Simulation of Vertical Surfactant Distributions in Drying Latex Films

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SUPPORTING INFORMATION

- 1. Comparison with the Model of Gundabala et al.
- 2. Effect of Surfactant Peclet Number in the First Drying Step

3. Supplements to the Part Dealing with Wet Sintering ($\overline{\lambda} = 0.5$)

4. Derivation of the Transport Equations by Means of a Variational Principle

1. Comparison with the Model of Gundabala et al.

Our simulation (Figures on the left) almost perfectly fits the profiles calculated by Gundabala et al.,^{1, 2} (Figures on the right. Reprinted with permission from reference 2 below. Copyright 2006 American Chemical Society) as shown in Figure S1 below.



Figure S1. Surfactant distributions just before the end of the first drying stage versus distance from substrate scaled by the film thickness. Surfactant concentration is expressed in percent of excess or depletion compared to the hypothetical situation where the surfactant was distributed homogeneously throughout the film thickness.

Top line: $\overline{A} = 1$; k = 10; Pe_S = 0.5; Pe_P as indicated.

Bottom line: $\overline{A} = 1$; Pe_S = 0.5; Pe_P = 1; k as indicated.

⁽¹⁾ Gundabala, V.R.; Zimmerman, W.B.; Routh, A.F. A Model for Surfactant Distribution in Latex Coatings. *Langmuir* **2004**, 20, 8721-8727.

⁽²⁾ Gundabala, V.R.; Routh, A.F. Predicting Surfactant Distribution in Dried Latex Films. in Film Formation; Process and Morphology. Provder, T.; Ed. ACS Symposium Series 941. American Chemical Society, Washington, DC. **2006**, 53-65.

2. Effect of Surfactant Peclet Number in the First Drying Step

This Figure complements Fig. 3 in the article. A small surfactant Peclet number tends to flatten the surfactant distribution.



Figure S2. Percent surfactant excess/depletion as a function of scaled distance from the substrate in the vertical direction. Vertical convection of surfactant taken into account. k = 4; $\overline{A} = 1$; Pe_P = 50; Pe_S as indicated in the insert.

3. Supplements to the Part Dealing with Wet Sintering ($\overline{\lambda} = 0.5$)

Figure S3 is to compare to Figure 6 in the text. It shows surfactant distributions when Peclet numbers are reduced. Excesses at the substrate are enhanced and minima in the curves are no longer observed.



Figure S3. Deformation by wet sintering. $\overline{\lambda} = 0.5$. Percent surfactant excess/depletion as a function of scaled distance from the substrate in the vertical direction.

 $Pe_P = 5$; $Pe_S = 0.1$; t = 1 when particle volume fraction has reached 0.64 in contact with the substrate.

Intermediate polymer / surfactant system (k = 4; \overline{A} = 1) at various times.

Figure S4 complements Figure 6a in the text. It shows how the surfactant is partitioned between the particle surfaces and the water phase.



Figure S4. Deformation by wet sintering. $\overline{\lambda} = 0.5$. Surfactant partitioning between particle surfaces and water phase as a function of scaled distance from the substrate in the vertical direction. Pe_P = 50; Pe_S = 0.5; t = 1 when particle volume fraction has reached 0.64 in contact with the substrate.

Intermediate polymer / surfactant system (k = 4; \overline{A} = 1) at various times.

4. Derivation of the transport equations by means of a variational principle

We provide below a derivation of the equations for the transport of latex beads and surfactant molecules, based on a least dissipation variational approach. The approach is based on a Rayleighian function $\mathcal{R} = \dot{\mathcal{G}} + \mathcal{D}/2$ sum of the Gibbs free-energy variation rate $\dot{\mathcal{G}}$ and one half of the dissipation rate $\mathcal{D}/2$. The minimization of \mathcal{R} with respect to each thermodynamic variable variation rate provides a set of dynamic equations, which can be interpreted as the kinetic linear response to the thermodynamic forces acting in the system (Onsager relaxation principle). Our derivation follows closely Doi [M. Doi, Onsager's Variational Principle in Soft Matter, *Journal of Physics : Condensed Matter*, **2011**, 23, 284118 and Soft Matter Physics, Oxford University Press, **2013**].

The free energy variation rate $\dot{\mathcal{G}}$ originates from a gradient of surfactant chemical potential and a gradient of osmotic pressure for the concentrated suspension (chemical potential of the beads). In expressing the first contribution, one must take care of the Langmuir equilibrium between surfactant adsorbed on the beads, and in solution. This equilibrium is assumed to hold everywhere and at all times.

Langmuir equilibrium and latex beads free-energy

Taking the latex solution as a suspension of identical spheres with radius R_0 and number concentration C_p . The bead volume fraction follows from simple geometrical considerations

$$\phi = \frac{4\pi R_0^3}{3} C_p.$$
 (1)

The surface to volume ratio of the suspension is $3/R_0$. In what follows, it turns out to be convenient to express the surfactant concentrations in terms of volume fraction ϕ . We therefore introduce $(1 - \phi)C_s$, average number density of free surfactant in solution and ϕC_a , equivalent fraction of surfactant adsorbed onto the surface. The total number of surfactant molecules in a volume reads

$$\int \mathrm{d}\mathbf{r} \left[(1-\phi)C_s + \phi C_a \right]. \tag{2}$$

The Langmuir equilibrium rules the exchange of surfactant molecules at concentration C_s in the solvent with single occupancy adsorption sites at the surface, and is characterized by an adsorption energy $-\varepsilon$ and a maximal coverage density ϕC_m . In other words, each latex bead carries at most $\frac{4\pi R_0^3}{3}C_m$ on its surface $(R_0C_m/3 \text{ molecules per unit surface})$. Within the previous assumptions and notations, the chemical potential of surfactant molecules adsorbed at the surface reads $\mu_a = kTC_a/(C_m - C_a) - \varepsilon$ and must match the chemical potential in solution μ_s . If in addition μ_s follows the Raoult law, the Langmuir equilibrium reduces to a standard relation between surface and volume concentrations

$$\frac{C_a}{C_m} = \frac{C_s}{C_s + A},\tag{3}$$

A being the volume concentration corresponding to a half-covered bead surface. In deriving the transport equations of both surfactant and particle beads, one must express the total Gibbs free-energy variation rate. The surfactant contribution to \dot{G} can be easily expressed in terms of chemical potential

$$\int d\mathbf{r} \left[\mu_a \frac{\partial}{\partial t} (\phi C_a) + \mu_s \frac{\partial}{\partial t} ((1 - \phi) C_s) \right]$$
(4)

Given that Langmuir equilibrium is assumed throughout the sample, one has $\mu_s = \mu_a$ and the expression becomes

$$\int \mathrm{d}\mathbf{r}\mu_s \frac{\partial}{\partial t} \bigg[\phi C_a + (1-\phi)C_s \bigg]. \tag{5}$$

The second contribution to the Gibbs free-energy variation rate originates from excluded volume, dispersion and electrostatic interactions. All these are summarized into a free-energy per volume $f(\phi)$. The contribution to \dot{G} simply reads

$$\int \mathrm{d}\mathbf{r} f'(\phi) \frac{\partial \phi}{\partial t}.$$
(6)

It is clear from eq (5) and (6) that the thermodynamic variables under considerations are ϕ and C_s (C_a being related to them through Langmuir equilibrium). These are the quantities for which a transport equation must be found.

Dissipation for moving beads and surfactants in a solvent at rest

The simplest model assumes that solvent particles remain, on average, at rest. Introducing the average velocity \mathbf{v}_s and diffusion coefficient D_s of surfactant molecules, one can express the viscous dissipation of molecules as

$$\int \mathrm{d}\mathbf{r} \frac{kT}{D_s} \mathbf{v}_s^2 (1-\phi) C_s. \tag{7}$$

One recognizes in the above expression the particle friction coefficient kT/D_s (Einstein relation). The product $(1-\phi)C_s d\mathbf{r}$ gives the number of surfactant molecules occupying a mesoscopic volume $d\mathbf{r}$, while C_s is the local concentration of tensioactive molecules, linked to the chemical potential μ_s .

An analogue expression accounts for the dissipation of latex beads drifting across the static medium. Denoting \mathbf{v}_p the local average bead velocity, the dissipation term reads

$$\int \mathrm{d}\mathbf{r} \frac{kT}{D_c(\phi)} \mathbf{v}_p^2 \frac{3\phi}{4\pi R_0^3}.$$
(8)

The ϕ dependence of the friction $kT/D_c(\phi)$ expresses the influence of hydrodynamic interactions acting in concentrated beads solutions, while the dilute limit $kT/D_c(\phi \simeq 0) = 6\pi\eta R_0$ reduces to the usual Stokes friction.

Rayleighian and transport equations

We obtain for a solvent at rest the following Rayleighian

$$\mathcal{R} = \int \mathrm{d}\mathbf{r} \left\{ \mu_s \frac{\partial}{\partial t} \left(\phi C_a + (1-\phi)C_s \right) + f'(\phi) \frac{\partial \phi}{\partial t} + \frac{kT}{2D_s} \mathbf{v}_s^2 (1-\phi)C_s + \frac{kT}{2D_c(\phi)} \mathbf{v}_p^2 \frac{3\phi}{4\pi R_0^3} \right\}, \quad (9)$$

the dynamic variables of interest being $\partial \phi / \partial t$ and $\partial C_s / \partial t$. They are related to drift velocities and currents by the usual flux balance relations :

$$\frac{\partial \phi}{\partial t} + \nabla \cdot (\mathbf{v}_p \phi) = 0 \tag{10}$$

for latex beads, and

$$\frac{\partial}{\partial t} \left(\phi C_a + (1 - \phi) C_s \right) + \nabla \cdot \left(\mathbf{v}_p \phi C_a + \mathbf{v}_s (1 - \phi) C_s \right) = 0 \tag{11}$$

for surfactant molecules. These two relations makes it possible to rewrite the Rayleighian in terms of bead and surfactant velocities only. Integrating by part, and assuming that no flux of surfactant or particles is allowed across the system boundaries, one obtains

$$\mathcal{R} = \int \mathrm{d}\mathbf{r} \left\{ (\phi C_a \mathbf{v}_p + (1-\phi)C_s \mathbf{v}_s) \cdot \boldsymbol{\nabla}\mu_s + \Pi'(\phi)\mathbf{v}_p \cdot \boldsymbol{\nabla}\phi + \frac{kT}{2D_s}\mathbf{v}_s^2(1-\phi)C_s + \frac{kT}{2D_c(\phi)}\mathbf{v}_p^2 \frac{3\phi}{4\pi R_0^3} \right\}$$
(12)

where the identity $\phi \nabla f'(\phi) = \Pi'(\phi) \nabla \phi$ is used to put the latex beads osmotic pressure $\Pi(\phi) = \phi f'(\phi) - f(\phi) + f(0)$ in evidence.

Setting the functional derivatives of \mathcal{R} with respect to $\mathbf{v}_p(\mathbf{r})$ and $\mathbf{v}_s(\mathbf{r})$ to zero (the Onsager-Rayleigh variational principle) determines both \mathbf{v}_p and \mathbf{v}_s in terms of gradients of ϕ and μ_s .

$$\frac{kT}{D_s}C_s(1-\phi)\mathbf{v}_s + (1-\phi)C_s\boldsymbol{\nabla}\mu_s = 0;$$
(13)

$$\Pi'(\phi)\nabla\phi + \frac{kT}{D_c(\phi)}\frac{3\phi}{4\pi R_0^3}\mathbf{v}_p + \phi C_a\nabla\mu_s = 0.$$
(14)

It is then straightforward to substitute for \mathbf{v}_p and \mathbf{v}_s in eqs (10,11), resulting in the transport equations for beads and surfactant. In the following expressions, gradients are given in terms of the vertical variable y.

$$\frac{\partial\phi}{\partial t} - \frac{\partial}{\partial y} \left(\frac{4\pi R_0^3}{3} \Pi'(\phi) \frac{D_c(\phi)}{kT} \frac{\partial\phi}{\partial y} \right) - \frac{\partial}{\partial y} \left(\frac{D_c}{kT} \frac{4\pi R_0^3}{3} \phi C_a \frac{\partial\mu_s}{\partial y} \right) = 0; \tag{15}$$

$$\frac{\partial}{\partial t} \left(\phi C_a + (1-\phi)C_s \right) - \frac{\partial}{\partial y} \left(\frac{D_s}{kT} (1-\phi)C_s \frac{\partial \mu_s}{\partial y} + \frac{D_c}{kT} \frac{4\pi R_0^3}{3} \phi C_a \frac{\partial \mu_s}{\partial y} + \Pi'(\phi) \frac{D_c}{kT} \frac{4\pi R_0^3}{3} C_a \frac{\partial \phi}{\partial y} \right) = 0.$$
(16)

Let us describe briefly the terms appearing in the above equations. Eq (15) relates the time variation of the bead volume fraction to the gradient of osmotic pressure (middle term) and a crossed diffusio-osmotic contribution proportional to the gradient of chemical potential μ_s (last term). This term is present because each latex bead carries along a number of adsorbed surfactant molecules proportional to ϕC_a , and therefore feels a thermodynamic force pushing it towards the chemical potential μ_s descent direction (see eq 14). In the improved treatment that follows below, we show that a different and more physical diffusio-osmotic term emerges, that is usually neglected in practice. Eq (16) relates the variation of surfactant molecules concentration (first term) to the gradient of chemical potential (second term) and the advection of surfactant molecules adsorbed on latex beads (last term). The third term is a counterpart of the crossed diffusio-osmotic term discussed above.

Neglecting the diffusio-osmotic term $\phi C_a \nabla \mu_s$ in eq (14) and assuming an ideal behavior for $\mu_s = \mu_s^{(0)} + kT \ln(C_s/C_0)$ leads to a basic set of equations, that constitute the starting point of the study by Gundabala et al.

$$\frac{\partial\phi}{\partial t} - \frac{\partial}{\partial y} \left(D_p(\phi) \frac{\partial\phi}{\partial y} \right) = 0; \tag{17}$$

$$\frac{\partial}{\partial t} \left(\phi C_a + (1 - \phi) C_s \right) - \frac{\partial}{\partial y} \left(D_s (1 - \phi) \frac{\partial C_s}{\partial y} + D_p(\phi) C_a \frac{\partial \phi}{\partial y} \right) = 0.$$
(18)

with a particle collective diffusion coefficient defined as

$$D_p(\phi) = \frac{4\pi R_0^3}{3} \frac{\Pi'(\phi)}{kT} D_c(\phi)$$
(19)

The connection with Gundabala et al follows from the following additional notations and adimensionalisation : C_{s0} initial surfactant concentration, $C_a \equiv 3\Gamma/R_0$, $3\Gamma_{\infty}/R_0 \equiv C_m$, $\overline{C_s} \equiv C_s/C_{s0}$, $\overline{\Gamma} \equiv 3\Gamma/(R_0 C_{s0}) = C_m/C_{s0}$.

Water exchange due to latex beads displacement

To improve upon the steady solvent assumption, we now account for the solvent incompressibility by modifying the conservation equation for beads and stating that the displacement of a bead results in the exchange with an equivalent volume of solvent moving opposite to the bead. This results in a different transport equation for the surfactants

$$\frac{\partial}{\partial t} \left(\phi C_a + (1 - \phi) C_s \right) + \nabla \cdot \left(\mathbf{v}_p \phi C_a - \mathbf{v}_p \phi C_s + \mathbf{v}_s (1 - \phi) C_s \right) = 0.$$
(20)

Reiterating the above steps leads to a modified Rayleighian

$$\mathcal{R}' = \int d\mathbf{r} \left\{ (\phi(C_a - C_s)\mathbf{v}_p + (1 - \phi)C_s\mathbf{v}_s) \cdot \nabla\mu_s + \Pi'(\phi)\mathbf{v}_p \cdot \nabla\phi + \frac{kT}{2D_s}\mathbf{v}_s^2(1 - \phi)C_s + \frac{kT}{2D_c}\frac{3\phi}{4\pi R_0^3}\mathbf{v}_p^2 \right\},$$
(21)

and to the following dissipation equations

$$\phi \mathbf{v}_p = -\frac{4\pi R_0^3}{3} \frac{D_c}{kT} \left(\Pi'(\phi) \nabla \phi + \phi (C_a - C_s) \nabla \mu_s \right);$$
(22)

$$C_s \mathbf{v}_s = -\frac{D_s}{kT} C_s \boldsymbol{\nabla} \boldsymbol{\mu}_s.$$
⁽²³⁾

A significant difference compared with the steady solvent case concerns the diffusio-osmotic term $\phi(C_a - C_s) \nabla \mu_s$. As expected, the gradient in chemical potential is now coupled the difference $C_a - C_s$ and the sign of the effective force is *a priori* undetermined. It depends on whether the amount of surfactant carried by a colloidal particle is higher or lesser than the amount of surfactant occupying an equivalent volume of solution. Neglecting again this contribution and combining with eq (20) leads to a slightly different set of equations, which account properly for a surfactant transport by a backflow around colloidal particles.

$$\frac{\partial\phi}{\partial t} - \frac{\partial}{\partial y} \left(\frac{4\pi R_0^3}{3} \Pi'(\phi) \frac{D_c(\phi)}{kT} \frac{\partial\phi}{\partial y} \right) = 0; \tag{24}$$

$$\frac{\partial}{\partial t} \left(\phi C_a + (1 - \phi) C_s \right) - \frac{\partial}{\partial y} \left(D_s (1 - \phi) \frac{\partial C_s}{\partial y} + \Pi'(\phi) \frac{D_c}{kT} \frac{4\pi R_0^3}{3} (C_a - C_s) \frac{\partial \phi}{\partial y} \right) = 0.$$
(25)

Simplifying by means of the collective diffusion constant D_p , one finally obtains :

$$\frac{\partial \phi}{\partial t} - \frac{\partial}{\partial y} \left(D_p(\phi) \frac{\partial \phi}{\partial y} \right) = 0; \tag{26}$$

$$\frac{\partial}{\partial t} \left(\phi C_a + (1 - \phi) C_s \right) - \frac{\partial}{\partial y} \left(D_s (1 - \phi) \frac{\partial C_s}{\partial y} + D_p(\phi) (C_a - C_s) \frac{\partial \phi}{\partial y} \right) = 0.$$
(27)

These equations are solved and compared to the results of Gundabala et al.

We note that for better consistency, diffusio-osmotic terms should be kept, and the non vanishing solvent velocity should also be accounted for in the dissipation terms. Hindered surfactant diffusion could also been introduced by means of a ϕ dependent coefficient $D_s(\phi)$. This leads to ever more complex transport equations that will be the subject of future work.