R. Bubeck
P. Leiderer
C. Bechinger

Structure and dynamics of two-dimensional colloidal systems in circular cavities

Abstract The properties of 2D colloidal crystals have been widely investigated over the last 20 years. Recently, it has been recognized that colloids are also useful for the investigation of systems comprised of only a few particles. We study the melting behavior of a finite number ($N < 30$) of paramagnetic colloidal spheres ($\sigma = 4.5 \mu\text{m}$) in 2D circular cavities. By applying a magnetic field, B , the interaction strength between the particles is varied. At high B , i.e. strong dipole interaction, the particles are arranged in a highly ordered shell-like structure. With decreasing B we observe a loss of

angular order between adjacent shells. Upon further reduction of the external field, however, different scenarios are observed. For cavities with hard-wall confinement and commensurate particle numbers angular order is restored again. In contrast, the latter effect is absent for soft-confinement potentials. In both cases the system melts completely for small magnetic fields.

R. Bubeck · P. Leiderer · C. Bechinger (✉)
University of Constance, Department of
Physics, 78457 Constance, Germany
e-mail: clemens.bechinger@uni-konstanz.de
Tel.: +49-7531-883562
Fax: +49-7531-883127

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Introduction

In the last few years there has been considerable progress in the field of localization and cooling of ions and electrons in artificial confining fields. Typical examples for 3D and 2D systems are ions in radio-frequency traps [1], electrons on the surface of liquid He [2], and electrons in quantum dots [3]. With the help of present-day powerful imaging techniques such examples may be promising subjects for the experimental investigation of systems in lateral confinements. Additionally, the structural and dynamical properties of few-body systems are also attractive from the theoretical point of view [4]. Several authors considered 2D systems with finite numbers of ions or electrons in lateral confinements using Monte Carlo (MC) simulations [5–8]. So far, the majority of theoretical studies investigated the behavior of Coulomb particles in a harmonic external potential. At low temperatures and in the case of a small number of particles, the particles are found not to crystallize in a

triangular lattice (Wigner crystal), but are arranged in a shell-like structure. Accordingly, it was pointed out that such systems might be a “realization” of a 2D Thomson atom, where the structure as a function of the particle number can be analyzed in terms of a Mendeleev-type table [6, 9]. The melting of laterally confined 2D systems with particle numbers of the order of 100 or smaller is predicted to occur via a two-step process [6–8]. Upon increasing the temperature, first intershell rotation becomes possible where orientational order between adjacent shells is lost. At even higher temperatures, radial diffusion between shells sets in, and this finally destroys the shell structure of the cluster. In recent experiments with magnetic colloidal particles in hard-wall confinements, however, a deviation from this scenario was found: when the effective temperature is increased beyond the point where intershell rotation sets in, angular order is restored again before the system melts completely [10]. In the meantime this reentrant behavior has also been confirmed by MC simulations

[11]. It has been pointed out that the occurrence of this effect is related to the boundary condition of the confinement, which determines to what extent the particles can escape in radial direction upon changing the temperature. This also explains why such behavior was not seen in previous calculations because they concentrated on the behavior of particles in parabolic, i.e. soft, confinements.

Here we present an experimental study of the phase behavior of 2D systems consisting of a small number of particles interacting via a dipole potential in different circular confinements. In the first part we discuss a system of 29 particles in a hard-wall confinement. These results are in excellent agreement with earlier experimental data [10] and recent numerical simulations [11]. In addition we also investigated a system of 26 particles in a soft potential. As shown, the properties in both cases are rather different, which is also in agreement with recent numerical simulations [11].

Experimental

The experiments were performed with superparamagnetic colloidal spheres with a diameter of $4.55\ \mu\text{m}$. Since the pair interaction potential between the spheres can be conveniently varied by means of a magnetic field such systems provide excellent model systems for the investigation of 2D systems. The advantages of colloidal suspensions are their convenient time (milliseconds) and length scales (microns), which allow the detailed observation of single particle trajectories by means of video microscope [12]. As a substrate for the 2D colloidal system we used fused silica plates onto which a $3\text{--}4\text{-}\mu\text{m}$ thick smooth film of poly(methylmethacrylate) (PMMA) was deposited by spin-coating. This was necessary to prevent the particles from sticking to the surface. The lateral confinements were realized by using a transmission electron microscope (TEM) grid made of copper that was pressed into the thin PMMA film, which was heated to about $150\ ^\circ\text{C}$. After this process typically several tens of identical circular hard-wall compartments with perpendicular wall were obtained (Fig. 1a). In addition to such hard-wall boundaries we also fabricated compartments with soft-wall potential. This was achieved by adding some additional PMMA solution to a sample after the TEM grid had been pressed onto the substrate. Owing to capillary forces the liquid

preferentially wetted the previously formed hard-wall compartments, where under the influence of the radial forces during spin-coating a radially symmetric meniscus was formed. After the solvent had evaporated this resulted in a soft-wall potential (Fig. 1b).

After insertion of the superparamagnetic colloidal spheres which were suspended in water (DynaBeads $4.55\ \mu\text{m}$, Dynal, lot no. B20100) and stabilized with $2.0\ \text{g/l}$ sodium dodecyl sulfate, the particles sedimented towards the patterned (see earlier) bottom plate, where they were confined by gravity to a 2D colloidal system in each compartment (Fig. 1). In our experiments the number density in different compartments varied statistically between about 25 and 45, depending on the particle concentration. The whole cell was placed in the center of a copper coil, which produced a magnetic field, B , perpendicular to the substrate. The magnetic field induces a magnetic moment, $M(B)$, within the particles which led to a repulsive magnetic dipole pair potential, $V_{ij} = \mu_0 M(B)^2 / 4\pi r_{ij}^3$, where μ_0 denotes the permeability of vacuum and r_{ij} the distance between particles i and j . The colloidal spheres were imaged with a home-built inverted video microscope onto a charge-coupled-device camera. An image processing system (Visiometrics IPS) with particle recognition facilities was used to determine the particle coordinates for each frame via a particle recognition algorithm. From these coordinates we determined the particle trajectories by using an object tracking software (Visiometrics TRACE).

To describe the effective interaction between the paramagnetic spheres it is useful to introduce the dimensionless plasma parameter, Γ , which can be defined in several ways. In order to avoid confusion and to allow direct comparison with the work of Schweigert et al. [11] we used their definition of the plasma parameter, where $\Gamma = q^2 / (a^3 k_B)$, with $q^2 = \mu_0 M(B)^2 / 4\pi$ and $a = 2R/N^{1/2}$. Here R denotes the radius of the circular hard-wall confinement, k_B the Boltzmann constant and T the temperature of the suspension. Within the range of magnetic fields used in this work, M is to a good approximation proportional to B . We want to emphasize that in our previous work we used a slightly different definition for Γ [10].

Accordingly the plasma parameter for $N=29$ in the present work is a factor of 2.2447 smaller than in the previous one.¹ In our experiments we varied Γ by changing B and kept T constant at $295\ \text{K}$. For each B , we measured the particle trajectories up to several hours with a lateral and temporal resolution of $0.25\ \mu\text{m}$ and $20\ \text{ms}$, respectively. In contrast to previous measurements where the measuring time was only 30 min, here the particle trajectories were taken up to several hours, which largely increased the statistics and allowed us to calculate dynamic properties such as mean square displacements.

Results

Hard walls

A real-space image for the case of $N=29$ particles in a hard-wall confinement at $\Gamma=64$ is shown in Fig. 1a. In this case the particles arrange in shells consisting of 3, 9 and 17 particles, respectively. Such a configuration is denoted in the following as (3, 9, 17) and has been shown to correspond to the ground state of such system [10]. In an earlier measurement we presented the structure of such a system as a function of Γ . In contrast to these experiments, where the measurement time was limited to 30 min, here the time was increased by a factor of 20.

¹In our previous work the plasma parameter was defined as $\Gamma = \langle V_{ij} \rangle / N k_B T$, where the angled brackets correspond to the sum over all particle pairs i, j

Fig. 1 **a** Bottom view of the $72\text{-}\mu\text{m}$ openings of a transmission electron microscope mesh, which serve as lateral hard-wall confinements for the particles. **b** An additional poly(methyl methacrylate) film on top of the openings produces a soft potential for the particles

This allowed us to calculate the angular diffusion coefficients of the shells.

To visualize the shell-like behavior of our system, the particle trajectories of the particles for $\Gamma = 17$ are plotted in Fig. 2a. The three particles of the inner ring also distort the symmetry of the second shell, which shows also a pronounced threefold symmetry, whereas the structure of the outer shell is only given by the circular hard-wall confinement. It can also be seen that the outer particles are more localized than the inner particles, which is a consequence of the hard-wall confinement. In addition the diffusion of the inner particles is highly anisotropic. Both findings are in good agreement with numerical calculations [7]. In order to characterize the angular movement of the innermost shell relative to the second shell, we first transformed the data shown in Fig. 2a into a reference frame, which follows the collective angular motion of the second shell. As a result, the angular positions of the particles of the second shell become rather localized, indicating that the particles move in a highly cooperative manner (Fig. 2b).

From the linear slope of the mean angular displacements of the particles in the first shell at long times one directly obtains the angular diffusion coefficient with respect to the second shell. In order to determine to which shell a particle belongs (this becomes increasingly difficult upon decreasing Γ) we used the minima in the radial distribution of particles, which show three maxima (corresponding to the three shells) with pronounced minima in-between, the latter characterizing the radial extension of the shells.

The angular diffusion constant, D_Θ , of the first shell is plotted against Γ in Fig. 3. At high Γ values, the energy barriers for shell rotation are rather small, corresponding to a small D_Θ . With decreasing Γ , however, D_Θ increases by more than a factor of 8 and indicates the high mobility of the second shell versus the first one. For even lower Γ values, D_Θ decreases again until the shell structure finally vanishes and an angular diffusion coefficient cannot be defined anymore. Such a maximum of the angular mobility was observed in earlier measurements [10] and

Fig. 3 Angular diffusion constant of the first shell over Γ for the system of 29 particles in a hard-wall confinement

has been explained by radial particle fluctuations, which tend to increase the registration between adjacent shells. With increasing Γ , the angular mobility of the first shell increases at first but is then reduced again by the increasing radial particle fluctuations of the second shell, which finally increase the registration between adjacent shells. This scenario has been supported by recent calculations of Schweigert et al. [11].

Soft walls

It has already been suggested that the occurrence of the previously discussed reentrance behavior is strongly related to the details of the confining potential. In the presence of a circular cavity with hard walls, the particles cannot escape in a radial direction, which seems to be important for the unusual Γ dependence of the angular diffusion coefficient. In contrast, if the confinement is comprised of soft walls, e.g. a parabolic potential, the whole system will expand if the magnetic field is increased and the melting scenario should be rather different [5, 6, 13–15].

Accordingly, we also performed measurements where the confinement was a soft wall. A typical snapshot at a plasma parameter of $\Gamma = 32.6$ with $N = 26$ is plotted in Fig. 1b. In contrast to the hard-wall potential, it can be clearly seen that now the particles are located in the center of the confinement with a configuration (3:9:14). Taking the preparation process of the samples into account (spinning of a liquid in a circular confinement), the shape of the confinement should roughly correspond to a rotational parabola. Owing to surface tension effects, however, deviations from a perfect parabolic potential might occur and we assume the potential to be given by $V(r) = \alpha r^\beta$. By comparing our ground-state configuration with the results from MC simulations² this suggests β is

Fig. 2 Particle trajectories over 10 h for $\Gamma = 32$: **a** raw data; **b** after correction of angular movement of the second shell

²The transition from ground-state configurations (4:9:13) to (3:9:14) takes place between $r^{2.04}$ and $r^{2.05}$ and that from (3:9:14) to (3:8:15) between $r^{6.57}$ and $r^{6.575}$

between 2.05 and 6.57. In contrast for $\beta = 2.0$, for example, a slightly different arrangement (4:9:13) should be observed. α can be estimated by the dynamical behavior of the particles. When the external magnetic field is turned off the particles begin to diffuse towards the center of the cavity, with their dynamics given essentially by their interaction with the confining potential, i.e. the meniscus of the polymer film. Since this dynamic is highly overdamped, the corresponding equation of motion can be easily solved, which allows us to obtain $\alpha = 0.3 \pm 0.1 \cdot 10^{-9}$ N/m. Accordingly the outmost particles are only raised about 270 nm (corresponding to 6% of the particle diameter) with respect to the center of the compartments; hence the a priori assumption of a 2D system is largely fulfilled in this situation.

Similarly, to the experiments described earlier we followed the particle trajectories at different Γ values and obtained the angular diffusion constants, which are plotted in Fig. 4. The experimentally accessible Γ range is now restricted to values above 20 since at smaller values it is difficult to define a shell structure and thus allow calculation of D_Θ . The available data, however, cover the region just above complete melting, where the reentrance has been observed in hard-wall potentials.

In contrast to Fig. 3, for soft walls we do not find any indications for a maximum as observed before, but the data points roughly show a linear Γ dependence. In addition the angular diffusion coefficient is higher compared to the hard-wall confinement. Both findings have also been observed in MC simulations [11]. Unfortunately, these studies were performed only with $N = 25$ particles in contrast to $N = 26$ in our case. This difference, however, should not affect the general diffusion behavior, since the configuration of the two inner shells is identical for $N = 25$ and $N = 26$.

Fig. 4 Angular diffusion constant of the first shell over Γ for 26 particles in a soft-confinement potential

Conclusion

In summary, we have studied the melting process of finite 2D systems in different external cavities. In the case of hard-wall confinements we find in agreement with recent theoretical studies reentrant behavior. This is interpreted in terms of radial particle fluctuations, which lead at lower Γ to a higher coupling of adjacent shells and, therefore, to higher angular order. In contrast, when the external 2D cavity is comprised of soft potentials the system size varies as a function of Γ . Consequently, the coupling of adjacent shells by radial particle fluctuation is smaller than in the hard-wall case. This finally results in a monotonic increase in the angular mobility of the shells with decreasing Γ as has been predicted by recent MC simulations.

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