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K. Mangold
R. Bubeck
P. Leiderer
C. Bechinger

Substrate-induced phase transitions in two-dimensional colloidal systems

K. Mangold · 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

Abstract We study the phase behavior of a 2D colloidal system in the presence of an external periodic 1D potential. As colloidal suspension we use an aqueous suspension of superparamagnetic spheres with a diameter of 4.5 μm. The periodic 1D potential is fabricated by evaporation of thin magnetic nickel lines onto a glass substrate, which is afterwards covered with a protective poly(methyl methacrylate) layer. When the phase behavior of the colloidal system is investigated as a function of the applied external magnetic field, we observe a promoting effect of the underlying periodic 1D potential to the crystallization of the 2D colloidal system.

Key words Colloids · Two-dimensional melting · Two-dimensional freezing · Phase transitions · Periodic potential

Introduction

The study of 2D melting by means of colloidal particles has attracted the interest of many researchers during the last few decades. The basic advantages of the use of such mesoscopic model systems are their convenient length and time scales which allow direct imaging of particle positions by means of optical methods, like video microscopy [1]. Additionally, the relevant interaction potentials in colloidal suspensions are well defined and can be adjusted over a wide range. During the last few years there has been strong experimental support of the basic ideas of 2D melting developed by Kosterlitz, Thouless, Halperin, Nelson and Young (KTHNY) [2, 3] by employing colloidal suspensions [4]. In particular, evidence for a two-stage melting process has been recently given by Zahn et al. [5].

While there exist numerous theoretical and experimental studies on 2D melting on homogeneous substrates, only little is known abut 2D melting in the presence of substrate potentials as typically provided by the atomic corrugation of a crystalline substrate [6]. Such studies, however, are highly demanding since the interplay of a 2D system with a periodic substrate will lead to strong changes in the phase behavior.

Here we demonstrate the effect of a periodic 1D potential on the phase behavior of a 2D colloidal system. The substrate potential is obtained by an array of thin paramagnetic Ni lines, which were deposited onto the substrate. As particles we used superparamagnetic colloidal spheres whose pair interaction potential can be varied over a wide range by an external magnetic field, B. Our results show that the presence of such a substrate potential drastically changes the dynamical and static properties of the colloidal system.

Experimental setup

In order to fabricate periodic 1D potentials we first deposited a Ni film of 3-nm thickness onto a glass substrate by thermal evaporation. During the evaporation process the substrate was masked with a grid, which resulted in equidistant quadratic Ni patches with a side length of 280 μm. The uncoated areas were used to compare the phase behavior of the colloids without the periodic potential. By a subsequent photolithographic process we then obtained periodically aligned Ni lines of 4 μm width and a periodicity of 10 μm. To protect the Ni grid when in contact with the aqueous colloidal suspension and to provide a smooth surface

to the particles, a 400-nm-thick poly(methyl methacrylate) (PMMA) film was spin-coated on top of the Ni stripes (Fig. 1). The resulting sample was used as the bottom plate of a sample cell, which contained the aqueous suspensions of superparamagnetic particles (DynaBeads) with a diameter of 4.55 μm [7]. The particles were additionally stabilized with sodium dodecyl sulfate (SDS), which causes a short-range steric repulsion between the spheres and prevents agglomeration in particular when the external field was absent. When the sample cell was filled with colloidal suspension the particles owing to their density (1.5 g/cm^3) immediately started to sediment towards the bottom plate, where they formed a 2D system. The cell was placed in the center of a copper coil, which could induce a magnetic moment, M, in the particles, leading to a magnetic dipole pair interaction given by $V_{\mathrm{mag}} = \mu_0 M(B)^2 (\pi\rho)^{3/2}/4\pi$, where $M(B)$ is the induced magnetic moment of the particles, ρ the single particle density and μ_0 the magnetic permeability. We found for small B that the magnetic moment of a sphere is a linear function of the field. To describe the effective interaction between the paramagnetic spheres it is useful to introduce the dimensionless plasma parameter $\Gamma = V_{\mathrm{mag}}/k_{\mathrm{B}}T$, with $k_{\mathrm{B}}T$ being the thermal energy in the system. In the following experiments variation of Γ was only achieved by changing the magnetic field, whereas the temperature was kept constant at room temperature.

To calculate the interaction between the colloidal spheres and the Ni lines we employed a finite-element method where the spheres and Ni lines were divided in small volume segments. Numerical integration of the dipole–dipole interaction over all the volume elements leads then to the potential energy of a single sphere above an array of Ni lines. The magnitude and direction of the moment of the particles is well known by the applied external magnetic field. In contrast, the magnetic moment of the Ni lines is more difficult to determine owing to the limited accuracy of the quartz mass balance method, which was employed to measure the thickness of the Ni layer. It is well known, however, that the direction (in plane or out of plane) of the magnetization of the ferromagnetic Ni lines strongly depends on the film thickness. In addition, a thin layer of antiferromagnetic nickel oxide will probably form on top of Ni immediately after the evaporation chamber is opened.

Characterization of the substrate

In order to determine how different directions of the magnetization affect the interaction between a colloidal sphere and a Ni line, we calculated the potential energy of a superparamagnetic particle above an array of Ni lines for both in-plane and out-of-plane magnetization. The resulting curves are shown in Fig. 2. When the orientation of the magnetic moment is in plane the minimum of the potential energy is close to the right or left edge of the Ni lines (depending on the directions of the in-plane magnetization and that of the vertical external B-field vector) as seen in Fig. 2a as open and closed symbols, respectively.

Accordingly, a rotation of the direction of the external B field by 180° should also induce in a change in the equilibrium position of the colloidal particles. Indeed, such behavior has been observed experimentally for Ni grids with about 20-nm thickness (Fig. 3a, b). In contrast, if the potential energy of a superparamagnetic sphere is calculated in front of an array of out-of-plane magnetized Ni lines, the minima are located in the middle of the Ni stripes (Fig. 2b). Such behavior was observed experimentally for Ni grids of 3-nm thickness (Fig. 3c). Upon reversal of the direction of B the position of the particles was not altered. This can be explained by the small coercive force of the Ni which causes the out-of-plane magnetization to be rotated together with B. Altogether, the thickness-dependent changes in the magnetic properties of Ni films are in good agreement with findings of other authors who observed that Ni layers below 20 nm are ferromagnetic with out-of-plane magnetization, whereas above 20 nm in-plane magnetization is observed [8].

Results

In the following we present data on the phase behavior of a 2D colloidal system in the presence of a pattern of Ni

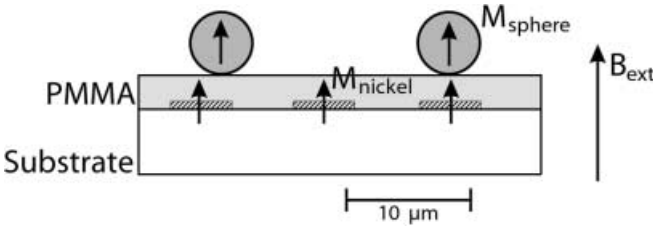

Fig. 1 Schematic side view of the experimental cell. Underneath a protective poly(methyl methacrylate) (*PMMA*) layer an array of Ni lines (*dashed regions*) has been formed on top of a silica substrate by means of photolithography. Also shown are the magnetic moments of the ferromagnetic Ni lines (M_{nickel}) and those of the particles (M_{sphere}), the latter being induced by the external magnetic field (B_{ext})

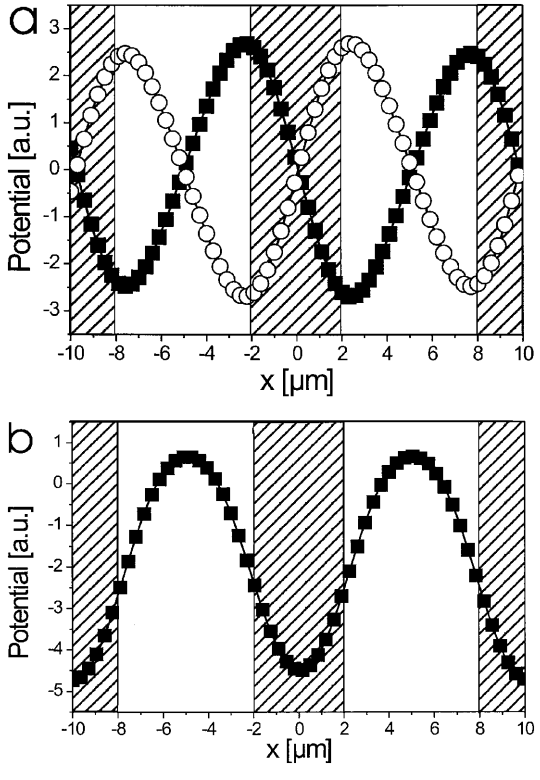

Fig. 2 **a** Numerical calculation of the potential energy of a superparamagnetic colloidal sphere in front of an array of in-plane-magnetized Ni stripes (*dashed areas*). After reversing the external field the induced magnetic moments of the particles are rotated by 180°, which causes the minima of the curves to be shifted in a horizontal direction. **b** The same calculation for out-of-plane magnetized Ni lines

lines as described earlier. In addition, we compare the results to that of a homogeneous substrate, which allows the influence of the Ni grid to be studied. The particles were observed by means of a homebuilt inverted microscope, which allowed the particles to be imaged onto a charge-coupled-device camera which was connected to a computer. With the help of a particle recognition algorithm we were able to identify the particle trajectories from which dynamical and static quantities were obtained.

The mean square displacements (MSD) for the *x*-(closed symbols) and *y*-directions (open symbols) directions are shown in Fig. 4 for the situation without and with Ni lines for different magnetic fields, i.e. Γ. The Ni lines were adjusted in such a way that the *x*- and *y*-directions corresponds to the orientation perpendicular and parallel to the lines. At first glance, the curves show similar behavior, i.e. a steep increase at short times which gradually decreases and becomes almost linear at longer times. The initial part of the curves is due to the short-

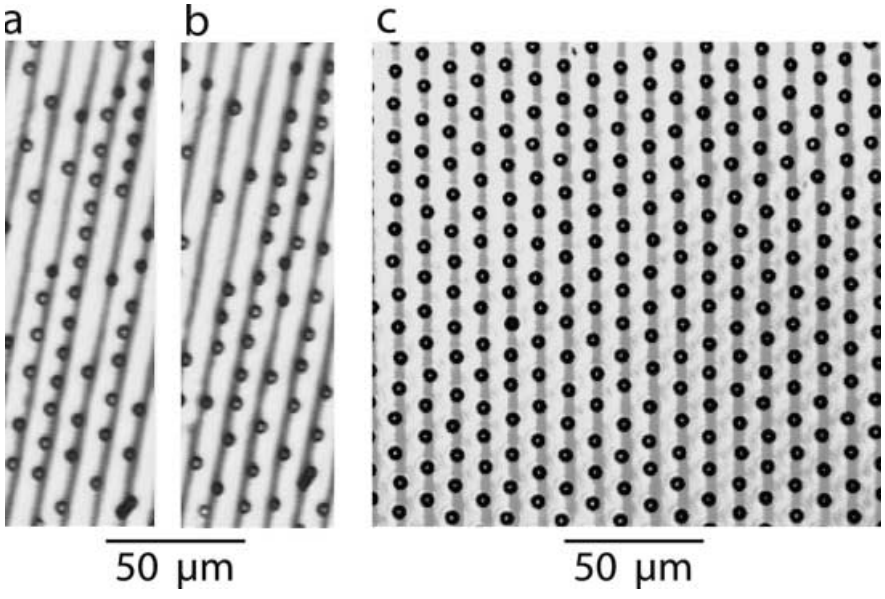

Fig. 3a, b Photos of colloidal particles on a Ni grid of 20-nm thickness, the latter corresponding to the almost vertical *black lines*. Upon reversing the external magnetic field the particles move to the opposite edge, which suggests in-plane-magnetization of the Ni. **c** Same situation for a Ni grid of 3-nm thickness. Upon reversal of the magnetic field no change in the particle positions is observed, which is in agreement with out-of-plane magnetization of the Ni at that thickness

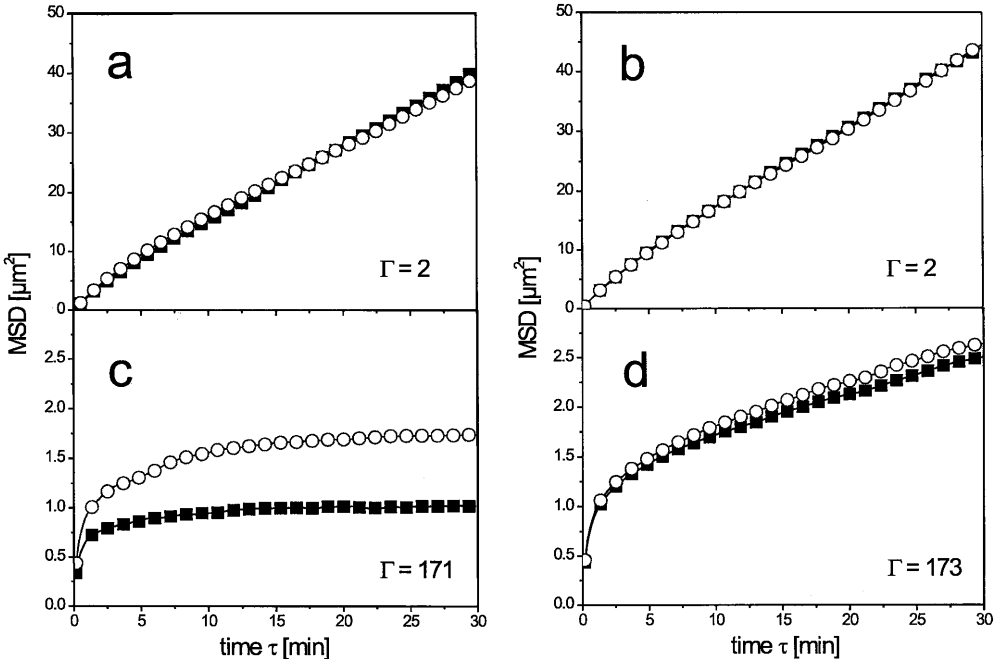

Fig. 4 Mean square displacements (*MSD*) at different plasma parameters for a system with (**a**,**c**) and without (**b**,**d**) Ni lines. The *closed symbols* denote the MSD perpendicular to the lines, the *open symbols* indicate the MSD along the lines

time diffusional behavior, which describes the motion of the particle at sufficiently small times (below 30 s) where the influence of the surrounding particles is negligible. From this we can calculate the diffusion constant $D_0 = 0.014\ \mu m^2/s$. The MSD at longer times is determined by particle–particle interactions, which generally leads to a smaller slope compared to the short-time behavior. At $\Gamma = 2$, the Ni lines show hardly any effect on the MSD as can be seen by the similar behavior of the data in Fig. 4a and b. Apparently, the influence of the Ni grid can be neglected in this case. With increasing Γ, however, the influence of the Ni stripes on the diffusional behavior of the particles becomes significant and manifests itself both in a smaller absolute value of the MSD and also in its different behavior for the x- and y-directions. At $\Gamma = 171$ the MSD perpendicular to the lines is almost constant, indicating the confinement effect of the Ni grid to the lateral movement of the particles, whereas the MSD parallel to the lines still shows a linear increase characteristic for free diffusion (Fig. 4c). At the same magnetic field the particles on the nonpatterned parts of the substrate still perform an isotropic free diffusion as can be seen from Fig. 4d and clearly demonstrates the influence of the Ni stripes on the dynamical properties of the particles.

To study additionally the effect of a periodic substrate potential on the phase behavior of the 2D particle system we calculated the mean square excursions. In analogy to the Lindemann criterion where the MSD of the particles $\left\langle \vec{u}(\vec{R})^2 \right\rangle$ is used as a melting criterion, Bedanov and Gadiyak [9] defined a similar melting criterion for 2D systems where the relative displacements of neighboring particles are considered, i.e.

$$\gamma = \frac{\left\langle \left[\vec{u}(\vec{R}+\vec{a}) - \vec{u}(\vec{R})\right]^2 \right\rangle}{a^2},$$

with $\vec{a}$ being the lattice vector of the system. It has been shown that, independent of the pair interaction potential, in 2D systems the melting transition occurs at $\gamma = 0.033$. From the experimentally determined particle positions we calculated the melting transition for different magnetic fields. As can be seen in Fig. 5, the freezing transition in the presence of the Ni stripes occurs at substantially smaller Γ values compared to the homogeneous substrate. This can be understood by the additional localization of the particles in the presence of the Ni lines, which support their crystallization. Accordingly, we call this effect magnetic-induced freezing.

The promoting effect of a periodic, 1D substrate potential to the freezing of 2D systems is not limited to the example described here but is also found for other particle–particle and particle–substrate interactions. It has been demonstrated that the presence of an optical interference pattern, which provides a periodic, 1D potential for highly charged dielectric polystyrene spheres, can induce crystallization into a previously disordered 2D colloidal suspension [10]. In addition, recent Monte Carlo simulations suggest a similar behavior to occur also in the case of 2D hard discs [11].

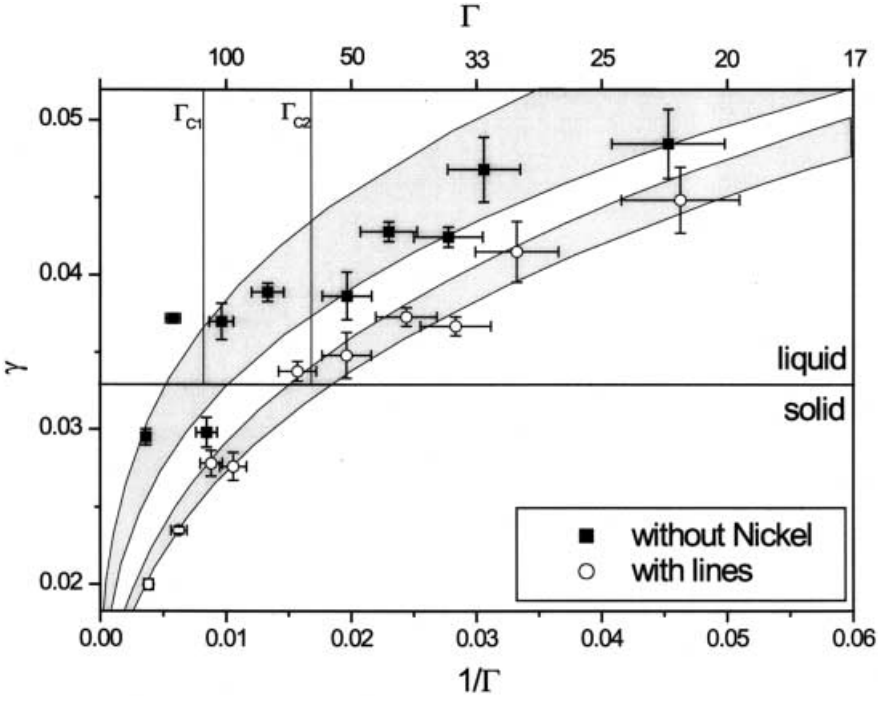

Fig. 5 Relative quadratic excursion, γ, of the colloidal particles as a function of $1/\Gamma$. Above $\gamma^{C}{}_{M} = 0.033$ (*horizontal line*) the system is liquid, below it is solid. The melting point for the system with additional Ni lines, Γ_{C2}, occurs at significantly smaller $1/\Gamma$ values than the melting point for the undisturbed system, Γ_{C1}. The *straight lines* with the *gray areas* are guides for the eye

Summary

In summary, we have studied the phase behavior of 2D superparamagnetic colloidal particles in the presence of a periodic, 1D substrate potential. The latter was obtained by photolithographically manufactured Ni lines, which additionally interact with the particles. It has been demonstrated that both the dynamical and the phase properties of the colloidal system are largely affected by the presence of the Ni grid. Owing to the presence of the substrate potential the freezing transition of the particles is shifted to smaller particle–particle interactions compared to a homogeneous substrate. This is in agreement with results of other systems, for instance, light-induced freezing, where a spatial periodic light field causes a colloidal suspension to freeze, and thus demonstrates the generic effect of substrate potentials.

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