Dynamics of Crystal Structure Formation in Spin-Coated Colloidal Films

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ABSTRACT The spin-coating of colloidal suspensions is an inherently nonequilibrium process that gives rise to highly reproducible, but polycrystalline, films with different symmetries depending on experimental parameters. In this study, we explore the transient dynamics of evaporative colloid spin-coating for the first time, via a combination of high-speed imaging, atomic force microscopy, static photography, and scanning electron microscopy. As the wet colloidal film thins and dries, we observe several symmetry transitions, while at the same time remarkably, the thinning rate (in nondimensional time units) collapses to one universal curve for all rotation rates. We correlate static and dynamic measures of crossovers in ordering regimes, and obtain an estimate of the evaporation rate in the late stage of drying. We conclude that the thinning dynamics controls the local volume fraction and stress profiles, which in turn drives the structural transitions.

SECTION Macromolecules, Soft Matter

Colloidal self-assembly is a facile and promising method for making photonic crystals,1 but the control of defects is a challenge. Nonequilibrium approaches to colloidal self-assembly are likely crucial to the making of large-area colloidal crystals.2,3 Colloid spin-coating has recently emerged as a highly robust and reproducible nonequilibrium method to make multilayer colloidal crystalline films.4−6 However, in spite of its robustness, the spin-coating route to colloidal crystals is fraught with challenges. The highly uniform structural colors exhibited by these films have been shown to arise from a polycrystal where different crystallites exhibit long-range orientational order.7 In order to develop strategies to produce crystals with a greater degree of translational order, a deeper understanding of the dynamical mechanisms of structure formation is required.

While the dynamics of spin-coating has been studied extensively and quantitatively in simple one-component fluids8−9 as well as in polymer solutions,10,11 the study of the dynamics of colloid spin-coating has been limited to numerical studies of thinning rates.12 A recent work demonstrates that spin-coating flows (in the absence of evaporation) control the local stress profiles, and drive crystallization when the Peclet number exceeds a critical value.6 Two questions that have remained unaddressed—how the dynamics interlinks with the emergence of different symmetries, and the role played by evaporation—are the focus of the experiments reported here.

We begin with our observations of the transient dynamics. Using high-speed imaging and the lighting configuration A (Figure 6), we are sensitive to changes in long-range orientational order via the appearance of symmetries in the optical reflections. In all experiments (at varying rotation speeds) common dynamical features are observed in the fluid phase. While the results presented here pertain to experiments using methyl ethyl ketone (MEK) as solvent, similar results were found with acetone as solvent. This phase is characterized (Figure 1a) by a set of von Kármán spirals13,14 that disappear when no more suspension is pipetted into the rotating substrate. Long-range orientational order with 6-fold symmetry extending over the whole surface is observed immediately after pouring of the suspension ceased. This symmetry (Figure 1b) prevails for at least half of the duration between pipetting and drying. Next, there is a transition to 4-fold symmetry (Figure 1c). This has been observed in dried structures5,7,15 but it has never before been observed in the wet phase. The 4-fold order encompasses the whole surface of the substrate for a short time (e.g., 10 and 100 ms at 6000 and 2000 rpm, respectively) before shrinking toward the center (Figure 1d). At this point, complete drying of the structure is observed. In all cases, this drying starts from the edges of the substrate and is directed inward, defining a circular drying front whose diameter decreases with time (Figure 1e).

Studies of these transient dynamics also show for the first time that the drying front is preceded by disordering, i.e., the disappearance of the symmetric reflections milliseconds prior to drying. A movie of the experiment is available in the Supporting Information.

The dried state is characterized by two cases that are distinguished through the symmetry observed in the outer...
A typical sequence illustrates the transient dynamics of long-range orientational order. (a) When the suspension is pipetted onto the rotating substrate, a set of von Kármán spirals appear. These spirals dissipate soon after the pipetting ceases. (b) With the disappearance of the spirals, six-arm symmetry is immediately observed along the whole surface of the substrate. (c) This order prevails for relatively long times but finally transitions to 4-fold symmetry. (d) The four-arm pattern rapidly shrinks toward the center. (e) The drying begins on the periphery, and the drying front (the interface between bright and dark regions) propagates radially toward the center, revealing the final dried symmetry. The wet region loses its six- or four-arm order in the milliseconds prior to the arrival of the drying front. (f) The dynamics in the fluid stage for varying experimental conditions (either decreasing concentration or increasing angular speed of the substrate) is qualitatively identical and quantitatively universal (see text). However, the dried structure presents two distinct symmetries depending on experimental conditions: pure 4-fold symmetry at low angular speeds or high concentration (top right, 20%, 4000 rpm, MEK solvent) and mixed structures, e.g., center 4-fold and the outer area 6-fold, at high angular speeds or low concentration (bottom right, 20%, 6000 rpm, MEK solvent). Real color versions of generic final state are shown at the rightmost of the figure. Red lines are drawn on top of the arms as a guide to the eye. The commonality in fluid structures, but not the two kinds of dried structures, indicates that the drying front might erase all memory of the structure observed prior to drying. Snapshots were digitally enhanced to improve visualization. An entire movie of this transient dynamics can be found in the Supporting Information.

Figure 1. A typical sequence illustrates the transient dynamics of long-range orientational order. (a) When the suspension is pipetted onto the rotating substrate, a set of von Kármán spirals appear. These spirals dissipate soon after the pipetting ceases. (b) With the disappearance of the spirals, six-arm symmetry is immediately observed along the whole surface of the substrate. (c) This order prevails for relatively long times but finally transitions to 4-fold symmetry. (d) The four-arm pattern rapidly shrinks toward the center. (e) The drying begins on the periphery, and the drying front (the interface between bright and dark regions) propagates radially toward the center, revealing the final dried symmetry. The wet region loses its six- or four-arm order in the milliseconds prior to the arrival of the drying front. (f) The dynamics in the fluid stage for varying experimental conditions (either decreasing concentration or increasing angular speed of the substrate) is qualitatively identical and quantitatively universal (see text). However, the dried structure presents two distinct symmetries depending on experimental conditions: pure 4-fold symmetry at low angular speeds or high concentration (top right, 20%, 4000 rpm, MEK solvent) and mixed structures, e.g., center 4-fold and the outer area 6-fold, at high angular speeds or low concentration (bottom right, 20%, 6000 rpm, MEK solvent). Real color versions of generic final state are shown at the rightmost of the figure. Red lines are drawn on top of the arms as a guide to the eye. The commonality in fluid structures, but not the two kinds of dried structures, indicates that the drying front might erase all memory of the structure observed prior to drying. Snapshots were digitally enhanced to improve visualization. An entire movie of this transient dynamics can be found in the Supporting Information.
Figure 2. Universality in transient film-thinning dynamics, light-
ing configuration B. (a) Pattern of alternating rings observed
during thinning ($\omega = 5000 \text{ rpm} = 523.6 \text{ rad/s, MEK solvent}$) at
0.21 and 0.44 s. The last image, $t = 0.438$ s, shows only the inner
region for enhanced detail of the drying front transition. (b) The
derivative of the thickness as a function of time measured from the
alternating ring pattern (at radial distances from 1 to 5 mm). A
rescaling of time ($\tau = \omega(t - t_{dry})$) leads to a collapse of data at all
rotation rates. $t = 0$ is the moment when the sample completely
dries. The results are well fit by the function in eq 1. Plotting the
two terms of the fit (non-evaporative, dotted line; evaporative,
dashed line) separately, we see that evaporation likely dominates
for $\tau > 80 \text{ rad}$. 

Out at ambient temperatures (20 °C) for two solvents (MEK
and acetone) which differ primarily in viscosity (0.42 mPa·s,
and 0.31 mPa·s respectively) and in equilibrium vapor pres-
sure (71 and 181 mmHg, respectively). The results from
acetone have not been reported, for clarity. However, all the
results presented, including the two-stage dynamics, are valid
for both solvents.

Finally, the thickness of the colloidal crystal was measured
using atomic force microscopy (AFM). Following techniques
described elsewhere,7 a scratch was made through the center of
the structure, and the height difference between the substrate and the top layer was determined as a function of
radial position. The heights showed a bimodal distribution
with one peak at the substrate location and the other on the top
layer of the colloidal sediment. They were fitted by gauss-
sians and the difference between the mean of those fits was
taken as the thickness of the structure.

In Figure 4a, we present the thickness profiles of the crystals obtained (MEK suspensions). At the same speed,
acetone profiles (not shown) are thicker. In all cases, thickness profiles present a plateau in the outer region and an increase
as we get closer to the center (radial distance $\rho = 0$). All

thickness profiles have an envelope similar to a bell function
with a global maximum at the center of rotation.

We can compare the static thickness profiles obtained
by AFM with optical thickness profiles extracted from the
ring-like interference patterns like the one shown in Figure 2a.
Although the interference fringes do not allow determination of absolute thickness for the fluid phase, a reasonable (upper)
limit is determined by utilizing the situation where the center
presented rings while the outer region was already dried (see
Supporting Information for details). The other fluid thick-
nesses were determined using this situation as a reference.
In Figure 4(b) we show thickness profiles obtained at different
dimensionless times. It is clear that the shape of the fluid
surface in the inner region, (i.e., $\rho < 1$ mm) is very similar for
$\tau = -91, -70,$ and $-40 \text{ rad},$ but different for $\tau = -14 \text{ rad}
\text{(when the outer region is dry).}$ This is consistent with observa-
tions (results of Figure 2(b)) that thinning rates (measured
prior to complete drying, $\tau < -40 \text{ rad}$) were independent of the radial distance.

Our study of transient dynamics (Figure 1) shows that
both kinds of previously reported long-range orientationally
ordered structures are found in a single system. On one hand,
the fluid phase presents 6-fold symmetry.4 On the other hand,
the final static structure after drying exhibits two different
symmetries (4- and 6-fold) that were previously seen in
 evaporative spin-coating.5,7,15 Remarkably, however, we find
other symmetry transitions in the transient dynamics. Sum-
marizing the results, we observe four different phases:

- Phase I: 6-fold symmetry (Figure 1b). This is identical to
the phenomenon reported by Jiang et al.,4 where the
interparticle separation reported was 1.41 $\sigma$ ($\sigma$ is the
particle diameter). Further assuming vertical compres-
sion, Jiang et al. deduced a particle volume fraction of
$\approx 52\%$. 

- Phase II: A transition to 4-fold symmetry (Figure 1c).
This has not been reported in the fluid phase before.

- Phase III: Loss of four-arm symmetry in the outer region,
milliseconds before drying (Figure 1d,e). This again is
new, and is specific to evaporative spin-coating (and
observable only because of the high-speed imaging).

- Phase IV: Dried close-packed structures with mixed
outer/linner (4/4 or 6/4) symmetries.

In the fluid phase (phase I), the shear stress $\sigma \sim p_{\text{MEK}} \omega^2 \rho^2$,
where $\omega = 500 \text{ rad/s}, h \approx 1 \mu m,$ and density $p_{\text{MEK}} \approx 800 \text{ kg/m}^3$.
The radial distance $\rho$ can be taken to be 1 mm in the inner
region and 5–10 mm in the outer region. The Peclet number
$Pe \sim \sigma \rho^2 h / \kappa T$ thus also increases with radial position from
0.8 to 8. This corresponds well to the findings in Shereda
et al. that shear-induced crystallization occurs when the
Peclet number is $O(1)$.

The origin of phase II appears to coincide with times where
the role of evaporation becomes more dominant in the
thinning rate (see Figure 2): i.e., both the radial variation in
Peclet number and evaporation must be taken into account.
The disordering in phase III is a more challenging question. Here, the dry–wet interface provides a perturbation to the shear stress profile imposed on the spinning fluid which induces disordering of a shear-induced crystal. The most direct consistency check for this is dynamical. Natural colloidal reorganization time scales are 

\[ t_{\text{Brownian}} \approx \frac{a^2}{D} > 15 \text{ ms} \]  

(a = 0.25 \mu m and \( D < k_B T / 6\pi \eta a \)). This time scale is a lower limit because \( \eta_{\text{eff}} \approx 10\eta \) at \( \phi = 0.5 \). The complete disappearance of the order occurs over \( \sim 10 \text{ ms} \).

The characteristic length- and time-scales for front motion in the movie shown are approximately 1 mm and 10 ms, respectively. For thin films in the outer region prior to drying, the volume fraction will increase rapidly: the Lindemann criterion ensures that, for thin enough films, the resulting change in lattice spacing will be large enough so as to result in crystal melting. There is not enough time before the front arrives for recrystallization at higher packing. Drying on the other hand forces local ordering at the drying front.

Another important aspect of the dynamics over times spanning phases I to III is the existence of an universal behavior in the thinning rate as a function of dimensionless time (Figure 2b). We attempted to fit the experimental data to a phenomenological form inspired by the thickness versus time equations for a simple fluid, but forcing the functional form to obey the experimentally observed time scaling:

\[ h = h_0 \left[ 1 + \alpha (\tau - \tau_0) \right]^{0.5} \]  

This functional form was not a good fit to the data at an early time \( \tau = 0 \) (not shown). Nevertheless, following Birnie et al. and Meyerhofer, a constant can be added to the thinning rate to properly take into account the evaporative phase:

\[ -\frac{dh}{d\tau} = \begin{cases} 0.5\omega h_0 \;/(1 + \alpha (\tau - \tau_0))^{1.5} + \epsilon & \text{if } \tau < \tau_0 \\ 0 & \text{if } \tau \geq \tau_0 \end{cases} \]  

This modified form is in excellent agreement with our measurements, with fitting parameters \( \alpha = 17 \text{ rad}^{-1} \), \( h_0 \approx 96 \mu m \), \( \tau_0 = -160 \text{ rad} \), and \( \epsilon = 0.015 \mu m/\text{rad} \). \( h_0 \) represents the starting height of the film at the end of the transient von Kármán spirals, and \( \tau_0 \) is the corresponding time. We find therefore that the dimensional evaporation rate \( \epsilon = \epsilon_0 \omega \) has a linear dependence on \( \omega \): for \( \omega = 500 \text{ rad/s} \), \( \epsilon = 7.5 \mu m/s = 0.75 \mu L/s/cm^2 \). In
addition, this universal behavior looks similar to (and can in principle be compared with) the numerical thinning rates calculated by Rehg and Higgins.12

Having considered the dynamics in the fluid phase, we next consider the movement of the drying front (Figure 3a). In all cases studied, the speed at which the interface moves toward the center presents two distinct dynamical regimes (Figure 3b): an early stage where front speeds are large and increase in magnitude with increasing rotation speed, and a late stage where front speeds are small and invariant with rotation speed. The radial crossover from sharp arms near the center of rotation to the broader arms far from it corresponds reasonably well with the dynamical crossover (Figure 3c) - the ratio of these two length scales is approximately 0.5 (with a standard error of ±0.25). Indeed, the much narrower arms in the central than in the outer regions (Figure 1) is also consistent with the front speeds measured (Figure 3b, slow/fast front speeds in the central/outer regions): the slower the front motion, the sharper the arms.

Finally, we compared static thickness profiles with the dynamic thickness profiles. We found that the thickness of the film is inhomogeneous even in the fluid state (Figure 4b), and there is always a maximum in thickness at the center of spinning. This inhomogeneity does not give rise to radial variations in the thickness in the center of rotation, for example, phase I (see Figure 6 and Figure 1b), while in the dried state, the change in thickness toward the center corresponds to a change in morphology (Figure 1f).

That the fluid is indeed not planar is shown clearly in both the dynamical optical and the static AFM measurements (Figure 4). It has been noted quite early by Acrivos et al.19 that it is much harder to planarize a non-Newtonian fluid. As pointed out by Rehg and Higgins,12 the functional relationship between viscosity and concentration appears to play a much more significant role in spin-coating of colloidal than in polymeric suspensions and the simple assumptions made for predicting coated film thickness in polymeric systems are inadequate for colloidal suspensions. Equation 1 is a phenomenological alteration of the Meyerhofer formula.9

At the late stage of drying (ρ < 1 μm), we may assume a disk-like shape for the suspension, since the maximum value of dh/dt is approximately 10⁻³ (Figure 4). Then, the rate of change in the volume of wet suspension is dv/dt = 2πρ(dp/dt)h + πρ²(dh/dt). Note that all the quantities in the above equation have been obtained in this experiment. The term dp/dt is obtained from the asymptotic fitting of the late stage (see Figure 4b). The thinning rate dh/dt in the second term in this equation is obtained from the fit to the thickness profile for τ = -40 rad (Figure 2b). However, the first term in this equation is the dominant one, i.e., the crystallization front is parallel to the outer meniscus of the wet film. In Figure 5 the rate of volume change is plotted as a function of the radial distance for the late stage of the drying front dynamics (Figure 3a). For this calculation the thickness profile h(ρ) was obtained from the static thickness profile (Figure 4a).

This calculation shows a linear decrease of the evaporation rate as we get closer to the center of rotation. Linear dependence of the dv/dt suggests that the capillary flow of solvent through the interface (i.e., the second term in dV/dt) is the primary contributor to the evaporation rate.

Why does the dried inner region always exhibit four-arm order? When the film is thin enough, the substrate will govern the ordering, and six-arm order is the result. For thicker films, the radial drying front dominates, and other orientations are possible. The increasing Peclet number with increasing radius probably also plays a role in generating the mixed symmetries.

In summary, we have studied the high-speed dynamics of evaporative spin-coating and found new structural transitions. In spite of the existence of these structural transitions, we find that the thinning dynamics exhibits no breaks at these transitions, and has a universal scaling form for all rotation speeds. On this basis, we suggest that the thinning dynamics controls the local volume fraction and stress profiles, which in turn drives the structural transitions. In addition, our quantitative measurements will enable detailed comparisons with numerical simulations of the spin-coating of colloidal suspensions in the presence of evaporative flows.

**EXPERIMENTAL SECTION**

We suspended silica particles (458 ± 2 nm diameter) in MEK or acetone at different initial volume fractions (φ₀ = 5, 10, 15, and 20%) by procedures described elsewhere.7 Substrates were made from silicon wafers cut approximately to 25 mm × 25 mm, rinsed with ethanol (96%) and distilled water, dried by blowing of N₂ gas, and stored in a clean box to avoid contamination until the moment of performing the experiment. Each experiment consisted of pipetting in continuous flow (“pouring”) 40 μL of suspension on the substrate.
spinning at a constant angular speed. The spinning was ceased in 10–15 s when the substrate was completely dry. Dynamics of the spin-coating process was obtained with a high speed camera at a rate of 1000 frames per second. A 500 W tungsten bulb was used as light source in two different lighting setups (Figure 6). To visualize long-range order in both the fluid (thinning) and dried states, the light source was located next to the camera (configuration A in Figure 6). Spatial and temporal thickness variations during the fluid stage were visualized (configuration B in Figure 6) via interference rings. In this case, the light source was placed such that the specular reflection of the bulb was observed by the camera; a band-pass filter set the imaging wavelength to λ = 540 nm ±40 nm and a diffuser placed in front of the light source homogenized the illumination. Radial thickness profiles of the colloidal films were determined by AFM scanning using a method similar to that reported by Arcos et al.7 Static optical images of the dried samples were visualized using a method similar to that reported by Birnie et al.8 In this case, the light source was placed such that the specular reflection of the bulb was observed by the camera; a band-pass filter set the imaging wavelength to λ = 540 nm ±40 nm and a diffuser placed in front of the light source homogenized the illumination.

SUPPORTING INFORMATION AVAILABLE Complete movies of the experiment on each configuration and detailed description of the measuring procedures for thickness-related data (fluid). This material is available free of charge via the Internet at http://pubs.acs.org/.

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