Two-dimensional colloidal structures responsive to external fields

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Recently advances in the area of ordering phenomena of colloidal suspensions under the combined action of external fields and spatial confinement have taken place. Colloidal systems confined to an interface are ideal models for the two-dimensional melting transition or light-induced crystallization and re-entrant melting.

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Abbreviation

DVLO-type Deryagin-Landau-Verwey-Overbeek-type

Introduction

Well-characterized and extremely monodisperse colloidal particles have become model systems for various problems in statistical physics such as phase transitions or self-organization of colloids. The use of colloidal particles bears two considerable advantages compared with atomic systems. First, the size of the particles in the micron range allows direct visualization by light microscopy with 'atomic' resolution. Second, because of friction with the surrounding solvent the dynamics of colloids is slowed down by more than six orders of magnitude when compared with atoms. The relaxation processes which appear almost instantaneous for the latter can therefore be resolved at all relevant time scales using colloidal particles. Past years have seen considerable advances in the development and investigations of colloidal model systems, in particular in restricted geometry such as quasi-two-dimensional layers of particles with or without lateral confinement. This is due to the great interest in packing phenomena and melting or glass-transition in finite systems or porous media. The scope of this review is to highlight the most recent experiments and related theoretical work on colloids in restricted geometry. Comparison of experimental data with computer simulations shows such striking agreement that certain colloidal systems come close to an analog computer. Other findings concern quantitative features of the classic Kosterlitz-Thouless two-dimensional melting, but also a two step-melting scenario of first order. Finally, a recent study of light-in-

duced melting in a colloidal system demonstrates the importance of fluctuations to stabilize a system of interacting particles.

Pieranski [1] was the first to develop a quasi two-dimensional colloidal system using polystyrene spheres trapped by surface tension at a water/air interface. Many alternative setups of colloids in restricted geometry have been realized since then. They differ by the 'degree or effectiveness of the confinement' and the interaction potential of the particles. While the trapping of colloids at solvent/air or solvent/substrate interfaces by interfacial tension [1] or gravity [2*,3*] leads to almost ideal two-dimensional systems, the confinement of charged or uncharged microspheres between charged or uncharged solid boundaries [4-6] imposes a much softer restriction to the motion of the particles perpendicular to the plane. This kind of system therefore, may be suited to study the transition between the two- and three-dimensional case [6*]. Three types of interaction potential can be distinguished: hard sphere, electric and magnetic (the electric and magnetic interactions causing long-ranged potentials). Uncharged (or weakly charged) colloids stabilized by polymer brushes at their surfaces interact effectively as hard spheres, despite subtleties arising due to additional short range attraction caused by the interaction of the polymer chains when two particles almost come into contact [7,8**]. Electric interaction originates from a surface charge induced Deryagin-Landau-Verwey-Overbeek (DVLO)-type potential or from dipole-dipole interaction. An electric dipole moment can thereby be caused by image-charge effects at the interface [1] or induced by an applied oscillating electric field [5]. Strong magnetic dipole-dipole interaction is obtained by Fe_2O_3 -doping of the particles and application of a magnetic field [9] or by magnetically 'inverting' the system using diamagnetic inclusions in a ferrofluid [10,11]. Layered colloidal systems are also easily influenced by light forces. Since the work of Ashkin [12,13] it is known that colloidal particles can be manipulated through their interaction with a focused laser beam because they are pulled into the maximum of the optical electric field if their dielectric susceptibility is greater than that of the surrounding medium (otherwise they are repelled). This enables micro-manipulation of individual particles with so-called 'optical tweezers' [13]. If the laser light intensity is modulated in space a spatially structured potential can be imposed on the colloids [14].

Structure and dynamics in two-dimensional model systems

Colloidal systems are widely used as model systems for the description of simple liquids [15]. In two-dimensional samples the structure and dynamics of all particles are directly accessible on all relevant time-scales through video-microscopy (VM). These experiments provide a crucial test for theoretical predictions, but applying theories to the analysis of the experimental data reveals properties of the individual particles and their interactions. Recently we developed a novel colloidal model system composed of super paramagnetic microspheres confined in two-dimensional [2]. The particle potential $U(r)$, which can be changed conveniently by an applied magnetic field, is dominated by the magnetic interaction and therefore has dipole-dipole character, in other words $U(r) \sim r^{-3}$ for two spheres at distance r . The potential can be precisely calibrated by the ratio, Γ , of the magnetic interaction energy to $k_B T$. So far, this is the only colloidal model system where the absolute strength of the particle interaction is known on all relevant length scales. Thus a qualitative and quantitative test of integral equation theories (such as the Ornstein-Zernicke equation with different closure relations) and computer simulations was possible. This is illustrated in Figure 1 where pair-correlation functions, $g(r)$, are shown (the distance, r , is normalized with respect to the mean particle density, ρ). The comparison of the experiments with theory reveals that despite the good qualitative agreement the theory still lacks a sufficient precision concerning the quantitative predictions, as the scaled interaction strength between theory, Γ_{theory} , and experiment/simulation, Γ_{exp} , differs considerably. The perfect agreement between experiment and simulation demonstrates that this colloidal model system behaves indeed like an analog computer.

Furthermore, we tested the validity of theoretical descriptions of the dynamic behavior of colloidal particles ([2^{*}], B Rinn, K Zahn, P Maass, G Maret, unpublished data). In agreement with results from mode-coupling theory and computer simulation [16] an enhancement of the self-diffusion of the particles due to the hydrodynamic interaction was found; this is because the precise knowledge of the colloidal potential is available. In contrast to the system mentioned above the particle potential $U(r)$ for charged colloids is less well known. Recently, charged polystyrene spheres confined between two charged glass plates have been used to determine $U(r)$ [17,18^{*}]. In the first setup the particles could move freely in the plane while in the second setup immobile large spheres were introduced as spacers between the confining glass plates and served as obstacles for the smaller species. The pair-correlation function, $g(r)$ (or $g_{ab}(r)$ $a, b = 1, 2$ for the binary mixtures) were determined by VM. Then $U(r)$ was ob-

Figure 1

The comparison of the measured pair correlation function $g(r)$ with theory and simulations reveals qualitative good agreement. The interaction strengths, Γ , however, are overestimated by the theories.

tained by a deconvolution of the Ornstein-Zernicke equation, which contains $g(r)$ and $U(r)$ in the form of an integral equation. In both experiments an attractive component in the potential of the moving species was reported. These findings are in agreement with earlier experiments [6^{*}] where a similar attraction of like-charged colloids between glass plates was observed by using two techniques: On the one hand, by application of an electric field colloidal particles were compressed towards confining glass walls. Due to this increase in density of the particles close to the boundaries a crystallization of the microspheres was induced.

Surprisingly, after switching off the electric field the crystallites remained metastable for up to an hour, an

observation which is not compatible with a purely repulsive potential between the colloids. On the other hand, two microspheres were positioned with optical tweezers at defined positions and their trajectories determined after switching off the light forces. Analyzing this data using the Smoluchowski equation, which describes the motion of interacting Brownian particles, the particle potential was calculated and revealed an increasing attraction if the particles were close to the confining glass walls. Recently, these controversial findings have been confirmed theoretically. By solving the nonlinear Poisson-Boltzmann equation for two like-charged spheres surrounded by a 1:1 electrolyte and confined in a charged cylinder, Bowen and Sharif [19*] found an attractive term in the potential between the two spheres. This effect is caused by a redistribution of the electrical double layers around the spheres due to the presence of the charged walls. In a second model proposed by Netz and Orland [20*] field theoretical methods were applied to obtain the partition function of two test particles immersed in a (multicomponent) electrolyte. A rigorous series expansion of the partition function is possible, where the first term is identical to the well known DLVO potential for the test particles. The other terms involve multibody interaction and the lowest order correction depends not only upon the screening length but also upon the composition of the electrolyte. For a net excess of positively- or negatively-charged species, as caused in the presence of charged glass walls, an attractive correction to the DLVO potential is found. Thus both theories support the conjecture of the attraction of like-charged particles in the presence of a charged wall.

The experiments [18*] on a binary solution of colloids with the larger species fixed in space provided additional interesting results. It was reported that if the concentration of the smaller (mobile) species is increased a long range attraction in the potential of the small particles occurs, in addition to the short range attraction discussed above. This might have consequences on the behavior of particles confined in porous media.

Phase transitions in confined geometry

Since the early work of Kosterlitz and Thouless [21] it was conjectured that the melting transition in two-dimensional is fundamentally different than in three-dimensional. According to the Kosterlitz, Thouless, Halperin, Nelson, Young (KTHNY) theory a two-dimensional crystal melts via two continuous transitions with an intermediate hexatic phase which is characterized by a short range translational but quasi-long-range bond-orientational order [22,23]. Despite the large number of colloidal and other systems studied the situation remains controversial which explains the great interest and activity in this field. We present recent results

which show that the phase behavior in two-dimensional, or generally in restricted geometry, shows an even more complex variety.

Colloids confined to two-dimensional+ ϵ dimensions

Some time ago systems of effectively hard colloidal spheres confined between two glass plates with continuously varying spacing were studied [24,25]. They showed that such a system undergoes a sequence of transitions $n\Delta \rightarrow (n+1)\zeta \rightarrow (n+1)\Delta$ between two- and three-dimensional. The symbols describe a system of n layers of particles with hexagonal Δ or quadratic ζ symmetry. The simple reason for this sequence lies in the fact that the height of an fcc stack of hexagonal layers (111) is greater than a corresponding stack of quadratic layers (100). In addition, the possibility of a transition $1\Delta \rightarrow b$ was pointed out [26], where b is a so-called buckling phase. In this phase individual lattice rows are lifted upwards out of the plane of the hexagonal closed packed crystal. This process will eventually lead to a 2ζ phase. Recently, combining computer simulation and theory Schmidt and Löwen [27] investigated the phase diagram (in the range $n=1,2$) of an ensemble of hard spheres in confined geometry as a function of the particle density and the spacing of the walls. They reproduce the whole variety of phases proposed and demonstrate for example that the transition $1\Delta \rightarrow b$ is of first order (due to the observed phase coexistence) and that $b \rightarrow 2\zeta$ is extremely weak or continuous. Finally, in a wedge geometry similar to the earlier experiments [24], Naser *et al.* [28,29] provided experimental evidence for the existence of a buckling mechanism even for $n > 1$, where prism shaped arrays of particles are lifted upwards.

Two-dimensional melting in the infinite system

Despite the observation [4,5,11] of a two stage melting with an intermediate hexatic phase in colloidal systems, the controversy about the nature of the melting transition is still ongoing. Apart from numerous simulations which seem to exclude an intermediate phase (see a review in ref. [30]) it is argued that the experiments so far lack the demonstration of thermal equilibrium and of the two-dimensional nature of the system. Recently, using the colloidal system introduced above [2*], we examined the melting scenario of magnetically interacting dipoles close to an interface (K Zahn, R Lenke, G Maret, unpublished data). As the particles are vertically confined to $< 1\%$ of their diameter the system is effectively two-dimensional. In addition, as the potential is tunable by an external field the 'heating' rate during the melting transition could be varied and the establishment of thermal equilibrium was controlled. Finally, as the absolute value of the interaction potential is known, the melting temperatures were determined and compared to theory and simulation. Considering all available quantities (correlation function, mean square dis-

Figure 2

If a two-dimensional crystal of paramagnetic colloids (inset) melts, the translational ξ_G and bond-orientational ξ_B correlation lengths vanish at different interaction strengths, Γ . This defines the limits of the hexatic phase.

placement, defect structure, melting temperature) an overall perfect agreement of the measurements with the KTHNY theory could be observed (Figure 2).

Marcus and Rice [7,8**] used a different system effectively consisting of hard sphere colloids with a short-range attractive part of the potential. According to ideas of Bladon and Frenkel [31] such a system supports two solid phases having the same symmetry but different densities. A first-order isostructural solid $\rightarrow$ solid transition is possible and its coexistence line ends in a critical point. There the bulk modulus, B , is zero and thus, in a finite region around the critical point, dislocation unbinding (i.e. spontaneous dissociation of pairs of dislocations into isolated dislocations) is possible. According to KTHNY the system is driven into a hexatic phase. If this phase extends as far as the melting line, a two stage melting scenario similar to KTHNY with first order transitions is possible [32]. Marcus and Rice [7,8**] demonstrated the occurrence of a hexatic phase in their system and found solid-hexatic and hexatic-liquid coexistence regions, which were distinguished by their respective densities. As coexistence is a unique feature of first order transitions this demonstrates the possibility of the proposed melting scenario.

New effects may arise when an additional external potential is imposed on the particles. One possibility consists of charged colloids confined between two glass walls and subjected to an external potential produced by two interfering laser beams [33,34]. The resulting interference fringes represent a system of parallel po-

Figure 3

Contour plot of the averaged particle density distribution function, showing a re-entrant modulated liquid structure of two dimensional colloids subject to a one-dimensional modulated laser potential. The light potential depth is $6 k_B T$ and the light-induced freezing occurs at around $2 k_B T$.

tential wells for the spheres. In such a setup Chowdhury *et al.* [33] have demonstrated light-induced freezing, light-induced freezing: a liquid $\rightarrow$ solid transition can be induced if the periodicity of the interference fringes is compatible with the mean particle density. Wei *et al.* [35**] discovered recently that beyond the light-induced freezing transition re-entrant melting may occur with increasing light intensity. This leads to higher potential wells between the particles thereby, according to ideas of Chakrabarti [36,37], reducing fluctuations and correlations of the particles perpendicular to the fringes. Eventually the crystal melts into a system of independent lines. This is shown in Figure 3 where the averaged particle density distribution function is plotted.

This effect can be understood as an effective reduction of the dimensionality of the system ($2\Delta \rightarrow 1\Delta$). As a one-dimensional system has a much lower (or vanishing) freezing temperature a melting transition is induced.

Two-dimensional melting in finite geometry

Lateral confinement of particles in two-dimensional can be obtained by hard walls. Bubeck *et al.* [3*] investigated a system of paramagnetic microspheres confined

to regions having boundaries of various geometric shapes (circles, hexagons, squares) containing up to a few tens of particles. The influence of the confining wall on the equilibrium structure and on the dynamics of the particles was analyzed. Of special interest are the results obtained with a circular cavity which are related to earlier theoretical works by Bedanov and Peeters [38]. These authors reported simulations on electrons in two-dimensional confined laterally by a $1/r^2$ and hard wall potential. In a circular cavity occupied by a few tens of particles at low temperature a structure consisting of concentric shells of particles is obtained, with a decreasing number of particles for the inner shells. With increasing temperature the shells start to decorrelate and become free to rotate with respect to each other, while the shells themselves remain stable. Indications for this interesting melting scenario was already presented in [3*] and recently the same authors provided convincing experimental data for such a process (C Bechinger, personal communication). Finally a recent theoretical paper should be noted [39] in this connection where a finite number ($N = 1-1000$) of hard disks in a spherical cavity was investigated using analytical methods and simulation. The authors proposed an interesting freezing criterion analyzing the dynamic behavior of the particles which changes from hydrodynamic relaxation to particle exchange hopping processes for increasing disk densities.

Conclusion

Recent progress in the field of colloids in restricted geometry was due to the use of well defined, typically micron sized particles with controlled interparticle interactions suspended in water near interfaces. Further advances are expected with smaller but otherwise similar particles because of their more vigorous and faster dynamics. This is of particular interest in studies of the dynamics of the two-dimensional glass transition or of two-dimensional crystallization kinetics. Direct observation of such particles and determination of their trajectories is possible down to sizes well below the diffraction limit of optical microscopes by labeling them with fluorescent dyes. In addition, various new ways to manipulate them by light forces are yet to be explored. Finally, colloidal particles can be levitated by electric, magnetic or optical forces opening the possibility to study their structure and novel collective dynamics when freely suspended in vacuum, in gases or plasmas [40], where motions become essentially undamped.

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