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Surfactant-induced delay of leveling of inkjet-printed patterns

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Due to its flexibility, inkjet printing has become a widespread technique for the non-contact deposition of liquids, solutions and melts on a variety of substrates with a lateral resolution down to about 10 μm . Because the patterns are formed via coalescence of many individual droplets, ripples and undulations can appear in the deposited layers, which gradually disappear if sufficient time before ink solidification is given. In this manuscript, we study this spontaneous leveling process of inkjet printed lines that is driven by surface tension and hydrostatic pressure gradients. We show that the process can be significantly retarded if the ink contains soluble or insoluble surfactants, which are common additives to improve print quality. We present qualitative experiments as well as theoretical and numerical models that allow estimation of the leveling time for arbitrary ripple amplitudes and realistic surfactant properties. © 2011 American Institute of Physics. [doi:10.1063/1.3560770]

I. INTRODUCTION

The leveling dynamics of thickness variations in thin liquid films has been studied extensively in the context of ripples and other irregularities in solution-deposited coatings and molten glass films as well as brush marks in paint layers.^{1–22} Orchard presented a Fourier series solution of the Stokes equation for the leveling process, considering both surface tension and gravity as the driving forces and allowing for temporal variations of surface tension and viscosity.^{1,2} Retaining the time derivatives in the Navier-Stokes equation, Woo considered one-dimensional and axisymmetric disturbances on molten glass surfaces.⁴ Degani and Gutfinger in addition conducted time-resolved measurements of the leveling dynamics⁸ and presented a numerical solution of governing equations for the case of large amplitudes.⁹ Khesghi and Scriven focused their attention on large amplitude disturbances and performed a disturbance expansion up to second order aside from numerical simulations.¹³ They also considered the case of large Reynolds numbers, for which an oscillatory behavior is observed.

Quach presented a qualitative overview of the impact of non-Newtonian rheology on the leveling dynamics.⁷ Keunings, Iyer, and Bousfield studied the effect of viscoelasticity and shear-thinning on the evolution of coating defects.^{12,20} Stillwagon and Larson studied the leveling of thin films deposited on topographically patterned substrates.¹⁴ Overdiep,^{10,11} Wilson,¹⁶ and Eres *et al.*²² considered the influence of evaporation as well as concentration- and surface-tension gradients on the leveling process. The effect of surfactants has been studied by Schwartz *et al.*^{18,19}

In the past decade, inkjet printing has matured as a flexible deposition technique for laterally structured coatings of

solvent- or melt-based ink formulations.^{23–31} For many applications, it is desirable to obtain a smooth film without ripples or other morphological traces of the individual droplets that had originally been deposited. The degree of leveling and the final ink morphology that are crucial for print quality typically improve with time. On the other hand, ink redistribution effects, for example, due to equilibration of capillary pressure or surface energy differences on the substrate, are usually unwanted. As an illustrative example, Fig. 1 shows the light emission patterns of two organic light emitting diode (OLED) devices fabricated by inkjet printing using an Agfa Orgacon hole injection layer and Merck Livlux light emitting polymer. A large line pitch d_l in Fig. 1(a) caused the occurrence of striations, that is, individual printed lines are distinguishable in the light output. After process optimization, a perfectly homogeneous light emission is visible in Fig. 1(b).

To optimize the layer formation, quantitative models are desirable. The leveling and redistribution processes are illustrated by experiments presented in Sec. II. In Sec. III, we introduce the theoretical models we applied for the description of the ink redistribution dynamics in the presence of insoluble and soluble surfactants. In Sec. IV A, we first consider their influence on the leveling rate of one-dimensional ripples and striations. Subsequently we discuss the equilibration dynamics of inkjet-printed multi-lines in Sec. IV B.

II. EXPERIMENTAL

For our experiments, we used a commercially available dispersion of 1 wt. % poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS, OrgaconTM HILHC5-IJ, Agfa Gevaert N.V.) in water. Due to the high surface tension of water, surfactants are added to improve print quality. Depending on surfactant additives, the equilibrium surface

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FIG. 1. (Color online) Inkjet-printed organic light emitting diode devices based on Merck Livlux light emitting polymer and an (a) large and (b) optimized line pitch.

tension of the PEDOT:PSS dispersion ranges between $\gamma_\infty = 25 - 40$ mN/m. Its viscosity at nominal concentration is $\mu = (12 \pm 2)$ mPa-s, its density $\rho = 1000$ kg/m³.³²

A piezoelectrically actuated Spectra Galaxy PH 256/50 AAA inkjet printhead with 256 nozzles with a diameter of 42 μ m and a nozzle pitch of 254 μ m was used for deposition. The lateral separation d_l of neighboring inkjet-printed lines was varied by adjusting the azimuthal orientation of the printhead with respect to the direction of substrate motion. The drop volume V_d and drop ejection frequency f_d were kept constant at 50 pl and 1 kHz, respectively.

The distance between individual inkjetted droplets along the y-direction is denoted $d_d = U_{\text{sub}}/f_d$. The cross-sectional area (volume per unit length) $A_{\text{sl}} = V_d/d_d = V_d f_d / U_{\text{sub}}$ of a *single* inkjet-printed line can be adjusted by means of the substrate speed U_{sub} . The width of a *single* printed line w_{sl} depends on the ink-substrate contact angle θ as illustrated in Fig. 2(a). For uniform, narrow *single* lines $w_{\text{sl}} \ll \ell_c \equiv \sqrt{\gamma/(\rho g)}$, the equilibrium line width is given by³³ $w_{\text{sl}} = 2 \sin \theta \sqrt{A_{\text{sl}}/(\theta - \sin \theta \cos \theta)}$. For narrow and *thin* single lines, that is, if $h_{\text{sl}} \ll w_{\text{sl}}$, the cross-sectional profile is to good approximation parabolic and thus $A_{\text{sl}} = \frac{2}{3} h_{\text{sl}} w_{\text{sl}}$. Disregarding end effects, the average height of a multi-line is given by $\langle h \rangle = A_{\text{sl}}/d_l$. Here, h_{sl} is the center height of a printed *single* line, g is the gravitational acceleration and ℓ_c is the so-called capillary length, a material parameter that typically

FIG. 2. (Color online) Definition of geometric parameters. (a) Inkjet droplets of volume V_d impinge on an impenetrable substrate moving with velocity U_{sub} in the y direction to form a single line of width w_{sl} , centerline height h_{sl} and cross-sectional area A_{sl} . (b) Wide lines and thin films of average film thickness $\langle h \rangle$ can be formed by controlled coalescence of single lines deposited with a spacing $d_l < w_{\text{sl}}$.

ranges between 1.5 and 3 mm. For dimensions below ℓ_c , the influence of gravity on the leveling and redistribution process can to good approximation be neglected for horizontally oriented substrates.

Generally, patterns were printed such that the center-to-center distance of neighboring lines was smaller than the line width, $d_l < w_{\text{sl}}$, which guarantees a certain minimum overlap [Fig. 2(b)]. Moreover, d_d was kept much smaller than d_l , such that the leveling dynamics in the printing direction (y axis) proceeds much faster than perpendicular to it. For this reason, only the lateral leveling along the x-axis will be considered in this manuscript, and the ink thickness profile $h(x, y, t)$ is assumed to be independent of y. For industrial applications, it is desirable to maximize d_l and U_{sub} because then a larger area can be patterned with the same number of nozzles in shorter time.

Figure 3 shows four series of inkjet-printed PEDOT:PSS multi-lines of various width that were deposited on a flat, non-porous substrate using different line-pitch values d_l between 50 and 200 μ m. The width of a single line was approximately $w_{\text{sl}} = 200$ μ m. The gray scale contrast of the microscope images is mostly due to interference effects of the substrate-PEDOT:PSS and PEDOT:PSS-air interfaces and reflects the thickness profile of the printed stripes. Figure 3(a) shows separated individual lines that have not merged laterally at all. The onset of coalescence is clearly observed in Fig. 3(b). The grayscale contrast in Fig. 3(c) is very uniform, indicating near-optimal leveling. In Fig. 3(d), a very small line pitch was chosen that resulted in a larger overall film thickness. The grayscale distribution indicates that the thickness profiles of the stripes are not flat but more closely resemble parabolas as a consequence of capillary redistribution.

FIG. 3. (Color online) Experimental inkjet-printed PEDOT:PSS stripes deposited with a line-pitch d_l of (a) $200\ \mu\text{m}$, (b) $160\ \mu\text{m}$, (c) $100\ \mu\text{m}$ and (d) $50\ \mu\text{m}$. The white scratches in the right half of (c) are the result of Dektak scanning-probe measurements. Image width $13.2\ \text{mm}$.

III. THEORETICAL MODELS AND NUMERICAL SIMULATIONS

The two principal stages of the leveling process of a multi-line are illustrated qualitatively in Fig. 4. The initial configuration is approximated by a linear superposition of truncated parabolas

$$h(x, t = 0) = \sum_{n=-4}^4 \max \left\{ 0, h_{sl} \left[1 - \frac{4(x - nd_l)^2}{w_{sl}^2} \right] \right\}, \quad (1)$$

which exhibits thickness variations corresponding to approximately 20% of the average film thickness $\langle h \rangle$. After a time t_{lev} the ripples in the initial ink thickness profile have leveled and the central part of the multi-line has an essentially uniform thickness. After a time t_{red} the height profile has adopted an approximately parabolic shape (if the total line width $w < \ell_c$), which corresponds to the liquid equilibrium conformation characterized by an x -independent pressure inside the line.³⁴ We define the leveling time t_{lev} as the time when the ripple amplitude has decayed to 10% of its initial value. The definition of the redistribution time t_{red} will be given in Sec. IV B. The aim of this manuscript is to identify the process window such that leveling can be achieved while

FIG. 4. (Color online) Exemplary ink thickness profile of $N = 9$ overlapping inkjetted lines for parameters $w_{sl} = 100\ \mu\text{m}$, $d_l = 50\ \mu\text{m}$, $h_{sl} = 20\ \mu\text{m}$, and $\Gamma(x, t = 0) = 0$. The black solid line represents the initial distribution immediately after deposition ($t = 0$). The dashed and dotted lines represent after the height profile after leveling ($t \approx t_{lev}$) and after capillary redistribution ($t \approx t_{red}$), respectively.

redistribution is avoided, resulting in inkjet-printed multi-lines with a homogeneous layer thickness.

The width of a multi-line w depends on the number of lines N , d_l , and w_{sl} and may change in time as a consequence of ink spreading or retraction. We shall assume, however, that the contact lines remain pinned, for example, as a consequence of contact angle hysteresis. Moreover, although the viscosity gradually increases during the solvent evaporation process, we consider the case of a constant Newtonian viscosity and neglect any influence of the solvent volatility.

A. Insoluble surfactants

In the case of small aspect ratios $\varepsilon \equiv h_{sl}/w_{sl} \ll 1$, the so-called lubrication approximation³⁵ can be applied to describe the leveling dynamics. In this limit, the equations describing the evolution of the height profile and the surfactant surface distribution of an *insoluble* surfactant are^{36,37}

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x} \left(\frac{h^2}{2\mu} \frac{\partial \gamma}{\partial \Gamma} \frac{\partial \Gamma}{\partial x} - \frac{h^3}{3\mu} \frac{\partial p}{\partial x} \right) = 0 \quad (2)$$

$$\frac{\partial \Gamma}{\partial t} + \frac{\partial}{\partial x} \left(\frac{h\Gamma}{\mu} \frac{\partial \gamma}{\partial \Gamma} \frac{\partial \Gamma}{\partial x} - \frac{h^2\Gamma}{2\mu} \frac{\partial p}{\partial x} - D_s \frac{\partial \Gamma}{\partial x} \right) = 0 \quad (3)$$

$$p = -\gamma \frac{\partial^2 h}{\partial x^2} + \rho gh, \quad (4)$$

where Γ is the surfactant surface concentration, p is the augmented pressure³⁵ and D_s is the surface diffusion constant. An assumption implicit in Eqs. (2)–(4) is that the substrate is oriented horizontally with its surface normal parallel to the positive z -direction, whereas gravity acts in the negative z -direction. This formalism can be applied when the ink-substrate contact angle is not too large, an upper limit³⁸ is on order of 30° .

FIG. 5. Nondimensional equation of state of an exemplary insoluble surfactant.

For the evaluation of the surface tension γ , we have used the equation of state

$$\gamma = \gamma_\infty + \Pi_{\max} \exp\left(-A \left[\frac{\Gamma}{\Gamma_c}\right]^2\right) \quad (5)$$

depicted in Fig. 5. The parameter values were chosen as $\gamma_\infty = 39$ mN/m, $\Pi_{\max} = 24$ mN/m, $\Gamma_c = 3.5 \mu\text{l}/\text{m}^2$, and $A = 6.125$, which to good approximation resembles the equation of state of oleic acid on glycerol.^{39,40}

For numerical simulations of the leveling dynamics, we first use the initial conditions

$$h(x, t = 0) = \langle h \rangle + a_0 \cos\left(\frac{2\pi}{\lambda} x\right) \quad (6)$$

$$\Gamma(x, t = 0) = \Gamma_0, \quad (7)$$

that is, we initially consider only the center region close to $x = 0$ as sketched in Fig. 4. In a second step, we discuss end-effects in the vicinity of the contact lines in Sec. IV B. Here a_0 is the amplitude of the ink thickness variations and λ is the ripple wavelength, which is determined by d_l . Equation (7) corresponds to a uniform initial surfactant concentration along the surface, which means that Marangoni stresses are induced by the leveling process. Although nonuniform initial surfactant distributions after inkjet deposition are conceivable, the authors are not aware of any existing experimental, theoretical or numerical data regarding $\Gamma(x, t = 0)$.

Equations (2)–(5) were nondimensionalized using the following scales

$$\bar{x} \equiv x/\lambda, \quad \bar{h} \equiv h/\langle h \rangle, \quad \bar{\Gamma} \equiv \Gamma/\Gamma_c \quad (8)$$

$$\bar{p} \equiv p/p_0, \quad \bar{\gamma} \equiv \gamma/\Pi_{\max}, \quad \bar{t} \equiv t/t_0 \quad (9)$$

where $p_0 \equiv \gamma a_0/\lambda^2$ and t_0 is defined in Eq. (10).

B. Perturbation analysis for small amplitudes and insoluble surfactants

Using a Fourier series solution of the Stokes equation, Orchard² derived the expression

$$t_0 = \frac{3}{16\pi^4} \frac{\mu}{\gamma} \frac{\lambda^4}{\langle h \rangle^3} \frac{1}{1 + \rho g \lambda^2 / 4\pi^2 \gamma} \quad (10)$$

for the leveling time of long-wavelength ripples on thin liquid films, that is, in the limit $2\pi\langle h \rangle/\lambda \ll 1$, in the absence of surfactants. This result can also be derived from a linearization of Eqs. (2) and (4) for the case when the ripple amplitude $a_0 \ll \langle h \rangle$ in Eq. (6).

Schwartz *et al.*^{18,19} considered the effects of surfactants on the leveling dynamics for the case of an idealized linear equation of state and when gravitational effects are negligible. We follow their procedure to derive an expression for the leveling time scale in the presence of surfactants for a realistic, nonlinear equation of state and with gravitational effects included. We consider the following harmonic variations of the height profile and surfactant concentration

$$h(x, t) = \langle h \rangle + h_1(t) \cos kx \quad (11)$$

$$\Gamma(x, t) = \Gamma_0 + \Gamma_1(t) \cos kx \quad (12)$$

$$\gamma(x, t) = \gamma(\Gamma_0) + \frac{\partial \gamma}{\partial \Gamma}(\Gamma_0) \Gamma_1(t) \cos kx \quad (13)$$

and determine the time dependence of the amplitudes h_1 and Γ_1 from linearized versions of Eqs. (2)–(4), that is, for the case when $h_1 \ll \langle h \rangle$ and $\Gamma_1 \ll \Gamma_0$. We point out that the Orchard time t_0 from Eq. (10), which we use for nondimensionalizing time in Eq. (9), depends on surface tension $\gamma(\Gamma_0)$ and thus on Γ_0 , that is, the linearization point in Eqs. (12) and (13). The following system of linear and homogeneous ordinary differential equations results

$$\frac{\partial \bar{h}_1}{\partial \bar{t}} + \frac{1}{2} \frac{-3\bar{\gamma}_0 \frac{\partial \bar{\gamma}}{\partial \Gamma}(\bar{\Gamma}_0)}{(\bar{\gamma}(\bar{\Gamma}_0)k^2 + \rho g/\Pi_{\max}) \langle h \rangle^2} \bar{\Gamma}_1 + \bar{h}_1 = 0 \quad (14)$$

$$\frac{\partial \bar{\Gamma}_1}{\partial \bar{t}} + \frac{-3\bar{\Gamma}_0 \frac{\partial \bar{\gamma}}{\partial \Gamma}(\bar{\Gamma}_0)}{(\bar{\gamma}(\bar{\Gamma}_0)k^2 + \rho g/\Pi_{\max}) \langle h \rangle^2} \bar{\Gamma}_1 + \frac{3\bar{\Gamma}_0}{2} \bar{h}_1 + Z\bar{\Gamma}_1 = 0, \quad (15)$$

which we solve for the initial conditions $\bar{h}_1(\bar{t} = 0) = \bar{a}_0 \equiv a_0/\langle h \rangle$ and $\bar{\Gamma}_1(\bar{t} = 0) = 0$ and find

$$\frac{1}{\bar{a}_0} \bar{h}_1 = \frac{1 + N_-}{N_- - N_+} \exp(N_+ \bar{t}) - \frac{1 + N_+}{N_- - N_+} \exp(N_- \bar{t}) \quad (16)$$

$$\bar{\Gamma}_1 = \frac{3\bar{\Gamma}_0}{2} \frac{\bar{a}_0}{N_- - N_+} (\exp(N_+ \bar{t}) - \exp(N_- \bar{t})), \quad (17)$$

where the rate constants $N_\pm$ are given by

$$N_\pm \equiv -\frac{1}{2} \left(S \pm \sqrt{S^2 - Q\bar{\Gamma}_0 - 4Z} \right), \quad (18)$$

and we defined

$$Q \equiv \frac{-3\bar{\gamma}_0 \frac{\partial \bar{\gamma}}{\partial \Gamma}(\bar{\Gamma}_0)}{(\bar{\gamma}(\bar{\Gamma}_0)k^2 + \rho g/\Pi_{\max}) \langle h \rangle^2} \quad (19)$$

$$S \equiv 1 + Q\bar{\Gamma}_0 + Z \quad (20)$$

$$Z \equiv t_0 D_s k^2. \quad (21)$$

We note that for $Q = 0$, Eq. (16) reduces to the Orchard solution $\bar{h}_1 = \bar{a}_0 \exp(-\bar{t})$. Had we chosen a locally non-uniform initial surfactant distribution $\bar{\Gamma}_1(\bar{t} = 0) \neq 0$, then the numerical prefactors of the exponential terms in Eqs. (16) and (17) would be different, but the rate-constants would remain unaffected.

For most surfactant systems, $\partial\bar{\gamma}/\partial\bar{\Gamma} \leq 0$, which implies that $Q \geq 0$ and that the rate constants $N_{\pm}$ are negative (semi)-definite, $N_{\pm} \leq 0$. This corresponds to a decay of both the ripples in the height profile and the surfactant concentration variations in the limit of long times. Because $|N_-| < |N_+|$, the rate constant N_- determines the long-time behavior.

C. Soluble surfactants

Jensen and Grotberg⁴¹ presented a theoretical model for the dynamics of thin liquid films in the presence of nonuniform distributions of a soluble surfactant. They assumed a linear equation of state $\gamma = \gamma(0) - B\Gamma$ with a positive constant B as well as a linear relation between the surfactant bulk concentration in the liquid film $c(x, y, z, t)$ and the equilibrium surface concentration

$$\Gamma_{\text{eq}} = \frac{k_1}{k_2} c_s(x, y, t) \equiv \frac{k_1}{k_2} c(x, y, z = h, t). \quad (22)$$

Here, the adsorption- and desorption rate constants $k_{1,2}$ are defined by a linearized Langmuir equation describing the bulk-surface exchange of surfactant as $J = k_1 c_s - k_2 \Gamma$, where J is the surfactant flux with units of mol/(m²s). Jensen and Grotberg⁴¹ simplified the equation for bulk transport of surfactant

$$\frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = D_b \nabla^2 c \quad (23)$$

for the case of fast vertical diffusion in thin liquid films considering Marangoni stresses as the only driving force

$$\frac{\partial C}{\partial t} - B \frac{h}{2\mu} \frac{\partial \Gamma}{\partial x} \frac{\partial C}{\partial x} = \frac{D_b}{h} \frac{\partial}{\partial x} \left(h \frac{\partial C}{\partial x} \right) - \frac{J}{h}. \quad (24)$$

Here $\mathbf{u}$ is the flow velocity, D_b is the bulk diffusion coefficient, and $C \equiv \frac{1}{h} \int_0^h c dz$ is the height-averaged bulk concentration. The corresponding surface concentration fulfills the equation

$$\frac{\partial \Gamma}{\partial t} + \frac{\partial}{\partial x} \left[-\frac{h\Gamma}{\mu} B \frac{\partial \Gamma}{\partial x} - D_s \frac{\partial \Gamma}{\partial x} \right] = J \quad (25)$$

with D_s the surfactant surface diffusivity.

We have extended this model by including flows due to pressure gradients, the full nonlinear Langmuir equation for bulk-surface exchange as well as the corresponding nonlinear equilibrium isotherm

$$J = k_1 C \left(1 - \frac{\Gamma}{\Gamma_{\infty}} \right) - k_2 \Gamma \quad (26)$$

$$\frac{\Gamma_{\text{eq}}}{\Gamma_{\infty}} = \frac{k_1 C}{k_2 \Gamma_{\infty} + k_1 C}, \quad (27)$$

where Γ_{∞} is the maximum surface concentration at complete coverage of the surface. The nonlinear equation of state derived from the Gibbs adsorption isotherm⁴² follows as

$$\gamma = \gamma(0) + RT\Gamma_{\infty} \ln \left(1 - \frac{\Gamma}{\Gamma_{\infty}} \right) \quad (28)$$

where R is the universal gas constant and T is the absolute temperature. We used Eqs. (27) and (28) to fit experimental data for the dependence of surface tension on bulk concentration, $\gamma(C)$, for the soluble surfactant sodiumdodecylsulfate (SDS) in glycerol,⁴³ which yielded the parameters $\Gamma_{\infty} = 4.2 \cdot 10^{-6}$ mol/m², $k_2/k_1 = 1.7 \cdot 10^6$ m⁻¹ as well as the maximum spreading pressure $\Pi_{\text{max}} = 23.7$ mN/m. Because we do not take the presence of surfactant micelles into account, the validity of this model is restricted to concentrations below the so-called critical micelle concentration (cmc).

We introduce the following new scaled variables

$$\hat{p} = \frac{p\lambda^2}{\langle h \rangle \Pi_{\text{max}}}, \quad \hat{\Gamma} = \frac{\Gamma}{\Gamma_s} \quad (29)$$

$$\hat{C} = \frac{k_1 C}{k_2 \Gamma_{\infty}}, \quad \hat{t} = \frac{t}{t_M} = t \frac{\langle h \rangle \Pi_{\text{max}}}{\mu \lambda^2}. \quad (30)$$

The scale Γ_s is chosen such that a nondimensional bulk concentration $\hat{C} = 1$ corresponds to a nondimensional surface concentration $\hat{\Gamma} = 1$ in the scaled version of Eq. (27), that is, $\Gamma_s = \Gamma_{\infty}/2$. We arrive at the following dimensionless equations

$$\begin{aligned} \frac{\partial \hat{\Gamma}}{\partial \hat{t}} + \frac{\partial}{\partial \bar{x}} \left[\bar{h} \hat{\Gamma} \frac{\partial \bar{\gamma}}{\partial \hat{\Gamma}} \frac{\partial \hat{\Gamma}}{\partial \bar{x}} - \frac{\varepsilon^2 \text{Bo} \bar{h}^2 \hat{\Gamma}}{2} \frac{\partial \bar{h}}{\partial \bar{x}} - \frac{\varepsilon^2 \bar{h}^2 \hat{\Gamma}}{2} \frac{\partial \hat{p}_c}{\partial \bar{x}} \right. \\ \left. - \frac{1}{\text{Pe}_s} \frac{\partial \hat{\Gamma}}{\partial \bar{x}} \right] = K [\hat{C}(2 - \hat{\Gamma}) - \hat{\Gamma}] \end{aligned} \quad (31)$$

$$\begin{aligned} \frac{\partial \hat{C}}{\partial \hat{t}} + \left[\frac{\bar{h}}{2} \frac{\partial \bar{\gamma}}{\partial \hat{\Gamma}} \frac{\partial \hat{\Gamma}}{\partial \bar{x}} - \frac{\varepsilon^2 \text{Bo} \bar{h}^2}{3} \frac{\partial \bar{h}}{\partial \bar{x}} - \frac{\varepsilon^2 \bar{h}^2}{3} \frac{\partial \hat{p}_c}{\partial \bar{x}} \right] \frac{\partial \hat{C}}{\partial \bar{x}} \\ - \frac{1}{\text{Pe}_b \bar{h}} \frac{\partial}{\partial \bar{x}} \left[\bar{h} \frac{\partial \hat{C}}{\partial \bar{x}} \right] = \frac{\beta K}{2\bar{h}} [\hat{\Gamma} - \hat{C}(2 - \hat{\Gamma})] \end{aligned} \quad (32)$$

$$\bar{\gamma} = \frac{1}{\Pi_{\text{max}}} \left[\gamma(0) + RT\Gamma_{\infty} \ln \left(1 - \frac{\hat{\Gamma}}{2} \right) \right]. \quad (33)$$

Here we introduced the capillary pressure $\hat{p}_c \equiv -\bar{\gamma} \partial^2 \bar{h} / \partial \bar{x}^2$ and the following dimensionless parameters

$$\begin{aligned} \varepsilon \equiv \frac{\langle h \rangle}{\lambda}, \quad \text{Bo} \equiv \frac{\rho g \lambda^2}{\Pi_{\text{max}}}, \quad \text{Pe}_s \equiv \frac{\langle h \rangle \Pi_{\text{max}}}{\mu D_s} \\ \text{Pe}_b \equiv \frac{\langle h \rangle \Pi_{\text{max}}}{\mu D_b}, \quad \beta \equiv \frac{k_1}{k_2 \langle h \rangle}, \quad K \equiv k_2 t_M. \end{aligned} \quad (34)$$

The Bond number Bo quantifies the relative importance of hydrostatic and capillary pressure gradients, whereas the Peclet numbers Pe_s and Pe_b compare the effects of convective and diffusive surfactant transport.

The initial conditions for the film thickness and surfactant surface concentration are the same as in the case of insoluble surfactants, Eqs. (6) and (7). We assumed that the height-averaged bulk concentration is initially uniform and in equilibrium with the surface concentration. Using the non-dimensional version of Eq. (27), we find $\hat{C}(\bar{x}, \hat{t} = 0) = \hat{\Gamma}_0 / (2 - \hat{\Gamma}_0)$.

IV. RESULTS AND DISCUSSION

A. Leveling dynamics

During leveling, liquid locally flows from the elevated regions toward the regions of reduced film thickness, which leads to a converging flow in the valleys and surface expansion on the hills. Considering an initially uniform surfactant concentration distribution, this surface compression and expansion induces Marangoni stresses, which oppose flow driven by capillary and hydrostatic pressure gradients and thereby slow down the leveling dynamics.

We solved Eqs. (2)–(5) and (31)–(33) numerically with the finite element software COMSOL MULTIPHYSICS 3.5 using quadratic basis functions. Figure 6 illustrates the relative increase of the leveling time $t_{lev}/t_{lev}(\bar{\Gamma}_0 = 0)$ when an insoluble surfactant is present at the air-liquid interface. The solid lines correspond to numerical solutions for different values of $\bar{a}_0$. The crosses indicate the results of the perturbation analysis according to Eq. (16) for $\bar{a}_0 = 0.01$, which agrees very well with the corresponding numerical solution.

When $\bar{\Gamma}_0 = 0$, the leveling time ratio is unity by definition. For $\bar{\Gamma}_0 \gg 1$, that is, in the saturation regime of the equation of state, a small change in the surfactant surface

concentration has no effect on the surface tension. Consequently, $t_{lev}/t_{lev}(\bar{\Gamma}_0 = 0)$ becomes independent of $\bar{\Gamma}_0$ in the limit $\bar{\Gamma}_0 \gg 1$. The saturation value corresponds to capillary/hydrostatic leveling with the reduced surface tension γ_∞ . In the intermediate regime $0 < \bar{\Gamma}_0 \lesssim 1$, the influence of flow-induced surfactant concentration gradients substantially increases t_{lev} above $t_{lev}(\bar{\Gamma}_0 = 0)$. The addition of surfactants thus can significantly slow down the leveling dynamics by more than a factor of 8.

Larger values of the ripple amplitude induce larger overall variations of the surfactant surface concentration $\Delta\bar{\Gamma} \equiv \max(\bar{\Gamma}) - \min(\bar{\Gamma})$. This tends to flatten the dependence of $t_{lev}/t_{lev}(\bar{\Gamma}_0 = 0)$ because a larger fraction of the concentration range relevant for the equation of state is involved in determining the dynamics. These larger variations are also the reason why the leveling time ratio increases with the ripple amplitude for $\bar{\Gamma}_0 \gtrsim 1$, although $\bar{\gamma}(\bar{\Gamma}_0)$ is already in the flat region of Fig. 5. We note that although the ratio $t_{lev}/t_{lev}(\bar{\Gamma}_0 = 0)$ primarily decreases for increasing ripple amplitudes above 0.5 in the region $\bar{\Gamma}_0 \lesssim 1$, the absolute leveling time t_{lev} typically *increases* due to a reduced mobility of the liquid film in the thin regions.

To illustrate the leveling dynamics, we plotted the dimensionless ripple amplitude $\bar{h}(\bar{x} = 0, \bar{t}) - 1$ for $a_0/\langle h \rangle = 0.01$ and different initial surfactant concentrations $\bar{\Gamma}_0$ in Fig. 7(a). The straight, black solid line corresponds to purely capillary leveling, that is, $\Gamma = 0$, for which the globally fastest leveling is observed. The remaining curves all exhibit two distinct time-scales corresponding to the rate constants $N_\pm$ given in Eq. (18). The non-monotonic behavior visible in Fig. 6 is a consequence of the superposition of these two processes. The curve for $\bar{\Gamma}_0 = 0.3$ shows the fastest asymptotic decay rate N_- , because the equation of state [Eq. (5)] attains its maximum slope $\partial\bar{\gamma}/\partial\bar{\Gamma}$ approximately at $\bar{\Gamma} \approx 0.3$ (see Fig. 5) and Q in Eq. (19), thus, its maximum value.

Figure 7(b) shows the variation of the surfactant surface concentration $\bar{\Gamma}(\bar{x} = 0, \bar{t}) - \bar{\Gamma}_0$ for $a_0/\langle h \rangle = 0.01$ and the same initial surfactant concentrations $\bar{\Gamma}_0$ as plotted in Fig. 7(a). The maximum concentration variation appears to increase with increasing $\bar{\Gamma}_0$. According to Eqs. (16) and (17), the asymptotic slopes of the curves are identical with the corresponding ones in Fig. 7(a).

Figures 8(a) and 8(b) show the relative increase of the leveling time when a soluble surfactant is present in the bulk liquid as well as at the liquid-air interface. A small value of the adsorption rate parameter K corresponds to a surfactant for which bulk-surface exchange cannot occur on the time scale of the leveling process. As in the case of insoluble surfactants, a significantly longer leveling time results. A large value of K implies that on the time scale of the flow the surfactant is always in equilibrium with the underlying bulk liquid, which strongly reduces its influence on the leveling process. In addition for sufficiently thick films, the height-averaged bulk concentration does not change much as a consequence of adsorption or desorption, and Marangoni stresses are strongly diminished. In this case, the capillary leveling dynamics are effectively recovered, and the only effect of the surfactant is to reduce the overall surface tension. For an equation of state like SDS in glycerol, this slows

FIG. 6. (Color online) Leveling time ratio $t_{lev}(\bar{\Gamma}_0)/t_{lev}(\bar{\Gamma}_0 = 0)$ as a function of initial insoluble surfactant concentration $\bar{\Gamma}_0$ for different topographical amplitudes $a_0/\langle h \rangle$ ranging from 0.01 to 0.9 as listed in the legend. The following parameter values were assumed: $Pe_s = 1000$, $\varepsilon^2 Bo = 0.004$, and $\varepsilon = 0.1$. Crosses correspond to results of the perturbation analysis for the case $\bar{a}_0 = 0.01$.

FIG. 7. (Color online) (a) Dimensionless ripple amplitude $\bar{h}(\bar{x} = 0, \bar{t}) - 1$ for $\bar{a}_0 = 0.01$ and different initial surfactant concentrations $\bar{\Gamma}_0$. Crosses correspond to results of the perturbation analysis for the case $\bar{\Gamma}_0 = 0.3$. (b) Dimensionless surface concentration $\bar{\Gamma}(\bar{x} = 0, \bar{t}) - \bar{\Gamma}_0$ for $\bar{a}_0/\langle h \rangle = 0.01$ and different initial surfactant concentrations $\bar{\Gamma}_0$. In both plots the parameters $\varepsilon \equiv \lambda/\langle h \rangle$, $\varepsilon^2 \text{Bo}$ and Pe_s were assumed to be 0.1, 0.004, and 1000, respectively.

down leveling by a factor of up to about 1.5, but for other surfactant/solvent combinations by typically no more than a factor of 2–3.

Figure 8(b) also illustrates the effect of the ripple amplitude. As in the case of insoluble surfactants, a larger ripple amplitude tends to somewhat lessen the retarding effect for small values of $K \lesssim 1$ and provided Γ remains considerably below Γ_s . For large values of $K \gtrsim 1$, Marangoni stresses are diminished and any remaining influence of the surfactant on the leveling time ratio becomes independent of the ripple amplitude.

B. Redistribution time of inkjet printed multi-lines

So far we have considered the leveling dynamics in the interior of a line array. If a uniform thickness is desired then the overall redistribution time t_{red} constitutes an upper bound for the device fabrication process. In this section, we discuss how t_{red} depends on the width of the multi-line w and the lateral line pitch d_l in the presence of insoluble surfactants.

FIG. 8. (Color online) (a) Leveling time ratio $t_{\text{lev}}(\bar{\Gamma}_0)/t_{\text{lev}}(\bar{\Gamma}_0 = 0)$ as a function of nondimensional surfactant concentration for $\bar{a}_0/\langle h \rangle = 0.01$ and different values of the adsorption rate parameter K . (b) Leveling time ratio $t_{\text{lev}}(\bar{\Gamma}_0)/t_{\text{lev}}(\bar{\Gamma}_0 = 0)$ as a function of the adsorption rate parameter K for $\bar{\Gamma}_0 = 0.3$ and two values of $\bar{a}_0/\langle h \rangle$. In both plots, the following parameter values were assumed: $\varepsilon = 0.1$, $\varepsilon^2 \text{Bo} = 0.004$, $\text{Pe}_s = 1000$, $\text{Pe}_b = 100$, and $\beta = 0.059$.

For $\lambda < \ell_c$, the capillary leveling time scales as $t_{\text{lev}} \sim \lambda^4/\langle h \rangle^3$ [Eq. (10)], where λ and $\langle h \rangle$ had been considered as independent parameters. For inkjet-printed structures, they are both, however, determined by the line pitch, $\lambda \sim d_l$ and $\langle h \rangle \sim 1/d_l$, such that we expect the leveling time to scale as $t_{\text{lev}} \sim d_l^7$. Provided that $w < \ell_c$, an equivalent scaling is expected for the multi-line redistribution time, if the wavelength λ is replaced by the width of the multi-line $w = (N - 1)d_l + w_{\text{sl}}$, leading to $t_{\text{red}} \sim w^4 d_l^3$. The exact definition of t_{red} that we have used is illustrated in Fig. 9(a), where we plotted the time evolution of the center height of a multi-line array $\hat{h}(\bar{x} = 0, \bar{t})$. Here, $\hat{h}$ is defined as $\hat{h} \equiv h/h_{\text{sl}}$. For $\bar{t} > \hat{t}_{\text{lev}}$ and sufficiently large $N \gg 1$, $\hat{h}(0, \bar{t})$ reaches a first plateau value, which we denote $\hat{h}_{\text{lev}}$. After completion of the redistribution, $\hat{h}(0, \bar{t})$ reaches a second plateau value denoted as $\hat{h}_{\text{red}}$. The redistribution time $\hat{t}_{\text{red}}$ is defined as the instant when the center height reaches a value halfway between the two plateau values, $\hat{h}(0, \hat{t}_{\text{red}}) = (\hat{h}_{\text{lev}} + \hat{h}_{\text{red}})/2$.

FIG. 9. (Color online) (a) Definition of the redistribution time $\hat{t}_{\text{red}}$. (b) Redistribution time $\hat{t}_{\text{red}}$ as a function of d_l/w_{sl} for $N = 99$ and insoluble surfactant concentrations of $\bar{\Gamma}_0 = 0$ and 0.3. The symbols represent numerical data, the red straight lines represent powerlaw relations $\hat{t}_{\text{red}} = B_1 w^4 d_l^3$ with fitted coefficients B_1 . (c) Redistribution time $\hat{t}_{\text{red}}(\bar{\Gamma}_0 = 0.3)$ as a function of the number of inkjet-printed lines N for a surfactant concentration of $\bar{\Gamma}_0 = 0.3$ and $d_l = 50 \mu\text{m}$. The symbols represent numerical data, the red straight line represents a powerlaw relation $\hat{t}_{\text{red}} = B_2 [(N-1)d_l + w_{sl}]^4$ with fitted coefficient B_2 . In all plots the following parameter values were used: $\text{Pe}_s \equiv h_{sl}\Pi_{\text{max}}/(\mu D_s) = 1000$, $\text{Bo} \equiv \rho g w_{sl}^2/\Pi_{\text{max}} = 0.0041$, $\varepsilon = 0.1$, $h_{sl} = 10 \mu\text{m}$, and $w_{sl} = 100 \mu\text{m}$.

Numerical results obtained for initial conditions equivalent to Eqs. (1) and (7) are presented in Figs. 9(b) and 9(c) and reproduce the expected scalings very well, both with and without an insoluble surfactant being present. The (small) deviations from the expected scaling behavior for small d_l/w_{sl} and small N are attributed to end-effects.

C. Implications for printing process windows

The effect of initially uniform surfactant distributions is to delay leveling and redistribution by a factor of up to approximately 8. Due to the highly nonlinear dependence of the leveling time t_{lev} on the line pitch d_l , the most crucial parameter for the leveling process is d_l . The redistribution time for narrow line widths $w < \ell_c$ scales as $t_{\text{red}} \sim w^4 \sim N^4$, that is, the process window for achieving leveling while avoiding significant redistribution effects becomes wider for larger N .

For wide lines $w \gg \ell_c$, we expect a different scaling owing to Eq. (10); however, for typical parameter values, t_{red} then becomes so large that this regime may not be of practical relevance.

Two obvious strategies for avoiding or minimizing surfactant related leveling delays is to either not add surfactants at all or to increase the surfactant concentration well beyond Γ_c , that is, $\bar{\Gamma}_0 > 1$, because then the leveling time ratio $t_{\text{lev}}/t_{\text{lev}}(\bar{\Gamma}_0 = 0)$ plotted in Fig. 6 is both reduced and remains unaffected by small processing-related variations in $\bar{\Gamma}_0$. In the case of soluble surfactants, rapid adsorption and desorption rates effectively eliminate Marangoni stress related effects for thick enough films, and the only retardation left is due to the reduced value of the surface tension, which amounts to typically no more than a factor of 2 or 3.

Whether these are viable solutions that are beneficial for the entire printing process depends not only on the functionality of the coating but also on the influence of the surfactant on, for example, solvent evaporation and the wettability of the solution on the substrate. For instance in the context of organic electronic devices, the device performance and efficiency may be adversely affected by a high surfactant concentration.

Our results have been obtained with two particular yet typical and representative equations of state. In the case of soluble surfactants, we considered the regime where surface adsorption is kinetics-limited as described by a Langmuir equation [Eqs. (26) and (27)] but not limited by diffusion in the bulk liquid, that is, we implicitly assumed that vertical concentration equilibration occurs rapidly compared to the leveling time scale, which is appropriate for thin films.

V. SUMMARY

We have studied the leveling and redistribution dynamics of inkjet-printed multi-lines in the presence of soluble and insoluble surfactants. While insoluble surfactants can slow down the leveling process up to a factor of approximately 8, the retarding effect of soluble surfactants can be lower in the case of fast rates of surfactant bulk-surface exchange. We presented numerical simulations as well as scaling relations for both the leveling and redistribution times of multi-lines as a function of the number of individual lines, the lateral pitch, and the average line height and width, which provide a basis for estimating optimal process conditions.

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