Leveling of thin films of colloidal suspensions

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ABSTRACT

We present an analysis of leveling in thin films of colloidal suspensions. The colloidal particles are assumed to be much smaller than the film thickness and influence the film rheology through a concentration-dependent viscosity and bulk diffusivity. A system of coupled nonlinear partial differential equations based on lubrication theory is used to describe the film height and the particle concentrations in the bulk and at the film surface. Linear stability analysis is applied to develop expressions for leveling rates in a number of limiting cases. It is found that for soluble particles, there exist regimes where increasing the Marangoni number slows down leveling at both short and long times, in contrast to the case of insoluble particles. Nonlinear simulations show that the linear theory accurately predicts leveling times even for large amplitude disturbances, and that the presence of a concentration-dependent viscosity and bulk diffusivity speed up leveling. The results of this work should be useful for estimating leveling rates in coatings laden with colloidal particles, and also in coatings containing soluble surfactant.

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1. Introduction

Liquids used in coating processes are often colloidal suspensions, and the resulting products are integral to numerous technologies such as abrasion-resistant coatings, displays, and solar cells [1]. In most coating applications, a thin film of uniform thickness is desired but may be difficult to achieve if irregularities in the coated liquid film do not level before the film solidifies. Often, there exists a finite time between the stage where liquid is applied to a substrate and downstream processes such as curing and drying. It is therefore crucial to understand the factors that influence the leveling of thin liquid films.

The importance of leveling to coating processes was recognized decades ago by Orchard, who developed expressions for leveling rates in films of Newtonian liquids from the linearized Navier–Stokes equations [2]. Kheshgi and Scriven further investigated leveling of Newtonian liquids through long-wave expansions and finite-element solutions of the Navier–Stokes equations [3]. In thin films of Newtonian liquids, the driving force for leveling is surface tension, which forces liquid movement through gradients in capillary pressure. There have also been studies of leveling in viscoelastic [4,5] and shear-thinning liquids [6], and a review of leveling research is given in Ref. [7].

When colloidal particles are added to a Newtonian liquid, new factors arise that can influence leveling such as non-Newtonian rheology and Marangoni flows caused by particle adsorption to the liquid–air interface. For particle diameters much smaller than the liquid film thickness, the presence of particles can fruitfully be described with continuum models. Such models generally involve mass and momentum conservation equations with a concentration-dependent viscosity, and convection–diffusion equations describing particle transport in the bulk and at the liquid–air interface. The lubrication approximation is also frequently invoked. As discussed below, different versions of these models have been used to study various phenomena in thin liquid films, but a comprehensive analysis of leveling in thin films of colloidal suspensions appears not to have been carried out.

Bousfield developed a lubrication model for leveling in a suspension that accounts for concentration-dependent viscosity, convection of particles in the bulk, and loss of liquid into the substrate and air, but not Marangoni flows [8]. A similar model accounting for Marangoni flows was developed by Wilson, but it assumes that the surface particle concentration is the same as the bulk particle concentration evaluated at the liquid–air interface [9]. Warner et al. studied evaporation and rupture in thin liquid films of colloidal suspensions using a model with surface concentration as a separate variable [10]. The films are assumed to be thin enough so that the the bulk concentration can be replaced by its value averaged over the film thickness. Yiantsios and Higgins also studied evaporation in thin films of colloidal suspensions [11]. Their model does not have surface concentration as a separate variable, but does account for thermal effects and the dependence of bulk diffusivity on particle concentration. Marangoni flows driven by gradients in

temperature, rather than concentration, are considered. Although the models of the latter two studies are more detailed than those of the former two, the issue of leveling was not specifically addressed.

The purpose of the present contribution is to investigate leveling in thin films of colloidal suspensions, accounting for Marangoni flows due to concentration gradients and particle adsorption to the liquid–air interface. Because we wish to focus on how these factors control leveling rates, our model does not incorporate evaporation, substrate absorption of liquid, or the van der Waals forces that induce film rupture. Our model is similar to that of Ref. [10], but also incorporates a concentration-dependent bulk diffusivity as in Ref. [11]. In one limiting case, the model reduces to that used for describing how insoluble surfactants affect leveling [12,13], and in another limiting case it generalizes that model to account for surfactant solubility. We thus expect that the results of our work will be useful for estimating leveling rates in coatings laden with colloidal particles or surfactants. The model is presented in Section 2, a linear stability analysis is given in Section 3, nonlinear simulations follow in Section 4, and conclusions are noted in Section 5.

2. Model

We consider a two-dimensional isothermal thin film of incompressible Newtonian liquid laden with hard, spherical particles which is resting on a flat, rigid, impermeable substrate as shown in Fig. 1. Here, x denotes the horizontal direction, z corresponds to the vertical direction, and t is time. Henceforth, subscripts of either x, z, or t denote partial derivatives with respect to the subscripted variable. The liquid–air interface is located at $z = h(x, t)$ and the substrate lies at $z = 0$. Particles can exist in two regions: at the surface and in the bulk. The particle concentration at the surface is represented by s, and c represents the particle concentration in the bulk. The adsorption and desorption of particles are the mechanisms which allow particles to move from the surface to the bulk and vice versa.

We note that our model cannot describe phenomena such as particle protrusion through the liquid–air interface and the formation of contact lines. Within our model, particles are treated in a manner similar to the way surfactants are described in thin-film studies; such an approach was used in Refs. [9,10]. Both insoluble and soluble particles will be considered, and by the former we simply mean that particles are confined to the surface and cannot desorb into the bulk as in the latter case. The following sections describe the equations that govern this model and simplify the equations down to three evolution equations: one governing film height, one describing surface concentration, and one accounting for bulk concentration.
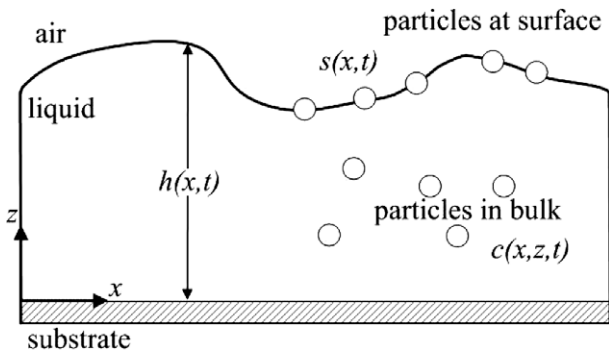

Fig. 1. A schematic of the model system.

2.1. Film height

A length scale in the x-direction is defined by a disturbance of wavelength L on an film with an initial uniform thickness of h_0. The disturbances can be considered long-scale if $\varepsilon \equiv h_0/L \ll 1$. To non-dimensionalize the governing equations, the horizontal and vertical dimensions are scaled so that $X = \varepsilon x/h_0$ and $Z = z/h_0$. The film height is scaled by the initial thickness, $H = h(x, t)/h_0$. The velocity in the x-direction is scaled so that $U = u/U_0$, where U_0 is a characteristic velocity of the problem, which is taken to be $\sigma_o \varepsilon^3/\mu_o$. Here, σ_o and μ_o are the surface tension and viscosity, respectively, of the liquid in the absence of particles. The velocity in the z-direction is non-dimensionalized so that $W = w/\varepsilon U_0$. Time is scaled so that $T = \varepsilon t U_0/h_0$. Using these scalings, the equation governing mass conservation in the liquid is

$$U_X + W_Z = 0. \tag{1}$$

The dimensional equations governing momentum conservation are

$$\rho(u_t + uu_x + wu_z) = -p_x + (\mu u_x)_x + (\mu u_z)_z, \tag{2}$$
$$\rho(w_t + uw_x + ww_z) = -p_z + (\mu w_x)_x + (\mu w_z)_z. \tag{3}$$

where ρ and μ are the density and viscosity, respectively. We will assume that the film is thin enough so that gravity can be neglected in the above equations. The viscosity is assumed to be a function of the bulk particle concentration (represented as a volume fraction) and is scaled so that

$$M(C) = \frac{\mu(C)}{\mu_0} = \left(1 - \frac{C}{0.64}\right)^{-2}, \tag{4}$$

where C is the z-averaged bulk particle volume fraction. The variable M thus represents a dimensionless viscosity. This Krieger–Dougherty-like relationship [14] is commonly used to calculate the viscosity of hard-sphere suspensions [15]. Pressure is scaled so that $P = \varepsilon h_0 p/\mu_0 U_0$. Using the above scalings and the lubrication approximation, which essentially eliminates $O(\varepsilon)$ terms, the dimensionless momentum conservation equations become

$$0 = -P_X + (MU_Z)_Z, \tag{5}$$
$$0 = -P_Z. \tag{6}$$

At the substrate, no-slip and no-penetration conditions hold

$$U(Z = 0) = W(Z = 0) = 0. \tag{7}$$

The dimensionless kinematic condition at the liquid–air interface ($Z = H$) is

$$W = H_T + UH_X. \tag{8}$$

The dimensional force balance at the liquid–air interface has the form

$$\mathbf{T} \cdot \mathbf{n} = -\frac{h_{xx}}{[1 + h_x^2]^{\frac{3}{2}}} \sigma \mathbf{n} + \nabla_I \sigma \quad \text{at } z = h(x, t) \tag{9}$$

where $\mathbf{T}$ is the stress tensor, ∇_I is the one-dimensional surface gradient operator, and σ is the surface tension. The normal and tangential vectors are

$$\mathbf{n} = \frac{(-h_x \mathbf{i}, \mathbf{k})}{(1 + h_x^2)^{\frac{1}{2}}}, \tag{10}$$

and

$$\mathbf{t} = \frac{(\mathbf{i}, h_x \mathbf{k})}{(1 + h_x^2)^{\frac{1}{2}}}, \tag{11}$$

respectively, where $\mathbf{i}$ and $\mathbf{k}$ are the unit vectors in the x- and z-directions. The non-dimensional form of the surface tension is taken to be