Final version: http://dx.doi.org/10.1088/1674-1056/27/2/024501

Analysis of thin film dynamics in coating problems using Onsager principle *

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September 28, 2017

Abstract

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 which is found consistent with the well-known scaling law as $Ca^{2/3}$.

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

PACS: 45.10.Db, 68.15.+e, 47.85.mb, 47.55.N-,

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*Project supported by the National Natural Science Foundation of China (Grant No. 91630208).

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1. Introduction

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} as illustrated in Fig. 1. 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. It is important to know the parameters that determine the thickness of the coating film, which must be controlled precisely in many applications. This set-up 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 $h_f \propto Ca^{2/3}$. We shall confine our attention here to wetting liquids.

Similar scaling relation is known for other problems. Brethertion [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 has shown 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.

The withdrawal of a solid substrate from a liquid reservoir is still a very active research subject, due to the technological importance in controlling the homogeneity and thickness in multi-layer coating in various applications. We refer to [7] for a recent review on the coating problem.

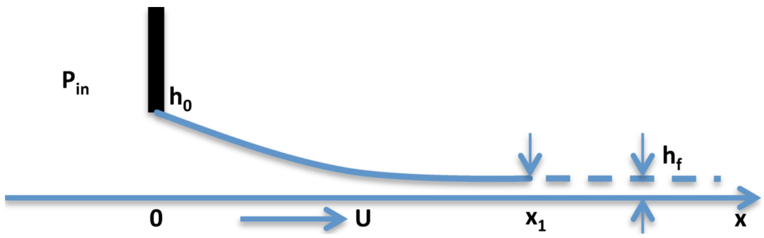

Fig. 1. Sketch of the coating system under consideration: driven by the pressure P_{in} in the reservoir, a flat film of the constant thickness h_f is dragged out on the moving substrate with speed U.

In this paper, we will study the dynamics of the thin film in the coating problem shown in Fig. 1 using Onsager principle. 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 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 we shall use 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 $a(t) = \{a_1(t), a_2(t), ...a_N(t)\}$ be a set of the parameters which specify the position of the boundaries. The time evolution of the system, i.e., the time derivative $\dot{a}(t) = \{\dot{a}_1(t), \dot{a}_2(t), ...\dot{a}_N(t)\}$ 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,

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

where γ is the surface tension, and P_{in} stands for the pressure in the bulk. Here we have assumed 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,

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

By equation (4), the following expression for $\dot{A}$ can be obtained:

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

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

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

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 $\partial\Phi/\partial v + \partial\dot{A}/\partial v = 0$,

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

and on the boundary, $x = 0$,

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

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

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

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 the equation (10) subject to boundary conditions (5) and (9) numerically. The calculated film profiles at successive times are shown in Fig. 2. Not surprisingly, a film of asymptotically constant thickness has been developed quickly.

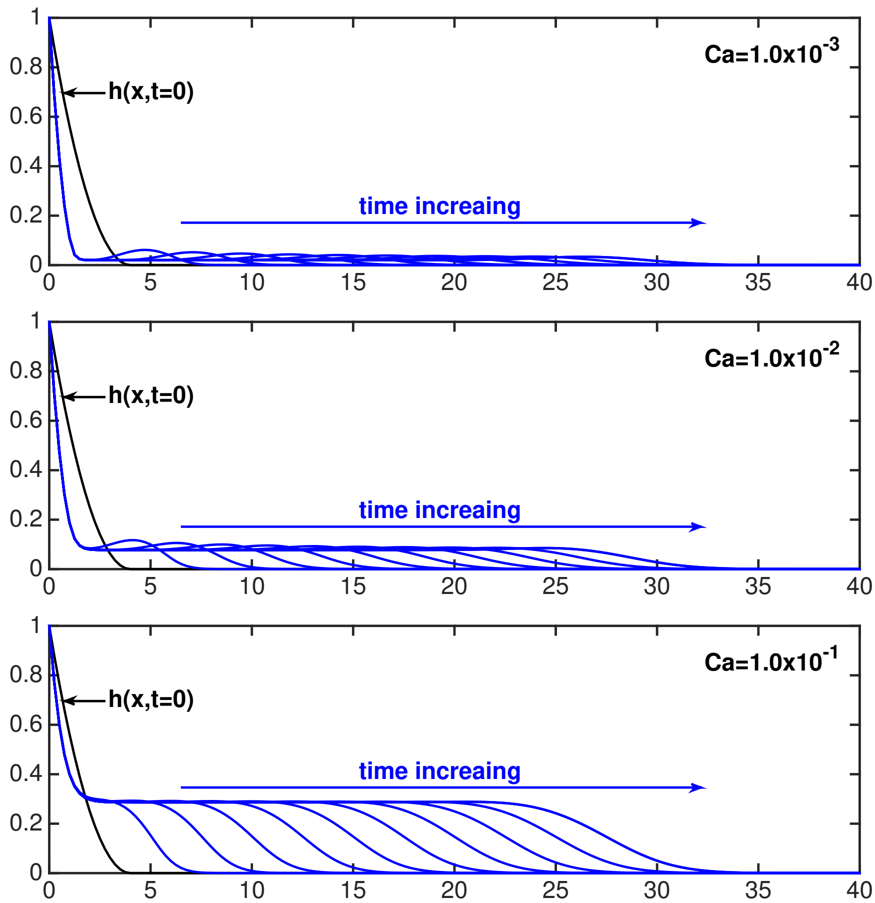

Fig. 2. The calculated film profiles at successive times with $\mathrm{Ca} = 1.0 \times 10^{-3}$, 1.0×10^{-2}, 1.0×10^{-1} and $\mathcal{P} = -P_{in} h_0/\gamma = 1.0$. Length scaled by h_0.

In Fig. 3 , we have plotted the film thickness h_f/h_0 solved numerically by the equation (10) with different Ca. The original 2/3 power law is recovered only for very small capillary number Ca and large negative pressure $\mathcal{P}$. The contour map of the film thickness in the parameter space $(\mathcal{P}, \mathrm{Ca})$ is shown in the right side of Fig. 3.

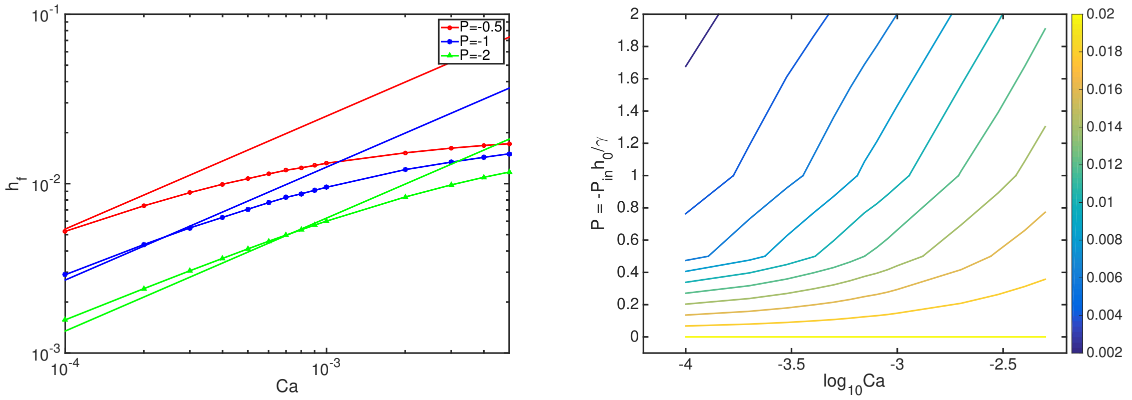

Fig. 3. (color online) Left: film thickness h_f/h_0 as a function of Ca. Different colored with symbols represent the numerical results for different driving pressure $\mathcal{P} = -P_{in}h_0/\gamma$. Solid lines without symbols represent the 2/3 power law. Right: Contour map of the film thickness in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

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 proposed a simplified model with a few slow variables, aiming to capture the evolution of the dynamical meniscus. We assume a simple parabolic formulation, where $h(x,t)$ is given by

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

where $\kappa(t)$, $x_1(t)$ and $h_f(t)$ are the three parameters characterizing the shape of the film. The dynamical meniscus merges with the planar film of thickness $h_f(t)$ 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 $h_f(t) = h_0 - \frac{1}{2}\kappa(t)x_1^2(t)$. 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

$$v(x,t) = \frac{h_f(t)}{h(x,t)}U + \frac{1}{h(x,t)}\int_x^{x_1(t)} dy\left[\left(\frac{1}{2}y^2 - x_1(t)y\right)\dot{\kappa}(t) - \kappa(t)y\dot{x_1}(t)\right]. \tag{12}$$

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,

$$\begin{aligned} \Phi &= \int_0^{x_1} \frac{3\eta}{2h}(v-U)^2 dx & (13)\\ &= \zeta_{\kappa\kappa}\dot{\kappa}^2 + \zeta_{x_1x_1}\dot{x}_1^2 + \zeta_{UU}U^2 + \zeta_{\kappa U}\dot{\kappa}U + \zeta_{x_1U}\dot{x}_1U + \zeta_{\kappa x_1}\dot{\kappa}\dot{x}_1, & (14) \end{aligned}$$

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

$$A = \frac{\gamma}{2}\int_0^{x_1}\left(\frac{\partial h}{\partial x}\right)^2 dx + \gamma Ut + \gamma h_f - P_{in}\int_0^{x_1} h(x)dx. \tag{15}$$

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),

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

The resulting time evolution follows ordinary differential equations (ODE) for $\kappa(t)$ and $x_1(t)$, which can be evaluated numerically.

In the steady state, $\dot{\kappa} = 0$ and $\dot{x_1} = 0$ and the ODE system is simplified as

$$3\text{Ca}\left[-\int_0^{x_1} \frac{\kappa y^5}{6h^3}dy + \int_0^{x_1} \frac{\kappa y^3}{2h^3}x_1^2 dy\right] + \frac{2}{3}\left(\kappa + \frac{P_{in}}{\gamma}\right)x_1^3 - x_1^2 \quad = 0, \tag{17}$$

$$3\text{Ca}\left[-\int_0^{x_1} \frac{\kappa^2 y^4}{2h^3}dy + \int_0^{x_1} \frac{\kappa^2 y^3}{2h^3}x_1 dy\right] + \kappa^2 x_1^2 + 2\left(\kappa x_1^2 - h_0\right)\frac{P_{in}}{\gamma} - 2\kappa x_1 \quad = 0. \tag{18}$$

Considering $h_f/h_0 \ll 1$, the leading order term of the equation (17) shows that,

$$\frac{2}{3}\left(\kappa + \frac{P_{in}}{\gamma}\right)x_1^3 = 0, \quad \Rightarrow \quad \kappa h_0 = \frac{-P_{in}h_0}{\gamma} := \mathcal{P}. \tag{19}$$

Substitute it into (18), make (18) $-$ (17) $\times\, \kappa/x_1$, and ignore the higher order term of h_f, we have

$$3\text{Ca}\left[-\int_0^{x_1} \frac{\kappa^2 y^4}{2h^3}dy\right] + 2\kappa h_f = 0, \tag{20}$$

where the integral can be approximated by

$$\int_0^{x_1} \frac{\kappa^2 y^4}{2h^3}dy \approx \frac{3\arctan\sqrt{\frac{h_0 - h_f}{h_f}}}{2\sqrt{2\kappa h_f}} \approx \frac{3\pi}{4\sqrt{2\kappa h_f}}, \tag{21}$$

which indicates that

$$\kappa h_f \approx \left(\frac{3\pi}{8\sqrt{2}}3\text{Ca}\right)^{2/3} \approx 0.885\,(3\text{Ca})^{2/3}. \tag{22}$$

The thickness h_f/h_0 can be estimated by

$$\frac{h_f}{h_0} \approx \frac{1.842}{\mathcal{P}}\,(\text{Ca})^{2/3}. \tag{23}$$

We compare the the numerical results of the ODE system derived from (16) to the numerical results of the PDE (10) and the prediction analysis (23) in Fig. 4.

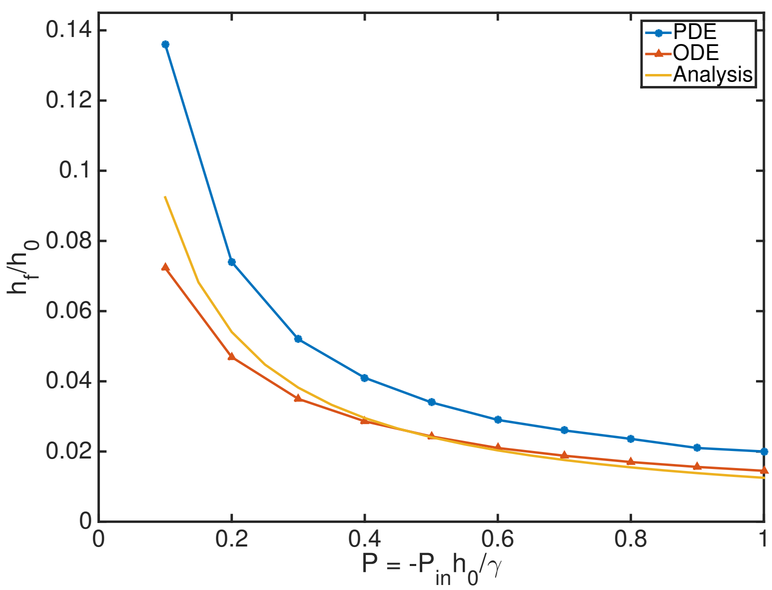

Fig. 4. (color online) Film thickness h_f/h_0 as a function of $\mathcal{P}$ with the same capillary number $Ca = 1 \times 10^{-3}$ for the numerical simulation of the ODE system (16), the numerical simulation of the PDE system (10) and the prediction analysis (23).

4. Conclusion

In this paper we 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 $h_f(t)$ using the approximate formulation (11). Both equations give similar prediction on how the steady film thickness h_f depends on the substrate velocity U and the reservoir pressure P_{in}. Also both equations indicate that the celebrated scaling law $h_f \propto (Ca)^{2/3}$ holds for very small capillary number Ca, but significant deviation is seen 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. The error may be reduced by introducing more parameters to approximate $h(x,t)$ or by considering more suitable form for $h(x,t)$, but this will be a future work.

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