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Spinodal decomposition in particle-laden Landau-Levich flow

Justin C. T. Kaoa) and A. E. Hosoi
Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
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We examine Landau-Levich coating by a suspension of spherical particles. For particles larger than the liquid film thickness, capillary forces lead to self-assembly of monolayer particle aggregates. We observe two regimes of deposition, find coating fraction as a function of wall speed, and propose a spinodal decomposition (Cahn-Hilliard) model for this pattern formation process.

Liquid coating processes are of widespread practical and scientific importance.1, 2 Researchers in this area since Landau and Levich,3 and even previously,4 have generally considered coating from a homogeneous liquid bath. However, one may also ask what kind of coating is produced from a heterogeneous source: for instance, a bubble in the liquid bath can produce a defect in the resulting coating.5 In this communication, we describe the Landau-Levich flow of a macroscopic suspension of spheres, a type of heterogeneous coating commonly observed in industrial processes, as well as in the deposition of foam bubbles in one’s beer glass. We show that this system exhibits particle aggregation and pattern formation driven by surface tension, and propose an analogy to the spinodal decomposition of binary mixtures.

A diagram of the experimental setup is shown in Fig. 1(a). The coating flow is produced by rotating partially filled glass media bottles (VWR 500 mL, I.D. = 8.0 cm) on fixed rollers, at wall speed $u$. To ensure a vertical wall at the meniscus, the total volume of suspension in each bottle is fixed to be half of the bottle volume. Solid particles comprise a fraction $\phi$ of the suspension volume, and deposition occurs continuously as the suspension leaves the bulk. Since the system is sealed, no evaporation occurs.

The particles used in our experiments are polystyrene beads (Glen Mills PB-4) with mean diameter $2a = 219 \mu m$ and polydispersity of $\sigma_{2a} = 33 \mu m$. These are suspended in a density-matched solution of water and table salt, with the surfactant polysorbate-20 added to ensure complete wetting of the beads ($\rho = 1.05 g/mL$, $\eta = 0.0011 Pa s$, and surfactant concentration 1 g/l, or roughly $10 \times$ the critical micelle concentration). The surface tension is found to be $\sigma \approx 30 mN/m$, decreasing about 10% with increasing particle volume fraction, apparently due to an increase in dust and other contaminants. All measurements and experiments are performed at $24 \pm 1 ^\circ C$.

Speed of rotation is set by a variable-voltage power supply and measured via an encoder on the drive motor. The experiment is operated in a parameter range such that the diameter of the particles, $2a$, exceeds the Landau-Levich thickness of deposited liquid film in the absence of particles,3, 6 $h_\infty \sim \ell_c Ca^{2/3}$, where $\ell_c \equiv \sqrt{\sigma/\rho g}$ and $Ca \equiv \eta u/\sigma$. The presence of a particle in the liquid film therefore causes a deformation of the free surface (Fig. 1), so that deposited particles are pinned to the wall by capillarity within a few millimeters of leaving the bulk suspension. Once pinned, particles remain fixed indefinitely;7 we may therefore stop the rotation for imaging, which is done at a marked location on the bottle. A digital camera views the middle of the cylindrical portion of the bottle, producing a usable imaging area of 5 cm wide by 2 cm high. Finally, a custom MATLAB
script processes the resulting photographs for texture on the scale of the particle size, yielding binary images indicating the spatial distribution of particle deposition.

Figure 2 shows some example deposition patterns, along with particle detection output (outlined regions). Several characteristic features are seen. First, the deposited particles form dense aggregates, with particles only rarely found in isolation (generally under low bulk volume fraction conditions). Second, these aggregates show a typical length scale of $\sim 3$–$10$ particle diameters. Finally, at intermediate coating fractions, the aggregates are elongated in the vertical (time-like) direction, showing history dependence of the deposition.

We consider the forces at work during the deposition of any individual particle, as it passes through the boxed region in Fig. 1. For the setup described here, typical capillary numbers are in the range of $Ca \equiv \eta u / \sigma \sim 10^{-4}$, with Reynolds number $Re \equiv \rho u a / \eta \sim O(1)$ and bond number $Bo \equiv \rho g a^2 / \sigma = 4.1 \times 10^{-3}$. The particles are large enough to deform the otherwise-flat liquid coating ($2a > h_\infty \sim \ell_c Ca^{2/3}$); therefore we expect surface tension to be the dominant force in the motion of our wall-coated particles.

Many researchers have considered the capillary attraction of floating particles,8–12 of particles confined to a horizontal surface,13,14 and even of swimming nematodes on a wall.15 Although none of these previous works match the details of our situation (where particles pass through a bulk meniscus, and the free surface is dynamic due to liquid drainage down a vertical surface), it is clear that a similar capillary attraction exists between our particles. Once particles are deposited on the wall, their surrounding liquid thins to less than a particle diameter, wetted particles distort the free surface, and capillary attraction acts to induce aggregation. (We note that a substantial body of literature exists in the area of self-assembly by evaporating colloidal suspensions,16–19 coffee rings,20 and gravitational drainage of thick suspension coatings.21 These phenomena depend on concentration of
solids via subsequent removal of liquid from the coating film, whereas in our system self-assembly occurs immediately and continuously upon passage through the bulk meniscus.)

Once deposited, our aggregates do not coarsen; particle motion is limited both by the range of capillary attraction (dependent on the size of the meniscus around each particle), as well as by immobilization of particles after deposition. Surface tension acts to press particles against the wall, resulting in rapid solid-solid contact with normal force increasing to $F_\perp \sim \sigma a$. We propose that the resulting sliding and rolling friction $F_f \leq k_F F_\perp$ prevents particle motion once $F_\perp$ is large compared to other forces affecting the particles. In our experiments, it is seen that particle pinning occurs within a few millimeters of leaving the bulk suspension, leaving the deposited aggregates no chance to coarsen beyond their initial length scale.

Finally, we observe that a particle moving from the bulk suspension to deposit on the wall must overcome both surface tension and gravity. However, both of these opposing forces are reduced when previously deposited particles extend the liquid meniscus. Thus, an initial particle deposition lowers the threshold to deposit subsequent particles, resulting in the observed vertically elongated structures.

We determine the expected range of the observed behavior by combining the requirements $h_\infty < 2a$ and $Bo \ll 1$. This yields $Ca^{2/3} < 2a/\ell_c \ll 1$, which we interpret as bounds on the size of particles displaying this aggregation, and an upper bound on the maximum wall speed producing this behavior. Violating the condition $h_\infty < 2a$ leads to substantial particle movement due to fluid drainage, as in Buchanan et al., while violating $Bo \ll 1$ results in no deposition. Within these bounds, systematic exploration of aggregation behavior with different-sized particles was impractical since the smallest particles available to us (Glen Mills PB-4, $2a = 219 \mu m$) have $2a/\ell_c \approx 0.12$, leaving little overhead for substantially larger particles. However, we do observe that aggregate sizes are roughly doubled when we use particles with twice the diameter (Glen Mills PB-2.5, $2a = 448 \mu m$); further details are given in the supplementary material.

Instead, we explore the effect of varying two other control parameters: the solid volume fraction of the suspension, from $\phi = 0.10$ to $\phi = 0.50$, and the wall speed (rotation rate) of the bottle, from $u = 0.47 \text{ cm/s}$ to $u = 4.3 \text{ cm/s}$ ($Ca = 1.7 \times 10^{-4}$ to $1.6 \times 10^{-3}$). Binary maps of the resulting deposition patterns are shown in Fig. 3. We observe two different types of behavior, depending on the volume fraction:

(1) At low fractions, below $\phi \approx 0.35$, we have isolated deposition of particles. Although deposition of one particle can nucleate deposition of some additional particles, the overall concentration of particles is too low to sustain continuous deposition, resulting in isolated aggregates of particles whose density increases relatively slowly with wall speed.

![FIG. 3. Regime map. Each binary image shows particle detection output from a photograph at the specified volume fraction ($\phi$) and capillary number ($Ca$, to within $\approx 10\%$). Black areas correspond to particle aggregates. Two regimes of behavior are seen, isolated deposition ($\phi \lesssim 0.35$) and sheet deposition ($\phi \gtrsim 0.35$). These are distinguished by the connectivity of the deposition patterns and the scaling behavior of the coating fraction (quantified in Fig. 4).](image-url)
(2) At higher volume fractions, a distinctly different behavior occurs, which we denote sheet deposition. In this case, the concentration of particles is sufficiently large as to produce continuous aggregates, resulting in labyrinthine deposition patterns. As the wall speed is increased, we see the emergence of patches of deposition coexisting with relatively bare regions. The size of these patches grows rapidly with wall speed until complete coverage is attained. (We attribute these patches both to the tendency of particle deposition to nucleate further particle deposition, as well as to slight variability of the inner surface of our cylinders.)

Let us define the coating fraction \( c \in [0, 1] \) as the fraction of the wall area which is coated by packed particle aggregates. Note that \( c = 1 \) corresponds to an area close packing of the particles, while \( c = 0 \) is a purely liquid coating with no particles at all. Absent any selective deposition effects (i.e., if particles merely followed liquid streamlines), the coating fraction should be proportional to the availability of particles, namely, the bulk volume fraction \( \phi \). Therefore, in Fig. 4, we plot \( c/\phi \) as a function of wall speed (capillary number). We see that this scaling results in collapse of the data for \( \phi \gtrsim 0.35 \), indicating that for dense suspensions, coating fraction is indeed controlled by availability of particles. Furthermore, we see speed independence for dense suspensions at \( \text{Ca} \gtrsim 4 \times 10^{-4} \) (corresponding to the upper right quadrant of Fig. 3), showing that in high speed sheet deposition, every available particle is eventually deposited. On the other hand, at low wall speeds (\( \text{Ca} \lesssim 4 \times 10^{-4} \)), particles in the bulk are “filtered” from the coating since they must first pass through the energy barrier of the bulk meniscus. This filtration is especially strong for \( \phi < 0.35 \) (isolated deposition), where the density of particles is insufficient to continuously disrupt the bulk meniscus.

To understand the deposition and pattern formation process, we seek a reduced model containing only the most essential features—due to the complexity of this system, our intent is to provide physical insight into the key driving mechanisms rather than to capture the microscopic interactions in full detail. Indeed, the nature of the problem precludes a rigorous derivation of the model equations discussed below, but we nonetheless include appropriate dimensional parameters where they may be rationalized on a physical basis.

The primary quantity of interest is the coating fraction \( c \), which we now consider as a continuous field \( c = c(x, z, t) \) on the wall \((x, z)\), where \( z = 0 \) is the bulk meniscus, \( z \rightarrow -\infty \) corresponds to the bulk suspension, and \( z \rightarrow +\infty \) is far up the wall. Since particles are conserved, \( c \) is governed by
the transport equation \( \partial_t c + u \partial_z c = -\nabla \cdot \mathbf{J} + q \), where \( u \) is uniform wall motion in the \( z \) direction, \( \mathbf{J} \) is flux relative to the wall (typically for \( z \geq 0 \)), and \( q \) represents exchange of particles with the bath (typically at \( z \approx 0 \)). We consider capillary-driven motion with linear resistance, so that we may express the flux as \( \mathbf{J} = -M \nabla \mu \), where \( \mu \) is a “chemical” potential associated with the surface energy \( f \), and \( M \) is the mobility.

We expect \( f \) to have a minimum in the absence of particles, \( c = 0 \), since the Landau-Levich film is nearly flat away from the bulk meniscus and hence its surface area cannot be further reduced. We also expect a minimum at the maximum packing, \( c = 1 \), since attractive capillary forces between particles are seen to result in the \( c = 1 \) state. Between these two limits, the surface area is larger due to menisci surrounding the particles. Hence, we conclude that the free energy of a homogeneous distribution of particles has the form of a double well potential, with energy scale set by surface tension. Thus, we take \( f_0 = k_n \sigma c^2(1-c)^2 + k_z m_p \kappa \ell_d \rho_p \) for the free energy density of a homogeneous distribution of particles on the wall, where \( k_n, k_z \) are unknown geometric factors, the first term is the double well potential, and the second term accounts for gravitational potential energy of particles on the wall with particle mass \( m_p = \rho a^3 \) and area per particle \( A_p = a^2 c \). An additional surface area is incurred at the boundary between a densely packed coating and a sparse coating; modeling this as energy contributions from gradients in \( c \) gives us the Cahn-Hilliard free energy, \( f = f_0 + k_{c2} a^2 \nabla^2 \nabla \cdot \mathbf{V} c^2 \).

As previously discussed, the capillary-driven evolution of \( c \) is predicated on particle diameter \( 2a \) being larger than liquid film thickness \( h \), a condition which is no longer satisfied as we descend through the meniscus and reach the bulk suspension where particles are fully immersed. We therefore represent the extent to which particles deform the liquid surface (i.e., the extent to which \( 2a > h \) is satisfied) by a smoothed Heaviside-like function \( b(z) = H_{z_0}(z) \) with characteristic length scale \( z_0 \sim \ell_a \), the meniscus size. In what follows, we take \( H_{z_0}(z) = [1 + \tanh(z/z_0)]/2 \) as an approximation which captures the exponential approach of the Landau-Levich solution to a flat film. Thus, accounting for spatial variation in the liquid film thickness, we define \( f = b f \), yielding a generalized form of Cahn’s chemical potential for spinodal decomposition, \( \mu = \delta f b c = b(\partial f / \partial c) - k_{c2} a^2 \nabla \cdot \mathbf{V} c \).

In our two-dimensional model, the sink term \( q \) provides for particle filtration by the meniscus. This occurs when capillarity and gravity prevent deposition: the bulk meniscus then accumulates particles, which are returned to the bath if the coating fraction would otherwise exceed \( c = 1 \). To approximate this effect, we take \( q = -k_n (u/a)(1 - b)H_{c-1} \), with constants \( k_n \) and \( c \), and characteristic time scale \( a \mu_t \). The factor \( (1 - b) \) ensures that filtration occurs at or below the meniscus, and \( H_{c-1} = \{1 + \tanh[(c-1)/\epsilon]\}/2 \) limits its effects to large concentrations near \( c = 1 \).

To complete the model, we need an expression for mobility. Particle motion in our system is opposed both by capillary-induced friction, \( F_f = k_f F_\perp \), as well as by viscous drag, \( F_s = 6\eta a u_p F_s^* + \alpha \nabla \cdot \mathbf{V}_s \), where \( k_f \) is the coefficient of friction, \( F_\perp \) is particle motion relative to the wall, \( \Omega \) is particle rotation, and \( \delta \) is the asperity scale or particle-wall separation. When the driving forces \( \mathbf{V} \) are balanced by resistance \( F_p = F_n + F_s \), we expect that mobility should satisfy \( J = c u_p \sim M F_s^*/\Omega_p \), yielding \( M \sim a^2 u_p (F_s^* + F_f) \). We have observed that typical \( u_p \) is such that the particle capillary number \( C_p = \eta u_p \sigma \) is small, so that \( F_p \ll F_f \), and thus \( M \sim a^2 u_p / F_f = (a k_\sigma \sigma) u_p \). However, \( u_p \) is undetermined in the context of this approximation, and indeed, the study of lubricated particle motion near a frictional surface continues to be an area of active research. In lieu of a mechanistic model for \( u_p \) which would be beyond the scope of this work, we assume that it decreases as one moves up the wall. This decrease is modeled as \( (ak_\sigma \sigma) u_p = M_0 (1 - b) \), with particles eventually stopping altogether as \( z \to \infty \). Last, we also expect \( M \sim c(1 - c) \), in order to account for the observed increased mobility of particles at intermediate densities, as well as for the expected \( c \)-dependence of flux at small \( c \) and small \( 1 - c \), in accordance with Cahn and Taylor. Combining the above, we finally obtain \( M = M_0 c(1 - c)(1 - b) \).

We may consider the foregoing equations in the absence of wall motion, gravity, and spatial variations, in order to find the characteristic scales of the aggregation instability. Taking \( c \to 1/2 + e^{j k_\sigma x + a t} \) for \( \epsilon \ll 1 \) yields characteristic length and time scales \( \lambda^* = 2^{1/2} \pi a k_\sigma / k_{c2}/\sqrt{k_{c0}} \) and \( \tau^* = 16(a^2/\sigma M_0)(k_{c2}/k_{c0}^2) \). The characteristic time is difficult to evaluate without a better
FIG. 5. Example solutions of our Cahn-Hilliard model for suspension coating. On the left of each pair is the computational domain, and on the right, a space-time plot of the top boundary of the domain, corresponding to the generated deposition pattern. Parameters are $z_0 = 4\ell_c$, $k_{\sigma_0} = 1.0$, $k_{\sigma_2} = 0.32$, and $k_q = 6.6$. The computational domain is 7.5 mm wide (30 mesh points), with the bulk meniscus ($z = 0$) occurring 2.5 mm from the bottom. Influx from the bottom boundary is a random field with length scale of $1/8$ mm. (a) $u = 1.8$ cm/s, mean influx density $c_0 = 0.50$, $k_q = 0.013$, and $\epsilon = 1$. (b) $u = 3.8$ cm/s, mean influx density $c_0 = 0.64$, $k_q = 0.0059$, and $\epsilon = 1$. The computational domain is 7.5 mm wide (30 mesh points), with the bulk meniscus ($z = 0$) occurring 2.5 mm from the bottom. Influx from the bottom boundary is a random field with length scale of $1/8$ mm. (a) $u = 1.8$ cm/s, mean influx density $c_0 = 0.50$, $k_q = 0.013$, and $\epsilon = 1$. (b) $u = 3.8$ cm/s, mean influx density $c_0 = 0.64$, $k_q = 0.0059$, and $\epsilon = 1$.

understanding of $M_0$, but the dependence of the characteristic length on particle size $a$ may be experimentally verified, and we have done so with the use of larger particles (see supplementary material). We further note that the predicted $\lambda^*$ is independent of wall speed $u$, as might be expected for a spinodal-type instability; this is corroborated by inspection of the patterns in Fig. 3. Interestingly, the characteristic length scales of irregular aggregates found in many drying colloidal systems are also seen to be on the order of several particle diameters, suggesting that capillary self-assembly of colloidal submonolayer aggregates may occur via a similar mechanism as that seen in our system.

Example solutions of our model equations are shown in Fig. 5, along with plots of the generated deposition patterns. We find that qualitatively the model captures behavior similar to that observed in experiment (cf. Figs. 1(b)–3), which is promising considering the simplification of the underlying physics. In particular, we observe features such as formation of dense irregular aggregates at high speeds, and at lower speeds, elongated deposition as well as concentration and filtration of particles by the meniscus. Thus, we have shown that the double well potential can, at leading order, account for many of the behaviors seen in this rather complicated system. (We note that one of the unknown parameters in our equations is redundant, and two more may be removed by nondimensionalization. Further numerical results are given in the supplementary material.)

We conclude by noting that the Cahn-Hilliard equation, combined with a moving front in its parameter values, describes not only suspension coating, but also many other systems, such as fabrication of polymeric solar cells, float-zone crystal growth, and slow cooling of metal alloys. Despite the substantial importance of these applications, only a few studies have considered the effect of a moving parameter front on the resulting spinodal decomposition patterns; much more remains to be learned.

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1 S. F. Kistler and P. M. Schweizer, Liquid Film Coating (Chapman and Hall, London, 1997).
7 One experiment, placed in a hallway display case at MIT, has retained its particle aggregates for over a year at the time of writing.
23 For normal force \( F_\perp \sim \sigma a \) and viscous resistance \( F_\eta = \frac{6 \pi \eta a^2}{\delta} \) for a separation \( \delta \), one obtains a time scale of \( \tau = \frac{\sigma}{6 \pi \eta a} = 7.6 \times 10^{-5} \) s.
25 See supplementary material at http://dx.doi.org/10.1063/1.3700970 for experimental data and photographs with larger particles, and additional numerical studies of the model.
29 Also, according to Dalbe et al. \( k_j \) may be as large as order unity for small particles such as ours.