Phase field crystal model of drying induced ordering of colloidal droplet

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Abstract. Controlled evaporation of solvent from a suspension of colloidal particles can induce interesting patterns of the residue on a substrate. Under certain circumstances, the colloidal particles can self-assemble in large crystalline arrays. The conditions needed for obtaining such a homogeneous pattern are poorly understood because of the complex interactions between many forces. Here we report on a simple phase-field crystal modeling of the phenomenon which shows that the ability to crystallize depends both on the initial density of the suspension as well as the drying rate.

1. Introduction
Self-assembly of colloidal particles into ordered arrays is interesting for various technological applications [1, 2] and also because it can involve ordering in systems driven far from equilibrium [3]. Many qualitatively different transitory structures can be formed by the colloidal particles, while evaporating the colloidal suspension. Ordered arrays of colloidal particles are often produced by evaporating a drop of colloidal suspension on a substrate [1, 3, 9]. Ordering upon evaporation is not well understood because of the complex interaction of many forces viz. lateral capillary forces, convection and floatation, as well as colloid-colloid interactions, and contact line pinning [7, 8, 9, 10, 11, 12].

Evaporation assisted ordering is usually a two-stage mechanism. In the pinned state, the contact line between the drop and the substrate is pinned. The area of the drop is fixed. Evaporation occurs primarily at the periphery [10] due to the increased local curvature. Therefore, solvent flows towards the periphery to replenish the liquid lost due to evaporation [8, 9]. It advects the particles with it and the build-up of particles at the periphery causes self-assembly due to attractive capillary forces, that has been investigated in the past [11, 9]. However, the contact line is eventually depinned and drying recommences when the drop area decreases [12], pushing the colloidal particles inward. The life time of these two states can be controlled by varying the contact angle between the droplet and the substrate. Here we try to understand the final structure at the end of the evaporation through depinned state via simple phenomenological continuum models. For simplicity we will not consider the effect of the substrate, hydrodynamics and polydispersity of the solute.
2. The Phase Field Crystal Model

Our approach is coarse-grained over the fluctuations at length-scale and time-scale of particle dynamics. We model the drying process as a two dimensional (2d) liquid-gas phase transition. The local density of the solvent \( \phi(r, t) \) at position \( r \), satisfies [13],

\[
\dot{\phi} = \Gamma \delta F_1 \delta \phi
\]  

with

\[
F_1[\{\phi\}] = \int \text{d}^2 r \left[ -a\phi^2 + b\phi^4 + c(\nabla \phi)^2 + h\phi \right]
\]  

where \( h \) is the chemical potential of the solvent controlling the rate of drying and \( a, b, c \) are parameters and \( a, b, c > 0 \). The free energy density has minima at \( \phi_1 \) and \( \phi_2 \) where \( \phi_1 > 0 \) and \( \phi_2 < 0 \). We denote the liquid \( \phi = \phi_1 \) and vapour \( \phi = \phi_2 \) phases of the solvent. The resulting partial differential equation is solved by an explicit Euler discretization scheme starting with an initial \( \phi(0, r) = \phi_1 \) within a circle of radius \( R \). For \( h > 0 \), \( R \) decreases at subsequent times as the drop evaporates and \( \phi \to \phi_2 \) everywhere.

We consider Phase Field Crystal (PFC) model for the solute particles. The simplest PFC model defined by the dimensionless free energy functional [14, 15] is

\[
F_2[\{\psi\}] = \int \text{d}^2 r \left\{ \frac{\psi}{2} \left[ \epsilon + (1 + \nabla^2)^2 \right] \psi + \frac{\phi^4}{4} \right\}
\]  

where \( \psi \) corresponds to dimensionless density field [14] of the solute. Note that it contains next order term in gradient expansion of the free energy \( (|\nabla^2 \psi|^2) \) besides the lowest order \( (|\nabla \psi|^2) \) term of the expansion to ensure the correct crystalline minima, which is triangular in 2d. A more detailed discussion is given in [14]. The dimensionless free energy functional in Eq.3 can be obtained by suitable rescaling of a dimensional free energy functional which is also related to classical density functional theory [14, 15, 16].

In our case the solvent evaporates continually from the surface of the droplet and thus the liquid-gas interface shrinks, pushing the solute particles inward. More specifically, the evaporating solvent will act as a time-dependent confinement to the solute particles. Therefore, there will be a term in \( F_2[\{\psi\}] \) which will couple with solvent density \( \phi(r, t) \). For simplicity, we assume the coupling to be linear and thus the dimensionless free energy functional of the solute becomes,

\[
F_2 = \int \text{d}^2 r \left\{ \frac{\psi}{2} \left[ \epsilon + (1 + \nabla^2)^2 \right] \psi + \frac{\phi^4}{4} + \phi \psi \right\}
\]  

The dimensionless equation of motion will be then

\[
\frac{\partial \psi}{\partial t} = \nabla \cdot \left( \mu \nabla \frac{\delta F_2}{\delta \psi} \right) = \nabla \cdot \left\{ \mu \nabla \left[ \epsilon + (1 + \nabla^2)^2 \right] \psi + \psi^3 + \phi \right\}
\]  

where the mobility \( \mu \) is given by

\[
\mu = (\tanh(\gamma \phi) + 1)/2
\]  

and \( \mu \) vanishes in the limit \( \phi \to \phi_2 \). The choice of the functional form of \( \mu \) is motivated by the fact that during evaporation if some solute particles go out of the droplet, the motion of
those particles cease. The parameter $\gamma$ will determine how sharply the velocity of the particles vanishes while crossing the perimeter of the drop. Here the control parameters are the average density of the particles in the drop, $\psi_{av}$, and the drying rate which is controlled by varying $h$ and $\Gamma$.

According to the model described here, there are two important time scales, which are involved in ‘drying induced ordering’ phenomena. One ($\tau_1$) corresponds to the drying rate of the solvent and other ($\tau_2$) corresponds to the relaxation of the solute to its crystalline minima. If initially $\psi_{av}$ is much lower than the critical value (i.e. initially solute is in disordered state) and $\tau_1 < \tau_2$, no ordering of the solute is expected, simply because in this case, before it finds the crystalline minima, the solvent will be completely evaporated. Only if $\tau_1 \geq \tau_2$, then ordering is expected. Such interplay between various time scales is important to understand the aforementioned phenomena.

From the phase diagram of a system obeying Eq. 3 [14], we know that for $\epsilon = -0.375$, triangular phase will be obtained when $\psi_{av}$ is in between $-0.32143$ to $-0.1543$, as well as in between $0.32143$ to $0.1543$. Beyond the range, striped phase will be obtained and below the range we obtain liquid like disordered phase. In our case, when the drop evaporates with a drying rate suitable for ordering (i.e. $\tau_1 \geq \tau_2$), the shrinking circular contact line pushes the solute inside the drop. Consequently, $\psi_{av}$ increases and when it is in the aforementioned range (in our case the range is between $-0.32143$ and $-0.1543$), ordered phase will be formed. But if the drying is slow enough or the initial density of the solute is high enough so that, final $\psi_{av}$ goes beyond the range, striped phase will be obtained according to the phase diagram given in [14]. In figure 2a and in 2b we show a typical striped and a typical ordered phase. In both the phases density is inhomogeneous over space but in the ordered state density peaks form a crystalline array (triangular) which is clearly absent in the striped phase. If the drying rate is such that the final $\psi_{av}$ remains below the range, we get a typical liquid-like disordered state, which is shown in figure 2c. The density in bulk of this state is homogeneous over space, as it should be and the ring pattern near the boundary (see figure 2c and 3a) appears due to the sharp change of density at the periphery of the drying droplet. When $\phi = \phi_2$ everywhere all the dynamics ceases (because, $\mu(\phi_2) = 0$).

A further simplification may be achieved by solving for the dynamics of the solvent analytically. For a given $\psi_{av}$, initial condition for solvent-field is

$$\phi(r, t = 0) = \begin{cases} \phi_1 & \text{for } |r| = R \\ \phi_1 + \frac{(\phi_1 - \phi_2)}{\xi}(R - r) & \text{for } R \leq |r| \leq (R + \xi) \\ \phi_2 & \text{otherwise} \end{cases}$$

(7)

Here $\xi = \sqrt{\frac{c(\xi_1 - \phi_2^2)}{I_s}}$ is the interfacial width for $\xi_1 \ll 1$, with $I_s = \frac{1}{3} - \frac{a(\phi_1^2 - \phi_2^2)}{3} + \frac{b(\phi_1^2 - \phi_2^2)}{3} + \frac{c(\phi_1^2 - \phi_2^2)}{2}$.

The rate of change of $\phi(r, t)$, $\frac{d\phi}{dt}$, is then obtained as,

$$\frac{d\phi}{dt} = \frac{dR}{dt} \frac{d\phi}{dr} \bigg|_{r=R}$$

(8)

which gives, after some straightforward algebra,

$$\frac{dR}{dt} = \dot{R} = \frac{\xi}{(\phi_1 - \phi_2)^2} \left[ -a(\phi_1^2 - \phi_2^2) + b(\phi_1^4 - \phi_2^4) + h(\phi_1 - \phi_2) \right] + \frac{2c}{R}$$

(9)
Where we have assumed that $\frac{\xi}{R} \ll 1$. Integrating Eq.9 we get

$$r = R_0 - \frac{2c}{D} \ln\left(\frac{DR_0 + 2c}{Dr + 2c}\right) + Dt$$

(10)

where $D = \frac{\xi}{(\xi_1 - \xi_2)^2}\left[-a(\phi_1^2 - \phi_2^2) + b(\phi_1^4 - \phi_2^4) + h(\phi_1 - \phi_2)\right]$ and $R_0$ is the initial radius of the drop.

We see that Eq.10 is a transcendental equation which is solved using bisection at every time step. Typical solutions for $R(t)$ are shown in Fig.1.

![Figure 1](image1.png)

Figure 1. (a) and (b) show how the radius of the drop ($R$) decreases with time for total drying time $t_d = 1568.15$ (fast drying) for $h = 0.006$ and $t_d = 6620.32$ (slow drying) for $h = 0.002$ respectively. In both cases the final radius of the drop is $R = 50.0$ which is greater than the values of $\xi$ for both cases.

3. Results

In our PFC simulations we choose $a = 0.008, b = 0.004, c = 1.0$ and $h = 0.006, 0.002$. Corresponding to these values, the dimensionless free energy $F_1$ has minima at $\phi_1 = 0.651$, $\phi_2 = -1.15$ (for $h = 0.006$) and $\phi_1 = 0.930$, $\phi_2 = -1.06$ (for $h = 0.002$). The interfacial width, $\xi = 31.77783$, for $h = 0.006$ and $\xi = 44.65193$, for $h = 0.002$. A system of size $512\Delta x \times 512\Delta x$ where $\Delta x = 1.0$ is chosen with periodic boundary conditions. Here we do not explicitly solve the dynamics of the solvent rather we use the solution given in Eq.10 which is valid for $\frac{\xi}{R} \ll 1$. At time $t = 0$ we take the radius of the drop $R_0 = 200$ and $\Gamma = 1.0$.

Initially $\psi(r, t = 0)$ is chosen randomly (because initially the solute is in disordered state) keeping its average density constant. The quantity $\left[+\left(1+\nabla^2\right)\right]\psi$ in Eq.5 (with $c = -0.375$), is calculated using fast fourier transformation (FFT) and Eq.5 is solved using Euler discretization scheme with $\gamma = 10.0$ in Eq.6. For $\gamma = 10.0$, $\mu(\phi_1) = 1.0$ and $\mu(\phi_2) = 0$.

We show a typical configuration for $\psi$ in Fig.2. While Fig.2(a) shows a striped pattern, $\psi$ shows ordered and liquid-like final configurations in Fig.2(b) and (c). Here the initial average value of $\psi$ is largest for Fig.2(a) but is smaller in the subsequent figures (b) and (c) with $\psi(a) > \psi(b) > \psi(c)$. In all these cases total drying time ($t_d$) i.e. drying rate, is taken to be same. This implies that for a fixed drying rate, for small as well as for large initial densities of solute, the typical final configurations are not in crystalline phase. For small initial densities, they are in liquid-like disordered phase and for large initial densities they are in stripe phase.
Figure 2. (a), (b) and (c) are the final configuration of $\psi(r,t)$ for three different initial, average solute densities which correspond to $\psi(a) = -0.7$, $\psi(b) = -1.0$ and $\psi(c) = -1.2$ respectively showing the striped phase, crystal and disordered liquid configurations respectively. Total drying time is 1568.15 (For $h = 0.006$) for all three cases.

Figure 3. (a) and (b) are the final configuration of $\psi(r,t)$ for $\psi_{av} = -1.2$ when total drying time $t_d = 1568.15$ (fast drying) for $h = 0.006$ and $t_d = 6620.32$ (slow drying) for $h = 0.002$ respectively. In (a) we get a typical liquid-like disordered configuration and in (b) a typical ordered (crystalline) configuration finally.

In intermediate initial densities we get crystalline phase. We also show a typical liquid-like disordered configuration for fast drying (i.e. $\tau_1 < \tau_2$) and a typical ordered (triangular phase) configuration for slow (i.e. $\tau_1 \geq \tau_2$) drying in Fig.3 (a) and (b) respectively. In both the cases the initial solute density is taken to be same and below the critical density. This implies that for slow drying, as was expected, we get crystalline order and for fast drying, we get liquid-like disordered structure. We also show how the radius of the droplet typically shrinks during evaporation in Fig.1 for fast as well as for slow drying.

4. Conclusions

In reality, drying induced pattern formation in colloidal drops is a very complex phenomena due to the interplay of various forces involved. One of the essential feature of the problem is dragging of the solute particles together by the solvent during evaporation in depinned state. This originates due to the surface tension between solute and the solvent. Here we have tried
to capture this effect by simple continuum models. According to the model described here, evaporation-assisted ordering depends on the drying rate as well as on the initial concentration of the solute. There is a critical density at which solute particles can be organised in space to form ordered arrays. For slow drying, the solute can reach to the critical density by the end of the evaporation and form the arrays. For fast drying, it may happen that before it reaches to the critical density, solvent is evaporated out completely and we have disordered structures at the end. A full description of this process together with Brownian dynamics simulations will be published elsewhere [6]

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