

**Final report**  
**Independent Junior Research Group**

**Colloids at Fluid Interfaces**

**Project N01 of the Transregional Collaborative  
Research Centre SFB–TR6**

# 1 General Information

## 1.1 Title

Colloids at Fluid Interfaces

## 1.2 Research Areas

Theoretical Physics, Soft Condensed Matter

## 1.3 Principal Investigator

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## 1.4 Duration

July 1, 2006 – September 30, 2011

## 2 Summary

The research of the Independent Junior Research Group in the period July 2006 – September 2011 is documented in 30 refereed publications [N01-1]–[N01-30], 2 refereed conference proceedings [N01-31, N01-32] and 2 completed dissertations [N01-33, N01-34]. Among the publications are 4 publications in *Physical Review Letters* [N01-4, N01-20, N01-22, N01-29]. The corresponding references are given in section 3.6 in chronological order and with full title.

The central research topic for the Junior Research Group was the *behaviour of colloids trapped near or at fluid interfaces*. These interfaces may alter the effective interactions between the colloids considerably, thereby giving rise to ordering and self-assembly phenomena different from bulk suspensions. Depending on the size of the colloids (coming from micrometers down to a few nanometers) different physical regimes are probed with an increasing influence of the substructure of the interface. We have investigated all these regimes, and the corresponding highlights can be summarized as:

- Analytical and numerical treatment of colloidal charge renormalization at interfaces, experimental confirmation [N01-4, N01-9, N01-26]
- Calculation of capillary-wave mediated interactions between isotropic and anisotropic particles as a novel example for the Casimir effect in Soft Matter [N01-1, N01-17, N01-19]
- Gravity in a Petri dish – investigations of systems with  $\sim 10\text{-}\mu\text{m}$ -particles at interfaces as systems analogous to screened gravity in two dimensions: prediction of novel dynamic behavior [N01-29]

Methodically, we also developed classical density functional techniques for inhomogeneous systems such as interfaces. Here, an important result was

- Development of multidimensional density functional methods for fundamental measure functionals: application to depletion interactions in hard systems and identification of a novel form for the colloidal limit [N01-15, N01-18]

The work on density functional theory led to insights on the *fluid-crystal and fluid-glass transition for hard spheres*, in collaboration with mainly other groups in Mainz. The highlights here are:

- Identification of a precursor-mediated process of homogeneous nucleation in hard sphere systems [N01-20]
- Investigation of the critical packing fraction  $\eta_c$  for the glass transitions for hard spheres confined in a slit of width  $H$ : oscillating behavior of  $\eta_c(H)$  [N01-22]

## 3 Research report

The target of our research in the documented period was mainly the investigation of the behavior of colloidal systems at fluid interfaces. At fluid interfaces, partially wetting colloids become strongly trapped and occasionally show unexpected self-assembly behavior. Such behavior can be attributed to effective interactions between the colloids which are qualitatively different from the corresponding ones in bulk systems and arise due to the very presence of the interface. In co-authorship with Dr. Fernando Bresme (Imperial College London), we have reviewed the experimental and theoretical progress which has been achieved in this field over the last years [N01-3]. In the first proposal for the Junior Research Group (2005) I identified three different regimes in which the effective interactions between the colloids are governed by different physical aspects of the fluid interface. These different regimes are roughly (but not exclusively) determined by the size of the colloids:

1. Classical capillary regime: colloid size  $\sim 1 \mu\text{m}$
2. Fluctuation regime: colloid size  $10 \text{ nm} \dots 1 \mu\text{m}$
3. Molecular regime: colloid size  $< \text{few nm}$

These colloid size regimes given above are valid for the case of interfaces between phases with truly molecular constituents such as air-water or oil-water interfaces. In the case of interfaces of more complex fluids such as colloid-polymer mixtures the “molecular” size (of the colloids and polymers) may be up to 100 nm, correspondingly one would expect that the molecular regime applies if other colloids trapped at the interface reach this “molecular” size. Our research in these three different regimes will be discussed in turn.

During the last 1.5 years we have started collaborations to investigate the phase behavior of hard spheres more closely. This will be summarized under the heading

4. Fluid-crystal and fluid-glass transition for hard spheres

### 3.1 The classical capillary regime

#### 3.1.1 Characteristics of capillary interactions

Partially wetting colloids of micrometer size become almost irreversibly trapped at fluid interfaces and thus form an effectively two-dimensional (2d), soft system. The progress in manufacturing such colloids with different shapes and varying surface properties, combined with the relative ease in observing them using optical microscopy, has triggered a number of experimental studies in the past twelve years. Some of these reported self-assembling behavior into clusters and froths which seemed to point at effective intercolloidal interactions

which are long-ranged and attractive. In this respect, the effective interactions at the interface would be qualitatively very different from the corresponding ones in bulk systems. For the discussion, it is useful to split these effective interactions between colloids at an interface into “direct” and “interface-mediated” interactions. Direct interactions are also present in the bulk but become modified through the presence of an interface (e.g. electrostatic interactions). It is the characteristics of the classical capillary regime that the interface-mediated interactions arise through static deformations of the soft interface, i.e. the interface acts as a 2d medium for the colloids and gives rise to capillary forces. Indeed these capillary forces can be long-ranged as the example of millimeter sized particles (say, needles) on water shows: they create dimples around them with a deformation varying logarithmically with the distance from the particles and ranging out a few millimeters. The particles are attracted towards each other through these dimples, with a potential also varying logarithmically with the interparticle distance. Contrary to a common misbelief, the logarithmic potential does not stem from the minimized free energy of the interface but rather one particle “falls” into the dimple around the other particle and thereby lowers its gravitational energy (for a review of these matters, see Ref. [N01-8]). It is tempting to attribute such a mechanism also to the capillary interactions of micrometer sized colloids. Unfortunately, the gain in gravitational energy scales  $\propto R^6$  (where  $R$  is the radius of a spherical colloid) and becomes unimportantly small in the micrometer domain. However, other direct interactions may also give rise to forces on the colloids perpendicular to the interfaces which drive them into one phase and create a dimple around them. Considering such systems, we have obtained the following results:

- In a mechanically isolated system (colloids and interface) the total vertical force on the colloids is balanced by a corresponding stress on the interface. As a consequence, the long-ranged attraction  $\propto \ln d$  (where  $d$  is the interparticle distance) is absent. We showed this result previously for planar interfaces but it holds also for colloids on droplets [N01-2, N01-10].
- External forces (gravity or an external electric field, say) may induce the logarithmic attractions, as well as restricted geometries (e.g. colloids floating on a thin film). A detailed analysis of an experiment using nematic films showed, however, that the magnitude of the such induced long-ranged attraction falls quickly with increasing film thickness [N01-13].
- Generally, the capillary interactions between particles can be cast into the form of two-dimensional electrostatics [N01-10]. In this picture, the long-ranged attractions are due to suitably defined “capillary charges”. The requirement of mechanical isolation (force and torque balance) corresponds to a zero net charge and zero dipole moment of “dressed” particles.
- Anisotropic particle shape gives rise to capillary multipoles, with the quadrupole being asymptotically dominant (the corresponding quadrupole–quadrupole interactions

decay  $\propto 1/d^4$ ). For the experimentally accessible case of ellipsoidal particles the orientation dependence of the capillary interaction is very pronounced [1, 2] and influences the self-assembling process at the interface considerably [3]. We have developed an efficient method, based on an expansion in elliptic multipoles, to calculate the capillary interaction for ellipsoids with arbitrary aspect ratio [N01-11]. This method appears to be fast enough for a direct implementation in a simulation code for studying the self-assembly of ellipsoids.

### 3.1.2 Charged colloids

The special case of surface-charged colloids is of great practical importance. When brought to an interface between a nonpolar and polar medium (e.g., air-water or oil-water interfaces), usually only the colloid surface facing the polar medium (water) becomes charged. The net effect of a double layer close to only one side of the colloid is an electric dipole moment  $p$  (oriented perpendicular to the interface). This gives rise to a “direct” repulsion between the colloids  $\propto p^2/d^3$ . For this system, we have obtained the following results:

- A simple argument within linearized Debye-Hückel theory gives  $p \propto q\kappa^{-1}$  where  $q$  is the charge on the water side of the colloid and  $\kappa^{-1}$  is the electrostatic screening length in the water which characterizes the extent of the double layer. However, an analysis of the nonlinear Poisson-Boltzmann equation in the interface geometry yields a drastically changed dependence due to charge renormalization:  $p \propto \ln(q\kappa^{-1})$ . This result also holds for arbitrary colloid geometry if the screening length is smaller than the local radii of curvature on the colloid surface [N01-4]. The relatively weak, logarithmic dependence of the colloid dipole moment on charge and screening length implies that the repulsion is robust with respect to variations in surface charge densities and electrolyte concentrations. In a collaboration with a group in Leuven (Jan Vermant) and at the University of Delaware (Eric Furst) we have experimentally confirmed this peculiar dependence of the renormalized dipole moment on the electrolyte concentration. This was done by measuring the force between isolated pairs of colloids (radius 1.55  $\mu\text{m}$ ) trapped at an oil-water interface and held by laser tweezers [N01-9].

Further, more precise experiments by Vermant and Furst [4] indicated a quantitative discrepancy with the renormalization theory for the absolute dipole strength. We have refined our theoretical analysis and found the absolute dipole strength to be proportional to the contact potential at the charge colloid surface [N01-26]. This contact potential is very sensitive to details of the double layer structure. We found that taking into account finite ion sizes and a nonlinear permittivity of water brings the experimental and theoretical results close together. Nevertheless, some discrepancies remain which call for yet more refined double layer theories. Thus, the measurement of the interaction of charged colloids gives a unique opportunity to judge these theories for the double layer.

- It is interesting to note that the effective dipole moment of an arbitrary charge distribution at an electrolyte interface always points perpendicular to the interface. This can be shown rigorously [N01-7] and corrects claims in the literature that longer-ranged attractions may arise due to the attraction between dipoles which are oriented in the interface plane [5, 6].
- Charges on the colloids always give rise to ensuing interface deformations and capillary interactions. For the experimentally relevant case of mechanical equilibrium (no external electric field) we have found that these capillary interactions are attractive and asymptotically vary  $\propto 1/d^3$  as the “direct” dipolar repulsion [N01-6]. However, the capillary attraction is smaller than the dipolar repulsion roughly by a factor  $F/(2\pi\gamma R)$  where  $F$  is the electrostatic force acting on one colloid perpendicular to the interface,  $R$  is the colloid radius and  $\gamma$  is the surface tension. Only for very large bare charge densities on the colloid surface ( $> 1 e/\text{nm}^2$ ) and low surface tensions (e.g. water surfaces with surfactant) the capillary attraction might overcome the dipolar repulsion. Usually, surface charge densities are lower, and the ensuing interface deformation is actually in the sub-nm range [N01-5].

### 3.1.3 Gravity in a Petri dish

Above, we have shortly discussed the long-ranged, logarithmically decaying capillary interaction energies between colloids due to their weight. For only a few colloids of micrometer size, this pair interaction is negligibly small. However, a large ensemble of these colloids evenly spread at the interface should be thermodynamically unstable and collapse to clusters in which the particle density is determined by the shorter-ranged repulsions (steric or electrostatic, say). The reason for this behavior is that the internal energy per colloid is not bound from below for logarithmic, attractive pair potentials. This potential corresponds to the gravitational potential in two dimensions; indeed the instability of a gravitating, homogeneous mass distribution is a phenomenon known in cosmology as the Jeans instability [7]. In a recent study [N01-21], Alvaro Dominguez (University of Seville) and I have analyzed this instability in a coarse-grained mean-field approach, and we have identified the characteristic time and length scales on which the collapse occurs. It turns out that for a standard colloidal system (oil-water or air-water interfaces, charged microcolloids), colloidal sizes of around  $10 \mu\text{m}$  and observation times of the order of 10 hours should lead to visible clustering effects. (Ensembles of smaller colloids are not affected noticeably.) Interestingly, this size regime for the colloids has not been studied experimentally before with sufficient care. A sharper focus here offers the possibility to study the structure formation in a two-dimensional gravitating “universe in a Petri dish”.

In contrast to the long-ranged gravitational attractions, the capillary attractions are cut off at the capillary length  $\lambda$ . Although very large for water-air interfaces ( $\lambda \sim 3 \text{ mm}$ ), it can be tuned by changing the surface tension and the mass density difference of the two phases forming the interface. Thus, in principle one has a system that has an interparticle

attraction with tunable range from  $10^3 R \dots 10^0 R$  (where  $R$  is the radius of the colloids) – “screened gravity”. The screening has a profound influence on the dynamics of the instability. Using Brownian dynamics simulations, density functional theory, and analytical perturbation theory, we have studied the collapse of a finitely-sized patch of colloids [N01-29]. Whereas the limit  $\lambda \rightarrow \infty$  corresponds to the global collapse of a self-gravitating fluid, for intermediate  $\lambda$  we predict theoretically and observe in simulations a ringlike density peak at the outer rim of the disclike patch, moving as an inbound shock wave. For smaller  $\lambda$  the dynamics crosses over to spinodal decomposition showing a coarsening of regions of enhanced density which emerge from initial fluctuations.

The theoretical results reported in this section have been obtained in collaboration with Siegfried Dietrich (MPI for Metals Research Stuttgart), Derek Frydel (MPI for Metals Research Stuttgart and later postdoc in the Junior Group), Johannes Bleibel (joint postdoc of the MPI for Metals Research Stuttgart and the Junior Group) and Alvaro Dominguez (University of Seville). The capillary interaction between ellipsoids has been calculated by my PhD student Hartwig Lehle (MPI for Metals Research Stuttgart). For the determination of the charged colloid interaction, I collaborated with Jan Vermant (Catholic University Leuven) and Eric Furst (University of Delaware) and their groups.

## 3.2 The fluctuation regime

When a fluctuating medium with long-ranged, power-law correlations is confined between a set of boundaries, forces with likewise long-ranged character are induced between the boundaries. There are different possible sources of such fluctuations in a medium: in a quantum-mechanical system it is the zero point energy of the vacuum (or ground state), and in a classical system it is the finite temperature which causes order parameter fluctuations. A classical variant of the Casimir interaction is found for the case of particles (colloids) that are trapped at membranes or at the interface of two fluid phases. In this two-dimensional latter instance, thermally excited height fluctuations of the interface which have long-ranged nature are disturbed by the presence of colloids. On a coarse-grained level, the energy spectrum of the fluid interface is very well described by an effective capillary wave Hamiltonian which governs both the equilibrium interface configuration and the thermal fluctuations around this equilibrium. Since capillary waves are the Goldstone modes of the broken translational symmetry pertaining to a free interface, their correlations decay logarithmically in the absence of gravity and the corresponding fluctuation-induced forces are a manifestation of the Casimir effect for a Gaussian theory in two dimensions. Compared to manifestations of the Casimir effect in a three-dimensional bulk medium, a new phenomenon arises here: The boundary of the fluctuating interface, which is represented by the contact line on the colloid surface, is itself mobile due to position fluctuations of the colloids and finite surface tensions of the colloid-liquid interfaces and thus the Casimir force receives another contribution due to these “fluctuating” boundaries.



Our research on the Casimir interaction at fluid interfaces has been focused on two aspects: the influence of the “fluctuating” boundaries and the consequences of possible anisotropic particle shape. In particular we have obtained the following results:

- For colloids at distance  $d$  with a circular cross section (spheres or circular disks, radius  $R$ ) we have examined the effect of the “fluctuating” boundaries in detail [N01-1]. In the long-range limit,  $d \gg R$ , the resulting Casimir force depends crucially on the boundary conditions at the three-phase contact line on the colloids’ surfaces. There one observes an interesting interplay between the attractive interaction from the interface fluctuations and a repulsive interaction caused by the fluctuating boundary conditions. This results in a cancellation of the leading terms up to a certain order in  $1/d$ , which is determined by the specific model considered for the boundary conditions. For freely fluctuating colloids – either with a pinned or unpinned contact line – the Casimir force is characterized by a fast decay  $\propto -d^{-9}$ . For a pinned contact line, fixing colloidal degrees of freedom leads to longer-ranged forces which are  $\propto -d^{-5}$  if the orientation of the colloids is fixed and  $\propto -1/d \ln d$  if both orientation and vertical position are fixed. Moreover, by combining different boundary conditions on the interacting colloids, a sign reversal of the Casimir force from attraction to repulsion may be observed. The cancellation of the leading terms from the mean-field and the fluctuation part can be understood in an alternative approach to compute the partition function of the system in which the analogy of the effective Hamiltonian to electrostatics is exploited.
- In Ref. [N01-31], we have further examined the effect of a three-phase line tension on the stability of a single colloid (radius  $R$ ) at a fluid interface and the Casimir interaction between two colloids, relevant for nanoscopic particles. Quite often, the stability of colloids at a fluid interface with respect to vertical displacements from their equilibrium position is discussed using a rigid interface model. For partially wetting colloids with a negligible line tension, this results in a steep potential well with spring constant  $k = 2\pi\gamma$  ( $\gamma$  is the surface tension of the fluid interface). A finite line tension  $\tau$  changes the spring constant by a term  $\propto -\tau/R$  and may induce metastability for the trapped colloids for certain positive values of  $\tau$ . Within a perturbative model we have found that the potential well is considerably broadened by capillary waves (qualitatively,  $k \rightarrow k/\ln(\lambda_c/R)$  where  $\lambda_c$  is the capillary length in the interface system). This suggests also a reduction of the metastability barriers in case of positive line tensions. The power-laws of the Casimir force found previously remain unchanged after inclusion of the line tension contribution. Only the respective amplitudes receive contributions which are line tension dependent.
- We have investigated the Casimir force between ellipsoidal colloids to examine the influence of particle anisotropy [N01-17]. The asymptotic expansion of the Casimir force was obtained in a *tour de force* using elliptic multipole expansions. We remark that our results complement current efforts of the quantum-mechanical Casimir community to obtain the interaction between anisotropic particles (see Refs. [8, 9]). Interestingly, the

force with the longest range ( $\propto 1/(d \ln d)$  in the case of fixed colloids and pinned contact lines) remains isotropic in the interface plane. Only when the fluctuations of the contact line are included, an orientation dependence of the Casimir force is observed.

- In collaboration with Fernando Bresme (Imperial College), we examined the effective interaction between truly nanoscopic colloids at a liquid–vapor interface of Lennard–Jones particles using Molecular Dynamics [N01-19]. For surface–to–surface distances between the colloids beyond already five Lennard–Jones diameters we could observe the characteristics of the Casimir force asymptotics which we derived in Refs. [N01-1, N01-31]. This provides some reassurance that the coarse–grained description of the interface using a simple capillary wave Hamiltonian is indeed valid down to microscopic distances and colloid sizes, and it only fails to capture the interaction at short distances.

The results reported in this section have been obtained mainly by my PhD students Hartwig Lehle (MPI for Metals Research Stuttgart) and Ehsan Noruzifar (Mainz University). For the Molecular Dynamics simulation of particles at the interface we collaborated with Fernando Bresme (Imperial College London).

### 3.3 The molecular regime

When the size ratio between colloids and solvent particles becomes smaller (down to a value of 10 and smaller), the thermally roughened interface will be about as broad as the size of the colloids. There it appears to be inappropriate to study effective interface models such as a simple capillary wave model to get a handle on the effective potential between the colloids. In general, the solvent–mediated part of the effective potential is  $\propto -\ln g_{cc}(z_1, z_2, r_{||})$  where  $g_{cc}$  is the colloid–colloid pair correlation function in the background of a solvent forming a liquid–vapor interface (at  $z = 0$ , say). Since the translational symmetry is broken by the interface,  $g_{cc}$  depends on both the distances  $z_1$  and  $z_2$  of the two colloids from the interface and their distance  $r_{||}$  in the interface plane. There is little to no previous theoretical work on such inhomogeneous pair correlation functions in colloid–solvent mixtures. From the simulation side, our already mentioned study of the Lennard–Jones solvent with colloids (size ratio 7) [N01-19] partly utilized this approach via  $g_{cc}$  to deduce the effective potential. As mentioned in Sec. 3.2, it is quite surprising to observe the signature of the Casimir interaction in this effective potential already at intermediate distances between the colloids. For smaller distances, the effective potential is very different from both the effective potential between the colloids in bulk liquid or vapor which calls for more detailed theoretical investigations.

The theory of integral equations and classical density functional theory are the methods of choice for studying pair correlation functions in liquids. Some time ago, I have developed an approach [10] utilizing reference system functionals in the closure to the Ornstein–Zernike equation which relates pair correlation to direct correlation functions. The parameters of the reference system are determined via an optimization criterion. This approach has proved to

be very successful for simple bulk liquids, owing to the fact that the hard sphere reference systems used there can be described by accurate density functionals of fundamental measure type [11, 12]. Several difficulties (numerical as well as conceptual ones) have to be overcome to employ this approach also to study the inhomogeneous pair correlation functions in the presence of the interface. We have not yet obtained a full solution in this case. Several developments on this way are reported below:

- Together with a French group (Said Amokrane, Paris) we have proved [N01-14] that the optimization criterion in the reference functional approach proposed by me in Ref. [10] is indeed a criterion for minimizing the bulk free energy of the system. The precision of the phase diagram following from this minimized free energy has been demonstrated for the case of the hard-sphere-Yukawa fluid with very short-ranged tails. Here, the binodal is notoriously difficult to obtain using theoretical methods, but these systems are very interesting since with the range of the interparticle attraction becoming shorter the liquid-vapor transition becomes metastable in favor of a liquid-solid or glass transition.
- Using the reference functional approach, I could contribute to a project between the Binder group, Mainz, and BASF Ludwigshafen. The target here was to develop robust coarse-grained models for solutions of alkanes in dipolar (e.g.  $\text{NH}_3$ ) and quadrupolar solvents (e.g.  $\text{CO}_2$ ) [N01-32]. The theoretical binodals for  $\text{CO}_2$  are in close agreement with experiment, except for the immediate vicinity of the critical point [N01-12]. The critical region for  $\text{CO}_2$  was analyzed in more detail in Ref. [N01-16], together with a critical assessment of the coarse-graining approach.
- We have analyzed the depletion potential in a binary hard sphere mixture (colloids and solvent) with large size asymmetry, considering both the colloid-colloid and the colloid-wall interaction where also the wall is hard. This has been done by explicitly calculating the solvent density profiles around two fixed objects (two colloids or colloid and wall) using fundamental measure functionals. Technically, the evaluation of these functionals in such geometries requires faster numerical methods than previously used. We have developed those successfully [N01-18]. (These methods can be transferred to the problem of finding the pair correlation functions in the presence of an interface.) The resulting solvent density profiles are in good agreement with simulations, done in collaboration with Tanja Schilling, Mainz [N01-18]. The results for the depletion force for size ratios up to 100 allowed us to establish a new approximation for the colloidal limit (the limit of infinite size ratio), replacing the venerable Derjaguin approximation [N01-15].
- Again in collaboration with the Binder group, we analyzed the long-standing problem of the Tolman length for simple fluids. The Tolman length  $\delta$  is the leading correction to the surface tension of a drop with radius  $R_d$ ,  $\gamma(R_d) = \gamma(\infty)/(1 + 2\delta/R_d)$ . and its sign and magnitude has been debated for long in the simulation community. Applying a thermodynamic analysis of finite system, the simulation results now point strongly to

negative and small values of  $\delta$ , in agreement with our density functional calculations. In contrast to the Tolman correction to the surface tension, higher-order corrections differ noticeably between simulation and density functional theory which calls for further analysis [N01-23].

The results on the depletion problem have been obtained mainly by my postdoc Vitalie Botan and PhD student Florian Pesth. The interpretation in the colloidal limit was developed together with Roland Roth (MPI for Metals Research Stuttgart) and Pawel Bryk (University Lublin). Complementary simulations have been performed by Tanja Schilling (Mainz). The formal proof for the minimization criterion in the reference functional has been performed in collaboration with Said Amokrane (University Paris Est). The application of the reference functional approach to coarse-grained models of CO<sub>2</sub> was done within the Mainz-BASF project of the Binder group, most notably with Bortolo Mognetti (now University of Oxford). The Tolman length project was in collaboration with Benjamin Block (diploma student) and Peter Virnau from the Binder group as well as Subir Das from Bangalore.

## 3.4 Fluid–crystal and fluid–glass transition for hard spheres

### 3.4.1 Hard spheres: Fluid–crystal coexistence and nucleation

The work reported here resulted from collaborations with Tanja Schilling (simulation, Mainz and Luxembourg), Hans-Joachim Schöpe (experiment, Mainz) and Hartmut Löwen (theory, Düsseldorf) and it was supported by a grant within the DFG Priority Program SPP 1296 *Heterogeneous Nucleation*.

We have carried out a large-scale Monte-Carlo simulation of 216,000 hard spheres, starting from an overcompressed, homogeneous melt. (For simple potentials and small translational Monte Carlo steps, Monte Carlo is mimicking Brownian dynamics on long time-scales. It thus provides a suitable model for the actual dynamics of colloidal hard spheres.) We monitored the nucleation process in Fourier space (by analyzing the spherically averaged structure factor) and in real space (by analyzing the local cluster configurations). The analysis in Fourier space is usually done in light scattering experiments on nucleation, and Hans-Joachim Schöpe, being an expert in light scattering methods, performed the corresponding analysis for the time series of the simulated structure factor. This Fourier analysis revealed a two-step process in the growth of crystalline material in the melt. First, slow growth of a broad structure factor peak around the fcc(111) peak is seen pointing to the growth of still quite amorphous precursor material. Second, fast growth of the distinct peaks of the rhcp (random hexagonally close packed phase) shows that the precursor material is transformed into rhcp after a certain induction time. These findings are consistent with recent experimental work on the HS system [13]. Our real-space analysis revealed more details about the precursor phase and the transformation into rhcp crystallites than could be extracted from the experiment. We identified precursors as clusters with lower symmetry, i.e. containing

particles with only 5 to 10 crystalline neighbours (ideal fcc/hcp structures have 12). Within these clusters crystallites (with 11 or 12 crystalline neighbours according to our definitions) grow.

Two-step crystallization with a precursor phase can be expected in systems with possible metastable fluid–fluid critical points (e.g. proteins, alkanes) but are surprising in such a simple system as HS. Thus, different dynamics for the two order parameters density and structure seem to suffice for a two-step nucleation process. This work has been published by Physical Review Letters [N01-20].

We have also performed a comparative study of equilibrium hard sphere crystal properties using FMT (Fundamental Measure Theory) and Monte Carlo simulation [N01-24]. Free energies (computed in simulations using a novel method developed by T. Schilling [14]) and density distributions in the unit cell from both methods are in good agreement. In that respect, FMT is clearly superior to the traditional Ramakrishnan–Yussouf density functional (for a recent investigation see Ref. [15]) and weighted–density approaches [16, 17], but the improved accuracy comes at the cost of substantially increased numerical effort in minimizing the functionals. The full minimization of different variants of FMT functionals yielded unexpected differences between them. Only for a recently optimized version (White Bear II [18]) the constrained chemical potential at fixed vacancy concentration in the crystal shows the physically correct behavior which is a weak divergence for vanishing vacancy concentration.

### 3.4.2 Glass transition for hard spheres confined between hard walls

The work discussed below resulted from a collaboration with Simon Lang, David Hajnal and Rolf Schilling (Mainz) as well as Thomas Franosch (Erlangen). The glass transition was analyzed using a novel formulation of Mode Coupling Theory derived for inhomogeneous systems. Our contribution was the calculation of precise equilibrium pair correlations and structure factors for the metastable, inhomogeneous fluid confined between walls. These calculations were mainly carried out by my postdoc Vitalie Botan.

Hard spheres of a high packing fraction confined between parallel hard walls show a characteristic layering in the equilibrium density profile and the correlation functions. This layering should also reflect in dynamical quantities. In the mode coupling formulation, the dynamic effect of an arrest at the critical packing fraction of the glass transition comes about by a complicated nonlinear feedback of the equilibrium correlation functions into the dynamics. However, the numerical results for the critical packing fraction show an oscillatory behavior with the slit width which is very much alike the oscillatory behavior seen in e.g. the diffusivities which are among the fundamental dynamic quantities. The behavior of the diffusivities in turn can be very well related to the layered structure of the fluid [19], thus also the glass transition reflects layering in a clear and visible manner. This work has been published by Physical Review Letters [N01-22].

In a side project, we investigated mixing effects on the glass transition in a two-component mixture of hard discs [N01-25]. Mode coupling theory has been shown to be very reliable in predicting these mixing effects as a comparison with simulation shows [20].

### 3.5 Teaching and supervision of PhD theses

Four PhD projects are associated with the topics of the Junior Research Group.

- Hartwig Lehle has been funded by the Max Planck Institute for Metals Research (MPI-MF) Stuttgart and worked under my supervision on the fluctuation induced force between spherical colloids and the capillary interaction of ellipsoidal particles. He has completed his thesis in February 2008 [N01-33] and has continued to work for three months with the Junior Research Group (partly funded by MPI-MF and SFB-TR6). He has now a position with the company Robert Bosch GmbH.
- Ehsan Noruzifar is funded by the SFB-TR6 and works on the fluctuation induced force between anisotropic particles and the self-assembly of ellipsoidal colloids. He will finish his thesis in December 2009 and continue with a postdoc position with Roya Zandi (University of California at Riverside). He successfully attracted funds from the DAAD-RISE program to support a three-month internship of a Canadian student in our group (Markus Karahka, Dalhousie University).
- Florian Pesth is funded by the SFB-TR6 and works on density functional theory and integral equations in inhomogeneous systems. Due to his strong commitment in the administration of the Junior Research Group computing resources he will finish his thesis only in June 2010.
- Marlon Ebert started November 2008 and is supervised jointly by Peter Virnau and myself. Funding comes from the Center for Computational Methods in the Natural Sciences Mainz (SRFN) and Graduate School of Excellence (MAINZ). He is working on test particle dynamics in colloidal fluids using density functional methods on graphics cards and is expected to finish end of this year.

Although there are no teaching obligations with my position, I have been teaching at least one course per semester since Winter 2006/07. These courses are:

- *Theoretische Physik II: Analytische Mechanik*  
(Theoretical Physics II: Analytical Mechanics)
- *Wahlpflichtvorlesung Weiche Materie* (credit course Soft Matter) 3×  
These were joined courses with experimental colleagues (Hans-Joachim Schöpe and Günter Auernhammer) featuring experimental and theoretical “lab” parts

- *Wahlpflichtvorlesung Weiche Materie II* (credit course Soft Matter II)  
Jointly with Dr. Thomas Gruhn.
- *Spezialvorlesungen* (special topics lectures) 4×  
(Statistical mechanics of Liquids and Gases, Introduction to Path Integrals, Biomaterials, The Birth of Quantum Mechanics)
- *Vorkurs Mathematik für Naturwissenschaftler* 2×  
(prep course mathematics for beginning students in the natural sciences)
- *Ergänzungen zur Experimentalphysik für Chemiker* (experimental physics for chemists: supplements)

### 3.6 List of publications of the Junior Research Group

- **Peer-reviewed publications**

- [N01-1] H. Lehle and M. Oettel,  
*Importance of boundary conditions for fluctuation-induced forces between colloids at interfaces,*  
Phys. Rev. E **75**, 011602 (2007).
- [N01-2] A. Dominguez, M. Oettel, and S. Dietrich,  
*Absence of logarithmic attraction between colloids trapped at the interface of droplets, Comment on “Capillary attraction of charged particles at a curved liquid interface by A. Würger,*  
Europhys. Lett. **77**, 68002 (2007).
- [N01-3] F. Bresme and M. Oettel,  
*Nanoparticles at fluid interfaces,*  
Topical Review, J. Phys.: Condens. Matter **19**, 413101 (2007) .
- [N01-4] D. Frydel, S. Dietrich, and M. Oettel,  
*Charge renormalization for effective interactions of colloids at water interfaces,*  
Phys. Rev. Lett. **99**, 118302 (2007).
- [N01-5] M. Oettel,  
*Entrapment of charged, nonwetting colloids near oil–water interfaces,*  
Phys. Rev. E **76**, 041403 (2007).
- [N01-6] A. Dominguez, M. Oettel, and S. Dietrich,  
*Theory of capillary-induced interactions beyond the superposition approximation,*  
J. Chem. Phys. **127**, 204706 (2007).

- [N01-7] D. Frydel, A. Dominguez, and M. Oettel,  
*Multipole expansion of the electrostatic interaction between charged colloids at interfaces,*  
Phys. Rev. E(R) **77**, 020401 (2008).
- [N01-8] M. Oettel and S. Dietrich,  
*Colloidal interactions at fluid interfaces,*  
Langmuir **24**, 1425 (2008).
- [N01-9] B. J. Park, J. P. Pantina, E. Furst, M. Oettel, S. Reynaert, and J. Vermant,  
*Direct measurements of the effects of salt and surfactant on interaction forces between colloidal particles at water-oil interfaces,*  
Langmuir **24**, 1686 (2008).
- [N01-10] A. Dominguez, M. Oettel, and S. Dietrich,  
*Force balance of particles trapped at fluid interfaces,*  
J. Chem. Phys. **128**, 114904 (2008).
- [N01-11] H. Lehle, E. Noruzifar, and M. Oettel,  
*Ellipsoidal particles at fluid interfaces,*  
Eur. Phys. J. E **26**, 151 (2008).
- [N01-12] B. M. Mognetti, M. Oettel, L. Yelash, P. Virnau, W. Paul, and K. Binder,  
*Spherically averaged versus angle-dependent interactions in quadrupolar fluids,*  
Phys. Rev. E **77**, 051406 (2008).
- [N01-13] M. Oettel, A. Dominguez, M. Tasinkevych, and S. Dietrich,  
*Effective interactions of colloids on nematic films,*  
Eur. Phys. J. E **28**, 99 (2009).
- [N01-14] A. Ayadim, M. Oettel, and S. Amokrane,  
*Optimum free energy in the reference functional approach for the integral equations theory,*  
J. Phys.: Condens. Matter **21**, 115103 (2009).
- [N01-15] M. Oettel, H. Hansen–Goos, P. Bryk, and R. Roth,  
*Depletion interaction of two spheres. Full density functional theory vs. morphometric results,*  
EPL **85**, 36003 (2009).
- [N01-16] B. M. Mognetti, M. Oettel, P. Virnau, L. Yelash, W. Paul, and K. Binder,  
*Structure factors of Carbon Dioxide using a simple Coarse Grained model,*  
Mol. Phys. **107**, 331 (2009).
- [N01-17] E. Noruzifar and M. Oettel,  
*Anisotropies in thermal Casimir interactions: ellipsoidal colloids trapped at a fluid*



- interface*,  
Phys. Rev. E **79**, 051401 (2009).
- [N01-18] V. Botan, F. Pesth, T. Schilling, and M. Oettel,  
*Hard sphere fluids in annular wedges: density distributions and depletion potentials*,  
Phys. Rev. E **79**, 061402 (2009).
- [N01-19] F. Bresme, H. Lehle, and M. Oettel,  
*Solvent-mediated interactions between nanoparticles at fluid interfaces*,  
J. Chem. Phys. **130**, 214711 (2009).
- [N01-20] T. Schilling, H. J. Schöpe, M. Oettel, G. Opletal, and I. Snook,  
*Precursor-Mediated Crystallization Process in Suspensions of Hard Spheres*,  
Phys. Rev. Lett. **105**, 025701 (2010).
- [N01-21] A. Dominguez, M. Oettel, and S. Dietrich,  
*Dynamics of colloidal particles with capillary interactions*,  
Phys. Rev. E **82**, 011402 (2010).
- [N01-22] S. Lang, V. Botan, M. Oettel, D. Hajnal, T. Franosch, and R. Schilling,  
*Glass Transition in Confined Geometry*,  
Phys. Rev. Lett. **105**, 125701 (2010).
- [N01-23] B. J. Block, S. K. Das, M. Oettel, P. Virnau, and K. Binder,  
*Curvature Dependence of Surface Free Energy of Liquid Drops and Bubbles: A Simulation Study*,  
J. Chem. Phys. **133**, 154702 (2010).
- [N01-24] M. Oettel, S. Görig, A. Härtel, H. Löwen, M. Radu, and T. Schilling,  
*Free energies, vacancy concentrations and density distribution anisotropies in hard-sphere crystals: A combined density functional and simulation study*,  
Phys. Rev. E **82**, 051404 (2010).
- [N01-25] D. Hajnal, M. Oettel, and R. Schilling,  
*Glass transition of binary mixtures of dipolar particles in two dimensions*,  
J. Noncryst. Solids **357**, 302 (2011).
- [N01-26] D. Frydel and M. Oettel,  
*Charged particles at fluid interfaces as a probe into structural details of a double layer*,  
Phys. Chem. Chem. Phys. **13**, 4109 (2011).
- [N01-27] D. Deb, A. Winkler, M. H. Yamani, M. Oettel, P. Virnau, and K. Binder,  
*Hard sphere fluids at a soft repulsive wall: A comparative study using Monte Carlo and density functional methods*,  
J. Chem. Phys. **134**, 214706 (2011).

- [N01-28] M. Bier, A. Gambassi, M. Oettel, and S. Dietrich,  
*Electrostatic interactions in critical solvents*,  
EPL **95**, 60001 (2011).
- [N01-29] J. Bleibel, S. Dietrich, A. Dominguez, and M. Oettel,  
*Shock waves in capillary collapse of colloids: a model system for two-dimensional screened gravity*,  
Phys. Rev. Lett. **107**, 128302 (2011).
- [N01-30] D. Frydel,  
*Polarizable Poisson–Boltzmann equation*,  
J. Chem. Phys. **134**, 234704 (2011).
- [N01-31] H. Lehle and M. Oettel,  
*Stability and interactions of nanocolloids at fluid interfaces: effects of capillary waves and line tensions*,  
Proceedings of CODEF II, Bonn, Germany, March 2008, J. Phys.: Condens. Matter **20**, 404224 (2008).
- [N01-32] K. Binder, B. M. Mognetti, L. Gonzalez Macdowell, M. Oettel, W. Paul, P. Virnau, and L. Yelash,  
*Towards the Quantitative Prediction of the Phase Behavior of Polymer Solutions by Computer Simulation*,  
Proceedings of the 6th International Symposium “Molecular Order and Mobility in Polymer Systems” Saint–Petersburg, Russia, June 2008, Macromol. Symp. **278**, 1 (2009).

• **Non peer-reviewed publications**

- [N01-33] H. Lehle,  
*Fluktuations- und Kapillarkräfte zwischen Kolloiden an fluiden Grenzflächen*,  
Dissertation, Universität Stuttgart (2009),  
<http://elib.uni-stuttgart.de/opus/volltexte/2008/3493/>.
- [N01-34] E. Noruzifar,  
*Thermal Casimir Effect at Fluid Interfaces: Fluctuation-Induced Forces between Anisotropic Colloids*,  
Dissertation, Johannes–Gutenberg–Universität Mainz (2009),  
[http://ubm.opus.hbz-nrw.de/frontdoor.php?source\\_opus=2138&la=de](http://ubm.opus.hbz-nrw.de/frontdoor.php?source_opus=2138&la=de).
- [N01-35] M. Oettel and P. Virnau,  
*Simulationen auf Grafikkarten: vom Videospiele zur Materialforschung*,  
Natur und Geist (Forschungsmagazin der Johannes Gutenberg–Universität Mainz) 2/2009, p.8.

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- [3] B. Madivala, J. Fransaer, and J. Vermant, *Langmuir* **25**, 2718 (2009).
- [4] K. Masschaele, B. J. Park, E. M. Furst, J. Fransaer, and J. Vermant, *Phys. Rev. Lett.* **105**, 048303 (2010).
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- [20] F. Weysser and D. Hajnal, *Phys. Rev. E* **83**, 041503 (2011).