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SPECIAL TOPIC — Soft matter and biological physics

Thin film dynamics in coating problems using Onsager principle*

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A new variational method is proposed to investigate the dynamics of the thin film in a coating flow where a liquid is delivered through a fixed slot gap onto a moving substrate. A simplified ODE system has also been derived for the evolution of the thin film whose thickness h_f is asymptotically constant behind the coating front. We calculate the phase diagram as well as the film profiles and approximate the film thickness theoretically, and agreement with the well-known scaling law as $Ca^{2/3}$ is found.

Keywords: Onsager principle, thin films, coating flows, interfacial flows

PACS: 45.10.Db, 68.15.+e, 47.85.mb, 47.55.N– **DOI:** 10.1088/1674-1056/27/2/024501

1. Introduction

The withdrawal of a solid substrate from a liquid reservoir is a very active research subject, due to the technological importance in controlling the homogeneity and thickness in multi-layer coating in various applications. It is important to know the parameters that determine the thickness of the coating film, which must be controlled precisely in many applications. This subject has received a lot of attention in the context of die coating and numerous extensions have been developed[1–3] since the original work by Landau & Levich.[4] An important dimensionless parameter in these problems is the capillary number defined by $Ca = U\eta/\gamma$, where η and γ are the viscosity and the surface tension of the fluid. It has been shown that when the capillary number Ca is small, the thickness of the film, h_f, satisfies the scaling law as $h_f \propto Ca^{2/3}$. Similar scaling relation is known for other problems. Bretherton[5] studied the propagation of a long bubble through a capillary filled with liquid. Using a lubrication approximation coupled with surface deformation of the bubble, he found that the thickness of the fluid film obeys the two-thirds power law. Aussillous and Quéré[6] reported more experimental data and analyzed the behavior using scaling arguments. We refer to Ref. [7] for a recent review on the coating problem.

However, our understanding of the fundamental mechanisms underlying the coating process is still limited. Specifically, none of the theoretical models of the coating flows cited above consider the flow driven by a reservoir pressure in addition to withdrawal as illustrated in Fig. 1. A film is deposited on a substrate which is moving with speed of U below a reservoir of viscous liquid under the driven pressure P_{in}. If the gap distance h_0 is sufficiently small for gravity to be negligible, a thin film of fluid is formed with a uniform thickness h_f along the substrate between the front and the rear meniscus. Moreover, existing studies on coating flows are mostly based on Newtonian fluids, while most of the fluids used in the coating industry are complex fluids, such as polymer solutions and colloidal mixtures. More complex rheological properties involve, so simpler approximations are highly desired.

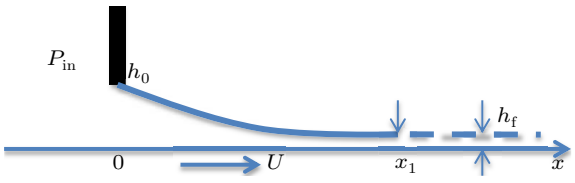


Fig. 1. Sketch of the coating system under consideration: driven by the pressure P_{in} in the reservoir, a flat film of the constant thickness h_f is dragged out on the moving substrate with speed U.

In this paper, we will study the dynamics of the thin film in the coating problem shown in Fig. 1 using Onsager principle. For simplicity, we shall confine our attention here to wetting liquids. The time evolution of the thin film is determined by a variational principle, i.e., by minimizing a certain functional with respect to the film shape change. Combined with the lubrication approximation, the thin film evolution equation governing the dynamics of the liquid film will be derived. In order to investigate the properties of the system dynamics, we carry out numerical simulations of the thin-film evolution

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equation. For small capillary number, the theoretical prediction can be obtained. We expect that the variational method presented here will provide additional insights to many other problems in coating because of its simplicity and susceptibility to asymptotic analysis.

2. Evolution equation for thin film in coating

We shall first briefly describe the variational principle used in this paper. Detailed description can be found in review papers and textbook.[8,9] Consider a Stokesian hydrodynamic system which includes many boundaries (boundary between fluid and solid, fluid and air, or between two immiscible fluids). If the boundaries are moving, driven by certain potential forces, such as gravity, surface tension, etc., the evolution of the system can be determined by the following principle: let $a(t)=\{a_1(t),a_2(t),\ldots,a_N(t)\}$ be a set of the parameters which specify the position of the boundaries. The time evolution of the system, i.e., the time derivative $\dot{a}(t)=\{\dot{a}_1(t),\dot{a}_2(t),\ldots,\dot{a}_N(t)\}$ is determined by the minimum condition for the following Rayleighian function of $\dot{a}$,

$$\mathscr{R}(\dot{a},a)=\Phi(\dot{a},a)+\sum_i\frac{\partial A}{\partial a_i}\dot{a}_i, \tag{1}$$

where $A(a)$ is the potential energy of the system, and $\Phi(\dot{a},a)$ is the energy dissipation function, defined as the half of the minimum of the energy dissipated per unit time in the fluid when the boundary is changing at the rate $\dot{a}$. Since the fluid obeys Stokesian dynamics, $\Phi(\dot{a},a)$ is a quadratic function of $\dot{a}$. The minimum condition of Eq. (1)

$$\frac{\partial\Phi}{\partial\dot{a}_i}+\frac{\partial A}{\partial a_i}=0 \tag{2}$$

represents the force balance of two kinds of forces, the hydrodynamic frictional force $\partial\Phi/\partial\dot{a}_i$, and the potential force $-\partial A/\partial a_i$ in the generalized coordinate.

The above variational principle can be proven directly from the basic equations of Stokesian hydrodynamics.[9] It can also be regarded as a special form of Onsager principle which describes the time evolution of non-equilibrium system characterized by certain set of slow variables.[9] Onsager principle has been successfully applied to various soft matter systems.[10–17]

Let us consider the evolution of the thin film in Fig. 1. Let $h(x,t)$ be the thickness of the liquid film at point x and time t. The free energy of the system is written as a functional of $h(x,t)$ by the sum of the wetting energy and the potential energy,

$$A=\frac{\gamma}{2}\int_0^\infty\left(\frac{\partial h}{\partial x}\right)^2\mathrm{d}x-P_{\mathrm{in}}\int_0^\infty h\,\mathrm{d}x, \tag{3}$$

where γ is the surface tension, and P_{in} stands for the pressure in the bulk. Here we assume that the substrate is fully wetted. By the lubrication approximation, let $v(x,t)$ be the depth averaged velocity of the fluid. The conservation condition of the fluid is written as

$$\dot{h}=-\frac{\partial}{\partial x}(hv). \tag{4}$$

The height function $h(x,t)$ satisfies the corresponding boundary conditions,

$$h(0,t)=h_0,\quad h(\infty,t)=0. \tag{5}$$

From Eq. (4), the following expression for $\dot{A}$ can be obtained:

$$\begin{aligned}\dot{A}&=\gamma\int_0^\infty\frac{\partial h}{\partial x}\frac{\partial\dot{h}}{\partial x}\mathrm{d}x-P_{\mathrm{in}}\int_0^\infty\dot{h}\,\mathrm{d}x\\&=-\gamma\frac{\partial^2h}{\partial x^2}hv\bigg|_{x=0}-P_{\mathrm{in}}hv\bigg|_{x=0}-\gamma\int_0^\infty\frac{\partial^3h}{\partial x^3}hv\,\mathrm{d}x.\end{aligned} \tag{6}$$

Using the lubrication approximation, the energy dissipation function is constructed as

$$\Phi=\int_0^\infty\left[\frac{3\eta}{2h}(v-U)^2\right]\mathrm{d}x, \tag{7}$$

where η is the viscosity of the fluid and U is the speed of the moving substrate.

The Onsager principle (2) indicates that v is determined by $\partial\Phi/\partial v+\partial\dot{A}/\partial v=0$,

$$v=U+\frac{\gamma}{3\eta}h^2\frac{\partial^3h}{\partial x^3}, \tag{8}$$

and on the boundary, $x=0$,

$$\frac{\partial^2h}{\partial x^2}\bigg|_{x=0}=\frac{-P_{\mathrm{in}}}{\gamma}. \tag{9}$$

Substituting the velocity (8) into the conservation law (4), the evolution equation for the film thickness $h(x,t)$ can be expressed as the following partial differential equation (PDE):

$$\dot{h}=-\frac{\partial}{\partial x}\left[\frac{h^3}{3}\left(\frac{\partial^3h}{\partial x^3}\right)+\mathrm{Ca}\,h\right], \tag{10}$$

where $\mathrm{Ca}=U/U^*$ represents the capillary number with $U^*=\gamma/\eta$ being the characteristic capillary velocity. The capillary number Ca measures the relative size of viscous drag and capillary retention in the film.

We solve Eq. (10) subjecting to boundary conditions (5) and (9) numerically. The time evolutions of the calculated film profiles for three scales of capillary number are shown in Fig. 2, where the black lines represent the initial profiles and the blue lines represent the time evolutions. It is obvious that a thin film of asymptotically constant thickness has been developed quickly for all cases and the thickness increases with capillary number.

In Fig. 3, we plot the film thickness h_{f}/h_0 solved numerically by Eq. (10) with different Ca. For relatively small capillary number Ca or relatively large negative pressure $\mathcal{P}$, the film thickness h_{f} increases with capillary number. Actually, under the circumstances that the surface tension force is the

dominant force in the coating process, the film thickness can be described theoretically by the well-known power law as $Ca^{2/3}$. This relationship was demonstrated in many experiments. When the capillary number Ca is larger or the negative pressure $\mathcal{P}$ is smaller, both the surface tension and viscous forces are significant. This is why the dependence of the film thickness on the capillary number is away from the power law. This phenomena can also be seen in the contour map of the film thickness in the parameter space $(\mathcal{P}, \mathrm{Ca})$ as shown in Fig. 3(b).

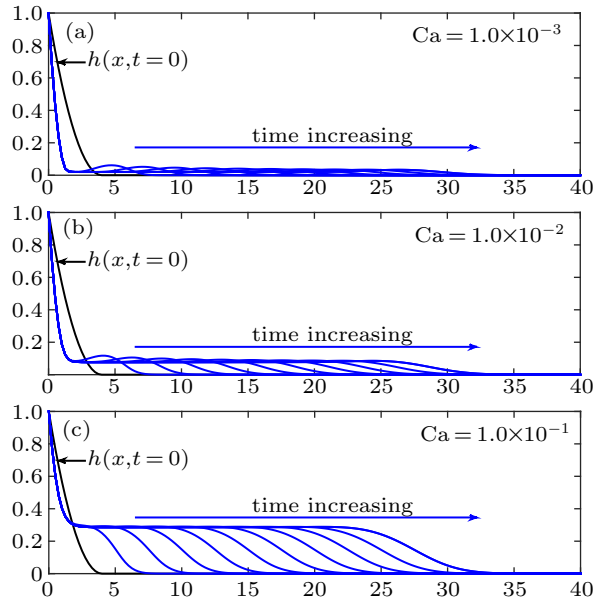


Fig. 2. (color online) Calculated film profiles at successive times with $\mathrm{Ca} = 1.0\times10^{-3}, 1.0\times10^{-2}, 1.0\times10^{-1}$ and $\mathcal{P} = -P_{\mathrm{in}}h_0/\gamma = 1.0$. Length scaled by h_0.

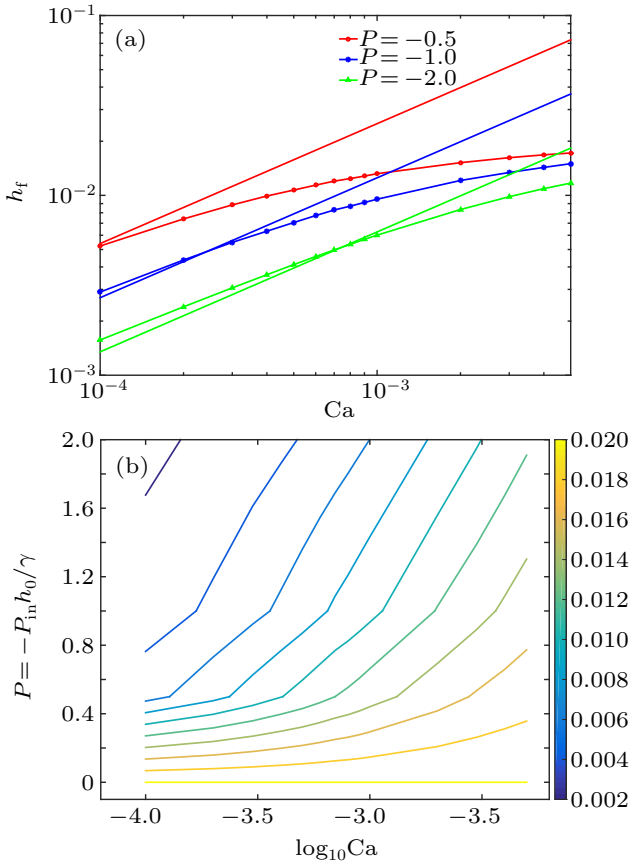


Fig. 3. (color online) (a) Film thickness h_{f}/h_0 as a function of Ca. Different color with symbols represent the numerical results for different driving pressure $\mathcal{P} = -P_{\mathrm{in}}h_0/\gamma$. Solid lines without symbols represent the 2/3 power law. (b) Contour map of the film thickness in the parameter space $(\mathcal{P}, \mathrm{Ca})$.

3. Approximating thickness of the film

The dissipation in the thin film takes place mostly in the intermediate region which connects the planar film and the bulk fluid, so-called dynamical meniscus (Fig. 1). Here we propose a simplified model with a few slow variables, aiming to capture the evolution of the dynamical meniscus. We assume a simple parabolic formulation,

$$h(x,t) = \begin{cases} \frac{1}{2}\kappa(t)\,(x_1(t)-x)^2 + h_{\mathrm{f}}(t), & 0 \le x \le x_1(t), \\ h_{\mathrm{f}}(t), & x_1(t) \le x, \end{cases} \tag{11}$$

where $\kappa(t)$, $x_1(t)$, and $h_{\mathrm{f}}(t)$ are the three parameters characterizing the shape of the film. The dynamical meniscus merges with the planar film of thickness $h_{\mathrm{f}}(t)$ at the position $x = x_1(t)$, as sketched in Fig. 1. The boundary condition, $h(0,t) = h_0$, constrains that only two parameters are independent. If $\kappa(t)$ and $x_1(t)$ are chosen as the unknown variables, then $h_{\mathrm{f}}(t) = h_0 - \frac{1}{2}\kappa(t)x_1^2(t)$. Approximately, the planar film moves with the same speed U as the substrate. Substituting Eq. (11) into Eq. (4) and performing an integration, we have

$$\begin{aligned} v(x,t) &= \frac{h_{\mathrm{f}}(t)}{h(x,t)}U + \frac{1}{h(x,t)} \\ &\quad \times \int_x^{x_1(t)} \mathrm{d}y \left[\left(\frac{1}{2}y^2 - x_1(t)y\right)\dot{\kappa}(t) - \kappa(t)y\dot{x}_1(t)\right]. \end{aligned} \tag{12}$$

The effects of viscous forces on the interface profile can be described by the lubrication equations. Therefore, the dissipation function Φ can be expressed as a quadratic function of $\dot{\kappa}$, $\dot{x}_1$, and U,

$$\begin{aligned} \Phi &= \int_0^{x_1} \frac{3\eta}{2h}(v-U)^2\,\mathrm{d}x \\ &= \zeta_{\kappa\kappa}\dot{\kappa}^2 + \zeta_{x_1x_1}\dot{x}_1^2 + \zeta_{UU}U^2 + \zeta_{\kappa U}\dot{\kappa}U \\ &\quad + \zeta_{x_1U}\dot{x}_1U + \zeta_{\kappa x_1}\dot{\kappa}\dot{x}_1, \end{aligned} \tag{13}$$

where the coefficients $\zeta_{\star\star}$ can be obtained by Eq. (12) explicitly. The free energy of the thin film can be calculated by

$$A = \frac{\gamma}{2}\int_0^{x_1}\left(\frac{\partial h}{\partial x}\right)^2 \mathrm{d}x + \gamma U t + \gamma h_{\mathrm{f}} - P_{\mathrm{in}}\int_0^{x_1} h(x)\,\mathrm{d}x. \tag{14}$$

Substituting the approximated formulation of the thin film profile (11), we can get

$$\begin{aligned} \dot{A} &= \left(\frac{\gamma}{3}\kappa x_1^3 + \frac{1}{3}P_{\mathrm{in}}x_1^3 - \frac{\gamma}{2}x_1^2\right)\dot{\kappa} \\ &\quad + \left(\frac{\gamma}{2}\kappa^2x_1^2 + P_{\mathrm{in}}\kappa x_1^2 - P_{\mathrm{in}}h_0 - \gamma\kappa x_1\right)\dot{x}_1 + \gamma U. \end{aligned} \tag{15}$$

In this simple model, the film profile is fully characterized by two slow variables: $\kappa(t)$ and $x_1(t)$. We then apply the Onsager principle (2),

$$\frac{\partial(\Phi+\dot{A})}{\partial\dot{\kappa}}=0, \qquad \frac{\partial(\Phi+\dot{A})}{\partial\dot{x}_1}=0. \tag{16}$$

The resulting time evolution follows ordinary differential equations (ODE) for $\kappa(t)$ and $x_1(t)$,

$$2\zeta_{\kappa\kappa}\dot{\kappa}+\zeta_{\kappa x_1}\dot{x}_1+\zeta_{\kappa U}U+\frac{\gamma}{3}\left(\kappa+\frac{P_{\rm in}}{\gamma}\right)x_1^3-\frac{\gamma}{2}x_1^2=0, \tag{17}$$

$$2\zeta_{x_1x_1}\dot{x}_1+\zeta_{\kappa x_1}\dot{\kappa}+\zeta_{x_1U}U+\frac{\gamma}{2}\kappa^2x_1^2+\left(\kappa x_1^2-h_0\right)P_{\rm in}-\gamma\kappa x_1=0, \tag{18}$$

which can be evaluated numerically.

In the steady state, $\dot{\kappa}=0$ and $\dot{x}_1=0$ and the ODE system is simplified as

$$3{\rm Ca}\left[-\int_0^{x_1}\frac{\kappa y^5}{6h^3}{\rm d}y+\int_0^{x_1}\frac{\kappa y^3}{2h^3}x_1^2{\rm d}y\right]+\frac{2}{3}\left(\kappa+\frac{P_{\rm in}}{\gamma}\right)x_1^3-x_1^2=0, \tag{19}$$

$$3{\rm Ca}\left[-\int_0^{x_1}\frac{\kappa^2y^4}{2h^3}{\rm d}y+\int_0^{x_1}\frac{\kappa^2y^3}{2h^3}x_1{\rm d}y\right]+\kappa^2x_1^2+2\left(\kappa x_1^2-h_0\right)\frac{P_{\rm in}}{\gamma}-2\kappa x_1=0. \tag{20}$$

Considering $h_{\rm f}/h_0\ll1$, the leading order term of Eq. (19) shows that,

$$\frac{2}{3}\left(\kappa+\frac{P_{\rm in}}{\gamma}\right)x_1^3=0 \quad\Rightarrow\quad \kappa h_0=\frac{-P_{\rm in}h_0}{\gamma}:=\mathcal{P}. \tag{21}$$

We substitute it into Eq. (20), make (20) $-$ (19) $\times\,\kappa/x_1$, ignore the higher order term of $h_{\rm f}$, and then have

$$3{\rm Ca}\left[-\int_0^{x_1}\frac{\kappa^2y^4}{2h^3}{\rm d}y\right]+2\kappa h_{\rm f}=0, \tag{22}$$

where the integral can be approximated by

$$\int_0^{x_1}\frac{\kappa^2y^4}{2h^3}{\rm d}y\approx\frac{3\arctan\sqrt{\frac{h_0-h_{\rm f}}{h_{\rm f}}}}{2\sqrt{2\kappa h_{\rm f}}}\approx\frac{3\pi}{4\sqrt{2\kappa h_{\rm f}}}, \tag{23}$$

which indicates that

$$\kappa h_{\rm f}\approx\left(\frac{3\pi}{8\sqrt{2}}3{\rm Ca}\right)^{2/3}\approx0.885\,(3{\rm Ca})^{2/3}. \tag{24}$$

The thickness $h_{\rm f}/h_0$ can be estimated by

$$\frac{h_{\rm f}}{h_0}\approx\frac{1.842}{\mathcal{P}}\,({\rm Ca})^{2/3}. \tag{25}$$

We compare the numerical results of the ODE system derived from Eq. (16) with the numerical results of the PDE (10) and the prediction analysis (25) in Fig. 4. It can be seen apparently that the simulating results of the ODE system catch the main trend described by the complex PDE system. Notably, there are only two variables, $\kappa(t)$ and $x_1(t)$, instead of the film profile $h(x,t)$ depending on both time and position, in the simplified ODE system. Meanwhile, for the small capillary number case, ${\rm Ca}=1\times10^{-3}$, the accuracy of the prediction analysis (25) has been demonstrated numerically.

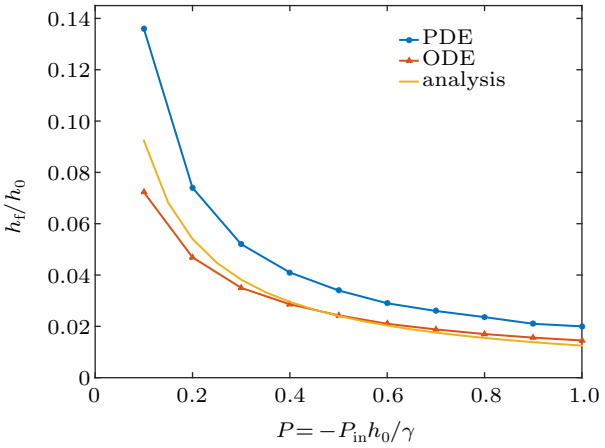


Fig. 4. (color online) Film thickness $h_{\rm f}/h_0$ as a function of $\mathcal{P}$ with the same capillary number ${\rm Ca}=1\times10^{-3}$ for the numerical simulation of the ODE system (16), the numerical simulation of the PDE system (10), and the prediction analysis (25).

4. Conclusion

In this paper, we have investigated the dynamics of the thin film deposited on a moving substrate through a fixed slot gap. We employed Onsager principle to derive an evolution equation (10) for the film thickness $h(x,t)$. We also derived an ODE system for the asymptotic value of the film thickness $h_{\rm f}(t)$ using the approximate formulation (11). Both equations give similar prediction on how the steady film thickness $h_{\rm f}$ depends on the substrate velocity U and the reservoir pressure $P_{\rm in}$. Also both equations indicate that the celebrated scaling law $h_{\rm f}\propto({\rm Ca})^{2/3}$ holds for very small capillary number Ca, but significant deviation is found for practical capillary numbers.

The approximate formulation based on the Onsager principle gives reasonably good results, but the result obtained by the approximate formulation is about 20% less than the exact result obtained by the PDE. As analyzed in Ref. [15], the error may be reduced by introducing more parameters to approximate $h(x,t)$ or by considering more suitable form for $h(x,t)$. It should be noted that the characteristic physics is correctly captured by the present simple variational calculation. However, more refined analytical work needs to be conducted in the future.

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