher order interaction terms, in particular, in three-body interaction potentials $\Omega^{(3)}$, restricting ourselves to limited sets of configurations (triangle-,mid-plane- and axial configuration).

Naively, one would expect the three-body potentials $\Omega^{(3)}$ for these configurations to have nothing in common. However, they show a surprisingly simple behavior. When plotted over the sum of the particle separations $L = r_{12} + r_{13} + r_{23}$, the three-body potentials for all three colloidal configurations collapse on one master curve, see Fig. 1. The line is a Yukawa-like potential $\propto -A^{(3)}e^{-\gamma L}/L$ with fit parameters $A^{(3)}$ and $\gamma$. This scaling behavior is most pronounced in solutions with a screening length larger than the particle diameter. For weakly charged colloids it breaks down which is no surprise because we are entering a regime where linearization of the PB equation is justified and where we do not expect any three body potentials at all. This scaling behavior enabled us to estimate the effect of many-body contributions on the phase behavior. There has been experimental evidence of a gas-liquid phase coexistence in charge stabilized colloidal suspensions. The standard van der Waals theory requires an attractive pair interaction for such a coexistence, while we have just repulsive pair interactions in our system. Still, the attractive triplet interaction might drive the phase-separation. We have extended the van der Waals theory taking triplet interactions into account and our calculations (see Fig. 2) indicate that for highly charged colloids (large $Z$) and low salt concentrations (large $\kappa^{-1}$), in principle, attractive three-body interactions can provide enough cohesive energy for a gas-liquid phase coexistence to take place.

Figure 1: Scaling behavior of the triplet interaction potential for relatively high charged colloids in a low salt solution. Scaled units as in [1].

Figure 2: Gas-liquid phase coexistence due to attractive triplet interactions in colloidal systems. For high charges $Z$ and high $\kappa^{-1}$ (states marked by crosses) a gas-liquid phase separation is possible. Circles stand for parameter sets where the triplet interaction is not strong enough for driving such a phase-separation.

C5 Investigation of three-body interactions in colloidal systems

M. Brünger, J. Dohnal, H.Hv. Grünberg, C. Bechinger

We typically treat interactions in a pairwise fashion, but this description is not always adequate. If the physical equations governing the interactions are non-linear, interactions between two particles can be modified by a close third or fourth particle. The total energy is then no longer described by summation of all pair-potentials but additional many-body interactions have to be considered. Physical examples, where many-body interactions are important, are abundant: nuclear structure and interactions [1], photo-ionization, adsorbate behavior on surfaces [2], and even noble gases which possess a closed-shell electronic structure [3,4]. In view of the general importance of many-body effects it seems surprising that until now no direct measurement of these interactions has been performed. This is largely because in atomic systems positional information is typically provided by structure factors or pair-correlation functions, i.e., in an integrated form. Direct measurements of many-body interactions, however, require direct positional information beyond the level of pair-correlations.

In contrast to atomic systems, length- and time-scales in colloidal systems are directly accessible with optical experiments and it is possible to obtain individual particle trajectories. Additionally, colloidal interactions can be tuned over a wide range, simply by changing the salt concentration (in contrast to atoms where interactions are unchangeably dictated by their electronic structure). At sufficiently small salt concentrations the interaction range can be several μm. If more than two colloids are within this range, a simple pairwise description breaks down and many-body interactions occur. Indeed, three-body effects have been found in recent computer simulations [5-7]. It was also demonstrated [8] [9], that the effective pair-potential of a colloidal liquid shows a density dependence which is a signature of many-body effects. Accordingly, colloidal suspensions represent an ideal model system for systematic investigations of many-body effects.

Here we present the first direct measurement of three-body interactions in a suspension of charged colloidal particles. As colloidal particles we used charge-stabilized silica spheres with 900nm diameter suspended in water. A highly diluted and deionized suspension was confined in a silica glass cuvette with 200μm spacing. As a trapping potential for the colloids we used line-scanned optical tweezers created by an Ar+ laser beam deflected by a galvanostatically driven mirror. The time averaged intensity distribution along the scanned line was chosen to be Gaussian distributed with the half-width σz = 4.5 μm. The laser intensity distribution perpendicular to the trap was also Gaussian with σr ≈ 0.5 μm. Due to the negatively charged silica substrate, the particles experience a repulsive vertical force balanced by the particle weight and the vertical component of the light force. The particles were imaged with a long-distance, high numerical aperture microscope objective onto a CCD camera.

We first determined the external potential acting on a single particle due to the optical line tweezers. A single particle was inserted into the trap where it diffused due to thermal fluctuations. The probability distribution \( P(x,y) \) was evaluated from the recorded positions. \( P(x,y) \) depends only on the temperature and the external potential created by the laser tweezers \( u_t(x,y) \) according to the Boltzmann probability distribution \( P(x,y) \propto e^{-\frac{u_t(x,y)}{k_B T}} \). Taking the logarithm yields the external potential \( u_t \) which is in good agreement with the gaussian light distribution.

Fig. 1: Measured \( U(r) \) (symbols) in the absence of the third particle. In the inset the potential is multiplied by \( r \) and plotted logarithmically.

Next, we inserted a second particle in the trap. The four-dimensional probability distribution is now \( P(x_1, y_1, x_2, y_2) = P_r e^{-u_t(x_1, y_1, x_2, y_2)/k_B T} U(r) \) with \( x_p, y_i \) being the position of the \( i \)-th particle relative to the laser potential minimum and \( U(r) \) the pair-interaction potential between the particles. Since it is reasonable to assume that the pair interaction depends only on the particle distance, we projected \( P(x_1, y_1, x_2, y_2) \) onto a one-dimensional distance distribution \( P(r) \). From the measured \( P(r) \) we obtained the total potential energy of the particles and after subtracting the external potential \( u_t \) we were left with the pair interaction potential \( U(r) \).

The pair-interaction potential of two charge-stabilized particles in the bulk is theoretically predicted to correspond to a Yukawa potential

\[
\beta U(r) = \beta u_{12}(r) = Z' \lambda_0 \frac{\exp(\kappa_1 r)}{1 + \kappa_1 r R} \frac{\exp(-\kappa_2 r)}{r} \tag{1}
\]

where \( Z' \) is the renormalized charge [10] of the particles, \( \lambda_0 \) the Bjerrum-length, \( \kappa_1 \) the Debye screening length, \( R \) the particle radius and \( r \) the center-center distance of the particles. Fig.1 shows the experimentally determined pair-potential (symbols) together with a fit
to Eq.(1) (solid line). As can be seen, our data are well described by Eq.(1).

Finally, we approached a third particle and localized it by means of an additional laser trap at distance \( d \) from the perpendicular bisector of the scanned laser line. From the distance distribution of the two particles in the laser trap, we can extract the total interaction energy which is now also dependent on \( d \). The total interaction energy in case of three particles should not simply be given by the sum of the pair-interaction potentials but will contain a three-body term. Following the definition of McMillan and Mayer, \( U(r_2,d) \) is given by [1]

\[
U(r_2)d = u_{12}(r_{12}) + u_{13}(r_{13}) + u_{23}(r_{23}) + u_{123}(r_{12},r_{13},r_{23})
\]

(2)

with \( u_{ij} \) being the pair-potential between particles \( i \) and \( j \) and \( u_{123} \) the three-body interaction potential. \( r_{12} \), \( r_{23} \) and \( r_{13} \) are the distances between the three particles which can - due to the chosen symmetric configuration - be expressed by the two variables \( r = r_{23} \) and \( d \).

Fig. 2: Experimentally determined interaction energy \( U(r) \) (symbols) for two particles in the presence of a third particle at distance \( d \). The superposition of three pair-potentials is plotted as lines.

The measured interaction energies \( U(r_2,d) \) are plotted as symbols in Fig.2 for several distances of the third particle. As expected, \( U(r_2,d) \) becomes larger as \( d \) decreases due to the additional repulsion between the two particles in the trap and the third particle. In order to test whether the interaction potential can be understood in terms of a pure superposition of pair-interactions, we first calculated \( U(r_2,d) \) according to Eq.(2) with \( u_{123} = 0 \). This was easily achieved because the positions of all three particles were determined during the experiment and the distance-dependent pair-potential is known from the two-particle measurement described above. The results are plotted as dashed lines in Fig.2. Considerable deviations from the experimental data can be observed, in particular at smaller \( d \). These deviations can only be explained, if we take three-body interactions into account. Obviously, at the largest distance, i.e. \( d = 4.1 \mu m \) our data are well described by a sum over pair-potentials which is not surprising, since the third particle cannot influence the interaction between the other two, if it is far enough from both.

![Fig. 3: Three-body potentials for different \( d \). Measured and calculated three-body potentials indicated by symbols and lines.](image)

According to Eq.(2) the three-body interaction potential is simply given by the difference between the measured \( U(r_2,d) \) and the sum of the pair-potentials. The results are plotted as symbols in Fig.3. It is seen, that \( u_{123} \) is entirely attractive and becomes stronger as the third particle is approached. The range of \( u_{123} \) is of the same order as the pair-interaction potentials.

To support our results, we also performed Poisson-Boltzmann (PB) calculations, in a similar way as in [7]. The results are plotted as lines in Fig. 3 and show reasonable agreement with the experimental data (in particular with respect to the range and size of \( u_{123} \)). This strongly supports our interpretation of the experimental results in terms of three-body interactions.

C6 Many-body interactions and the solid-liquid phase-behaviour of charge-stabilized colloidal suspensions

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For charged colloidal particles in suspensions, the well-known Derjaguin-Landau-Verwey-Overbeek (DLVO) pair-potential does not always provide a valid description of the intercolloidal interactions. This interaction depends on the density distribution of the ionic fluid between the colloids, which can be influenced by other colloids in the neighborhood of the interacting pair. Therefore, colloidal interactions in suspensions are in principle non-additive, that is, the total potential energy cannot be written as a sum of simple pair-interactions.

In a series of papers [1-3] we have been concerned with the general question how many-body forces affect the melting behavior of colloidal crystals. Starting from crystalline configurations, we computed the mean-square displacement of colloids about their lattice site and used Lindemann’s rule to estimate the solid-liquid phase-boundaries. The (PB-BD) simulation technique we used [4] combines a Poisson-Boltzmann (PB) field description for the microions with a Brownian dynamics (BD) simulation for the macroionic colloids, an approach which ensures that many-body interactions between the colloids are fully included.

Effective force calculations: In order to identify many-body effects we had to contrast the phase-diagram resulting from these simulations to the predictions based on the established description of colloidal suspensions in terms of pairwise Yukawa potentials. This requires a procedure by which we can map our original many-body non-linear system onto an effective linear pairwise additive Yukawa system. This was done by calculating effective pair-forces between colloids which are then fitted to Yukawa pair-potentials.

We considered a fixed configuration (either FCC or BCC) of $N$ colloidal spheres of radius $a$ inside a cubic box with periodic boundary conditions, solved the multi-centered PB equation to determine the electrostatic potential in the region between the colloidal spheres, and deduced the total force acting on each colloid by integrating the stress-tensor over a surface enclosing the respective particle. To numerically solve the PB equation we used $N$ spherical coordinate systems - centered on the colloids - together with a Cartesian system in the cubic simulation box. To derive effective forces, we considered the force $\mathcal{F}_{A,B}$ exerted by particle $A$ on particle $B$ which is obtained as the difference between the total force acting on particle $B$ with particle $A$ present, $\mathcal{F}_{B,A}^0$, and the total force acting on particle $B$, $\mathcal{F}_{B}^0$, after removing particle $A$ while leaving all other particles at their positions. Varying the position of particle $A$ results in the effective force curve $\mathcal{F}_{A,B}(r) = \mathcal{F}_{B,A}^0(r) - \mathcal{F}_{B}^0$. With this procedure, many-body interactions, if present, are folded into an effective pair-force curve.

Typical effective force curves resulting from this procedure are presented in Fig. (1). We observe a perfect Yukawa-like behavior at small distances, but systematic deviations starting around the mean distance $d_{m} = \rho^{-1/3}$ and developing into a cut-off at distances $r > 2d_m$. The force curves are compared to the predictions of DLVO theory, for different salt concentrations: the cut-off feature, observable under low salt conditions, vanishes at high ionic strength ($\kappa a = 2.0$) where perfect agreement with the predictions of DLVO theory is observed at all probed distances. We also found a systematic configuration dependence of the effective forces, being quite small at high ionic strength ($\kappa a = 2.0$), but becoming appreciable on reducing the salt concentration to $\kappa a = 0.2$. If the interactions in the system were pairwise additive, the resulting effective interaction would by construction be identical to the presupposed pairwise interaction potential, no matter how the surrounding particles (all particles but A and B) are arranged. Together with the cut-off feature, the configuration dependence of the effective interaction is a clear fingerprint of many-body interactions.

![Effective colloid-colloid force](Figure 1: Effective colloid-colloid force $f(r)$ between two out of $N = 108$ macroions arranged in a FCC configuration at a volume fraction $\eta = 0.03$ and for different salt concentrations ($\kappa a = 0.1, 0.2, 0.5, 1.0, 2.0$, from bottom to top). The calculated forces $f(r)$ are plotted such that a Yukawa pair-force following the DLVO theory appears as a straight line with the slope $-1$ (solid line). Systematic deviations from Yukawa-like behavior become visible for $\kappa a < 1.0$ which are due to many-body interactions. The curves $\kappa a = 0.1$ and $\kappa a = 0.2$ fall on top of each other (colloidal charge $Z = 1000$, Bjerrum length $\lambda_B/a = 0.012$).]
becoming important in low-salt colloidal systems.

Phase diagram of charge-stabilized colloids: Guided by this finding, we proposed to model the effective pair-force between colloids in suspensions by

\[
 f(r) = -\frac{du(r)}{dr} = \begin{cases} 
  U_0 e^{-\lambda r/d_m} / (r/d_m) & r \leq r_c \\
  0 & r > r_c 
\end{cases} 
\]  

(1)

with a prefactor \( U_0 \), a screening constant \( \lambda \) and a density-dependent cut-off \( r_c \propto d_m = \rho^{-1/3} \). Through this density-dependent cut-off the many-body interactions are included (to some extent, at least) in the pair-potential. Using this model potential, we carried out MD simulations and determined the solid-liquid phase-boundary by the Lindemann melting criterion, computing the rms displacement for various combinations of \( U_0 \) and \( \lambda \) in FCC and BCC crystals and for cut-offs directly behind the first, second, third neighbor shell. For a system of point-like Yukawa particles, interacting via \( u(r) = U_0 e^{-\lambda r/d_m} / (r/d_m) \), Robbins, Kremer and Grest (RKG) [5] determined the melting line (solid line in Fig. (2)). For \( r_c = 3.0 d_m \) (the cut-off used in [5] for numerical reasons), we could reproduce the RKG melting line using the pair-force in eq. (1). Decreasing then the cut-off, we observed systematic deviations from the RKG melting line occurring first at small values of \( \lambda \). The dashed lines in Fig. (2) are the melting line obtained choosing \( r_c = 1.35 d_m \) (\( r_c = 1.50 d_m \)) in a FCC (BCC) configuration. Such phase behavior of the simple model system (eq. (1)) is compared to the results of a full PB-BD simulation (symbols in Fig. (2)). It shows good agreement with RKG if obtained under high-salt conditions \( \kappa a = 2.0 \), \( (\lambda \approx 10) \), which is consistent with our finding that at high salt neither a cut-off behavior nor a configuration-dependence of the pair-potential could be observed. Obviously, in this salt regime the colloidal suspension can be represented quite well by a Yukawa system. However, reducing the amount of salt, i.e., decreasing \( \lambda \), we observe pronounced deviations from the RKG line. Again, this matches with the behavior of the calculated effective force curves at low salt, showing a configuration dependence but also the cut-off feature. Evidently, at low ionic strength the colloidal suspension can no longer be represented by a simple Yukawa system. The interactions are not pair-wise anymore, and many-body interactions have to be included. One possibility to do so is to use density-dependent pair-potentials, obtained for example from effective force calculations. The good agreement between our full PB-BD simulation results and the truncated (and density-dependent) Yukawa results shows how well this works and that it is indeed the many-body interactions that are responsible for the observed differences in Fig. (2) between the RKG and our melting line.

C 7 Tailored colloidal particles for photonic applications

S. Eiden, J. Widoniak, B. Lindlar and G. Maret

Mesoscale spheres of ceramic materials have recently attracted much interest. It has been shown that the structure, size and composition of these particles could be altered in a controllable way to tailor their optical, electrical, thermal, mechanical, electro-optical, magnetic, and catalytic properties over a broad range [1]. In the following the synthesis of monodisperse particles of titania, mesoporous silica and magnetic PMMA is described.

1. Monodisperse spherical TiO$_2$ particles were prepared by controlled hydrolysis of titanium tetraethoxide in ethanol. Ethanol was mixed with 0.1 M salt or polymer solution and furthermore with titanium tetraethoxide at ambient temperature using a magnetic stirrer. After a few seconds or minutes, depending on the concentration, precipitation occurred and homogene-neous TiO$_2$ beads were formed. After two hours the reaction was finished and the spheres were filtered and washed with ethanol. Raster electron micrographs (Fig.1) of the TiO$_2$ particles illustrated the perfectly uni-form spherical shape. The size and the size distribution was affected in a rather sensitive way by the concentration of water and salt or polymer. The X-ray powder diffraction pattern showed that the obtained TiO$_2$ phase was amorphous. Thermal analysis, $^1$H MAS NMR, IR- and X-ray absorption spectroscopy were carried out to determine the local structure. Thermal analysis clearly demonstrated the release of two water molecules per unit cell, i.e. the amorphous phase contains water molecules and/or hydroxide ions.

The presence of hydroxide was not evidenced by IR-spectroscopy, but the $^1$H MAS NMR spectra clearly showed two signals, according to hydrogen atoms of the hydroxide and of the water species. So the analytical techniques suggest the idealized chemical composition TiO$_{1.95}$(OH)$_{0.3}$(H$_2$O)$_{0.9}$. The particles can be sintered at 1000 °C, so that rutile particles were obtained which are very interesting for different applications because of their high refractive index.

2. The monodisperse mesoporous silica particles were synthesized via a seeded growth process. The silica seeds of 400 nm diameter were produced according the original Stöber process. The 100 ml seed suspension, containing 2.5 g silica, was gently stirred in a flask while 33 ml TEOS premixed with 41 ml Ethanol and 6 ml surfactant on one side and 16 ml water/ 5 ml 29 % ammonia/ 60 ml Ethanol on the other side was added. The rate of addition could be adjusted by two peristaltic pumps and was set in this case to 4 ml/h. It was important to avoid any hydrolysis and condensation reaction in TEOS/ethanol drops by nitrogen flow before they reached the seed suspension. After around 3 days the addition of reactants was finished and the reaction solution was centrifuged several times to remove the ammonia and at last to remove the ethanol. After drying the particles at 100 °C they were calcinated at 600 °C to remove the surfactant. In a second step the dye Fluorescein isothiocyanate was imbedded. The synthesis of the fluorescent mesoporous silica colloids yielded particles with a highly monodisperse size distribution as illustrated by confocal microscopy (Fig. 2). Depending on the seed size and on the time of addition of reactants the size of the particles can be varied between 300 and 1000 nanometers.

3. Based on the work of J. Ughelstad [2] we obtained magnetic particles with different sizes and magnetic properties. The synthesis of tailored magnetic polymer colloids of 400 – 800 nm required several steps, i.e. the synthesis of the parent methyl/glycidyl methacrylate copolymer particles, their chemical modification with ethylenediamine in order to obtain internal anchor groups, and the final generation of super paramagnetic magnetite nanoparticles by impregnation and subsequent hydrolyzation of Fe$^{2+}$ and Fe$^{3+}$ chlorides inside the methacrylate matrix. The magnetic particles were exactly characterized by several methods: EDX, TEM, SQUID and XANES measurements.

In summary, we have demonstrated three different synthesis routes for the fabrication of tailored colloidal particles. These particles have well-defined sizes and composition which can be changed in a controllable way to tailor their optical or magnetic properties. These spheres can be used as buildings block of photonic crystals, too.

C8 Interaction and flocculation of spherical colloids wetted by a surface-induced corona of paranematic order

H. Stark

In recent years the dispersion of colloidal particles in a nematic liquid crystal emerged as a novel type of soft matter with interesting properties [1]. A nematic liquid crystal consists of rodlike organic molecules which align approximately parallel to a common axis called director pointing along the unit vector \( \mathbf{n} \). In this report, we will concentrate on the new features which arise when the nematic liquid crystal is kept above but close to the nematic-isotropic phase transition at temperature \( T_c \).

Then every colloidal particle is surrounded by a surface-induced nematic wetting layer. In the easiest approximation, we describe it by the reduced Landau-de Gennes free energy in harmonic and one-constant approximation

\[
F[\mathbf{Q}(\mathbf{r})] = \int \left[ Q_{ij}^2 + (\nabla_k Q_{ij})^2 \right] d^3r + \frac{1}{\gamma} \int (Q_{ij} - Q_{ij}^{(0)})^2 d^3r ,
\]

(1)

where \( \mathbf{Q}(\mathbf{r}) \) is the symmetric and traceless alignment tensor of second rank. It quantifies both the preferred axis and the degree of orientational order. All lengths are in units of the nematic coherence length \( \xi_N = \sqrt{L/\alpha_0(T - T^*)} \) \( (L \) is an elastic constant, \( \alpha_0(T - T^*) \) is the Landau coefficient of the second-order term, and \( T^* < T_c \) is the temperature where the isotropic phase becomes unstable). The second term describes the coupling of the orientational order to the surface of the particle with the strength \( \gamma \). The free energy is given in units of \( \gamma L \xi_N/2 \).

To describe the nematic wetting layer of one particle with radius \( R \) [2], we choose, in accordance with the boundary conditions and the symmetry of the system, a uniaxial order parameter

\[
Q_{ij} = \frac{3}{2} S (n_i n_j - \frac{1}{3} \delta_{ij}) ,
\]

(2)

where the director \( \mathbf{n} \) points along the radial direction and the scalar order parameter \( S \) quantifies the degree of orientational order. From Eq. (1), we derive the Euler-Lagrange equations in the bulk and at the surface whose solution reads

\[
S(r) = S_0 A^{-1} \left( R, \gamma \right) \exp \left[ -\frac{(r - R)}{r} \right] \left( 1 + \frac{3}{r} + \frac{3}{r^2} \right) ,
\]

(3)

with the factor

\[
A(R, \gamma) = \frac{\gamma + 1}{R} + \frac{4\gamma + 3}{R^2} + \frac{9\gamma + 3}{R^3} + \frac{9\gamma}{R^4} .
\]

(4)

The wetting layer is given by an exponentially decaying scalar order parameter on a length scale \( \xi_N \). We note that the electric double-layer around a charged particle also follows from a variational approach with the same type of a bulk free energy as in Eq. (1) but with \( Q(\mathbf{r}) \) and \( \xi_N \) replaced, respectively, by the scalar field \( \Phi(\mathbf{r}) \) of the electrostatic potential and the Debye screening length \( \kappa^{-1} \). The surface free energy is replaced by \( 2\sigma \int \Phi d^2r \)

where \( \sigma \) is a reduced surface charge density.

The two-particle interaction [2] is calculated in analogy to the Debye-Hückel approximation for electrostatically stabilized colloids [3]. We approximate the alignment tensor field around two particles by a linear superposition of the two one-particle solutions \( \mathbf{Q}^{(i)}(\mathbf{r}) \) centered on particles 1 and 2,

\[
\mathbf{Q}(\mathbf{r}) = \mathbf{Q}^{(1)}(\mathbf{r}) + \mathbf{Q}^{(2)}(\mathbf{r}) .
\]

(5)

The field \( \mathbf{Q}(\mathbf{r}) \) solves the bulk Euler-Lagrange equation. The boundary condition, however, is satisfactorily fulfilled only in the limit of distance to contacts \( d > 2R \gg 1 \) since then, e.g., \( \mathbf{Q}^{(1)}(\mathbf{r}) \) has nearly decayed to zero at the location of particle 2. As usual, the interaction energy is defined by

\[
U_{LC} = F[\mathbf{Q}^{(1)}(\mathbf{r}) + \mathbf{Q}^{(2)}(\mathbf{r})] - 2F_S[\mathbf{Q}^{(i)}(\mathbf{r})] ,
\]

(6)

where \( F_S \) denotes the self energy of one particle. It can be transformed to a surface integral over the midplane \( M \) between the two particles plus a negligible second term:

\[
U_{LC} \approx -4 \int_M Q_{ij}^{(1)} \mathbf{\hat{v}} \cdot \nabla Q_{ij}^{(1)} d^2r ,
\]

(7)

where \( \mathbf{\hat{v}} \) is a unit vector normal to \( M \) and pointing towards sphere 1. For particle radii much larger than \( \xi_N \), which implies that the particle separations \( d \gg 1 \), the interaction energy is strongly attractive and of Yukawa type:

\[
\frac{U_{LC}}{12\pi} \approx -\left( \frac{S_0}{A} \right)^2 \exp \left[ -\frac{(d - 2R)}{d} \right] .
\]

(8)

The result agrees with an alternative derivation based on an expansion of the two-particle field \( \mathbf{Q}(\mathbf{r}) \) into spherical harmonics [4,5]. Furthermore, numerical calculations show that it very well approximates the two-particle potential down to distances of contact of the order of \( \xi_N \). It has recently been measured in experiments [6].

The fact that the range of \( U_{LC} \) (given by \( \xi_N \)) and its strength \( A^{-2} \) are easily tunable by temperature has inspired us to study a flocculation transition mediated by \( U_{LC} \) close to the nematic-isotropic phase transition in an...
Figure 1: Flocculation diagram in terms of the tunable parameters of the electrostatic interaction, i.e., the surface charge density $q_s$ and the Debye length $\kappa^{-1}$. The four different regions I-IV characterize how a colloidal dispersion of charged particles reacts on $U_{LC}$.

electrostatically stabilized colloidal dispersion [7]. The surface charge of the colloids, given by the density $q_s$, is screened by counterions with concentration $n_p$ in the host fluid, giving rise to the electric double layer. Its thickness is determined by the Debye length $\lambda_D$, where $\varepsilon$ denotes the dielectric constant of the solvent and $e$ is the fundamental charge.

The two-particle potential in the Derjaguin approximation under the assumption of $q_s \ll \kappa^{-1}$ is then [3]

$$U_E = -\frac{8\pi^2}{\varepsilon_2} \frac{Rq_s^2}{\kappa^2} \ln \left(1 - e^{-\kappa(d-2R)}\right). \quad (9)$$

We reexamined this flocculation transition [5]. To be concrete, we consider silica particles of radius $R = 250$ nm dispersed in the liquid crystal 8CB and also take into account the attractive van der Waals interaction [3]. In Fig. 1 we plot a flocculation diagram as a function of $\kappa^{-1}$ and $q_s$. We can distinguish between four regions: For small $\kappa^{-1}$ and $q_s$ (region I), the electrostatic stabilization is not sufficient to overcome the van der Waals forces. At large $\kappa^{-1}$ and $q_s$ (region II), $U_{LC}$ is too small to create a minimum at finite distances which would cause aggregation of the particles. In the intermediate regime (region III) such a minimum occurs when the temperature is lowered towards $T_c$. Especially Fig. 2(a) demonstrates that, for the parameters chosen, the flocculation transition occurs in a narrow temperature interval of 0.5 K. Finally, in region IV a potential minimum is still present [see Fig. 2(b)] but flocculation is hindered by a potential barrier; the dispersion is kinetically stabilized.

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C9 Non–linear rheology of colloidal suspensions

M. Fuchs and M. E. Cates,*

Soft materials, such as particle dispersions, exhibit a wide range of rheological properties. While dilute colloids flow with a viscosity only slightly higher than that of the solvent, concentrated dispersions behave as weak amorphous solids and elastically withstand (small) finite stresses. For intermediate concentrations, one generally observes, upon increasing the external shear rate, first, a strong decrease of the dispersion viscosity (‘shear thinning’), and then often a dramatic increase (‘shear thickening’). While shear induced crystallization of particle suspensions causes a marked decrease of the viscosity, shear thinning is not always accompanied by a flow–induced ordering, but appears connected more generally to a decrease of the Brownian contribution to the stress. In shear–thinning concentrated suspensions of polydisperse colloidal particles the structure remains amorphous during the application of shear. Therefore a mechanism explaining the reduction of the viscosity in disordered systems needs to be discovered.

For its theoretical description, the familiar framework of linear response theory cannot be used, because the effect of the external driving on the microstructure and its dynamics needs to be understood. In this project, thus a framework for the non–linear response of a colloidal dispersion to arbitrary shear rates is developed, which is then basis for approximation schemes to study specific mechanisms caused by shearing.

![Diagram](image)

Figure 1: Advection by steady shear of a fluctuation in \( x \)-direction with wavelength \( \lambda_x \) at time \( t = 0 \). Internal motion like particle diffusion is neglected. At later time \( t \), the wavelength \( \lambda_x \) in the gradient \( y \)-direction obeys: \( \lambda_x / \lambda_y = \Delta x / \Delta y = \gamma t \).

Fundamental starting point for the development of a non–linear response formalism under applied shear rate \( \gamma \) is the ‘Smoluchowski equation’ for the time–evolution of the many–body distribution function \( \Psi \) which depends on all particle coordinates \( r_i \):

\[
\frac{\partial}{\partial t} \Psi = \Omega^{(\gamma)} \Psi
\]

Here, \( N \) is the (large) number of particles, which interact with forces \( F_i \), and have diffusion coefficient \( D_0 \sim 1/\tau_{\infty} \) set by the solvent viscosity at infinity dilution. Simulations by Strating [1] show that Eq. 1 captures shear thinning in response to the imposed solvent flow, which points in \( x \)-direction, with constant gradient along the \( y \)-direction set by the shear rate \( \gamma \).

Projection operator techniques allow to derive general steady state quantities of the sheared system [2]. It is driven far from equilibrium because the shear–dependent term in Eq. 1 cannot be obtained from an external potential and thus stationary fluxes, which are absent in thermal equilibrium, can be shown to exist. Of interest is the transverse stress \( \sigma \), which can be obtained from the stationary average of the microscopic stress tensor element, \( \sigma = \langle \sigma_{xy} \rangle^{(\gamma)} \). It can be connected via an exact generalized Green–Kubo expression to the stress auto–correlation function averaged in the quiescent system \( \langle \ldots \rangle^{(0)} \) but with \( \gamma \)-dependent dynamics:

\[
\sigma = \frac{\gamma}{k_B T} \int_0^{\infty} dt \langle \sigma_{xy} e^{\Omega^{(\gamma)} t} \sigma_{xy} \rangle^{(0)},
\]

where the integrand defines a non–Newtonian shear modulus \( g(t, \gamma) \). Calculations of stress versus shear rate curves (called ‘flow curves’) can proceed from Eq. 2 either via exact calculations (as far limited to low densities) or via approximations building on the knowledge about the dynamics of the quiescent system. Because the viscosity, \( \eta = \sigma / \gamma \), at small shear is dominated by the slow dynamics in \( g(t, \gamma = 0) \), shear–thinning can be expected to originate in an acceleration of the dynamics in \( g(t, \gamma) \) reducing the integral in Eq. 2.

In Refs. [2,3], we argued that advection of wavevectors is the physical mechanism how shearing accelerates the structural dynamics in dense dispersions. Figure 1 shows that an arbitrary fluctuation with wavevector initially along the \( x \)-axis, \( \mathbf{q}_0(t = 0) = \frac{2\pi}{\lambda_x} \mathbf{e}_x \), obtains a growing component along the \( y \)-direction, \( \mathbf{q}_y(t) = q_y(0) \gamma t \). Brownian particle motion assisted by the interaction forces, will smear out and decorrelate the fluctuation at late times. Because the wavelength in the gradient direction \( \lambda_y(t) \) decreases with time under shear, smaller and smaller motions can cause the fluctuation to decay. Internal stresses thus relax more quickly and the viscosity shear–thins.

While this mechanism should be rather universal, at present it has only been worked out for dense colloidal
dispersions, because there the interesting question arises how it interferes with incipient solidification [2-4]. Mode coupling approximations are required and lead to closed non-linear equations describing the structural relaxation under shear. Figure 2 shows the non-Newtonian shear modulus for various distances to the density \( \phi_c \) where the unsheared system would undergo an idealized glass transition.

![Figure 2: Transient non-Newtonian shear modulus \( g(t, \dot{\gamma}) \) (in units of \( k_B T/\eta \)) of a model for colloidal hard spheres with diameter \( d \) for packing fractions close to solidification at \( \phi_c \) and for increasing shear rates \( \dot{\gamma}_0 \) as labeled; \( \dot{\gamma}_0 \) increases from right to left. The fluid lines (\( \varepsilon < 0 \)) for the 3 smallest \( \dot{\gamma}_0 \) overlap; from [3].](image)

Even though small shear rates are considered and the (bare) Peclet number \( \dot{\gamma}_0 = \gamma_0 d^3/\eta_0 \) (it compares \( \dot{\gamma} \) with the time it takes a particle at infinite dilution to diffuse its own diameter) is small, the final relaxation of the modulus is strongly accelerated by shear. For states which would be solid without shear, and where \( g(t,0) \) would decay to a (finite) elastic constant at long times, enforcing stationary shear leads to a finite relaxation time which is of the order of \( \dot{\gamma}^{-1} \) [2,3]. The solids are shear-melted, as stress fluctuations decay to zero with rate set by the external drive. The 'flow curves' in Fig. 3 of these melted states exhibit a 'yield stress', \( \sigma^+ = \lim_{\dot{\gamma} \to 0} \sigma(\dot{\gamma}, \varepsilon \geq 0) > 0 \). It gives the stress which needs to be overcome in order to retain the stationary shearing. A discontinuous transition from this solid-like yielding behavior (above the transition for \( \varepsilon \geq 0 \)), to dissipative fluid flow (for \( \varepsilon < 0 \)) with a finite Newtonian viscosity \( (\eta = \lim_{\dot{\gamma} \to 0} \sigma(\dot{\gamma}, \varepsilon < 0)/\dot{\gamma}) \) is obtained. In the fluid flow curves in Fig. 3, the Newtonian region (indicated by dashed lines), is followed by shear-thinning where the stress grows sub-linearly with shear rate, viz. the viscosity decreases. Interestingly, the solid requires a much larger power, \( \dot{E} = \sigma \dot{\gamma} \sim \dot{\gamma} \), to keep flowing than the fluid, where the power is dissipated \( (\dot{E} = \sigma \dot{\gamma} \sim \dot{\gamma}^2) \). Comparisons with computer simulations of Eq. 1 are possible for \( \dot{\gamma}_0 \ll 1 \), see Fig. 4, and support the universal predictions.

![Figure 3: Steady-state shear stress, \( \sigma = \langle \sigma_{yy} \rangle^{(s)} \), in units of \( k_B T/\eta \) versus Peclet number \( \dot{\gamma}_0 \) for a model of colloidal hard spheres at various distances from solidification, as labeled. The line labeled \( \gamma \eta_{pe} \) gives the contribution from the solvent. For the fluid cases, \( \varepsilon < 0 \), dashed lines mark Newtonian fluid behavior, \( \sigma \sim \dot{\gamma} \). Sublinear increase of \( \sigma(\dot{\gamma}) \) for larger \( \dot{\gamma} \) indicates shear thinning. For solid cases, \( \varepsilon \geq 0 \), a yield stress plateau exists for small \( \dot{\gamma} \). At the critical density, \( \phi_c \), a power-law, \( \sigma - \sigma^+ \sim \dot{\gamma}^m \) holds for \( \dot{\gamma}_0 \to 0 \) (thin line, exponent \( m = 0.15 \)) [3].](image)

![Figure 4: Steady-state viscosities (symbols) from Brownian dynamics simulations of hard spheres [1] versus Peclet number \( \dot{\gamma}_0 \) for packing fractions \( \phi \) as labeled. Fits by eye to the data for \( \phi \geq 0.50 \) with a model for colloidal hard spheres for varying separation parameters \( \varepsilon \) are given as solid lines, and lead to the estimate \( \phi_c = 0.59 \) [4].](image)

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C10 Elastic constants of a two-dimensional colloidal crystal near melting

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We describe a new method to determine the elastic constants of colloidal crystals and glasses which is based on controlled displacements of groups of particles using optical tweezers. We have studied 2D colloidal crystals of super-paramagnetic microspheres confined by gravity to the flat water-air interface. Under an external vertical magnetic field the particles arrange in a crystalline triangular phase because of repulsive dipole-dipole interaction. One triangle formed by three neighboring spheres is rotated, or stretched, respectively, by the threefold optical tweezer and the corresponding structural relaxations after switching off the tweezer are analyzed using video-microscopy. The relaxation times obtained are directly related to the shear modulus $\mu$, and elastic modulus $K + \mu$, respectively, of the crystal.

Since the pioneering work of Kosterlitz and Thouless [1] (KT) the melting transition in two dimensions (2D) is a fascinating field of research. Halperin, Nelson and Young [2,3] expanded KT to the so called KTHNY theory which suggests that a 2D crystal melts in two continuous (second order) steps, first into a hexatic phase which, in turn, transits into the isotropic liquid at slightly higher temperature. Both transitions are mediated by dissociation of pairwise creation of topological defects. The theory predicts, amongst other quantities, the temperature dependent behaviour of the elastic constants [5]. Despite of many experiments and simulations on various 2D-systems there is still no clear-cut answer about the universality of KTHNY melting which may, or may not, be preempted by a first order melting transition depending on the system parameters. In particular, the expected [4,5] softening of the 2D crystals near melting has not been observed directly.

We have described earlier [6] how the shear modulus of 2D magnetic colloidal crystals was measured by rotation of a triangle of neighboring particles off the lattice positions and subsequent observation, without tweezer, of the relaxation into equilibrium. Here we report additional data determining the bulk modulus of the 2D crystal from a radial stretch of the triangle. The 2D sample consisting of 4.7 $\mu$m diameter Dynal beads was observed by a CCD-camera through a (x 100) microscope objective which was also used to focus the beam of an Ar-laser (wavelength 514nm) onto the selected particles to be tweezed. A computer-controlled biaxial scanning galvano-mirror moves the tweezer in the sample plane to displace the particles in a well defined way. In order to measure $K + \mu$ three adjacent particles forming an equilateral triangle were displaced radially by 15% of the lattice constant $a$ as sketched in fig.1.

Figure 1: The labeled particles were displaced radially to stretch the 2D crystal locally.

The interparticle interaction strength $\Gamma$ is given by the dipole-dipole interaction compared to $k_B T$:

$$\Gamma = \frac{E_{\text{magn}}}{k_B T} = \frac{\mu_0 (\chi B)^2 (\rho \rho')^2}{k_B T},$$

$\rho$ is the 2D particle density and $\chi$ their susceptibility. $\Gamma$ is thus the effective inverse system temperature which is controlled over more than three orders of magnitude by variation of $B$.

Figure 2: Relaxation of the normalized displacement $u_r$ for $\Gamma = 334$ and three other crystal temperatures (inset).

Fig.2 shows a typical exponential relaxation curve of the particle’s displacements after switching off the tweezer. These data were obtained by averaging 346 measurements at $\Gamma = 334$ (which is deep inside the crystalline phase, melting occurs at $\Gamma_m = 60$). The dependence of the relaxation time $\tau$ upon $\Gamma$ shown in the inset illustrates that the crystal becomes more...
compressible with increasing temperature resulting in an increase of $\tau$.

From these measurements the bulk modulus was obtained by using a 2D elastic continuum model of a deformed circular disk embedded in an elastic membrane. Within this model the total energy of the deformed disk is related to the radial deformation amplitude $\Delta r^2$ by $E = 2\pi(K + \mu)\Delta r^2$ and hence the force driving the relaxation is $F_R = 4\pi(K + \mu)\Delta r$. Because the colloidal movement is totally overdamped due to the viscosity of the suspension we can equate $F_R$ with the Stokes friction of the displaced particles to obtain the time dependent particle relaxation:

$$F_S = 6\pi\eta R_P \sum_j \frac{\partial u_j(r)}{\partial t}$$

where $\eta$ denotes the viscosity of water, $R_P = 2.25\mu m$ is the particle radius and $j$ is an index running over all particles participating in the relaxation process. It turned out in the experiment that only 12 particles were displaced significantly i.e. beyond the thermal noise level. This leads to an exponential decay of the displacements, with a relaxation time $\tau = 11.76 \frac{K + \mu}{K + \mu}$. From the measurements of $K + \mu$, combined with the measurements of $\mu$ [6] we immediately obtain the coupling constant $K = \frac{4a^2}{\pi\gamma} \frac{\mu}{K + \mu}$. The temperature dependent behavior of the elastic moduli in the vicinity of $1/\Gamma_m$ as predicted by KTHNY gives $K(\Gamma) = \frac{16\pi C}{1-1+1/\Gamma_m}\Gamma^{-\nu}$. $C$ is a non-universal parameter which depends on the core energy $E_c$ of a dislocation, $\nu$ is a universal critical exponent. Deeper in the crystalline phase ($\Gamma \geq 100$) the coupling constant $K$ is proportional to $\Gamma$. The temperature dependence of the experimentally obtained values of $K$ is shown in fig.3 in comparison with the theory [5,6] and with measurements on the same system obtained from analysis of fluctuations of the strain tensor [7].

In the tweezer experiment no clear-cut softening (deviation from the linear $\Gamma$-dependence) can be observed within experimental accuracy. The data obtained from the fluctuation analysis are in agreement with the low temperature behaviour over the entire $\Gamma$-range explored, even close to $\Gamma_m$. This is expected since regions containing dislocations were excluded from the analysis in [7]. The data obtained by tweezing show significant deviations at high $\Gamma$. The origin of these deviations as well as the role of dislocations on $K$ in the tweezer technique remains to be explored.

In conclusion, measurements of elastic constants from local deformations of the 2D-lattice are in qualitative agreement with data based on a strain fluctuation analysis [7], but so far not reliable enough to observe the renormalization of the elastic constants predicted by KTHNY. We believe, however, that in contrast to ref.[7] the tweezer method is sensitive to renormalization because of the averaging of many sets of relaxation data including particle configurations containing dislocations.

Figure 3: The coupling constant $K$ plotted versus $\Gamma$. The solid line represents a fit of the KTHNY theory.

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C11 Novel glassy states in dispersions with short–ranged attractions

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Aggregation in a colloidal dispersion can be induced by adding a quite small amount of non–adsorbing polymer. For small polymer–colloid size ratios ξ it is known since the work of Asakura and Oosawa that the polymers induce a ‘depletion attraction’ between the colloidal particles. The equilibrium phase diagram of particles interacting with steric repulsion and a shorted–ranged depletion attraction is understood rather well. Yet, aggregation and vitrification prevent the system to reach thermal equilibrium in large areas of the phase diagram. Such metastable states are ubiquitous in colloidal dispersions, and often crucially determine their technological applica-
tion. Because of the good control of effective interactions in colloid–polymer mixtures, this mixture is thus an important model system for studying metastable states and aggregation phenomena.

The connection between the formation of glasses and aggregation to colloidal gels has recently become of interest and is studied in this project by theory, simulations and experiments. The specific question addressed concerns the conditions on the attractive part of the potential to cause aggregation. While in the classical Smoluchowski theory of coagulation, any two particles which come close are postulated to stick together because of strong dispersion forces, in the case of aggregation studied here, the strength of the (depletion) attraction is moderate and not much stronger than thermal fluctuations. Thus, the conditions on strength and range of the interaction need to be found, where ‘bond–formation’ between particles can take place [1]. The transition lines where long–lived bonds between particles become possible then form parts of the border of the regions in phase space where metastable colloidal gels are formed, and where thermal equilibrium may be approached on time scales too long to explore experimentally. At higher colloidal density (measured by the packing fraction φ), colloidal gels are also called ‘attraction driven glasses’ and their properties are dominated by rather local structural correlations. At lower packing fractions, bond–formation still is required for the existence of gels, but the buildup of long–ranged structural correlations is also required because the gels form open ramified networks.

At high packing fractions, inducing a short–ranged attraction by e.g. addition of polymers, has a counter–intuitive effect on metastable arrested states resulting from repulsions. As seen in Fig. 1, the attraction at first does not enhance the tendency of the system to form metastable states, quite on the contrary metastable ‘repulsion driven glasses’ are melted by a weak attraction. Adding polymers to state A, which is a glass of (slightly polydisperse) hard spheres, weakens the local ordering (it opens holes in the neighbor shells that cage particles), and at state B (which has almost the same packing fraction as A), structural relaxations have become fast enough, for the equilibrium state to be reached during the experiment [2]. Yet strengthening the attraction even further (states C, D and E), bond–formation between particles sets in and causes a strong slowdown of the particle rearrangements making it impossible for the sample to reach equilibrium for periods of weeks and longer.

Identification of the mechanism leading to metastable states at points C, D and E in Fig. 1 being ‘bond–formation’ can be made by simulations of the mean–squared displacements ⟨r²(t)⟩ of the particles [2,3]. For states close by where final decay into equilibrium is possible, Fig. 2 shows that pure repulsion causes a slowdown of ⟨r²(t)⟩ on length scales connected with the particle size. (The relevant length is the localization or ‘Lindemann–length’ which is found to be around 20% of the particle radius.) At first, a short ranged attraction speeds up ⟨r²(t)⟩ as discussed above for states A and B in Fig. 1, but then particles become progressively more trapped in potential wells, and the mean–squared dis-

Figure 1: Equilibrium and nonequilibrium behavior of a colloid–polymer mixture at ξ = 0.08; from [2]. Samples that reached thermal equilibrium are fluid (crosses), fluid–crystal coexistence (open squares), and fully crystalline (open inverted triangles); dashed–dotted lines sketch the equilibrium phase boundaries. Samples that did not reach thermal equilibrium are repulsion driven glass (full diamonds) and attraction driven glass (full triangles). Dashed curves are guides to the eye of the observed glass transition lines. Solid curves are the corresponding theoretical predictions.
Figure 2: Plots of mean squared displacements \( \langle r^2(t) \rangle \) in units of particle radius squared as function of time \( t \) from simulations at packing fraction \( \phi = 0.50 \) for increasing strengths of attraction as labeled; from [2]. The inset shows the dependence of the (normalized) single–particle long–time diffusion coefficient on attraction strength.

Figure 3: Normalized self–intermediate scattering functions at packing fraction \( \phi = 0.55 \) and polymer concentration relative to overlap \( c_p/c_p^* = 0.38 \) for various wavevectors; from [3]. Dotted lines give logarithmic fittings to the correlators in a time window around \( t_1 \) (marked by a vertical line).

Placement shows an incipient saturation (‘plateau’) at a distance connected to the range of attraction \( \xi(t) \); for even stronger attractions in the gel \( \langle r^2(t \to \infty) \rangle/R^2 \sim \xi^2 \).

Thus, studies of the equilibration behavior (Fig. 1) and observations of the dynamics (Fig. 2), identify caging and bond–formation as mechanisms causing metastable states as predicted by theory [1]. Quite intriguingly, a transition line separates both non–equilibrium ‘phases’ (making gel–to–glass transitions possible in principle), which ends in a special higher–order transition point. In the vicinity of the latter, anomalously slow dynamics, \( S_q(t) - F_q \sim \ln(t/t_1) \) had been predicted, which preliminary simulation results support, Fig. 3.

While at higher packing fractions bond–formation as described in the present theoretical framework (the idealized mode coupling theory) appears to be the rate–limiting step for gelation, at lower packing fractions (fractal) structure formation needs to be incorporated into the theoretical approach [4]. Figure 4 shows that various non–equilibrium processes are observed at low \( \phi \), and cannot be understood from considering one mechanism alone. Rather, the limit of equilibrium behavior, where fluid and fluid–crystal coexistence is found, differs from the (transient) gelation line, where solidification occurs. While the theoretical bond–formation line lies parallel to the gelation line for not too low packing fractions, it may also be connected to the cessation of crystallisation. Work on these questions is in progress, where the kinetics of structure formation is considered. Experimental and simulation studies could provide crucial information.

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C12 Local structural analysis of a binary 2d colloidal glass former: concept of local density-optimised crystallite-clusters

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A glass can be considered as a supercooled melt, forming a solid with a liquid-like structure and with frozen-in particle dynamics. Nevertheless, there are a lot of open questions regarding the physical properties of glass formers in the supercooled or glassy state as well as at the glass transition itself. Up to now no theory is available to explain all of the typical physical properties of glass formers which are characterized by averaged structural and dynamic functions.

In order to study the glass transition we investigated a very simple model system - a two-dimensional (2d) mixture of two kinds of different sized and repulsively interacting colloidal particles, dispersed in water. In a hanging droplet geometry the water-air interface was adjusted completely flat and perpendicular to the gravitational field. At room temperature, $T$, the colloids gathered on the water-air interface due to gravity and formed a monolayer. From the approximately 100,000 colloids in the cell, the time-dependent particle positions of about 1000 particles were observed by video-microscopy, far away from the cell edge. During the measurements the coordinates of the labelled particles were calculated and stored in real-time.

The PMMA colloids used are doped with superparamagnetic magnetite which makes the particles paramagnetic. The larger colloids possess a diameter of 4.7 $\mu$m and a magnetic susceptibility of $6.2 \times 10^{-11} \text{Am}^2/\text{T}$ and the smaller colloidal particles a diameter of 2.8 $\mu$m and a magnetic susceptibility of $6.8 \times 10^{-12} \text{Am}^2/\text{T}$. Using an externally tuneable magnetic field, $B$, applied perpendicular to the water-air interface, the colloidal particles interact by a repulsive $1/r^4$ dipole potential, where $r$ is the distance between two particles. The system itself is characterized by an interaction parameter, $\Gamma$, which consists of the magnetic energy $E_{\text{mag}}$ ($\sim B^2$) divided by $k_B T$. From this relationship, $\Gamma$ corresponds to an inverse system temperature, $T_{\text{gs}}$, tuneable by the external magnetic field.

Depending on different system temperatures, partial radial pair correlation functions and mean squared displacements were calculated from the coordinates of the labelled particles and compared with the shape of other glass formers. This is how the binary colloidal system used here has been identified as a 2d glass [1].

Additionally, we considered the characteristic local particle arrangements as well. Three point correlation functions were calculated for two nearest neighbouring particles for all particle combinations of the different kinds of colloids ($b$: big, $s$: small), i.e. $bb$, $bs$, and $ss$ [1]. With those, we found local density-optimised isosceles triangles, the so called elementary triangles, one for each of the four three-particle combinations of the big and small colloids, $bbb$, $bsb$, $bs$, and $ss$, shown in Fig. 1.

In order to analyse the characteristic local configurations of the amorphous colloidal 2d system for different system temperatures, triangles of nearest neighbouring particles were introduced minimizing the distances between the particle surfaces [1]. Therefore, the colloids are not treated by their hardcore radius, but by their so called magnetic field radius. This comes from the repul-
sive magnetic particle interaction which produces areas around one central colloid where no other particle can enter. Even though the potential is soft, the hardcore approximation is well defined since the first maximum of the partial radial pair correlation functions is quite sharp, shown in Fig. (2). The ratio of the two magnetic field radii was determined as 2.15 while the absolute values of the magnetic field radii depended on the 2d particle density. Nevertheless, the construction of the triangles of nearest neighbouring particles needs some special arrangements in order to be able to cover the observed colloidal area [1].

Looking directly to the arrangement of the colloids in the 2d system at low system temperatures and after some waiting time, elementary triangles are easily visible as shown in Fig. 3. The elementary triangles of the same three-particle combination tended to aggregate into crystallite-clusters. In addition, these crystallite-clusters tended to form multi-crystallite-clusters.

![Figure 2: Partial radial pair correlation functions for bb, bs, and ss. The sharp first maximum of the pair ss and bb allows the measurement of the absolute values of the magnetic field radii. That is how the ratio of the two different magnetic field radii can be calculated as 2.15.](image1)

![Figure 3: A part of a 2d colloidal image with sketched in triangles of nearest neighbouring particles which are comparable with the different elementary triangles. Parts of perturbed local structures, e. g. not local density-optimised areas, are highlighted by ellipses. A large rectangular bbbs and hexagonal bb crystallite-cluster as well as multi-crystallite-clusters are clearly visible.](image2)

Geometric properties of the triangles of nearest neighbouring particles were compared to each other for different system temperatures and at different time steps [1]. Already in the liquid state the distributions of the geometric properties show the maximum positions at the values of the elementary triangles. However, for decreasing system temperatures the deviations of the geometric properties decrease or the local density of the structure is more optimally packed. Since such ordered regions do not have free space, structural relaxation processes are blocked there. This is the reason for the well-known heterogeneous relaxations in the supercooled state. Also in the regions of fast moving particles, structurally stable clusters are visible moving like an ice floe in water. Therefore, density-optimised sections are able to flow, too.

These observations led to the concept of local density-optimised crystallite-clusters [1], which explains the glass transition as a percolation of elementary triangles, stabilised by the local density-optimised packing of the particles. In between the connected crystallite-clusters, disordered and spatially separated areas with frozen-in structural relaxations are found. That is why relaxation processes are not able to happen in a glass state any more.

With the concept of local density-optimised crystallite-clusters a lot of typical glass properties can be explained. For example, at the glass transition no density jump occurs coming up from the percolation of crystallite-clusters. Additionally, the increasing cage effect for decreasing system temperatures happens because of the growth of locally ordered structures.

C13 Hydrodynamic coupling of two rotating spheres

Michael Reichert and Holger Stark

Colloids are widely used to model atomic systems. However, there is one feature specific to colloidal suspensions: the so-called hydrodynamic interactions. A particle moving in a viscous fluid interacts with all the other particles in the surrounding fluid via the long-range flow field it creates. Hydrodynamic interactions are a complicated multi-body problem since the motion of one particle depends on the translations and rotations of all the other particles in the fluid.

The physical systems we have in mind are colloidal suspensions of spherical, birefringent particles. In contrast to conventional isotropic colloids, both their positions and orientations can be manipulated by optical tweezers. With optical traps generated by linearly polarized laser light, e. g., the orientation is controlled.

Our aim in this project was to determine the collective motions of two trapped particles and to investigate correlations in their thermally induced fluctuations. Our work extends recent investigations on translational correlations [1]. By taking into account the rotational degree of freedom, we obtain a rich spectrum of collective modes and correlations [2].

In the regime of low Reynolds numbers and on the Brownian time scale, the fluid flow obeys the linear Stokes equation (also called creeping flow equation), supplemented by stick boundary conditions on the surfaces of all particles. Due to the linearity of the equations, the translational and rotational velocities of the \( N \) particles, \( v_i \) and \( \omega_i \), depend linearly on all external forces \( F_i \) and torques \( T_i \). Defining \( 6N \)-dimensional vectors \( P := [v_1, \ldots, v_N, \omega_1, \ldots, \omega_N] \) and \( S := [F_1, \ldots, F_N, T_1, \ldots, T_N] \), we write compactly

\[
P = MS ,
\]

where the mobility matrix

\[
M := \begin{bmatrix}
  \mu^t_{ij} & \mu^r_{ij} \\
  \mu^r_{ij} & \mu^t_{ij}
\end{bmatrix}
\]

constitutes the central quantity in the hydrodynamic coupling. It consists of \( 3 \times 3 \) mobility tensors \( \mu^t_{ij}, \mu^r_{ij}, \mu^r_{ij} \), and \( \mu^r_{ij} \), which describe the mutual coupling of translations (t) and rotations (r) of two particles i and j. They depend on the configuration of all particles. A general theorem predicts that \( M \) is symmetric [3].

There are several techniques to calculate the mobility tensors for a given many-particle system, e. g., the method of reflected flow fields or the method of induced force multipoles. The latter was implemented in the numerical library HYDROLIB [4].

The axial symmetry of a system of two equally sized spheres greatly reduces the complexity of the \( 12 \times 12 \) mobility matrix. The collective motions parallel to the particle-particle axis decouple completely from perpendicular motions. In addition, there is no coupling of translation and rotation in the parallel motions. Furthermore, for the perpendicular motions only a \( 4 \times 4 \) mobility matrix is necessary since translations in \( x \)-direction only couple to rotations about the \( y \)-axis, and vice versa (for the definition of the coordinate system, see Fig. 1). We assume small displacements of the particles in the optical traps and therefore consider harmonic forces and torques, i. e., \( F_i^a = -K_i r_i^a \) and \( T_i^a = -K_i \chi_i^a \). Besides the particle positions \( r_i^a \), we introduce angular variables \( \chi_i^a \) for rotations about the coordinate axes (\( \alpha = x, y, z \); \( i = 1, 2 \)). Since they are small, the relation \( \omega_i^a = \chi_i^a \) holds. For the coupled translational and rotational motions, we define a four-dimensional vector of generalized coordinates, \( q := [r_1^x, r_1^y, \chi_1^x, \chi_1^y] \), and a diagonal force constant matrix \( k := \text{diag}(K_1, K_1, K_1, K_1) \). According to Eq. (1), the overdamped motions of two trapped particles then follow from

\[
\dot{q} = -mkq ,
\]

where the appropriate \( 4 \times 4 \) mobility matrix \( m \) is taken at

\[\text{symmetric translation}
\]

\[\text{antisymmetric rotation}
\]

\[\text{symmetric}
\]

\[\text{antisymmetric}
\]

Figure 1: Relaxational eigenmodes of two trapped spheres (white: relaxed state). Top: Only the translational parallel modes are shown. They are decoupled from the symmetric and antisymmetric rotational modes about the z-axis. Bottom: For each of the two perpendicular modes, there is a second mode where the sense of rotation is opposite to the one shown.
the equilibrium particle distance. The relaxational eigenmodes with relaxation times \( \tau_i \) are now determined by the eigenvalue problem

\[
\mathbf{m} \mathbf{k} g_i = \tau_i^{-1} g_i \quad (i = 1, \ldots, 4)
\]

(4)

for the non-symmetric matrix \( \mathbf{mk} \) with the eigenvectors \( g_i \). The eigenmodes are illustrated in Fig. 1.

In order to treat thermal fluctuations, a time-dependent random force \( \mathbf{s}(t) \) is added to the trap force: \( \mathbf{s} = -\mathbf{k} q + \mathbf{q} \), and Eq. (3) is extended to the Langevin-type equation

\[
\mathbf{m}^{-1} \mathbf{q} + \mathbf{k} q = \mathbf{s}(t).
\]

(5)

The random force is assumed to be a Gaussian white noise with zero mean, \( \langle \mathbf{s}(t) \rangle = 0 \), and time correlations determined by the fluctuation-dissipation theorem

\[
\langle \mathbf{s}(t) \otimes \mathbf{s}(t') \rangle = 2 k_B T \mathbf{m}^{-1} \delta(t - t').
\]

(6)

From Eqs. (5) and (6), any time correlation function of the generalized coordinates can be calculated:

\[
\langle q_i(t) q_j(0) \rangle = \frac{k_B T}{k_{ij}} \sum_n g_{in} h_{nj} e^{-t/\tau_n} \quad (t > 0),
\]

(7)

where \( g_{in} \) is the \( i \)-th component of the eigenvector \( g_n \), and \( h_{nj} \) denotes the dual vector \( (g_n^\dag h_{nj} = \delta_{nn'}) \). If \( q_j \) is a position coordinate, \( k_{jj} = K_i \), for angles, \( k_{jj} = K_i \).

To calculate the correlation functions, explicit values for the mobilities were obtained by using the numerical library HYDROLIB [4]. Fig. 2 shows two examples for fluctuations perpendicular to the particle-particle axis: the auto- and cross-correlation for rotations about the \( y \)-axis (\( \chi^y \)) and translations along \( x \)-direction (\( \chi^x \)).

The striking feature of both correlation functions is that they exhibit a “memory effect”. They vanish at \( t = 0 \), in contrast to what one expects for the instantaneous hydrodynamic forces in Stokesian dynamics, and show an extremum after a characteristic time. Consider, e. g., the cross-correlation in Fig. 2. The motion of particle 1 creates a fluid flow which instantaneously reaches particle 2. However, due to the trap, particle 2 can only “react” in finite time. Thus, the correlation evolves on a characteristic time scale which is related to the relaxation times and thereby to the trap stiffness.

For a single sphere, translation and rotation are not coupled [5]. However, there exists a surprising auto-correlation, as shown in Fig. 2, that is mediated by the neighboring particle. The auto-correlation is much weaker than the cross-correlation since the flow field created by particle 1 has to be reflected by particle 2. Then, in turn, particle 1 also “reacts” with a finite delay. Hence, we always expect \( t_a > t_c \).


C14 Entropic forces induced by rigid rods

L. Helden, R. Roth, G.H. Koenderink, P. Leiderer, C. Bechinger

Though the entropy of an isolated system is maximized in thermal equilibrium, this does not necessarily apply to the corresponding degree of disorder. For example, binary hard-sphere mixtures in equilibrium can form amazingly ordered solid structures for certain size ratios and packing fractions [1],[2],[3]. From a microscopic point of view, this crystallization can be understood by considering two large hard spheres suspended in a fluid of smaller spheres. If the distance between the large particles becomes smaller than the diameter of the smaller spheres, the concentration of the latter becomes depleted in the gap and an effective osmotic pressure imbalance causes a net attraction between the large particles. Consequently, this effect has been termed depletion force with the smaller particles often being referred to as depletion agent [4]. Because depletion forces are not restricted to particular length scales, the underlying principle is also applicable to macromolecular and biological systems. Accordingly, such interactions are of general interest for physicists, chemists and engineers. While there has been tremendous progress regarding the understanding of depletion forces in binary sphere systems [5],[6] and colloid-polymer mixtures [7],[8], less is known about systems where non-spherical objects such as rods are employed as depletion agent. However these particles are particularly interesting. Owing to their orientational degree of freedom, rods with high aspect ratios are much more effective as depletion agent than spherical objects. Thus only minute volume fractions (typically below 1%) are needed to induce phase separation in sphere-rod systems [9],[10],[11],[12].

In this Letter we report on the first direct measurements of depletion potentials using rigid rods as the depletion agent [13]. Since electrostatic and dispersion forces were largely screened in our experiments, only hard-body interactions had to be considered and depletion forces of entirely entropic origin could be observed. For this model-like system, we have calculated the depletion potential within density functional theory (DFT) for the exact sphere-wall geometry of our system finding excellent quantitative agreement [14] with the experimental results.

Using total internal reflection microscopy (TIRM), we were able to obtain the depletion potential of a single polystyrene (PS) sphere (diameter \( \approx 3.7 \mu m \)) close to a flat wall as a function of the rod volume fraction \( \phi \). The basic idea of TIRM (see [15],[16] for detailed reviews) is to collect the scattered light from a spherical micron-sized probe particle fluctuating due to its Brownian motion close to a horizontal planar wall. The particle-wall separation can be obtained from the scattering intensity, when the particle is illuminated by an evanescent light field from below. Using the Boltzmann distribution, a distance-dependent particle-wall interaction potential with a resolution of about 0.3k_BT can be deduced from the separation histogram.

As depletion agent we used colloidal rods consisting of a boehmite (\( \gamma \)-ALOOH) core [17] coated with a 4.5 nm thick silica layer [18]. The average length \( L \) and diameter \( \sigma \) of the resulting rods as determined by transmission electron microscopy (TEM) are 203±93 nm and 18±3 nm, respectively. A typical TEM-picture is shown in Fig.1. To minimize attractive dispersion forces which could lead to considerable changes in the depletion interactions [19] a practically index matched combination of solvent N,N-dimethylformamide (DMF, refractive index \( n=1.43 \)) and surfaces (coated silica \( n\approx1.45 \)) was used. As a result, the suspension remained stable up to at least 0.25M LiCl. The following measurements were all performed at 0.2M LiCl corresponding to a Debye screening length well below 1 nm. The plain probe particle-wall interaction potential shown in Fig.2 (a) demonstrates, that the interaction can be regarded as hard-core-like to very good approximation. In particular attractive dispersion forces, which typically can be detected for separations \( z<100 \) nm [20] were not observed, demonstrating the effectiveness of the silica coating in suppressing these forces.
When rods are added to the system, depletion forces modify the effective interaction potential between the PS-sphere and the wall. Fig. 2 shows the measured potentials (symbols) for different volume fractions $\Phi$ of the rods. Obviously the potential minima become deeper with increasing rod concentration and are also slightly shifted closer to the wall. The theoretically expected onset of the depletion forces corresponds to the length $L$ of the rods, i.e. $\approx 200$ nm. While this onset is difficult to resolve clearly at the smallest rod concentrations, data for higher concentrations (Fig. 2(e,f)) confirm this theoretical expectation. For the two highest rod concentrations (Fig. 2(g,h)), depletion effects became so strong that the PS-particle was trapped in the potential minimum and did not fluctuate more than 100 nm away from the surface. Accordingly no statistics could be acquired for larger distances. If spheres with a diameter equal to the length of the rods would be used at the same volume fraction instead, the maximum depletion attraction at $z=0$ would be less than 4% of the corresponding rod values [9]. In order to achieve a quantitative theoretical description of the experiment, we regarded the rods volume fraction $\Phi$ as an adjustable parameter and varied it until best agreement between calculated and measured potentials was obtained. Details of the DFT-calculations used for the fits are described elsewhere [14]. The results are plotted as solid lines in Fig. 2 and show very good agreement with our experimental data. Only for the smallest distances $z<20$ nm in Fig. 2 some deviations between the theory and the experiments can be observed. This is due to remaining repulsive interactions having a finite length scale. The volume fractions $\Phi_{th}$ obtained from the fits agree with the experimentally determined values within a standard deviation of 12% having exactly the same mean value. We attribute this statistical deviations to the uncertainties in preparing and handling the small amounts of stock solution.

C15 The nucleation process and elastic properties of colloidal crystals in 3D

U. Gasser, Ch. Eisenmann, D. Reinke, and G. Maret

Mono-disperse colloidal suspensions are good model systems for studying fundamental aspects of the liquid-solid phase transition as well as properties of simple crystals and fluids, since they show a phase diagram that is analogous to that of atomic or molecular substances. An important advantage of colloidal suspensions is that the colloidal particles can be chosen to be large enough for direct observation by light microscopy; as a consequence the ‘atoms’ of the system can be imaged and tracked directly. This makes it possible to study various local properties of crystals, liquids, and glasses that usually are not accessible with other methods. Moreover, the transition from the liquid to the solid takes much longer than in molecular substances, such that modern confocal microscopes can yield a detailed picture of the transition with good time-resolution.

We use mono-disperse poly(methyl methacrylate) spheres with a diameter \( d \approx 1.8 \mu m \) that are sterically stabilized. They are fluorescently labeled with rhodamine in order to make them visible with fluorescence microscopy. The solvent is a mixture of decahydronaphthalene and cycloheptylbromide, which has the advantage to yield good refractive-index matching of the particles when the density of the particles matches that of the solvent at the same time. Due to a small charge of the particles that is most likely caused by the rhodamine, the observed phase diagram is shifted to lower volume fractions when compared to hard spheres [1].

A laser scanning confocal microscope is used to take stacks of 2d-images. This allows an accurate determination of the particle positions in a small volume (usually 60 \( \mu \)m \( \times \) 60 \( \mu \)m \( \times \) 20 \( \mu \)m) inside the sample cell. The algorithm for determining the particle positions is based on a method that was first used by Crocker et al. [2]; the error in the positions is \( \leq 40 \mu m \). Due to the good refractive-index matching, the samples are transparent, and, therefore, it is possible to take images far from the cover glass in the bulk of the sample.

**Nucleation**

For an investigation of the nucleation process it is essential to have a method for identifying regions with crystalline order. We use a bond-order parameter method [1,3], which is independent of the lattice that forms eventually. Moreover, it is a local method that allows to identify very small ordered regions. The basic idea is to get a quantitative measure for the orientation of the bonds of a particle with its nearest neighbors, and to compare this orientation for neighboring particles.

When this method is applied to the experimental data, it turns out that, surprisingly, the crystal nuclei are fractal with a dimension \( d_f \approx 2.3 \). Their shape is very irregular and far from compact, as it would be expected for an object with surface-tension. This is consistent with the surprisingly small value that was determined for the surface tension and it shows that the nuclei are unable to reach their ideal shape, since particles are continuously joining or leaving the nuclei. These surprising properties of very small crystal nuclei show that their basic properties and their growth mechanism are still not well understood on a microscopic scale. One important open question concerns the relation between translational and orientational order in a crystallizing sample. While translational order is always accompanied by orientational order of the bonds, the opposite does not hold: there can be long range orientational order without translational order. The most striking example for this is the melting transition in 2D, where the translational symmetry is broken before the orientational order is lost. Since crystal nuclei are detected by looking for orientational order with the bond-order parameter technique, it is of interest to study the appearance of translational order in crystal nuclei.

Although very small crystal nuclei are too small to yield sharp Bragg peaks, one obtains maxima from the structure function \( S(\mathbf{q}) \) that indicate approximate translational symmetries. For a comparison of orientational with translational order we have calculated the correlation function of the bond order parameter \( q_0 \) and the correlation function \( q_0 \) of the translational order with respect to the reciprocal lattice vector \( \mathbf{G} \), which belongs to the maximum of \( S(\mathbf{q}) \):

\[
p_0(r) = \frac{4\pi \sum_{j \neq k, m} q_{0m}(j) q_{0m}(k) \delta(r - |r_j - r_k|)}{13 \sum_{j \neq k} \delta(r - |r_j - r_k|)}
\]

![Figure 1: Comparison of averaged orientational (full symbols) and translational (open symbols) correlation functions from crystal nuclei of different sizes in a sample with \( \phi = 0.44 \).](image)
\[ g_{ij}(r) = \frac{\sum_{j\neq k} \exp(i \vec{G} \cdot \vec{r}_{jk}) \delta(r - |\vec{r}_j - \vec{r}_k|)}{\sum_{j\neq k} \delta(r - |\vec{r}_j - \vec{r}_k|)} \]

Fig. 1 shows a comparison of averaged \( g_{66} \) and \( g_{ij} \) correlation functions for crystal nuclei of different sizes. The correlation length of the orientational order (full symbols) is always longer than that of the translational order (open symbols). This suggests that orientational order leads the way for the formation of a crystal lattice. Surprisingly, the correlation functions of nuclei that contain between 3000 and 7000 particles show a minimum in the range 20 \( \mu \)m \( \leq r \leq 30 \mu \)m. This must reflect a typical internal structure of the nuclei, which often consist of a small number of regions with somewhat different bond orientation. The mechanisms that lead to the formation of a well-defined crystal lattice continue to be the subject of our investigations.

**Elastic properties of colloidal crystals**

The elastic properties of a polycrystalline material depend strongly on its structure on a mesoscopic scale, since the size and the structure of the crystal grains as well as the amount of defects determine its strength. Elastic constants are usually defined via a macroscopic continuum-description of a piece of material. On the other hand, it must be possible to get the same information about elastic properties from microscopic information like time-dependent particle positions, which are accessible by direct imaging of colloidal crystals with confocal microscopy. Local elastic properties of mono crystals as well as several crystal grains together with the domain walls in between can be imaged, and, therefore, a link between microscopic properties of the crystal lattice, domain walls, and defects on one side and the macroscopic elastic properties of colloidal crystals on the other side can be obtained experimentally.

The colloidal model system that is described above is used to develop an experimental method for local measurements of elastic constants. Such a method was proposed by Sengupta et al. [4] and has been successfully tested with computer simulations of hard disks and experimentally on colloidal particles with dipole interaction in 2D [5]. In this method, the elastic constants are extracted from measured strain fluctuations. Its main advantage is the general applicability, even the interaction potential between the particles need not be known.

The particle positions that are obtained as described above are used to calculate the local strains in the observed volume. For this purpose, the particles are tracked, the average drift of the observed particles is determined and subtracted, and the deviations \( \vec{d} \) from the ‘lattice’ sites are determined by subtracting the average particle positions from the time-dependent positions. The components of the position- and time-dependent strain tensor \( \epsilon \) are then obtained by calculating \( \nabla \vec{d} \) from the deviations of neighboring particles. These local strains are averaged over sub-blocks of the observed volume; preliminary histograms of strain fluctuations for different sub-block sizes are shown in Fig. 2. The elastic constants of an infinite crystal are connected to the dependence of the half width of the histograms on the block size, and they can be determined in a way that is analogous to the method that was used by Sengupta et al. [4]. Since this method does not necessarily require that the particles fluctuate around the equilibrium positions of a well-defined crystal lattice, this method might also be applied to crystallites that contain defects or even to glasses.

**Figure 2:** Histograms of the strain fluctuations averaged over sub-blocks of different sizes (where \( b \) is the ratio of the sub-block size and the total size of the observed volume in \( z \)-direction) in two samples with volume fractions \( \phi = 0.30 \) and \( \phi = 0.55 \).

C16 Quasicrystalline order in 2D binary dipolar systems

F. Scheffler, P. Maaß, J. Roth, and H. Stark

Super-paramagnetic colloidal particles suspended in a solvent experience a dipole-dipole interaction under the influence of a magnetic field. In experiments on two-dimensional monodispersed systems of this type the KTHNY theory could be verified [1], which predicts the occurrence of a hexatic phase of bond-orientational order when a hexagonal crystal melts. Recently, locally quasicrystalline patterns were observed in binary mixtures of dipolar colloids [2]. Quasicrystals possess a long-range positional order which cannot be periodic due to the non-crystallographic point group symmetry as first reported by Shechtman et al. in rapidly quenched Al-Mn alloys [3]. In 2D the Penrose tiling, which consists of two types of rhombs put together by certain matching rules, is a typical example for a quasicrystalline pattern with fivefold symmetry.

In this project, we investigate if binary dipolar systems in 2D show stable or at least metastable quasicrystalline order by decorating the Penrose pattern with strong (A) and weak (B) dipoles following the rules of Ref. [4] (see Fig. 1, the ratio of the number of A and B dipoles is \( \phi = \frac{1 + \sqrt{5}}{2} \) is the golden mean). In the simulation of atomic binary quasicrystals, Lennard-Jones pair potentials are used, which favor certain particle-particle distances. To stabilize a quasicrystal, these distances have to be tuned to the characteristic lengths in a Penrose pattern. The interesting point is that the dipole-dipole interaction in our treatment does not possess such an intrinsic length scale. The only tunable parameter to stabilize a quasicrystalline pattern is the ratio of the dipole moments.

In a first step we compare the energy per dipole for a periodic approximant of the Penrose pattern with various versions of hexagonal structures (see Fig. 2): (i) two phase-separated lattices of A and B dipoles, (ii) B dipoles in the center of triangles made up by A dipoles plus a phase-separated A lattice, (iii) like (ii), however the B dipoles only occupy every second triangle and a phase-separated B lattice remains. Note that the average dipole density was fixed and the lattice constants of the coexisting structures were optimized. We find that the quasicrystalline structure has lowest energy for dipole ratios between 4 and 6.5 with an optimum at 5. Interestingly, the version (ii) with the “diluted” A lattice is otherwise the structure of lowest energy suggesting that a mixture of A and B dipoles is more stable than a phase separated structure.

In a second step, we assign noise to the dipole positions with respect to the optimum quasicrystalline structure and let it relax via the method of “steepest descent”. Up to an average dipole displacement of 0.1 (in units of the edge length of the Penrose rhombs), the system relaxes back to the optimum structure. At an average displacement of 0.2, numerous defects remain. This is reminiscent to the empirical Lindemann criterion, which predicts the melting of a crystal for an average displacement of 0.14 in units of the lattice constant.

We are currently performing Monte Carlo simulations to investigate the absolute stability of the quasicrystalline structure and the transition to a disordered phase. So far, our results hint to a remarkable stability of quasicrystalline structures in binary dipolar systems despite the missing intrinsic length scales.

D Biological Systems
Macrosions at the air-water interface

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The general interest in macroionic systems at the air-water interface has been triggered by the experiment of Pieranski [1] who demonstrated that a polystyrene sphere can be trapped at an air-water interface in a large surface energy well. Since then, observing particles at the air-water interface has been a common and convenient way of investigating 2D or quasi-2D colloidal systems, e.g., proteins. The need to obtain 2D arrays of proteins arises due to the fact that large 3D single crystals are often difficult to obtain, and the subsequent structural analysis by x-ray techniques can be rather time-consuming. On the other hand, 2D arrays of proteins if obtained lend themselves to rapid analysis by electron microscopy techniques and requires only small amounts of sample material.

We have first investigated, within the framework of the Poisson-Boltzmann theory, any possible electrostatic contribution to the trapping of a macroion at the air-water interface [2]. We found that electrostatics mainly serve to isolate particles already trapped at the interface since a charge particle is repelled from the air-water interface due to image forces. The study further shows that while one can make an argument for electrostatic trapping, the stability of a trapped particle at the air-water interface is essentially dominated by surface tension forces as suggested by Pieranski [1]. We then considered, within the linear Debye-Hückel theory, the pair interaction potentials of macroionic spheres assumed trapped at this interface [3]. We showed that introducing additional substrate interfaces parallel and very close to the air-water interface can affect the pair potentials in a particular way, depending on the dielectric constant of the substrate relative to water. Applying the pair potentials in a one-component Monte Carlo simulation we obtained fluid – crystal phase diagrams in the [\( \phi_{\text{surf}} \) \( L/a \)] parameter plane, where \( \phi_{\text{surf}} \) is the separation distance between the two interfaces (the air-water interface and the water-substrate interface) and \( \phi_{\text{surf}} \) is the surface fraction of the interfacial colloids at the air-water interface. The main result is as follows (see figures): A substrate whose dielectric constant is much smaller than that of the solvent, e.g. air, enhances the repulsive pair interaction and consequently induces crystallization of the 2D protein array at the air-water interface, at much lower densities, compared to the freezing density of the system without additional substrate.

D2 DNA molecules under mechanical stress

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Within the last few years methods to manipulate and observe single molecules, in particular optical tweezers and scanning force microscopy, have provided unprecedented insights into the micromechanics of DNA. The force-extension curve of double-stranded (ds) DNA is accurately described by the wormlike-chain model for semiflexible polymers by application of forces up to 20–30 pN, at extensions up to the full contour length $l_0$. At higher forces (at about 80 pN for $\lambda$-DNA) a completely new behavior is observed: the slope of the force-extension curve now becomes flat, and the double helix can be overstretched at an almost constant force up to an extension of $1.7l_0$ [1]. This transition to an overstretched state is reversible, the exact force for overstretching depending on ionic strength and on the relative contents of dG-dC and dA-dT pairs. The observed plateau in the force-extension curve has been interpreted as a coexistence of B-DNA and a new conformation called S-DNA where base pairs are thought to be strongly tilted with respect to the helical axis.

Overstretched states of dsDNA have been known for some time from electron microscopic studies of complexes with the recombination enzyme RecA. Indeed, recent investigations into the kinetics of RecA binding to DNA have shown a maximum in the binding rate constant if the double helix is pre-stretched by a force of about 75 pN. From force measurements it is known that the free energy per base pair in B-DNA differs by about $3k_BT$ from that of S-DNA. This has led to the conjecture that the plateau in the force-extension curve is due to the coexistence of B-form and S-form segments. The structure of DNA-RecA complexes is not known; however, X-ray diffraction studies of oligonucleotides complexed with the TATA-box binding protein TBP show that the native double helix is strongly extended by the protein. Computer simulations show that the overstretched conformation is an energy minimum, which would support a two-state model for the B-S-transition.

Changes of the base-pair stacking, on the other hand, also influence the interaction between the base pairs, which directly affects the compression modulus accessible by inelastic scattering experiments. Therefore, the hypothetical base pair tilting during the B-S transition should entail a significant change of the longitudinal sound speed. In addition, the hypothetical strong conformational fluctuations at and near the B-S transition should give rise to significant enhancement of the quasi-elastic light scattering.

In order to use techniques such as quasi- and inelastic light scattering for the study of isolated, highly oriented DNA molecules, we have developed a surface force apparatus specifically designed for the requirements of optical experiments. The plates of the apparatus consist of glass surfaces to which DNA functionalized at both extremities can be coupled. Using $\lambda$-DNA with a 48’000 basepairs and a contour length of 15.8 $\mu$m we arrive at packing densities of about 40% relative to close packing of random coils with a radius of gyration $R_G = 0.9\,\mu$m. Using confocal laser scanning microscopy on fluorescently labelled DNA allows to resolve individual DNA coils. Upon application of an electric field the DNA is extended, allowing to discern molecules unspecifically adsorbed to the substrate from those attached via their functional end-group (see Fig. 1). These experiments have shown that our surface modification and DNA functionalization protocols lead to highly selective end-attachment of DNA. First experiments on DNA functionalized with two different end labels demonstrate that double-sided attachment is possible (see Fig. 2). However, at this stage the density of double-sided attachment still needs to be enhanced for scattering experiments to be feasible.

Figure 1: (a) $\lambda$-DNA molecules stretched by an electrical field parallel to the substrate surface. End-attachment is shown by the monodisperse length distribution. (b) End-attached DNA stretched by an electrical field perpendicular to the surface (bright points). Field of view: $35\,\mu$m x $35\,\mu$m.

Figure 2: $\lambda$-DNA molecules attached at both extremities between closely separated glass surfaces. Extended molecules are marked by the arrows. Field of view: $60\,\mu$m x $30\,\mu$m.

Wrapping in colloid-membrane complexes

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When a charged spherical particle adsorbs on an oppositely charged flexible membrane, the membrane deforms and wraps around the particle. This mechanism plays an important role in many physical and biological processes. The most prominent is probably the transport of particles into a cell - known as endocytosis. But also in experiments measuring the motion of latex spheres attached to a large vesicle the wrapping of the particle by the membrane is important [1]. In order to investigate the wrapping of charged colloid-membrane complexes we model the membrane as a two dimensional elastic surface with a homogeneous charge density $\sigma$, a bending rigidity $K_0$ and a surface tension $\gamma$. The sphere has radius $R$ and charge $Z$. We consider the membrane as being a small part of a much larger charged vesicle which serves as a reservoir for the membrane area, since not the true area is preserved as the membrane wraps the sphere, but the projected area is preserved. This means that also the total charge of the system is not preserved. The reservoir generates an osmotic pressure $\Pi$ and a chemical potential $\mu$ which couples to the charged area of the system. These terms have to be added to the surface tension $\gamma$ of the system, which gives rise to an effective tension $\gamma_e := \gamma + \Pi - \mu\sigma$. We describe the electrostatic interactions by Deybye-Hückel potentials, introducing the additional parameters $\ell_B$, the Bjerrum length, and $\kappa_s$ the inverse screening length. As a reference state we use always the state in which the membrane is flat and touches the sphere in one point. The simplest hamiltonian to describe the system considered here, in units of $k_B T$, is given by:

$$H = \frac{K_0}{2} \int d^2 \rho \sqrt{g(\rho)} (\Delta X(\rho))^2 + \gamma_e \int d^2 \rho \sqrt{g(\rho)}$$

$$+ \frac{1}{2} \int d^2 \rho \int d^2 \rho' \sqrt{g(\rho)g(\rho')} v_m(X(\rho) - X(\rho'))$$

$$+ \int d^2 \rho \sqrt{g(\rho)} v_a(X(\rho)) + \int d^2 \rho \sqrt{g(\rho)} v_h(X(\rho))$$

where $X_m$ denotes the configuration of the membrane, which minimizes the hamiltonian (1). We analyze the ground state of the system in a twofold way. First, we minimize (1) numerically, applying a step-length corrected Newton-Raphson scheme. The second way consists of investigating the hamiltonian (1) in a simplified geometry on a scaling level. We distinguish between three different states of the system:

- Point contact state. The membrane touches the sphere just in one point.
- Touching state. The membrane touches the sphere over a finite area, but wraps less then half of the sphere.
- Wrapping state. The membrane wraps more then half of the sphere.

On the scaling level we try to identify the dominant contributions to the free energy for the transitions between the different states of the complex. To reduce the parameter of the system, we use dimensionless parameters:

$$\tilde{Z} := \frac{Z}{\kappa s \sigma}, \tilde{\epsilon} := \sqrt{\frac{\epsilon_{R} B_{s}}{K_0}}, \tilde{\gamma} := \frac{\gamma}{K_0} \text{ and } \kappa R.$$

The shape of the membrane, as it wraps around the sphere, depends on the rescaled inverse screening length $\kappa R$. For small $\kappa R$ (low salt concentration, small spheres) the membranes wraps into a cymbal-like shape shown in Fig. 1. In this case the long-ranged electrostatic attraction pulls the membrane closer to the sphere, producing the cymbal-like shape.

Figure 1: A wrapping state of the membrane for $\kappa R = 0.1$, $\tilde{\epsilon} = 1$ and surface tension $\tilde{\gamma} = 0$. The long-ranged electrostatic attraction pulls the membrane closer towards the sphere and creates a cymbal-like shape of the membrane. The change of the sphere is $\tilde{Z} = 2.6$.

In the case of large $\kappa R$ (high salt concentration, large spheres) the electrostatics is strongly screened. Thus, away from the sphere the dominating energy contributions stem from the mechanical bending energy and the mechanical surface tension. The membrane wraps in this case into a catenoid-like shape, shown in Fig. 2, reducing in this way its elastic bending energy. A catenoid is the only non-trivial minimal surface (surface with vanishing mean curvature) in two dimensions.
Figure 2: Three different wrapping states of the membrane for $\kappa R = 10$, $\delta = 1$ and surface tension $\gamma = 0$. Away from the sphere the electrostatic interaction between the sphere is low. The membrane therefore minimizes the bending energy and acquires a catenoid-like shape. The change of the sphere is $\tilde{Z} = 1.4, 1.8, 2.1$ (from bottom to top).

From the scaling model, we obtain the following dominant contributions for the transitions for $\kappa R \ll 1$:

- **Touching transition.** The dominant contributions to the free energy are the repulsive bending energy of the curved membrane segment and the attractive membrane sphere interaction. Both terms are independent of $\kappa R$ and if these two terms are balanced one obtains for the touching transition:
  \[
  \tilde{Z}_t \sim \frac{1}{2\pi \sigma^2}.
  \tag{2}
  \]

- **Wrapping transition.** If the membrane wraps the sphere, the area of the membrane increases and therefore additional surface has to be pulled out of the reservoir. Since the membrane is charged, this moves charges closer together and thus creates a repulsion. For $\kappa R \gg 1$ this contribution is negligible, but for $\kappa R \ll 1$ this term becomes dominant. This term plus the purely mechanical contributions have to be balanced by the membrane-sphere attraction. One obtains for $\tilde{Z}_w$:
  \[
  \tilde{Z}_w \sim \frac{4 + \tilde{\gamma}}{8\pi \sigma^2} + \frac{1}{8\kappa R}.
  \tag{3}
  \]

In the case of $\kappa R \gg 1$ we find:

- **Touching transition.** The dominant contributions to the free energy are the repulsive bending energy of the curved membrane segment and the attractive membrane sphere interaction. If these two terms are balanced, the membrane goes from the point contact state into the touching state:
  \[
  \tilde{Z}_t \sim \frac{\kappa R}{2\pi \sigma^2}.
  \tag{4}
  \]

- **Wrapping transition.** The dominant contributions to the free energy are the bending energy, the repulsive surface tension and the membrane sphere interaction. Balancing these terms yield the value $\tilde{Z}_w$ for the wrapping threshold:
  \[
  \tilde{Z}_w \sim \frac{4 + \tilde{\gamma}}{8\pi \sigma^2} \kappa R.
  \tag{5}
  \]

For $\gamma = 0$ we find $\tilde{Z}_t = \tilde{Z}_w$, i.e., the membrane goes in this case directly from the point contact state to the wrapping state. The resulting complementation diagram is shown in Fig. 3. For small as well as for large $\kappa R$ the membrane wraps the sphere only for large $\tilde{Z}$. If one fixes $\tilde{Z}$ in such a way that the membrane is in the wrapping state and decreases $\kappa R$ the membrane will unwrap and finally leave the wrapping state. The same holds in the case of increasing $\kappa R$. This means that the membrane wraps the sphere optimally only in an intermediate regime of $\kappa R$.

The surface tension is known to be an important control parameter for the clathrin-independent endocytosis [2], where increasing the surface tension of the membrane decreases the rate of endocytosis and vice versa. This can be easily explained in our model. The effect of increasing the surface tension is to enhance the touching region, whereas it is more pronounced for large $\kappa R$ (see eq. (3) and eq. (5)). If one increases $\gamma$ the membrane unwarps and leaves the wrapping state at a critical tension $\gamma^*$. Certainly, wrapping is a prerequisite for endocytosis which means, that a decrease in wrapping leads to a decrement in the endocytosis rate.

![Diagram](image)

Figure 3: Complementation diagram for the membrane-sphere system as a function of the rescaled charge $\tilde{Z}$ and the rescaled inverse screening length $\kappa R$. The lowest line denotes the touching transition and the lines above the wrapping transition, where the solid line shows the wrapping transition with vanishing surface tension ($\gamma = 0$), whereas in the case of the dashed line the surface tension is finite ($\gamma = 10, \delta = 1$ in both cases). In case of the lower dashed line, the membrane goes directly from the point contact state to the wrapping state. The effect of the surface tension is to increase the touching area. The black dots denote the numerically obtained results for the wrapping transition with $\gamma = 0$, while the stars denote the results obtained with $\gamma = 10$. The labels A and B symbolize the different wrapping shapes of the membrane. The cymbal-like shape is denoted by A, while in the case of B the membrane wraps into a catenoid-like shape.

D4 Bundling of actin filaments induced by depletion forces

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During recent years there has been growing interest in depletion forces between colloids in suspension which can be induced by the addition of smaller particles to the background solvent. It has been demonstrated that such forces are responsible for the phase separation and flocculation of binary hard-sphere mixtures, colloids in the presence of micelles, and of colloid-polymer mixtures. Accordingly, depletion effects are also important in many technological applications such as the stabilization of emulsions and drug formulation [1].

The mechanism underlying depletion interactions is easily understood when two hard spheres of radius $R$ suspended at distance $r$ in a fluid containing smaller macromolecular species (depletion agent) of radius $r$ are considered. If the distance $r$ between the large spheres is decreased below the diameter of the smaller ones, the latter are expelled from the region between the large spheres. Consequently, the concentration of macromolecules becomes depleted in this region compared to the bulk concentration and an effective osmotic pressure imbalance causes a net attraction between the large spheres [2]. Since depletion interactions are based on excluded volume effects, they are a generic phenomenon and thus not limited to particular systems, but also observed in biological environments where they are often referred to as macromolecular crowding. Here depletion forces arising from the high packing fraction and large size asymmetry of macromolecules in the cytoplasm have been suggested as the main origin for the enhanced kinetics of many cytoplasmic reactions in the presence of proteins which themselves do not specifically bind to either of the reactants [3,4]. Specifically, it was observed that condensation of E. coli DNA is promoted by adding inert polymer coils [5]. Also, the organization of cytoskeletal filaments into bundles has been attributed to depletion forces induced by small inert polymers. Several groups have monitored the bundling of actin filaments by static light scattering when polyethylene glycol (PEG) as inert polymer was added [6]. Indeed, they found that the scattering intensity after addition of PEG increases strongly and that actin bundling apparently only occurs above a critical PEG concentration. Since the strength of depletion forces increases monotonically with the number density of the depletion agent, however, it is unclear whether the observed critical concentration can be explained in terms of depletion interactions.

In this Letter we report on a systematic study of PEG-induced bundling of F-actin using transmission electron microscopy (TEM) and quasi-elastic light scattering (QELS). We demonstrate that the bundle thickness and the slowing-down of the bundle dynamics increase monotonically with increasing PEG concentration. This is in contrast to the observation of a threshold behavior as suggested by other authors [6]. By comparing the decay times of the QELS data with theoretical predictions for solutions of semiflexible polymers we are able to obtain the persistence length of the actin bundles as a function of the concentration and molecular weight of the added PEG. Our findings are consistent with depletion forces as the driving mechanism for the bundling of actin.

With increasing amount of PEG (Fig. 1 a-d) the semidilute F-actin solution develops into a network consisting of actin bundles. Using image analysis software to measure the average bundle thickness $d$ we estimated $d$ to be 12.2 nm, 28.5 nm and 54.0 nm at $c_{PEG}=4\%$, 6% and 8% w/w, respectively. The artificial enlargement due to the staining procedure are taken into account by scaling the values to the single filament diameter $d=6$ nm. The mesh size $\xi=1.2 \mu m$ reported for a pure semidilute F-actin solution of the same monomer concentration [7], is in good agreement with Fig. 1a). A similar behavior, i.e. a PEG induced bundling of actin, was also observed with confocal fluorescence microscopy (data not shown). While the optical resolution in these experiments did not allow to directly resolve the increased bundle thickness when adding PEG, the mesh size of the actin network was found to increase to $\xi=4.1 \mu m$, 5.0 $\mu m$, 7.1 $\mu m$ and 8.6 $\mu m$ at $c_{PEG}=2\%$, 4%, 6% and 8% w/w, respectively. Due to mass conservation, such an increase in $\xi$ is equivalent to an increase in the average bundle thickness. Both, the TEM and the confocal microscopy results are consistent with depletion induced actin bundle formation.

![Fig. 1: Transmission electron micrographs of F-actin at c_{PEG}=0.1 mg/ml with a) 0%, b) 4%, c) 6%, and d) 8% w/w PEG 6kDa, respectively. The images show strong actin bundle formation with increasing c_{PEG}.](image-url)
As seen in Fig. 1, increasing the PEG concentration leads to an actin network with thicker bundles. This is expected to have a strong effect on the bundle dynamics which depends sensitively on the local mechanical properties. We have thus measured the dynamic structure factor for different ϕ_{PEG} and molecular weight M_w. As in case of actin filaments, the dynamic structure factor of actin bundles is well described by the stretched exponential derived for semiflexible polymers [8]

\[ F(q,t) = \exp(-\frac{\eta(q)}{\zeta_1} \gamma(q)^{\eta(q)}) \]  

(1)

At PEG concentrations lower than 6% the value of α is for all M_w close to 0.75 which is the characteristic for transverse bending dynamics of semiflexible filaments. At higher concentrations and in particular for M_w>600Da, α decreases to about 0.5 being characteristic for networks with unrelaxed mechanical stress.

If we assume the bundles to correspond to weakly bending rods with \( l_p \) much larger than both \( \lambda \) and \( \xi_m \), the \( q \)-dependence of the decay rate \( \gamma(q) \) is given by [8]

\[ \gamma(q) = \frac{k_B T}{\zeta_1} l_p^{-1/3} q^{2/3}, \]  

(2)

where \( k_B T \) is the thermal energy and \( \zeta_1 \) is the effective transverse friction coefficient. The latter quantity is related to the hydrodynamic screening length \( \xi_0 \) the concentration dependent solven tot viscosity \( \eta \) and the bundle diameter \( d \) by \( \zeta_1 = 4\pi \eta n_0 \xi_0 / d \); assuming that \( \xi_0 \) is of the order of \( \xi_m \sim d \alpha_{\text{min}} \), \( \zeta_1 \) is independent of the bundle size and the PEG concentration.

For all the PEG molecular weights investigated we find a clear scaling of \( \gamma(q) \) with \( q^{2/3} \). In addition the slope \( \gamma(q)q^{2/3} \) decreases with increasing ϕ_{PEG}. It should be mentioned that for ϕ_{PEG}>6% deviations from a \( q^{2/3} \)-behavior occur. This is consistent with the observation that in this regime the assumption of unconstrained filaments breaks down. From linear fits of \( \gamma(q) \) to Eq. (2), we extract the concentration dependence of the bundle persistence length for various M_w (Fig. 2). In the absence of PEG we find \( l_p=4.7\mu m \). This is in reasonable agreement with QELS results on unlabelled F-actin [9], but lower than in a more recent image analysis study of labelled F-actin yielding \( l_p=16.2\mu m \) [10].

Addition of PEG leads for all molecular weights to an increase of \( l_p \). It is important to realize that even at very small ϕ_{PEG} the increase of \( l_p \) is significant. At ϕ_{PEG} around 6% (for PEG with M_w=6kDa and 8kDa) and about 8% for 2kDa \( l_p \) shows a sudden increase. As these concentrations are identical to those where \( \alpha \) deviates from 0.75, this effect is likely to be caused by the fact that in this concentration regime the validity of Eq. (2) comes into question. The data in Fig. 2 also show a slight increase of the \( l_p \) with increasing PEG molecular weight at a given PEG concentration. Since the depletion strength is a function of the size and the concentration of the macromolecules, the continuous increase of \( l_p \) together with the observed dependence on M_w is consistent with depletion effects as the driving mechanism for actin bundling.

Fig. 2: Persistence length as a function of c for various M_w calculated from \( \gamma(q) \) using Eq. (2) (● 600, □ 2, ○ 6, and ● 8kDa). The values above the broken line are beyond the range where Eq. (2) is valid. The solid line is guides to the eye.

In conclusion we found that with increasing ϕ_{PEG} the thickness of the actin filament bundles increases. In addition, we studied the fluctuations of bundle segments by means of QELS which provides evidence for semiflexible behavior and detailed, quantitative information on the persistence length reflecting the bending rigidity of the actin bundles. Our results demonstrate that the decay rate of the dynamic structure factor decreases with increasing concentration and molecular weight of PEG which suggests an increasing persistence length of the bundles. Both findings are consistent with depletion forces as the driving mechanism for actin bundling by PEG.


E  Multiple Light Scattering
Persistent random walk in a honeycomb structure: Light transport in foams

MF. Miri and H. Stark

Foams, i.e., cellular structures where air bubbles are separated by thin liquid films, constitute an appealing form of soft matter. They represent a truly interdisciplinary research field with, on the one hand, theoreticians addressing fundamental questions about geometrical and topological properties of foams and, on the other hand, engineers who are interested in their rheological behavior due to applications in oil recovery and fire fighting [1]. Diffusing-wave spectroscopy based on the diffusion limit of multiply scattered light is an indispensable tool for studying dynamic processes in turbid media. Experiments confirm the diffusive transport of light or photons in foams [2]. However, there is a debate in literature about the main mechanism of the underlying random walk [3]. One suggestion is that light mainly scatters from the Plateau borders where three liquid films always meet. On the other hand, since the cells are much larger than the wavelength of light, one employs geometrical optics and follows a light beam as it is reflected by the liquid films with a probability \( r \) called the intensity reflectance. This naturally leads to a random walk of the photons in space.

As a first approach to study the second mechanism [4], we choose the honeycomb structure which serves as the simplest two-dimensional model foam. We neglect the thickness of the liquid films and simply consider constant reflection \( r \) and transmission \( t = 1 - r \) coefficients to implement the geometrical-optics rules. Fig. 1 illustrates the different photon paths in a honeycomb lattice depending on the angle of incidence \( \varphi \). In general, due to symmetry, only three angles of incidence appear within each photon path: \( 0^\circ \leq \varphi \leq 30^\circ \), \( 60^\circ - \varphi \), and \( 60^\circ + \varphi \). The angle \( \varphi = 90^\circ \) corresponds to a classical one-dimensional persistent random walk with a well-known diffusion constant. The paths for \( \varphi = 30^\circ \) and \( 60^\circ \) only contain a finite number of step lengths and directions and therefore can be treated analytically by a set of twelve master equations. They demonstrate that these random walks represent twelfth-order Markov chains. Nevertheless, with the method of characteristic functions, we were able to extract the diffusion constants [4]. All the analytically determined diffusion constants contain the characteristic term \( It(1 - r)/r \), where \( I \) is the edge length of a hexagon and \( c \) the speed of light. The prefactors satisfy \( D(60^\circ) : D(90^\circ) = 1/2 : \sqrt{3}/2 : \sqrt{3}/2 \).

For any other angle of incidence, we determined the diffusion constants numerically by a standard Monte Carlo procedure (see Fig. 2) [4]. They all show a significant deviation from the simple \( (1 - r)/r \) law of the analytic cases. Furthermore, they depend on the angle of incidence which is a remarkable property since usually the diffusion process erases the memory for the initial conditions. Thirdly, we find that \( D(\varphi \rightarrow 30^\circ) \neq D(30^\circ) \). For \( \varphi \rightarrow 30^\circ \) the motion of the photon switches between a one- and two-dimensional diffusion state which we are able to treat analytically within a two-state model [4].

Reasonable estimates of \( r \) give the same order of magnitude for \( D \) as recent experiments on dry foams [3]. This demonstrates that the investigated mechanism contributes significantly to the diffusive behavior of light. We currently extend our study to disordered Voronoi foams and include a more realistic model for the reflection coefficient \( r \) based on the Fresnel formulæ.

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E2 Measurement of the magneto-optical correlation length in turbid media

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In multiple light scattering media magnetic field induced circular birefringence (Faraday effect) influences interference effects such as speckle pattern or coherent backscattering. It was predicted that in the diffusive regime the relevant correlation length with respect to the Faraday rotation \( \ell_F \) differs, in general, from the transport mean free path \( \ell^* \). We have verified experimentally the prediction, that the ratio \( \ell_F^*/\ell^* \) equals 2 for Rayleigh scattering and decreases to one with increasing scatterer size.

Coherent Backscattering (CB) of multiply scattered light originates from the constructive interference between each light path and its reversed path. In the exact backscattering direction both paths always have exactly the same length thus leading to a constructive interference enhancement of a factor of two in the exact backscattering direction with respect to the ‘incoherent background’ of diffuse scattering at wide angles [1].

Faraday rotation (FR) introduces a phase shift of \( \pm V B \cdot \hat{r} \) for circular polarized light (handedness \( \pm 1 \)) propagating a distance \( r \) parallel to a magnetic field \( B \). \( V \) is the specific Verdet constant.

In the first models describing the influence of FR on CB, the average distance between two scattering events \( \langle |r| \rangle \) was approximated by the transport mean free path \( \ell^* \) and it was assumed that the handedness changes randomly after each scattering event. Consequently, the phase of a light amplitude experiences a mean square deviation of \( \frac{2\pi}{\ell^*} (V B)^2 \) along a path of length \( s \) resulting in a destruction of the CB cone with increasing magnetic field.

However, this approximation of a random helicity flip after each scattering event turns out too strong. In fact, the circular depolarization is strongly correlated with the scattering angle \( \theta \), normally. In case of Rayleigh scattering, for example, there is a complete helicity flip only for \( \theta = \pi \), but none for \( \theta = 0 \). Therefore, it was suggested [2] to introduce a new correlation length for the influence of FR according to a modified differential cross section \( d \sigma V (\theta) \sim d \sigma^+ + (\theta + \pi) \) corresponding to the parts of the light that are scattered into the same ‘+’ and into the orthogonal ‘−’ circular polarization state. Finally, the correlation length is obtained in analogy to the definition of \( \ell^* \) in case of non-isotropic scattering: \( \ell_F^*/\ell^* = (1 - \langle \cos \theta \rangle)^{-1} \), where the average is taken according to \( d \sigma V (\theta) \) now.

Experimentally, the specific value \( \ell_F^*/\ell^* \) can be obtained by measuring the CB cone without FR, \( E(q_b) \), and comparison to the maximum enhancement factors, \( E(V B) \) at \( q_b = 0 \), as a function of \( V B \). \( q_b \approx 2\pi/\ell^* \) is the backscattering vector for a given back-scattering angle \( \theta_b \) with respect to the reverse direction of the incident light. The rescaling factor \( \ell_F^*/\ell^* \) is obtained independent of the path length distribution \( p(s) \) and \( \ell^* \).

We measured the CB cone of polystyrene spheres suspended in water for magnetic fields up to 23 T, using beads of radii between 23.5 nm and 112.5 nm. As an example, Fig. 1 shows the destruction of a CB cone with increasing magnetic field. Fig. 2 shows the measured values \( \ell_F^*/\ell^* \) for different scatterer sizes in comparison to the calculations [2]. The coincidence with the theoretically predicted values is very good, showing the importance of correlations between depolarization and scattering angle for multiple scattering.

Figure 1: Destruction of the CB cone with increasing magnetic field for a sample of polystyrene spheres (radius \( r \approx 23.5 \) nm, volume fraction 4.92\%) in water. \( \lambda = 458 \) nm, circular polarization.

Figure 2: Measured [3] and calculated [2] values \( \ell_F^*/\ell^* \) as a function of the polystyrene sphere radius \( r \). \( \lambda = 458 \) nm, \( \ell^* \approx 0.5 \) mm.

E3 Laser-induced Nanostructuring and Nanocleaning

M. Bertsch, H-J. Münzer, M. Mosbach, R. Wannenmacher, J. Boneberg, P. Leiderer

The irradiation of surfaces with short laser pulses can be used both for the generation of nanostructures and for the removal of unwanted nanoscale particles from surfaces, two important challenges in nanoscience. We have used colloidal nanoparticles for investigating the distribution of optical near fields of small objects on surfaces both theoretically and experimentally. The results have important consequences for laser-assisted particle removal, where field enhancement may cause local surface damage and is one of the physical key processes in this cleaning method. On the other hand, the application of near fields at particles allows structuring of surfaces with structure dimensions on the order of 100 nm and even below.

As samples we used industrial silicon wafers with (100) orientation. After an appropriate cleaning procedure a suspension of monodisperse polystyrene (PS) spheres with diameters between 320 nm and 800 nm was applied to the samples by a spin coating process. Alternatively, hexagonally close-packed colloidal monolayers were directly prepared onto the surface in a self-organized process [1]. To illuminate the samples, we used two different laser systems, in most of our experiments a pulsed Ti:Sapphire-laser with a wavelength of 800 nm and 150 fs pulse duration, and alternatively a ns-Nd:YAG-laser with a pulse duration of 8 ns.

Upon irradiation of the test particles with pulsed laser light two prominent effects are observed: i) on one hand, the particles are removed from the Si surface, if the laser pulse has sufficient intensity; ii) on the other hand, holes appear in the Si substrate at the previous positions of the particles. These holes are ascribed to local ablation of the silicon by the optical near field under the particles [2]. The local intensity can be enhanced considerably compared to the incident plane wave of the laser pulse, and thus lead to laser-induced evaporation underneath the particles already at average laser fluences well below the melting threshold of Si.

In order to investigate this effect in more detail, as a first approach we have calculated the scattered field of a spherical particle of arbitrary size in free space, as it is described by the well-known Mie theory [3]. The patterns resulting from these calculations are shown in Fig. 1a for a 320 nm (bottom) and an 800 nm (top) particle illuminated by a plane wave with a wavelength of 800 nm. They exhibit a double-peak structure with a distance between the maxima of about 300 nm for both particle sizes, whereas the absolute value of the intensity enhancement differs by a factor of 4.5.

![Figure 1: Field intensity enhancement and ablation pattern underneath colloidal particles with diameters of 800 nm (top) and 320 nm (bottom) on a silicon substrate. The direction of the electrical field is oriented vertically. The Fi numbers indicate the field intensity enhancement in the maximum (as compared to the incident intensity) a) Calculated field enhancement by neglecting the influence of the substrate. b) Ablation pattern resulting from illumination by a fs laser pulse. c) Calculation including the influence of the substrate.](image)

In a next step we compared these calculations to the experimental results shown in Fig. 1b. As previously demonstrated [4], fs laser irradiation of particles on surfaces creates an ablation pattern underneath each illuminated particle. For constant laser fluences, all sites of ablation exhibit the same morphology. Underneath particles 320 nm in diameter, the ablation pattern shows a double hole structure, yet the distance between the maxima is obviously smaller than for the free space calculation. The pattern formed underneath 800 nm particles does not show two peaks at all.

Apparently, the Mie calculations differ substantially from the experimental findings. However, since this theory holds only for an illuminated sphere in free space, one might expect that the differences are due to the influence of the silicon substrate. We have therefore performed semianalytical field calculations using the Multiple Multipole (MMP) technique [5]. As it is obvious from Fig. 1c, much better agreement with the experimental findings is achieved in this way.

Besides the mapping of the field at particles, the creation of holes can also be used for nanolithography. As colloidal particles can be deposited onto various materi-
als including polymeric, biological, and semiconducting ones, this method seems to be feasible for nanostructuring of such technologically important substrates. An intriguing possibility besides the fabrication of single holes is in this context the exploitation of self-organization processes, e.g. the utilization of 2-D colloidal monolayers, for the structuring process [1]. Illumination of such a colloidal monolayer by an ultrashort laser pulse leads to a regular array of holes. Since it is a parallel technique, it allows the structuring of large substrate areas and can result in a million holes and more for a single shot, limited only by the size of the laser spot.

![Figure 2: Hole arrays formed after illumination of a hexagonal colloidal monolayer (sphere diameter 800nm) with a fs laser pulse. Left: silicon substrate, right: germanium substrate.](image)

Apart from its impact on nanostructuring and on the mapping of field distributions, the local substrate ablation induced by field enhancement is also important in the so-called “Laser Cleaning” process [6]. Laser cleaning as a contactless process is currently discussed as an alternative technique for the removal of ultrasmall particle contaminants from surfaces of, e.g., silicon wafers used by the semiconductor industry. Originally, the observed particle lift-off was attributed to the acceleration of the particles resulting from the thermal expansion of the substrate surface upon irradiation with the laser pulse. Only very recently it could be shown experimentally [4] that local ablation of the substrate can also play a dominating role in the cleaning process. This is further confirmed by the results discussed above. Especially for the case of fs pulses, particle removal always comes along with hole creation, i.e. local substrate ablation. In order to avoid the damage of the substrate by the cleaning process - which is if course unacceptable for microelectronics - a modification of pulsed laser cleaning has been developed, which is called “Steam Laser Cleaning”. There a thin liquid layer is adsorbed on the substrate just before the laser pulse is applied, and the rapid evaporation of this film after laser heating leads to a very gentle and efficient particle removal without surface damage [7].

The results presented here are of relevance for the nanostructuring of surfaces, for the mapping of field distributions and for applications such as laser cleaning. From our investigations it is obvious that underneath the irradiated spheres one deals with light intensities far above the nominal applied ones, a phenomenon which has to be taken into account as a primary source for local damage at surfaces irradiated by short laser pulses. Well-defined colloidal particles as they have been used in this research have proven as valuable test samples for systematic studies of these effects.

E4 Light propagation in concentrated, strongly scattering media and localization of light

R. Tweer, R. Lenke, S. Eiden, M. Störzer and G. Maret

The problem of light propagation in strongly scattering systems can in principle be treated by solving Maxwell's equations. However, this is a very complicated task - analytically as well as numerically - and considerable simplifications are necessary before qualitative and quantitative predictions can be made. The most common approach uses a Green's function formalism [1] resulting in a diagrammatic path model of amplitudes and - under the assumption of no correlations - in a path model of intensities. The latter can be mapped onto a random walk of photons with a characteristic Boltzmann diffusion constant $D_B = v_B \ell^* / d$, $v_B$ being the energy transport velocity, $\ell^*$ the transport mean free path of uncorrelated, random steps and $d$ is the dimensionality.

Most experimental results are accounted for by the diffusion model, even in cases where the diffusion constant cannot be forecast explicitly. A result of the diffusion theory is, for example, that the total transmitted intensity through a non-absorbing 2D or 3D slab of thickness $L$ follows Ohm's law (i.e. $\propto L^{-1}$).

However, there are correlations between each path and its reversed counterpart - giving an effect not considered in the diffusion model. Both paths have exactly the same length and thus are always in phase at each starting and end point of a loop. This correlation results in a constructive interference enhancement of a factor of two at these points. This so-called coherent backscattering (CB) increases the probability of light paths to form closed loops by a factor of two with respect to models neglecting all interferences. As a consequence, CB reduces the diffusion constant. In very strongly scattering samples, where $k e \ell^* \approx 1$ (Ioffe-Regel criterion, ‘$e$’ for effective medium), a ‘non-classical’ transport behavior was predicted, called strong or Anderson localization [2]. Anderson localization of light, solely due to disorder, has not yet been observed beyond any doubt [3,4].

We have studied the transition to Anderson localization within a self-attracting random walk model basing on our well established Monte-Carlo simulations [5,6,7]. In a random walk without CB, the next scattering event $(n+1)$ after point $r_n$ is chosen at random angle and at a distance $dr$ with an exponential distribution $p(dr) \propto \exp(-dr/\ell^*)$ according to Lambert-Beer's law. Including CB, the wave feels "earlier visited" scattering positions through an increased attraction. This is taken into account by a "CB-region" of volume $\lambda^2$ around every previous visited position. In our model we approximate this regions by gaussians.

$$p(r_{n+1}) = C e^{-dr/\ell^*} \left( 1 + \sum_{i=1}^{n-2} \exp \left[ -\frac{|r_{n+1} - r_i|^2}{2\sigma^2} \right] \right)$$

(1)

with $\sigma = 1/2k e$, $dr = |r_{n+1} - r_n|$ and a normalization constant $C$. The 1 in the sum represents the incoherent summation of all paths corresponding to the incoherent background of the CB-cone. The $(n-1)th$ point is excluded from the sum as single scattering does not contribute to CB. Within the explored range of simulated path lengths, our results reproduce the behavior which was found by other theories (see fig.1): A phase transition from weak to strong localization is observed at a value of $k e \ell^* \approx 2$. The jump in the curves seen in fig.1 are due to the limited computational-power. By the change from simulations of $10^4$ to $10^5$ scattering events (change from line to marks), the number of photons for averaging decreases from $10^4$ to some hundred. It’s important to notice that the error in the slope is much smaller than the error in the absolute value. This means that each photon is localized sooner or later - only the center of every localized photon is different. We have also used these simulations to study the diffusion of photons transmitted through a slab with the contribution of CB. We find a broadening of the pulses (see fig.2). The photons are "stored" inside of the sample for some time. On the other hand, the total transmission changes from the 1/$L$-behaviour in the diffusion limit to an exponential decay at $1/k e \ell^* = 1$ (see inset of fig.2). While this model reproduces features of current localization theories, it only...
applies to the weak scattering limit where correlations (other than CB) between different scattering events can be neglected. For strongly scattering media this simplification is not longer correct and overlapping of different scattering areas (cross sections) has to be taken into account as sketched in fig. 3: CB creates a twofold interference enhancement around any scatterer. The dashed line in fig.3 indicates the result of equation (1) with a maximum above 2 for correlated scatterers while CB allows an enhancement at most, or in other words: with an intensity ratio $R_I = \frac{coh}{(incoh + coh)} \leq 0.5$. Therefore we corrected the probability distribution by replacing the summation with the envelope. This correction gives substantial different results: The onset of localization shows up for $R_I \simeq 1$ (see fig. 1) while in the corrected model $R_I$ is always below 0.5 (see fig.4). Here the diffusion constant is still reduced by CB, but stays finite at all (simulated) times. Within this refined model, all indicators of strong localization related to CB disappear.

It would be interesting to study, wether this model can be mapped onto more rigorous localization theories and wether the refinements suggested here would affect the strong localization there as well.

On the experimental side the observability of Anderson localization requires samples with $k_c \ell^* \rightarrow 1$.

The scattering cross section $\sigma_{sca}$ of a (spherical) particle with given radius $R$, index of refraction of the particle $n_i$ and surrounding matrix $n_m$ can be calculated with Mie-Theory [8]. In very dilute systems with a density of scatterers $\varrho$ the transport mean free path is $\ell^* = \frac{1}{\varrho \sigma_{sca}}$. In systems with increasing volume fraction $f$ strong deviations from this law are found [9] due to correlations between the scatterers. The scattering cross section is then calculated by convoluting the form factor $F(\theta)$ with the structure factor $S(\theta)$.\footnote{The structure factor was calculated in the Percus-Yevick closure relation of the Ornstein-Zernike-equation.}

$$\sigma_{sca} = \frac{\pi}{k^2} \int_0^\pi F(\theta) S(\theta) \sin \theta d\theta$$

Another problem to be solved for highly concentrated media is the calculation of the averaged index of refraction. Mean field theories like the Maxwell-Garnett (MG) theory [8] are often used, but in order to take the Mie-resonances into account, we decided to use the energy density coherent potential approximation (ECPA) [10]. The idea of this theory is to take one representative scatterer and to substitute the surrounding medium by an effective and homogenous medium with $n_{eff}^2 = \epsilon_{eff}$.

The positions of the particles are expected to be random under the condition that there is no overlapping between them. In the distribution of distances one finds a maximum at $R_{\epsilon} = R/f^{1/3}$ (see fig. 5). This distance is taken as the radius of the basic scattering volume. From this, we get a self-consistent Ansatz with the postulation that the energy content of a wave $\Psi_{in}$ passing through a
sphere filled with effective medium should be the same compared to a sphere filled with the scatterer coated with a surface of the matrix medium $\epsilon_{m}$.

The resulting effective index of refraction is used to calculate $F(\theta)$ and $S(\theta)$. In figure 6 we compare the results for the $l^{*}$ values using a mean field calculation (MG) and the ECPA. The most obvious difference is the divergence of $l^{*}$ (i.e. $1/l^{*} \rightarrow 0$) around the Mie-resonances in the calculations using the ECPA. The mean field approach of Maxwell-Garnett can be interpreted as a thorough polydisperse medium, whereas the ECPA results represent a perfect monodisperse system. The real samples will be located between both cases.

The experiments we use to measure $l^{*}$ from coherent backscattering and diffusion coefficients by a time of flight setup (ToF) have been described in earlies publications [11,12]. The data was extracted by fitting simulated curves to the CB-data and by comparing the ToF-data with classical diffusion theory (fig. 7+8).

We used samples of different TiO$_2$ powders from Dupont. The calculated scattering values were averaged over the polydispersity of the powders. We found very good agreement comparing the experimental data of the transport mean free path (see fig.9) and the diffusion constant

\[ l^* \approx \frac{1}{7 \mu m} \] at a volume fraction of $f = 0.6$ or in other words $k_{e} l^* \approx 3.5$.

In order to increase the scattering strength of the particles we studied coated sphere. They were synthesized by coating a core particle with another material. We used core spheres of silica and coated them with titanium dioxide. We extended our calculations for coated spheres to

Figure 5: Sketches to explain the energy density coherent potential approximation.

Figure 6: Calculations of $1/l^{*}$ with the Maxwell-Garnett theory (circles) and with the ECPA (line) for spheres of TiO$_2$ with a volume fraction of $f = 40\%$. This corresponds to a polydisperse or a perfect monodisperse sample respectively.

Figure 7: Typical CB-cone measured with the wide-angle setup and fitted by simulations.

Figure 8: Typical pulse broadening for different sample thicknesses and densities measured with the time of flight setup. The data is compared with theory curves calculated with classical diffusion theory. (see fig.10) with our calculations – without any adjustable parameter used for fitting.

On the other side, the calculated minimum value of the transport mean free path for titanium dioxide spheres is

\[ l^* \approx \frac{1}{7 \mu m} \] for different volume fractions. The experimental data is compared with averaged ECPA-calculations.
find the parameters with the largest scattering cross sections. The samples we produced were close to this regions and had a polydispersity of about 10 - 20 %. Now the ECPA calculations had to be averaged over the polydispersity of the core and of the total radius. Because of numerical difficulties, we kept the inner radius fixed while averaging over the total radius distribution. This is done for the mean radius we found when analyzing SEM-pictures and the neighbor radii. Again the results showed good agreement between calculations and experiment (see fig.11 and fig.12). The deviation seen in the results of the diffusion coefficient (fig.12) for small volume fractions are caused by an approximation we had to use. The ECPA actually assumes a homogeneous sphere as the scatterer. The expansion to a sphere with different shells would have gone beyond the scope of this work. Therefore we used the Maxwell-Garnett approach to homogenize the index of refraction. This approximation is acceptable for higher volume fractions where single particle effects loose importance.

At the moment, we are trying to create hollow spheres for a maximal index-jump inside of the sample. With this particles the calculations give a value of \( k_e \ell^* \approx 1.45 \). This should allow samples showing large deviations from classical diffusion behavior.

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M.F. Miri and N. Rivier

*The equilibrium state of 2D foams*


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*Continuum elasticity with topological defects, including dislocations and extra-matter*

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### Scientific Staff

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Goldbach, Christoph (Lei)
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Möbius, Walter (Ma)

Abbreviations:
(Di): Dieterich; (Kr): Klein; (Lei): Leiderer; (Ma): Maret; (Ni): Niehara; (Sta): Stark; (Fu): Fuchs;