Watching paint dry: Evaporation mediated self assembly of nanoparticles

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Encapsulation via a self assembly method (Colloidosomes)





Encapsulation of living bacteria





Living cells

Dead cells

Transmission image

Encapsulation with responsive shells



Create capsules with triggerable shell to allow release of agents at specific points in well For pH sensitivity: Poly(4-vinyl pyridine) (PVP) For a timed release: poly(lactic acid)





Water core capsules containing Poly(N-isopropylacrylamide) with a PVP shell





×9,500

5.0kV

1 um WD 4

Poly(lactide-co-glycolide) 50/50 microcapsules with methylene blue in water as core

Microgels

Particles that swell in response to certain triggers









Engine oil additives













 \bigcirc

Water layer thickness is electrolyte type and concentration dependent





Drying

Drying is non-uniform We start with a fluid thin film fluid mechanics - surface tension driven flow





0 min



40 min



140 min



190 min



90 min



250 min 200 nm polystyrene in water

Outline

- Drying is non-uniform
- Surface tension driven thin film flows
- Pressure distribution in drying films
- Cracking of drying films
- Crack spacing
- Segregation in drying films

Fluid flows in thin films subject to evaporation



Fluid flows in thin films subject to evaporation

Particles consolidate first in thinner region



Evaporation from consolidated region causes flow from bulk to the edge

Particles carried to the edge

No need to invoke faster evaporation from the edge



Drying – Open Time

To complete problem we need to estimate

- u* Characteristic horizontal velocity
 - Characteristic horizontal length scale

estimated earlier



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Directional drying

Dispersion dries from the edges inwards.

The particles consolidate into a solid.

This solid is rigid, but may remain saturated with water.





Directional drying

observe film during drying

Fronts propagate along drying direction



- ~100 nm hard spheres in water
- ~100 μm thick dried film
 - Blow nitrogen across film to dry.

Dry from right to left

Dynamics ~5000x real time



Directional drying fronts



Front Positions x = 0 $x = x_s$ $x = x_c$





Two-stage solidification

Using 200 nm particles

Changes in colour mean changes in spacing

Solidification happens in two stages.

The first stage is reversible



The two fronts advance intermittently, with coupled motion.

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Two-stage solidification



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Two-stage Solidification



The two stages correspond to consolidation, and aggregation.

To understand these processes, we consider the inter-particle forces.



Liquid



theory





 $A = 5 \times 10^{-21} \text{ J}$ (estimated)

 $\sigma_0 = 0.5 \ \mu C/cm^2$ (measured)

van der Waals attraction Electrostatic repulsion

$$F = -\left(\frac{Aa}{12}\right)\frac{1}{x^2} + 2\pi\varepsilon\varepsilon_0 a\Phi^2 \kappa e^{-\kappa x}$$



theory



DLVO + capillary forces





The front separation and velocity are inversely related. Their product decreases with added salt.

Dynamics of Cracking



Crack jumping



The drying fronts appear to be correlated with the fracture front.

Notice how regular the crack spacing is

20 nm Ludox silica particles in water



Checking the wavelength





Two propagating cracks

Assumptions: Constant elasticity Linearisation – small amplitude wavelength

$$\ln\left(\frac{C_1\lambda}{h}\right) = \frac{1}{2}\ln C_2 + \frac{C_1b}{2h}$$







Capillary pressure reduces as the body yields



Pressure ~ surface tension x surface curvature

Network of particles is elastic

Yield occurs until a local force balance is achieved

Pore elasticity or stress in bed

$$\nabla \bullet (\mathbf{\sigma} - P\mathbf{I}) = 0$$
 Stress balance
 $\nabla p = \frac{\mu}{k_p} \mathbf{u}$ Fluid pressure from Darcy

flow

 σ is the stress on the particles

 $\sigma - PI$ is called the total stress

One solution is $\sigma = PI$ This assumes no shear stresses stress is a diagonal tensor OK far from edges Cracking of Elastic films under constant stress



Energy released per unit advance of crack:

$$\frac{dU_{el}}{da} = \frac{h^2 \sigma^2}{cE} \tanh\left(\frac{c\lambda}{h}\right)$$

Energy cost of crack propagation:

$$\frac{dU}{da} = G_c h$$

Spacing for elastic films



Film Cracking



New area created – energy cost

Elastic energy relieved – energy gain

Flow of fluid – energy cost

Inclusion of flow term



Energy cost of fluid flow for unit advance of crack: $-\frac{Q\Delta P}{v}$

$$=\frac{\mu}{k_p}\frac{2v(1-\phi)^2h^3\sigma^2}{\pi c^2E^2}\tanh^2\left(\frac{c\lambda}{h}\right)\ln\left(\frac{\lambda}{\delta}\right)$$

Energy balance becomes

Elastic energy released

Energy consumed by creation of crack surface Energy loss due
 to viscous flow of solvent

$$\frac{h^2 \sigma^2}{cE} \tanh\left(\frac{c\lambda}{h}\right) = G_c h + \frac{2\mu vh}{\pi k_p} \left(\frac{(1-\phi)h\sigma}{cE} \tanh\left(\frac{c\lambda}{h}\right)\right)^2 \ln\left(\frac{\lambda}{\delta}\right)$$

When $\lambda \to \infty$ then $\sigma \to \sigma_{\infty}$

=

$$\left(\frac{\sigma}{\sigma_{\infty}}\right)^{2} \tanh\left(\frac{c\lambda}{h}\right) + 1 = \frac{2\mu vh(1-\phi)^{2}}{\pi k_{p}cE} \left(\frac{\sigma}{\sigma_{\infty}}\right)^{2} \tanh^{2}\left(\frac{c\lambda}{h}\right) \ln\left(\frac{\lambda}{\delta}\right)$$

Spacing for elastic films with flow from crack



Film Cracking: next steps

Selection rules - experimental data indicates a specific spacing

What determines the selection?

Can we template a specific spacing?



Vertical Segregation



Using one coat can we get a layered coating



Many potential applications:

Expensive active agent at surface Adhesive component at substrate

Commercial paints have as many as 15 different components

Particles in a film diffuse Evaporation reduces the top surface If diffusion is slow then top surface acts like a piston





Particles in a film diffuse Evaporation reduces the top surface If diffusion is fast then particles remain dispersed





Combine the two effects



Governing equations

$$\begin{split} &\frac{\partial \phi_1}{\partial t} + \nabla \cdot \phi_1 \mathbf{U}_1 = 0 & \text{Conservation equation} \\ &\mathbf{U}_1 = -\frac{K(\phi_1, \phi_2)}{6\pi\eta R_1} \nabla \mu_1 & \text{Volume average velocity} \\ &n_{P_1} \frac{\partial \mu_{P_1}}{\partial \hat{z}} + n_{P_2} \frac{\partial \mu_{P_2}}{\partial \hat{z}} + n_s \frac{\partial \mu_s}{\partial \hat{z}} = 0 & \text{Gibbs-Duhen equation} \\ &\mu_1 = \mu_{P_1} - \frac{1 - \phi_1 - \phi_2}{1 - \phi_1} \frac{\frac{4}{3}\pi R_1^3}{\nu_s} \mu_s - \frac{\phi_2}{1 - \phi_1} \left(\frac{R_1}{R_2}\right)^3 \mu_{P_2} & \text{Chemical potential} \\ &\Pi = -\frac{\mu_s - \mu_s^0}{\nu_s} = \left(\frac{\phi_1}{\frac{4}{3}\pi R_1^3} + \frac{\phi_2}{\frac{4}{3}\pi R_2^3}\right) kTZ(\phi_1, \phi_2) & \text{Osmotic pressure} \end{split}$$



 $φ_1(\xi,t)$ $φ_2(\xi,t)$

z=0 ξ = 0

Governing equations

$$\begin{aligned} \frac{\partial \phi_1}{\partial \tau} + \frac{\xi}{1-\tau} \frac{\partial \phi_1}{\partial \xi} &= \frac{1}{Pe_1(1-\tau)^2} \frac{\partial}{\partial \xi} \\ \left[\left[\frac{K(\phi_1,\phi_2)\phi_1 \left[\phi_1(1-\phi_1) \frac{\partial \mu_{P1}/\partial \xi}{\partial \mu_{P2}/\partial \xi} - \phi_1 \phi_2 \left(\left(\frac{Pe_1}{Pe_2} \right)^3 + \frac{\partial \mu_{P1}/\partial \xi}{\partial \mu_{P2}/\partial \xi} \right) + \phi_2(1-\phi_2) \left(\frac{Pe_1}{Pe_2} \right)^3 \right] \right] \\ & \left(1-\phi_1 \right) \left(\phi_1^2 \frac{\partial \mu_{P1}/\partial \xi}{\partial \mu_{P2}/\partial \xi} + 2\phi_1 \phi_2 \left(\frac{Pe_1}{Pe_2} \right)^3 + \phi_2^2 \left(\frac{Pe_1}{Pe_2} \right)^6 \frac{\partial \mu_{P2}/\partial \xi}{\partial \mu_{P1}/\partial \xi} \right) \\ & \left. \frac{\partial}{\partial \xi} \left[\left(\phi_1 + \left(\frac{Pe_1}{Pe_2} \right)^3 \phi_2 \right) Z(\phi_1,\phi_2) \right] \right] \end{aligned}$$

Governing equations

$$\frac{\partial \mu_{P1}/\partial \xi}{\partial \mu_{P2}/\partial \xi} = \frac{\phi_2}{\phi_1} \frac{\partial \phi_1/\partial \xi}{\partial \phi_2/\partial \xi}$$
$$K(\phi_1, \phi_2) = (1 - \phi_1 - \phi_2)^{6.55}$$
$$Z(\phi_1, \phi_2) = \phi_m/(\phi_m - \phi_1 - \phi_2)$$

Numerical Results



Evolution of profile



Changing initial concentrations



$$au=0 \ \phi_1+\phi_2=0.2$$

 $\phi_2=0.15$

Changing initial concentrations







Changing initial concentrations



 $au = 0 \ \phi_1 + \phi_2 = 0.2$ $\phi_2 = 0.15$

$$\phi_2 = 0.1$$

$$\phi_2 = 0.05$$

Asymptotic solution



Asymptotic solution



Atomic Force Microscopy



- Made trays with laminate coating to prevent edge drying
- Dried films under controlled conditions in suitable chambers

AFM Results





Summary

Films dry non-uniformly

Capillary pressure gradients build up across the film

Water can recede from film edge

Pressure can cause film to crack

Cracks can display oscillatory behaviour

There is a definitive crack spacing

Segregation can be achieved in drying films

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