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Particle interactions near the contact line in liquid drops

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Micrometer-sized particles distributed in a drop of water are drawn toward the contact line upon evaporation, where they arrange themselves into a crystal structure. Here we report experiments with paramagnetic particles, which make it possible to measure the particle interactions by tuning an external magnetic field. By aligning the magnetic dipoles, we are also able to redistribute the particles back into the bulk of the droplet. This method allows us to assemble and disassemble colloidal crystals simply by applying a magnetic field.

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Two-dimensional self-assembly of colloidal particles using thin liquid films or evaporating drops has recently attracted considerable interest due to the possibilities of creating regular mesoscopic structures and also for its usefulness as a model system for solid deposition on substrates [1–8]. Micrometer-sized particles distributed in a drop of water are drawn towards the contact line upon evaporation, where a colloidal crystal structure is formed. The flow can carry most of the colloidal particles toward the edge, and the ring mass grows as a power law with time [1]. Studies of DNA molecules show that they are in the random coil state in the central part of the drop, whereas close to the contact line they transfer into a highly stretched state [9]. Recently it was shown that surfactants may enhance the Marangoni-Benard instability, thereby allowing one to control the pattern formation in a relatively simple way [10]. Here we report experiments with paramagnetic particles, which make it possible to tune the particle interaction by an external magnetic field [11,12]. By aligning the magnetic dipoles, we are able to the reverse the flow process, thereby redistributing the particles back into the droplet. This method allows us to assemble and disassemble the colloidal crystal simply by applying a magnetic field.

As a starting point, we deposited drops of approximate diameter 5 mm onto carefully cleaned glass slides. The drops contain around 0.01 mg/ml paramagnetic beads (Dynabeads M-270 coated with carboxylic acid), each with radius $a=1.4\,\mu$m, and an effective magnetic susceptibility $\chi_{eff}\approx 0.17\pm 0.03$. In absence of magnetic fields they do not exhibit a magnetic moment. The carboxylic acid group covering the particles makes them hydrophilic. The beads close to the contact line were visualized with a polarization microscope (Olympus A70, used in reflection mode) equipped with a camera. After the drop has been deposited, and before the capillary flow generated by evaporation sets in, the beads are drawn toward the boundary of the drop, where they come to rest at a distance D from the contact line [1]. Here D can be varied by changing the volume of the drop. If two or more beads settle down, they will attract each other in the direction of the contact line, despite their identical electric charges. This can be explained by capillary forces giving an efficient attractive long range potential [3]. Attempting to measure this potential, we apply a magnetic field in the vertical direction (perpendicular to the glass slide), see Fig. 1, thereby creating a repulsive force given by

$$F_m=\frac{3\mu m^2}{4\pi R^4},\quad m=(4\pi/3)a^3\chi_{eff}H, \tag{1}$$

where μ is the permeability of water, m the magnetic moment, R the distance between the two beads, and H the external magnetic field in the z direction. In the middle of the

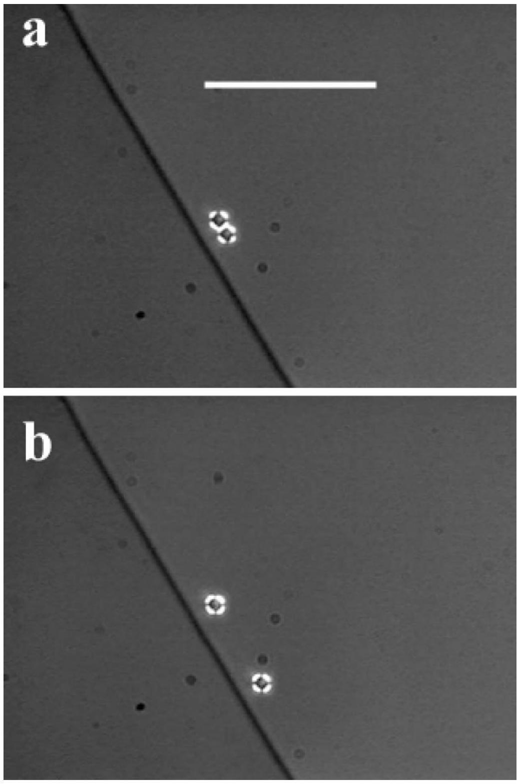

FIG. 1. In (a) the two particles residing near the (dark) three phase contact line are drawn towards each other due to capillary forces. In (b) a vertical magnetic field of 10 kA/m is applied, thus driving the beads apart. The scale bar is 30 μm.

drop, the beads sometimes collide with each other (but never attach), suggesting that the electrostatic screening energy is comparable to the thermal energy. It is also worth pointing out that we used deionized pure water from a Millipore system to disperse the paramagnetic beads, which means that the effective interaction range of the electrostatic forces is much smaller than the resolution of our microscope ($\sim 1\ \mu$m). Moreover, we do not measure the capillary forces for beads that are very close to each other. Thus, we will here neglect electrostatic interactions, only considering magnetic and capillary forces.

Identical beads immersed in planar thin liquid films exert capillary forces which can be approximated by $F_c \propto -1/R$ [3]. This expression is valid when R is sufficiently larger than the bead size, much less than the capillary length of water, and if the water surface is free to deform around the bead (see Refs. [2,3] for a general derivation). In a water drop, the expression must be modified due to the presence of the three phase contact line. The droplet meniscus h is described by the Laplace equation [3]

$$\nabla^2 h = 0. \tag{2}$$

In order to solve the Laplace equation, we assume particles of radius $a \ll D, R$, both residing at a distance D from the three phase contact line. Moreover, we assume that the meniscus satisfies the conditions $h(y=0)=0$ and $h(y\to\infty) = y\tan\theta$ (θ is the angle the water interface makes with the substrate). Using the method of image charges, we find the following solution:

$$h = y\tan\theta + \frac{\delta}{2\ln(a/2D)}\ln\frac{x^2+(y-D)^2}{x^2+(y+D)^2} + \frac{\delta}{2\ln(a/2D)}\ln\frac{(x-R)^2+(y-D)^2}{(x-R)^2+(y+D)^2}, \tag{3}$$

where δ is the deformation of the water surface at the surface of the identical beads. The force may be evaluated as the derivative of the energy with respect to the separation of both particles:

$$F_c = -\frac{\partial}{\partial R}\frac{\sigma}{2}\int_{-\infty}^{\infty} dx \int_0^{\infty} dy (\boldsymbol{\nabla} h)^2, \tag{4}$$

where σ denotes the surface tension of water ($\sigma = 72$ mN/m). One finds

$$F_c = -\frac{2\pi\delta^2\sigma}{[\ln(a/2D)]^2}\left(\frac{1}{R} - \frac{R}{R^2+4D^2}\right). \tag{5}$$

It should be noted that we have assumed $qD \ll 1$, where $q^{-1} = \sqrt{\sigma/\rho g}$ denotes the capillary length, such that the limit $D\to\infty$ is not allowed, and Eq. (5) does not reduce to the formula given in Ref. [3]. On the other hand, it is clearly seen that at large D the dominant contribution to the force is proportional to $-1/R$. At smaller D, the second term in Eq. (5) introduces a larger correction, resulting in a more rapid decay of the capillary force with increasing R. Due to the finite size of the particles, Eq. (5) cannot be expected to be valid when R and D are comparable to the particle radius a, but represents a reasonable starting point to explain the phenomena seen in this work.

In the presence of an external magnetic field the capillary attraction Eq. (5) is balanced by the magnetic repulsion. We are therefore able to measure the capillary attraction simply by finding R, D, and H experimentally, and then calculate F_m using Eq. (1). Figure 2 shows the capillary force measured in this way as a function of interparticle distance R. The crosses correspond to $D_1 = 11\ \mu$m and the boxes to $D_2 = 4.6\ \mu$m. The theoretical lines were fitted to Eq. (5) with $\delta_1 = 1.1$ nm and $\delta_2 = 0.7$ nm. The small values of δ provide some evidence for the assumption that the beads are almost totally immersed in the liquid, thus floating between the glass substrate and the meniscus. In the experiments we also observed fluctuations of the particles of the order of the particle radius, which we interpret as thermal fluctuations. The associated "thermal force" is roughly estimated to be $kT/a \sim 10^{-15}$ N, i.e., comparable to the smallest forces measured here.

Immediately after the magnetic field is turned off, the particles start to move toward each other. We measured the time it took the beads to get in close contact, and the result is shown in Fig. 3. To obtain an expression for the time versus

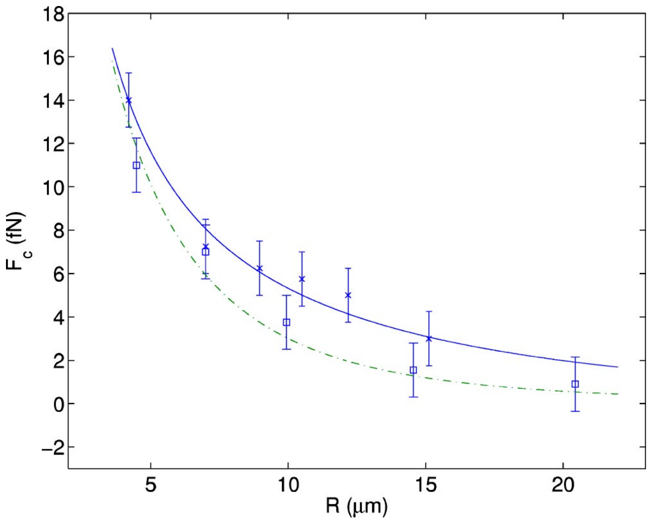

FIG. 2. The force as a function of distance R when $D_1 = 14\ \mu$m (crosses) and $D_2 = 4.6\ \mu$m (boxes). The solid line is a theoretical fit using Eq. (5) to the case $D_1 = 14\ \mu$m, and the dash-dotted line to $D = 4.6\ \mu$m. Note that the forces measured here are very small, and therefore given in 10^{-15} N.

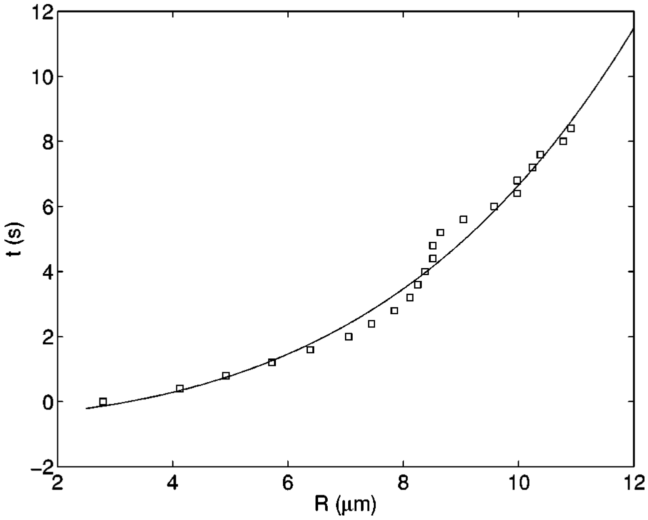

FIG. 3. The relaxation time vs the distance R for the two beads shown in Figs. 1 and 2, where $D=4.6$ μm. The solid line is a theoretical fit to the experimental data using Eq. (6).

interparticle distance, we assume that the capillary force is balanced by the viscous drag, $F_d = f\eta a v$, where η is the viscosity of water, f the drag coefficient, and v the particle velocity. We then obtain

$$t - t_0 = \frac{\eta f a [\ln(2D/a)]^2}{2\pi\delta^2\sigma}\left(\frac{R^4}{16D^2} + \frac{1}{2}R^2\right), \tag{6}$$

where t_0 is a constant. The solid line in Fig. 3 shows the best fit to Eq. (6) with $t_0 = -0.5$ s, $D = 4.6$ μm, $\eta = 0.893 \times 10^{-3}$ Ns/m^2, and $f=5$. The drag coefficient of a bead at a compressible interface is 3π, whereas that in bulk is 6π. It is seen that the drag coefficient found here is slightly lower than both, which may suggest that the interfaces influence the bead dynamics.

When the evaporative flow sets in, a larger amount of particles move towards the contact line, where they form a colloidal crystal structure, see Fig. 4(a). Note that the contact line is rough due to evaporation and the fact that we have tuned the magnetic field on and off many times before taking the picture. Each such operation slightly deforms the contact line. Upon applying a vertical magnetic field, the beads repel each other, and the colloidal crystal at the contact line starts to disassemble. If the field is strong enough, we obtain a nearly regular lattice of particles repelling each other, see Fig. 4(b). The repulsive force on a single bead separated by a distance d_0 from a chain consisting of $2N$ beads is given by

$$F_{mt} = \frac{3\mu m^2 d_0}{4\pi} \sum_{m=-N}^{m=N} \frac{1}{[d_0^2 + (2na)^2]^{5/2}}. \tag{7}$$

Experimentally, we find that at an external field of $H = 32$ kA/m, the particle will come to rest at $d_0 = 8 \pm 1$ μm.

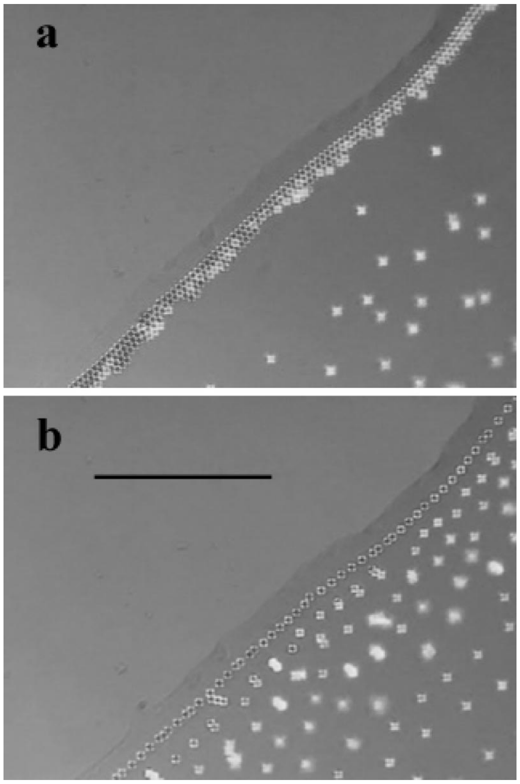

FIG. 4. Figure (a) shows a colloidal crystal assembled by the evaporative flow. In (b) we apply a magnetic field to tear the crystal apart, and then reassemble it again. The scale bar is 50 μm.

This value was obtained with only one particle in presence of the chain at the contact line (i.e., before a colloidal crystal was assembled). Inserting the numbers in Eq. (7), assuming $N \rightarrow \infty$, we find that $F_{mt} \approx 1$ pN. Thus, the evaporation induced forces driving the beads from the middle of the drop to the boundary are considerably larger than the capillary forces at the boundary. In the case of many interacting particles, see Fig. 4(b), one observes a slightly lower d_0 due to dipolar interactions. Note also that in a lattice structure the average distance may vary slightly due to fluctuations or disorder.

In conclusion, we have studied the interaction of spherical beads near the contact line of liquid drops. We found that the capillary forces are of importance for understanding the attraction between the particles. Using a magnetic field, we were able to measure these forces. Moreover, we could control the assembling process of the colloidal crystal at the boundary. We believe that magnetic beads can also assist and enhance colloidal self-assembly in other systems, e.g., the ones studied in Ref. [6]

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