Crystallization and chain formation in liquid drops

L. E. Helseth* and T. M. Fischer
Max Planck Institute of Colloids and Interfaces, D-14424 Potsdam, Germany
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Colloidal crystals are easily formed in liquid drops and thin films upon evaporation. In this study we use spherical paramagnetic beads, which make it possible to manipulate them by an external magnetic field. We show that the hydrophilic beads position themselves at a distance from the contact line so that they barely touch the water-air interface. Upon applying a magnetic field, the magnetic beads can either arrange themselves in a two-dimensional repulsive lattice or form attractive vertical chains, depending on the contact angle of the drop. We also demonstrate that the vertical chains' position from the contact line is quantized and depends on the number of beads in the chain.

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I. INTRODUCTION

In the last decades colloid science has been of considerable importance in industry as well as for understanding basic physical processes. The fact that colloids can be visualized directly using a microscope has made them ideal for model studies of structure and crystallization processes [1–4]. To this end, monolayers at the air-water interface have been used as model systems for understanding pattern formation of micron sized colloidal particles [5,6]. Two-dimensional self-assembly of colloidal crystals is also revealed in thin liquid films or evaporating drops [7–13]. This process is often seen in coffee drops spilt on a table, where the particles form a ringlike structure when the water disappears. This process is driven by two different forces. First, the evaporative flow carries the particles toward the contact line. Second, the attractive capillary forces at the contact line drive the particles together, thereby forming a well-ordered structure, where the crystallinity depends on the shape and homogeneity of the particles. Understanding colloidal crystallization is therefore not only important in fundamental research, but also necessary in order to understand the nature around us. If we instead of coffee particles substitute spherical magnetic beads, we are able to form colloidal crystals which can be manipulated with an external homogenous magnetic field. This kind of system may function as a model system for studying the influence of magnetic fields on growth of thin organic films. It is known that certain molecules behave as magnetic dipoles, and that the alignment and growth of crystals can be controlled with a magnetic field [14]. To this end, it should be emphasized that magnetic control of crystal patterns have already been demonstrated by Skjeltorp and co-workers [2–4]. Moreover, crystallization and pattern formation assisted by ac and dc electric fields were demonstrated in Refs. [15–18], where novel colloidal phases were constructed and particle interactions measured. In the current paper we intend to demonstrate direct manipulation of the crystallization process, i.e., how to disassemble the colloidal crystal using a magnetic field, and show that the magnetic beads can either form attractive chains or arrange themselves in a repulsive lattice, depending on the three-phase coexistence contact angle of the drop. Interestingly, the position of the vertical chains from the contact line depends sensitively on the number of beads in the chain, and only certain ''quantized'' positions are preferred.

II. EXPERIMENTAL SYSTEM

We deposited water drops of diameters around 5 mm onto clean glass slides [19]. The drops contain around 0.01 mg/ml magnetic beads (Dynabeads M-270 coated with carboxylic acid), each with radius $a=1.4\ \mu$m. The carboxylic acid group covering the particles makes them hydrophilic. Together with gravity, hydrophilicity eventually makes them sink to the bottom of the drops. In the middle of the drop, the beads sometimes collide with each other (but never attach), suggesting that the electrostatic screening energy is comparable to the thermal energy. The main reason for using charged beads here is indeed to avoid that the beads stick together. 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.

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, 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_1 from the contact line. Here D_1 can be varied by changing the volume of the drop, which also takes place upon evaporation.

If two beads separated by a distance R settle down near the contact line, their surfaces will deform the water/air interface, resulting in a capillary attraction, as can be seen in Fig. 1(a). In a recent work it was shown that in the case $a \ll D_1, R$ this force can be approximated by [20]

*Present address: Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306-4390, USA.

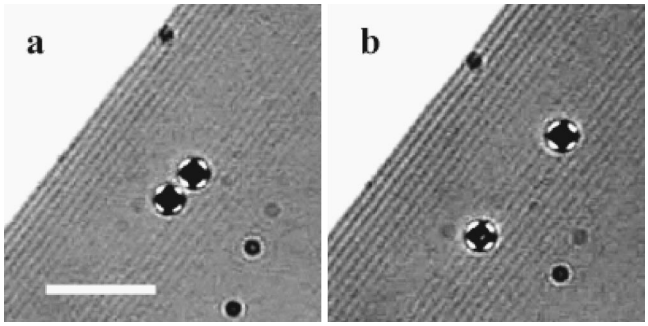

FIG. 1. Interference reflection microscopy image of two particles near the contact line. In picture (a) they are glued together by capillary forces, whereas in picture (b) they are separated with a magnetic field of $H=11$ kA/m. The white bar is of 10 μm.

$$F_c = -\frac{2\pi\delta^2\sigma}{[\ln(a/2D_1)]^2}\left(\frac{1}{R}-\frac{R}{R^2+4D_1^2}\right), \tag{1}$$

where δ is the deformation of the water surface at the surface of the identical beads and σ is the surface tension of water. If we apply a magnetic field in the z direction normal to the glass slide, the magnetic moment of the paramagnetic beads will align along the field, resulting in a magnetic force between them. The magnetic dipole energy is given by

$$U_m = \frac{\mu m^2}{4\pi R^3}, \tag{2}$$

where μ is the permeability of the surrounding medium and $\boldsymbol{m}$ the magnetic moment of the identical particles. In the case of paramagnetic beads, the magnetic moment is given by $\boldsymbol{m}=(4\pi/3)a^3\chi\boldsymbol{H}$, where a is the bead radius and χ the effective susceptibility. The magnitude of the repulsive force is found to be

$$F_m = \frac{4\pi\mu a^6\chi^2H^2}{3R^4}. \tag{3}$$

In equilibrium, the repulsive magnetic force must balance the attractive capillary force.

A. Bead location

In Fig. 1(b) the beads are at rest when $R\approx 9a$ and $D_1 \approx 8a$ in a magnetic field of $H=11$ kA/m. Then Eq. (3) gives $F_m \approx 5\times 10^{-15}$ N. Using Eq. (1), we find that the corresponding surface deformation is $\delta\approx 1$ nm. Since the beads are covered by a hydrophilic acid group and appears nonbuoyant at the contact line, it follows that they are completely immersed in the water and that their contact angle with the water/air surface is small, and therefore rest at a position where the height $h\approx 2a$ of the water level equals the diameter of the bead. The distance D_1 can be related to the contact angle by the following relationship:

$$\tan\theta = \frac{2a}{D_1}. \tag{4}$$

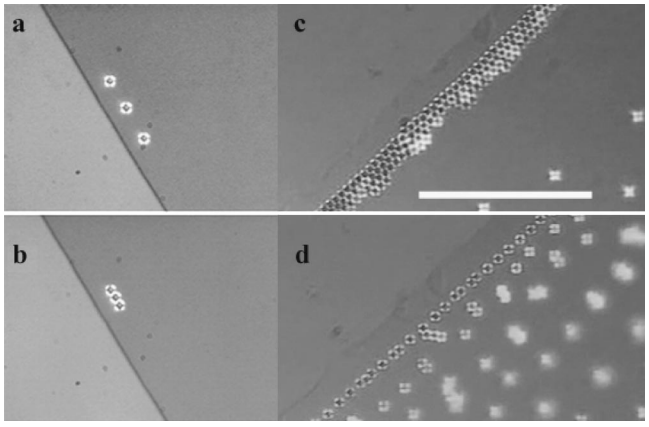

FIG. 2. Reflection microscopy images of various stages in the formation of a colloidal crystal in a liquid drop. In pictures (a) and (b) three particles form a horizontal chain along the contact line. In (c) we see the formation of a crystal at a later stage, whereas picture (d) shows the disassembly in a magnetic field. The white bar is of 50 μm.

Additional evidence for the validity of this relationship can be found by looking at Fig. 1. Here the small inclination of the water film near the contact line results in an optical interference pattern, and the path difference between two interference maxima is $\approx\lambda_0/2n_w$, where $\lambda_0=0.54$ μm is the wavelength of the mercury light source and $n_w=1.33$ the refractive index of water. We count 14 maxima between the contact line and the middle of the beads, which correspond to a height difference 2.84 μm, in good agreement with the result $2a=2.8$ μm expected from Eq. (4) [21]. From Fig. 1 we find $D_1=8a$, which means that the contact angle for this particular case is $\theta=14°$.

B. Crystallization

Figure 2 demonstrates how a colloidal crystal is self-assembled through the combined action of evaporative flow and capillary attraction. In Fig. 2(a) three beads have just encountered the contact line, whereas some seconds later they are glued together by capillary forces, as can be seen from Fig. 2(b). We will refer to the chains formed by capillary action along the contact line as horizontal chains. As more beads are drawn to the contact line, two scenarios are possible. First, if the contact line remains pinned as discussed in Ref. [7], the particles form a colloidal crystal as a result of an undisturbed self-assembly process. On the other hand, if the contact line is not fixed, but moves with a certain speed, this may influence the crystallization process. If the speed is too high, the particles will be more or less randomly distributed, in which case we could not observe any well-defined crystal. However, if the speed is slow enough, the crystallization is not affected by the receding contact line, as can be seen from Fig. 2(c). Here a colloidal crystal is formed near a contact line moving with a speed of 1 μm/s to the right. Since the particle distribution in the drop is somewhat random, one cannot control exactly how the crystal is assembled, and crystal defects are often the result of this randomness, which may be enhanced by contact line movement.

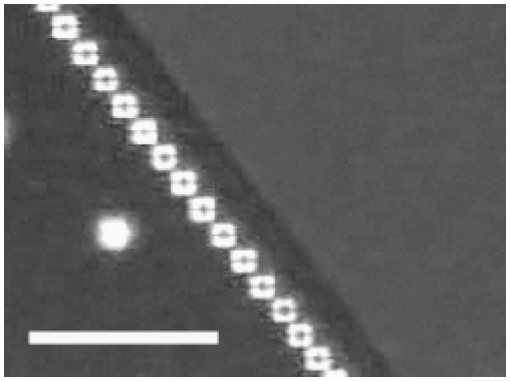

FIG. 3. A single bead ''levitating'' above a horizontal chain. The white bar is of 20 μm.

III. MAGNETIC DISASSEMBLY

If we apply a magnetic field as in Fig. 1, the aligned dipoles repel each other, and the crystal is torn apart. The three-phase coexistence contact angle (glass/water/air) is very important during this process. If the contact angle is small, the beads are effectively confined to two dimensions near the three-phase contact line. An example of this is shown in Fig. 2(d), where a magnetic field of $H=32$ kA/m was applied to disassemble the crystal shown in Fig. 2(c). Here the beads behave like they were moving on a two-dimensional lattice, i.e., they do not move substantially in the vertical direction. On the other hand, if the contact angle is sufficiently large, we have a three-dimensional system, and the beads are allowed to align in the vertical direction. Equation (4) predicts that two beads must be at least a distance $D_2=2D_1$ from the contact line in order to align completely along the magnetic field in the vertical direction. In Fig. 2(d) we find that $D_1\approx 8a$, which means that the beads must move a distance $8a$ to $D_2=16a$ in order to align in the vertical direction. Thus it is clear that as long as the magnetic beads are confined near the contact line, they prefer to stay within a two-dimensional lattice, whereas further away they may align vertically as well.

For two dipoles in a two-dimensional system, the interaction energy is purely repulsive and given by Eq. (2). Figure 3 shows a single bead repelled by a horizontal chain located a distance $D_1\approx 5a$ from the contact line. Theoretically, the force on a single bead from a chain consisting of $2N$ beads is given by

$$F_{me}=\frac{4\pi\mu\chi^2a^6H^2d_0}{3}\sum_{m=-N}^{m=N}\frac{1}{[d_0^2+(nR)^2]^{5/2}}, \qquad (5)$$

where d_0 is the distance from the chain, and we will here assume that $N\to\infty$ in order to obtain some simple estimates.

Experimentally, we found that a field of $H=4$ kA/m must be applied before the beads starts moving away from the chain. In this case $R=2a$ and $d_0=2a$, which means that $F_{me}\approx 7\times 10^{-13}$ N. On the other hand, in a field of $H=36$ kA/m the single bead comes to rest at a distance $d_0\approx 7.6a$ from the chain when $R=3a$ (see Fig. 3), thus giving $F_{me}\approx 5\times 10^{-13}$ N. In equilibrium the magnetic forces must balance those generated by the evaporative flow. The fact that the measured forces only change slightly upon moving the beads from $d_0=2a$ to $d_0=7.6a$, suggests that the evaporative forces decay relatively slowly close to the contact line. Moreover, we see that they are two orders of magnitude larger than the capillary forces. Therefore, it is clear that if proper care is not taken, they may damage the colloidal crystal. That is, if the droplet start to evaporate too fast (e.g., by some kind of thermal excitations), these forces may counteract the capillary action pulling beads together, thereby destroying the crystal. In order to produce a nice crystal, both capillary and evaporative forces must cooperate in harmony.

If the contact angle is large enough, and the beads are free to move in three dimensions, they always align along the magnetic field direction. In particular, two isolated beads minimize their energy to be

$$U_m=-\frac{\mu m^2}{2\pi R^3}. \qquad (6)$$

Let us now estimate the magnetic field required to reconfigure two isolated magnetic beads from forming a two-bead chain along the contact line to a two-bead chain in the direction of the magnetic field. Here the gain in magnetic energy obtained by aligning the magnetic moments must overcome the gravity as well as capillary energy. To obtain a simple estimate, we neglect the capillary energy, thus finding the critical magnetic moment m_c using

$$-\frac{\mu m_c^2}{2\pi R_c^3}-\frac{\mu m_c^2}{4\pi R_c^3}=\frac{4\pi}{3}a^3(\rho_b-\rho_w)g2a, \qquad (7)$$

resulting in

$$H_c=\frac{4}{\chi_{eff}}\sqrt{\frac{(\rho_b-\rho_w)ga}{\mu}}. \qquad (8)$$

Here $R_c=2a$, $\chi_{eff}\approx 0.17$, $\rho_b\approx 1600$ kg/m^3 the density of the beads, $\rho_w\approx 1000$ kg/m^3 the density of water, and $g=10$ N/kg, which results in a critical magnetic field $H_c\approx 1.9$ kA/m.

A typical example of the observed behavior is shown in Fig. 4. In Fig. 4(a) several beads are glued together in two separate chains along the contact line. Beads 1, 2, 3, and 4 are placed directly above the two chains in a close-packed formation. In Fig. 4(b) we have gradually increased the applied field in the vertical direction (perpendicular to the glass slide) up to 1.8 kA/m. Now bead 4 has been displaced slightly, and the close-packed condition is no longer fulfilled. If we increase the field by a very small amount, the situation in Fig. 4(c) occurs. Here beads 1 and 2 have detached and formed a vertical chain. In Fig. 4(d) also bead 3 has been displaced slightly from the close-packed condition. In Fig. 4(e) the field has been increased to 2.5 kA/m, and bead 4 has now formed a vertical two-bead chain with its neighboring bead from the horizontal chain. Finally, increasing the field

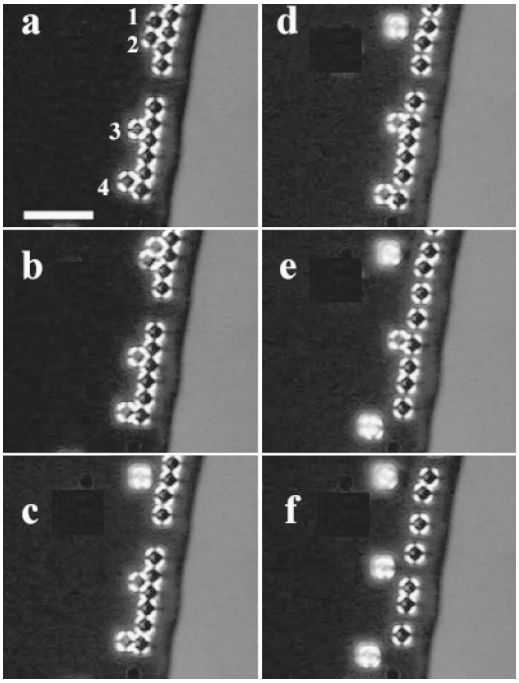

FIG. 4. Various stages in the disassembly of a colloidal structure. See the text for details. The white bar is of 10 μm. Beads being attracted toward the contact line from the bulk during this process have been eliminated from the images for clarity.

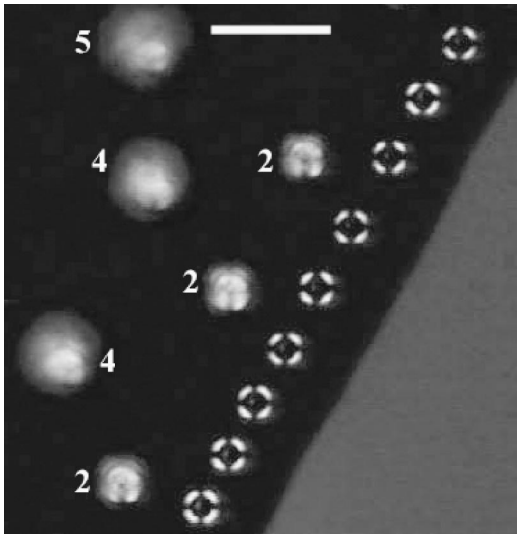

FIG. 5. Quantization of position from the contact line for vertical chains with 2, 4, and 5 beads. Note that the image blur increases with axial distance from the geometrical focus. The white numbers indicate the number of beads in the chain. The applied field is 36 kA/m, and the white bar is of 10 μm.

by a very small amount, also bead 3 forms a vertical chain with its neighboring bead.

The observations made in this experiment can be explained qualitatively by considering the interaction between capillary and magnetic forces.

First of all, if we use Eq. (5) with $d_0=2a$, $R=2a$, and $N=2$, we find $F_{me}\approx 1\times 10^{-13}$ N. This force is smaller than that found in the system of Fig. 3, which can be explained by smaller evaporative forces due to smaller flow. We find that upon evaporation the contact angle becomes smaller and smaller, and the evaporative flow stronger. Thus, since Fig. 4 depicts an early stage of the process, the flow is rather small.

Second, we note that in our experiment $D_1\approx 2a$, which gives $\theta\approx 45°$. Equation (4) suggests that the closest distance at which these vertical dipoles may be located from the contact line is $D_2=4a$, which is consistent with the observations done here. In fact, beads 1, 2, 3, and 4 all form vertical chains initially located at a distance $D_2\approx 4a$ from the contact line. If we assume that the assumptions behind Eq. (4) are valid for any integer n of beads, one expects that $D_{n+1}=[(n+1)/n]D_n$. A pictorial evidence for this kind of quantization can be found in Fig. 5. Here chains with 2, 4, and 5 beads have arranged themselves at different positions after fast ramping of the field to 36 kA/m, in very good agreement with the quantization ''rule.'' Dipolar interactions alter the distances slightly, in particular, for the chains that are close to each other. The effect of this repulsion can be seen in Figs. 4(c–f), where the vertical chain formed by beads 1 and 2 is gradually moving away from its initial location ($D_2\approx 4a$) as the magnetic field increases.

Third, we see that our theoretical estimate of H_c fits quite well with the experimental measured values, in particular, for the vertical chain formation in Fig. 4(c). Because beads 1 and 2 are not in the horizontal chain close to the contact line, the capillary forces are expected to be relatively small, since they may not even touch the water/air interface. On the other hand, the repulsive magnetic force results in a small push, and one should therefore expect that the two beads form a vertical chain at fields lower than H_c, which appears to be in agreement with our observations. The vertical chain formation in Fig. 4(e) takes place at a larger magnetic field, which can be explained qualitatively by observing that it is more difficult to remove a bead in the horizontal chain closest to the contact line, since the capillary forces are stronger here. Thus, bead 4 must struggle to remove another bead from this chain. It is even more difficult for bead 3, which must remove a bead with two neighbors, thereby increasing the capillary forces.

IV. CONCLUSION

We showed that in a magnetic field, magnetic beads in a liquid drop can either arrange themselves in a two-dimensional repulsive lattice or form attractive vertical chains, depending on the contact angle of the drop. We also demonstrate that the vertical chains' position from the contact line is quantized and depends on the number of beads in the chain.

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