Polymer film deposition from a receding solution meniscus: The effect of laminar forced air convection

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HIGHLIGHTS
- The solution deposition of polymer films is studied.
- The effects of air convection and coating speed are elucidated.
- A coating instability is observed for low air flow rates and small substrate speeds.

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ABSTRACT
When the meniscus of a polymer solution with a volatile solvent recedes over a wettable substrate, a polymer layer is deposited onto it. Even for chemically homogeneous and topographically flat substrates and constant coating speeds, the layer can exhibit quasi-periodic line patterns extending parallel to the contact line of the liquid meniscus. In this manuscript, we study such unstable solution deposition processes by means of well-controlled, systematic experiments and numerical simulations. The presence of laminar forced air convection gives rise to a linear increase in the average layer thickness with air flow rate. Initially, the line patterns increase in width and height with increasing air flow rate. However, beyond a certain critical value the coating instability is suppressed.

1. Introduction
Applying a thin film of non-volatile solute on a solid substrate by means of a solvent-based coating process in the presence of evaporation has received considerable interest in the past years. Le Berre et al. (2009) used a receding meniscus to deposit a phospholipid film with a controlled thickness. They identified the existence of two different regimes of coating. For a high substrate speed $U_{\text{sub}}$, the thickness of the dried film $h_{\text{dry}}$ follows the classical Landau-Levich scaling (Landau and Levich, 1942) $h_{\text{dry}} \sim U_{\text{sub}}^{2/3}$, since the evaporation rate is insufficient to directly dry the film. For a low substrate speed, a cross-over occurs and $h_{\text{dry}}$ is found to decrease with increasing $U_{\text{sub}}$. In this so-called ‘evaporative’ regime, the dry deposit directly emerges from the contact line. Based on the mass balances for the solvent and solute, Le Berre et al. (2009) deduced that in this regime the thickness scales as $h_{\text{dry}} \sim U_{\text{sub}}^{-1}$. The same exponent of $-1$ was found by a number of authors (Faustini et al., 2010; Jing et al., 2010; Rogowski and Darhuber, 2010; Vital et al., 2017).

Even on a flat, smooth and chemically homogeneous surface, a coating process can result in a non-uniform deposit. Masuda et al. (2004) placed a substrate vertically in a colloidal suspension and evaporated the solvent at a controlled temperature. The
colloidal particles deposited in the form of regularly spaced lines oriented parallel to the contact line of the liquid meniscus. The width and spacing of the lines could be modulated by controlling the temperature of the solution. Similar experiments were conducted by Abkarian et al. (2004) and Ghosh et al. (2007) found analogous patterns while dip-coating a colloidal suspension with a low substrate withdrawal rate. They reported a disordered particle deposit in case of a high substrate speed. The deformation and rupture of the liquid meniscus, leading to the line formation, were monitored in situ by Mino et al. (2015) and Nadir Kaplan et al. (2015).

Bodiguel et al. (2009, 2010) measured the pinning force, induced by the solute deposit to pin the contact line. Noguera-Marín et al. (2014) studied the effect of the wetting properties of the substrate and found that the pinning of the contact line is enhanced by contact angle hysteresis of the substrate. Later, the same authors also varied the pH of the colloidal suspension, in order to alter the particle interactions and thus the importance of collective diffusion effects (Noguera-Marín et al., 2016). Similar experiments were conducted by Hsueh et al. (2013); Lee et al. (2009) varied the diameter of the colloidal particles and related the distance between two deposit lines to the particle size using a geometrical model. A similar correlation between the line width and spacing was found by Watanabe et al. (2009).

Pattered deposits have been observed with a large variety of material systems such as colloidal suspensions of gold (Ming et al., 2008; Nakanshi et al., 2011; Watanabe et al., 2012; Watanabe and Miyahara, 2013), silver (Sambandan et al., 2010; Watanabe and Miyahara, 2013), polymer (Abkarian et al., 2004; Ray et al., 2005; Ghosh et al., 2007; Han et al., 2011; Noguera-Marín et al., 2016; Zhang et al., 2016) or silica (Masuda et al., 2004; Lee et al., 2009; Bodiguel et al., 2010; Watanabe and Miyahara, 2013; Li et al., 2014; Noguera-Marín et al., 2014, 2016; Mino et al., 2015; Nadir Kaplan et al., 2015) nanoparticles, carbon nanotubes (Zeng et al., 2011; Xiao et al., 2012; Joo et al., 2014), nanofibers (Gao and Han, 2013) and nanowhiskers (Xiao et al., 2012), protein molecules (Lin et al., 2010), virus capsules (Lin et al., 2010), silica and titania sol-gel films (Uchiyama et al., 2012; Uchiyama, 2015), phospholipid (Le Berre et al., 2009) and polymer solutions (Yabu and Shimomura, 2005; Lin and Granick, 2005; Hong et al., 2005, 2007a; Xu et al., 2006; Byun et al., 2008; Kim et al., 2008; Lin, 2010; Kwon et al., 2011a,b; Park et al., 2012; Chen et al., 2012; Hsueh et al., 2013; Men et al., 2014; Sun and Yang, 2015; Sun et al., 2017). Yabu and Shimomura (2005) studied the pattern formation process from a receding meniscus of a polymer solution. Depending on the initial concentration of the polymer, they found different deposition patterns, namely dot arrays, stripes parallel to the contact line and ladder structures. Park et al. (2012) created an array of polymer stripes over a distance of several cm by confining a polymer solution between the substrate and a roll, which was moving over the substrate. They demonstrated the possibility to control the size of the stripes by varying the speed of the roll. Kim et al. (2008) prepared a micropatterned film of a diblock copolymer. Upon thermally annealing this structure, they demonstrated the molecular alignment of the block-copolymer in a lamellar morphology in the coating direction.

The formation of non-uniform deposits has also been studied by numerical simulations (Nomonura et al., 2003; Lara-Cisneros et al., 2008; Doumerc and Guerrier, 2010, 2013; Frastia et al., 2012; Colosqui et al., 2013; Dey et al., 2016; Zigelman and Manor, 2016; Jung et al., 2017; Zigelman and Manor, 2018), Frastia et al. (2012) used a thin film model to study the solution deposition process in a receding meniscus. The contact line was allowed to recede either by evaporation or by dewetting of the partially wettable substrate. Unlike in a dip-coating process, there was no imposed (average) speed of the contact line. They found that the contact line receded by a periodic pinning-depinning cycle and identified various deposition patterns depending on the system parameters. Doumerc and Guerrier (2010) studied the drying of a polymer solution in a receding meniscus in a dip-coating geometry, i.e. with an imposed contact line speed. The evaporation rate was assumed to be limited by the diffusion of solvent vapor in the gas phase, while the hydrodynamics in the solution was described with a thin film model. Their model reproduced the evaporative regime and the Landau-Levich regime and obtained only homogeneous deposits. However, by including a solutal Marangoni stress (Doumerc and Guerrier, 2013; Dey et al., 2016), they obtained patterned deposits in the evaporative regime for certain ranges of the control parameters.

This manuscript focuses on the periodic pattern formation that occurs during deposition of a polymer solution from a receding meniscus in a horizontal die-coating geometry. The die-coating setup comprises an air nozzle to induce well-controlled, laminar gas-phase convection, which allows to increase the effective evaporation rate. Several authors had already employed forced air convection to introduce ‘dry’ air devoid of solvent vapor (Lee et al., 2009; Jing et al., 2010; Bodiguel et al., 2010; Zeng et al., 2011; Noguera-Marín et al., 2014, 2016), most likely to maintain the evaporation rate at a steady-state value for extended times. However, they did not study the influence of the gas phase convection itself on the pattern formation process. We conducted systematic experiments and numerical simulations to study the effect of the two main control parameters: the substrate speed and the air flow rate. Section 2 focuses on the experimental setup and procedures. Section 3 describes the details of the numerical model, which is similar to the one developed by Doumerc and Guerrier (2010, 2013) and Dey et al. (2016). The experimental and numerical results are discussed in Section 4.

2. Materials and methods

Fig. 1(a) shows a sketch of the experimental setup. A custom-made slot-die is placed at a height $H \approx 500 \mu m$ above a horizontal glass substrate. The slot-die is mounted on several mechanical stages, that allow it to be tilted around three perpendicular axes of rotation. The substrate is placed horizontally on a sample holder, which is connected to a computer-controlled translation stage (Newport XMS 160). We use a Cartesian coordinate system for describing positions and orientations. The $x$-axis is oriented in the direction of substrate motion, the $z$-axis vertically upwards. Fig. 1(b) shows a bottom view of the slot-die. The slot-die consists of two metal parts, both with a width $w_{s} = 1 \text{ mm}$, that are fastened together. One of the parts contains a rectangular slot with dimensions $w_{s} = 0.1 \text{ mm}$ in the $x$-direction and $w_{y} = 1 \text{ cm}$ in the $y$-direction. The coating liquid is injected through this slot and is confined between the slot-die and the substrate by capillary pressure. The receding coating meniscus is monitored from below using a microscope, consisting of a long working distance objective (Mitutoyo, M Plan Apo 10X, 0.28) and a CCD camera (AVT Pike F-145B). The optical axis of the microscope is oriented along the $y$-direction and extends into a cavity in the sample holder. A small mirror is connected to the objective with its surface normal oriented at an angle of 45° relative to the $z$-axis for looking upwards. A separate air nozzle can be connected to the slot-die on the side of the receding meniscus. This creates a rectangular slot with dimensions $w_{s} = 0.75 \text{ mm}$ in the $x$-direction, $w_{y} = 1 \text{ cm}$ in the $y$-direction and $L_{z} = 11 \text{ mm}$ in the $z$-direction. The exit of the air nozzle is placed 0.5 mm above the exit of the slot-die. A large volume syringe (Hamilton, product number 86020, 100 ml) placed on a syringe pump (KDS Gemini 88) is used to drive the flow of air.
through the nozzle. The entire setup is placed in an enclosure, to minimize dust contamination.

The coating liquid is a solution of the polymer poly(methyl methacrylate) (PMMA, Sigma Aldrich 182230, average molecular weight approximately 120,000) in either toluene (Sigma Aldrich 34866) or in o-xylene (Sigma Aldrich 95662). For both solvents, the initial concentration used in all coating experiments is 1 wt%. Solutions with higher concentrations were prepared in order to measure the viscosity and surface tension. The viscosity was measured with a Brookfield LVDV-II+PRO viscometer and the surface tension with a Krüss K10ST digital tensiometer (Wilhelmy plate method). The circles in Fig. 2 represent the viscosity of the toluene based solution at different solute concentrations. The surface tension of pure toluene was measured to be 28.1 mN/m at a temperature of 23°C. An increase of 0.2 mN/m and 0.7 mN/m was found at PMMA concentrations of 14.9 wt% and 29.2 wt%, respectively.

The substrate is a glass cover slip (Gold Seal, dimensions 48 × 60 mm, thickness 150 μm). It is cleaned by subsequent immersion into a detergent solution (Contrad 70) and de-ionized water in an ultrasonic bath for 15 min each. The substrates are dried using a nitrogen jet and placed in a UV/ozone cleaner (Jelight model 42-220). For each experiment, the substrate is coated over a distance of at least 5 mm. Multiple experiments are performed on one substrate. During each experiment, coating liquid is injected through the slot-die in order to keep the volume of liquid in the coating meniscus approximately constant in time. The liquid is added using a syringe (Hamilton, product number 81220, 500 μl) placed on a syringe pump (KDS Gemini 88). After an experiment, images of the polymer deposit are taken with an Olympus BX51 microscope (M Plan Apo 1.25X/0.04 and U Plan FI 10X/0.3 objective lenses). Subsequently, the topography of the deposits are measured with an atomic force microscope (AFM, Park XE7, 90 × 90 μm scan range, PPP-NCHR probe).

Fig. 1(c and d) show typical microscope images of the receding meniscus during an experiment with \( U_{\text{sub}} = 9 \) μm/s. The air nozzle is not connected to the slot-die. The substrate speed direction is from the top to the bottom of the image. The receding meniscus extends from the slot-die onto the substrate and is located in-between the two dotted lines in Fig. 1(c and d). In this experiment, the polymer deposit on the substrate is not homogeneous, but consists of lines oriented in the \( y \)-direction, parallel to the contact line, i.e. perpendicular to the substrate speed. The lines are deposited during a periodic displacement cycle of the receding meniscus. Fig. 1(c and d) show the meniscus at the start of a cycle and 4 s later. During this period, the polymer transported to the contact line causes the meniscus to elongate along the \( x \)-axis. After some time, this elongation reaches a maximum value, a polymer line is deposited on the substrate and the meniscus relaxes back to its position at the start of the cycle (Fig. 1(c)). The dry polymer lines then are translated along with the substrate.

Fig. 3 shows an AFM topography scan, i.e. the layer thickness profile \( h_{\text{dry}}(x, y) \), of a polymer line formed during the experiment illustrated in Fig. 1(c and d). The substrate speed direction is from the left to the right of the image. The scan is made in the center of the substrate in the \( y \)-direction and is leveled in both the \( x \)- and the \( y \)-direction.

3. Numerical model

Fig. 4 shows the 1D computational domain that is used to model the solution deposition process in a receding meniscus. The model...
is similar to the one developed by Doumenc and Guerrier (2010, 2013) and Dey et al. (2016). The thickness profile $h$ of the volatile solvent film is described by the lubrication equation (Oron et al., 1997)

$$\frac{\partial h}{\partial t} + \frac{\partial Q}{\partial x} = -F.$$  

(1)

The solvent flux $Q$ is given by

$$Q = \frac{h^2}{2 \mu(c)} \tau - \frac{h^3}{3 \mu(c)} \frac{\partial \rho}{\partial x} + U_{\text{sub}} h$$  

(2)

of the non-volatile solute,

$$h \frac{\partial c}{\partial t} + \frac{Q}{c} \frac{\partial c}{\partial x} = -\frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right) + cF.$$  

(3)

The solute concentration is assumed uniform across the thickness of the liquid film. The first term on the right hand side of Eq. (3) describes the diffusion of the solute, while the second term appears, since the solute is assumed non-volatile.

The evaporation rate $F$ (with units of m/s) is assumed to decrease linearly with the local solute concentration and is represented by the phenomenological model equation

$$F = F_0 \left( 1 - \frac{c}{c_{\text{max}}} \right).$$  

(4)

where $F_0$ is the evaporation rate of the pure solvent and $c_{\text{max}} = 100$ wt%. This is different from the original model by Doumenc and Guerrier (2010, 2013) and Dey et al. (2016), where the evaporation rate is obtained by solving a diffusion equation for the solvent vapor in a separate 2D computational domain for the gas phase. In this case the evaporation rate $F$ strongly increases near the contact line. This effect, which was first described by Deegan et al. (1997), cannot be captured using Eq. (4). However, Dey et al. (2016) compared the 2D and 1D evaporation models and found very similar deposit patterns for comparable values of $F$.

The capillary pressure

$$P = -\gamma(c) \frac{\partial^2 h}{\partial x^2}$$  

(5)

represents the influence of surface tension. The effect of gravity is neglected. The viscosity $\mu(c)$ depends on the local solute concentration $c$ according to the following function (Doumenc and Guerrier, 2010)

$$\mu [\text{Pa s}] = 10^{5.27-13.1c+6.99 c^2+1.25 c^3},$$  

(6)

where $c = \log_{10}(c/c_{\text{max}})$. Eq. (6) is based on the experimental data in Fig. 2. The surface tension $\gamma(c)$ linearly increases with the solute concentration according to

$$\gamma = \gamma_0 + d \gamma/c,$$  

(7)

where $\gamma_0 = 28$ mN/m and $d \gamma/c = 0.01$ mN/m (wt%). The solutal Marangoni shear stress $\tau = (d \gamma/c)(\partial c/\partial x)$ arises due to the dependence of surface tension on the solute concentration. Doumenc and Guerrier (2013) showed that for polymer solutions, patterned deposits are obtained only for $\tau \neq 0$. The substrate moves with speed $U_{\text{sub}}$ in the positive $x$-direction. $x = L$ is the location of the drying front, which can also occur outside of the computational domain. The diffusion coefficient of the solute in the solvent is set to $D = 1 \cdot 10^{-10}$ m$^2$/s and is assumed to be independent of $c$ for reasons of computational efficiency. The initial concentration is $c_i = 1$ wt%.

The following boundary conditions are used

$$h(x=0) = h_0, \quad \frac{\partial h}{\partial x}(0) = C_0, \quad c(0) = c_i.$$  

(8)

$$\frac{\partial h}{\partial x}(x=x_1) = 0, \quad \frac{\partial p}{\partial x}(x_1) = 0, \quad \frac{\partial c}{\partial x}(x_1) = 0.$$  

(9)

At the reservoir side $x=0$ (Eqs. (8)), the film thickness is fixed at $h_0 = 100$ μm, the surface curvature at $C_0 = 2$ mm$^{-1}$ and the solute concentration at the initial concentration $c_i$. The right side of the computational domain is located at $x_1 = 1$ mm, which is sufficiently large such that all the solvent has evaporated from the film. It is assumed that at this outlet, the gradients of the film thickness, the pressure and the solute concentration are equal to 0. The model is solved with the finite-element software Comsol 3.5a.

### 3.1. Periodic deposits

The receding meniscus can display a periodic displacement cycle (similar to that shown in Fig. 1(c and d)) for certain values of the substrate speed $U_{\text{sub}}$ and evaporation rate $F$. Fig. 5(a) shows a typical example of liquid film thickness profiles and Fig. 5(b) of corresponding solute concentration profiles at different moments.
in time during one cycle. The curves were obtained from a numerical simulation with $c_i = 1$ wt%, $F_0 = 2$ $\mu$m/s and $U_{sub} = 25$ $\mu$m/s. At the start of the cycle (illustrated by the curves labeled with ‘0’), the liquid film thickness profile displays a bulge. In time, the bulge grows and the drying front moves in the direction of the substrate speed. The bulge dries out and the drying front quickly moves against the substrate speed direction. The deposited bulge is advected along with the substrate, due to the strong increase in its viscosity. The receding meniscus develops a new bulge and the periodic cycle repeats itself.

4. Results and discussion

4.1. Variation of substrate speed

Fig. 6(a) shows dry layer thickness profiles $h_{dry}(x)$ of individual lines from deposit patterns obtained from experiments with different values of $U_{sub}$. The air nozzle was not connected to the slot-die. A 1D layer thickness profile $h_{dry}(x)$ is obtained by averaging the corresponding 2D profile $h_{dry}(x,y)$ (an example of which is shown in Fig. 3) in the $y$-direction. The profiles are shifted along the x-axis so that the maximum layer thickness occurs at $x = 0$. Furthermore, it is assumed that the minimum layer thickness is equal to 0. The amplitude of the line deposit decreases with increasing substrate speed. Fig. 6(b) shows the average layer thickness, defined as

$$h_{avg} = \frac{1}{L_z} \int h_{dry}(x) \, dx,$$

as a function of $U_{sub}$. The integral is taken over the period $L_z$ of one individual line. Fig. 6(b) displays multiple values for the same $U_{sub}$. They represent different lines from the same deposit pattern and indicate the typical spread in the average layer thickness. The solid line is a power-law fit of the form $h_{avg} \sim U_{sub}^{-a}$, with an exponent $a = 1.13$. When the substrate speed is increased to larger values ($U_{sub} \gtrsim 100$ $\mu$m/s), the line structures disappear and a uniform and homogenous deposit is obtained.

In the so-called evaporative regime (Jing et al., 2010) (where $h_{dry}$ decreases with increasing $U_{sub}$), the average dry film thickness is described by

$$h_{avg} = \frac{Q_{ev} c_{max} c_i}{U_{sub} (c_{max} - c_i)}.$$  

(11)

Here, $Q_{ev}$ is the evaporation rate integrated over the receding meniscus, i.e. the total evaporative volume flow per unit length of contact line in the $y$-direction. We note that there is no evaporation beyond the drying front. It is assumed that the solute does not evaporate and that the diffusive flux of the solute is negligible. Since $c_i \ll c_{max}$, Eq. (11) reduces to

$$h_{avg} \approx \frac{Q_{ev} c_i}{U_{sub}}.$$  

(12)

Although the deposit displays a periodic pattern, the average film thickness still follows the scaling behavior of Eq. (12), as the exponent $a = 1.13$ is close to the expected value of $a = 1.13$. This implies that in the experiment, $Q_{ev}$ is to good approximation independent of $U_{sub}$. Hsueh et al. (2013) performed 2D numerical simulations on the dip-coating geometry and demonstrated the occurrence of a flow that transports the solute back to the reservoir, at relatively high substrate speeds. This resulted in a value of $h_{avg}$ lower than expected from Eq. (11). Doumenc et al. (2016) studied the evaporative dip-coating of colloidal suspensions, where even in the evaporative regime, the film that is drawn from the meniscus can be saturated with solvent. This film subsequently dries over a certain drying length, which scales as $L_{avg} \sim c_i/U_{sub}$ in a certain regime (Doumenc et al., 2016). In this limit, the scaling relation of Eq. (12) is replaced by $h_{avg} \sim Q_{ev} c_i^2 / U_{sub}^2$.

Fig. 6(c) displays the period $\lambda$ of individual lines as a function of the substrate speed. For $U_{sub} \lesssim 20$ $\mu$m/s, $\lambda$ is found to decrease with increasing $U_{sub}$, while for larger substrate speeds it remains approximately constant.

Fig. 7(a) shows numerical simulations of one period of the dry deposit thickness profile $h_{dry}$ for different values of $U_{sub}$. The values of the other parameters are the same as those used in Fig. 5. The profiles are shifted along the x-axis so that the maximum thickness occurs at $x = 0$. Both the amplitude and the period of the deposit are reduced by an increase of the substrate speed. Also the minimum film thickness (between subsequent peaks) varies with $U_{sub}$.

Fig. 7(b) displays $h_{avg}$, scaled by the factor $Q_{ev} c_i$, from Eq. (12), as a function of $U_{sub}$. Due to the periodic displacement cycle, the total evaporation rate $Q_{ev}$ becomes time-dependent. The value of $Q_{ev}$ that is used in Fig. 7(b) corresponds to the time-average over one period. In the numerical simulations, $Q_{ev}$ also depends on the substrate speed, since the location of the drying front moves towards the reservoir upon decreasing $U_{sub}$. This limits the length over which the evaporation takes place. Doumenc and Guerrier (2010) showed that in the case of 2D diffusion-limited evaporation, the total evaporation rate $Q_{ev}$ is to good approximation independent of $U_{sub}$, while the location of the drying front does depend on the substrate speed. The average layer thickness follows the scaling behavior of Eq. (12), as illustrated by the dotted line in Fig. 7(b).

For values of $U_{sub} \gtrsim 40$ $\mu$m/s, i.e. outside of the range used in Fig. 7(a), the receding meniscus reaches a stationary state and a homogeneous deposit is obtained. The red circles in Fig. 7(b) are obtained in the periodic regime, the blue asterisks outside of this regime. The green triangles are obtained when the solutal Marangoni stress is not taken into account. Fig. 7(c) shows the period of the dry deposit as a function of $U_{sub}$. The period appears to diverge near the lowest values of $U_{sub}$, where periodic deposits are still observed. For higher values of the substrate speed, the period decreases much less rapidly. This trend compares well with that
observed in Fig. 6(c). However, the range of substrate speeds that result in a patterned deposit in the experiments is larger than predicted by the numerical model.

4.2. Variation of evaporation rate

The experiments described in Section 4.1 were performed without the air nozzle attached to the slot-die. Placing the air nozzle onto the slot-die reduces the volume of open space above the receding meniscus. Fig. 8(a) shows layer thickness profiles of line deposits, obtained when the air nozzle is attached to the slot-die, but without any air flow through the nozzle \( (q_{\text{air}} = 0 \, \text{ml/min}) \). The green squares in Fig. 8(d) show the corresponding average layer thickness \( h_{\text{avg}} \) as a function of \( U_{\text{sub}} \), while the red circles represent the data of Fig. 6(b). Comparing these two data sets illustrates that \( h_{\text{avg}} \) is reduced by the presence of the air nozzle. Since the air nozzle is located closely above the receding meniscus, it hinders the diffusion of the solvent vapor and thus reduces the evaporation rate over the receding meniscus (when \( q_{\text{air}} = 0 \, \text{ml/min} \)). A similar observation was made by Chen et al. (2010).

Fig. 8(b) shows layer thickness profiles when there is an air flow present through the nozzle, with \( q_{\text{air}} = 10 \, \text{ml/min} \). This results in laminar air flow with an average speed of approximately 2 cm/s at the exit of the air nozzle and a Reynolds number (based on the width of the nozzle \( w_{\text{n}} \)) of \( Re \approx 1 \). The blue diamonds in Fig. 8(d) show the corresponding values of \( h_{\text{avg}} \). Comparing the green and blue data sets in Fig. 8(d) indicates that the average layer thickness increases due to the air flow over the receding meniscus. This flow enhances the convection of solvent vapor away from the meniscus and thus the total evaporation rate.

The evaporation rate over the receding meniscus also depends on the solvent that is used. Fig. 8(c) shows layer thickness profiles obtained from experiments where the polymer was dissolved in o-xylene instead of toluene; the cyan open circles in Fig. 8(d) display the corresponding values of \( h_{\text{avg}} \). The air nozzle was attached to the slot-die, but no airflow was present \( q_{\text{air}} = 0 \, \text{ml/min} \). The vapor pressure of o-xylene is more than four times lower than that of toluene (Haynes, 2016), which results in a lower evaporation rate. Correspondingly, \( h_{\text{avg}} \) is significantly decreased, as is illustrated by a comparison of the green and cyan data sets in Fig. 8(d).

The experimental results from Figs. 6 and 8 were fitted with power-law functions \( h_{\text{avg}} = \beta U_{\text{sub}}^a \). In all cases the power-law
exponent (as listed in Table 1) is close to the expected value \( x = -1 \). The total evaporation rate \( Q_{\text{ev}} \) is obtained from the parameter \( \beta \) by comparing the power-law fit with a modified version of Eq. (11), where \( U^{-1}_{\text{sub}} \) is replaced by \( U_{\text{sub}}^{-1} \). The resulting values are listed in Table 1 and confirm the observations that the evaporation rate can be enhanced by an air flow over the receding meniscus and reduced by using a solvent with lower volatility.

In Fig. 9 we systematically study the effect of the air flow rate on the solution deposition process. Fig. 9(a) shows layer thickness profiles for different values of the air flow rate \( q_{\text{air}} \) and \( U_{\text{sub}} = 20 \) \( \mu \text{m/s} \). The polymer was dissolved in toluene. The amplitude of the line deposit increases with increasing \( q_{\text{air}} \). Fig. 9(b) illustrates that the increase in the average layer thickness scales linearly with the air flow rate, \( \Delta h_{\text{avg}} \equiv (h_{\text{avg}} - h_{\text{avg}}(q_{\text{air}} = 0)) \sim q_{\text{air}} \). Comparing this relation to Eq. (12) suggests that the increase of the total evaporation rate over the meniscus \( Q_{\text{ev}} \) is proportional to \( q_{\text{air}} \). The solid line in Fig. 9(b) is a guide to the eye. When the air flow rate is increased to values much larger than those illustrated in Fig. 9, for \( q_{\text{air}} \geq 20 \) ml/min, the line structures disappear and a uniform and homogeneous deposit is obtained.

Fig. 10(a) displays dry thickness profiles from numerical simulations for different values of the evaporation rate constant \( F_0 \) and \( U_{\text{sub}} = 10 \) \( \mu \text{m/s} \). The period of the dry deposit increases with \( F_0 \), while its maximum thickness increases only weakly. The deposit profile develops a ‘tail’ at the side further away from the liquid reservoir (higher values of \( x \)). Although the exact shapes differ from the experimental data shown in Fig. 9(a), where the maximum film thickness increases more strongly with increasing \( Q_{\text{ev}} \), the model reproduces the increase in line width qualitatively correctly.

Fig. 10(b) shows \( h_{\text{avg}} \) scaled by the factor \( c_{i}/U_{\text{sub}} \) from Eq. (12), as a function of \( Q_{\text{ev}} \). As in Fig. 7(b), the red circles are obtained in the periodic regime. The average layer thickness increases linearly with \( Q_{\text{ev}} \) in perfect qualitative agreement with the experimental results of Fig. 9(b).

### Table 1

<table>
<thead>
<tr>
<th>Case</th>
<th>( x )</th>
<th>( Q_{\text{ev}} ) (( \mu \text{m}^2/\text{s} ))</th>
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<tr>
<td>Fig. 6(a)</td>
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<td>414</td>
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<tr>
<td>Fig. 8(a)</td>
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<td>Fig. 8(b)</td>
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<td>Fig. 8(c)</td>
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</table>

### 4.3 Uniformity of the line deposits

An interesting question concerns the uniformity of the width, height and period of the line deposits. Fig. 11 shows optical micrographs of line deposits obtained for different values of the substrate speed \( U_{\text{sub}} \). Generally the period of the line pattern appears quite uniform. The line width strongly decreases and the uniformity of the width improves with increasing \( U_{\text{sub}} \). In Figs. 11(c,d), the width non-uniformities of neighboring stripes are spatially correlated in the coating direction, which points at a transverse polymer concentration instability in the coating meniscus. The scatter in the datapoints in Figs. 6(b and c), 8(d) and 9(b) indicate a non-uniformity of the average height \( h_{\text{avg}} \) of \( \pm 10\% \) to \( \pm 25\% \) and of the line period of approximately \( \pm 10\% \). The non-uniformity of the line width and height in our experiments is comparable to the range of results in published literature (Men et al., 2014; Jing et al., 2010; Kwon et al., 2011a; Xu et al., 2006; Hong et al., 2007a,b; Lin and Granick, 2005; Park et al., 2012).

Xiao et al. showed that the ageing of a P3HT solution has a drastic impact on the line uniformity (Xiao et al., 2012). According to the authors, P3HT nanowhisker aggregates form in solution, the effective molecular weight of which increases with increasing solution age, which positively affects the uniformity of the line.
width and height. However, in the case of our PMMA solutions in toluene no such aggregate formation is expected.

5. Summary and conclusions

We studied the deposition of polymer films from a receding solution meniscus by means of experiments and numerical simulations. The substrate speed and the evaporation rate of the solvent were identified as the main control parameters. In the experiments, the evaporation rate was varied by applying a forced air flow over the receding meniscus. Periodic deposit patterns, consisting of lines parallel to the receding contact line were observed for certain ranges of the control parameters. Systematic series of experiments were conducted by varying the experimental conditions and by measuring the resulting dry layer thickness profiles with atomic force microscopy.

The average layer thickness was found to scale approximately inversely proportionally with the substrate speed. This is consistent with a relation derived for the so-called evaporative regime of coating, where the flow in the receding meniscus is dominated by the evaporation of the solvent. The numerical model correctly describes the trend of decreasing stripe amplitude and period with increasing substrate speed as observed in the experiments.

Regarding the variation of the evaporation rate, the numerical model predicts a change in the morphology of the stripe deposit while the maximum film thickness is affected only weakly. This is different from the experiments, where the maximum film thickness noticeably increases with increasing total evaporation rate. At sufficiently high air flows, the coating instability is no longer observed.

In order to improve the comparison with the experiments, possibilities for further study are to implement diffusion-limited evaporation at the liquid-air interface (Dey et al., 2016) and to include the forced convection in the model via a two-dimensional computational domain representing the gas phase (Wedershoven et al., 2018).

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References


