STABILITY OF ELECTROLYTE FILMS ON STRUCTURED SURFACES

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We investigate the stability of a thin film of liquid electrolyte on an electrically charged structured surface with a periodic array of gas-filled grooves. We derive a nonlinear evolution equation for the film thickness by taking into account the effects of structuring into our system of lubrication-type equations. We analyze how the introduction of structuring destabilizes the film by increasing either the Navier slip length or the length of the groove at the no-shear segments. We perform nonlinear simulations for the evolution of the film thickness to show that structuring decreases the rupture time with respect to a thin film on a solid surface.

KEY WORDS: thin films, rupture, stability analysis, electrostatic forces, structured surfaces

1. INTRODUCTION

In multiphase flows, the transport of bubbles and drops is critical in the development of many applications such as cooling/heating devices (Kabov et al., 2011), dynamics of the tear film in the eye (Braun, 2012), and microfluidic systems (Stone et al., 2004). Gravity-driven and pressure-driven flows become ineffective on the micro- and nanoscale. Also, as the length scale decreases, surface tension, electrostatic, and dispersion effects become more predominant than inertial effects. One of the limitations of pressure-driven flows at small scales is related to the fact that the liquid has to satisfy the no-slip condition at the solid wall.

Liquid flows in microfluidics can be enhanced with the introduction of hydrophobic surfaces; a hydrophobic surface repels the liquid and reduces the friction between the solid and the liquid, thus enhancing the flow by increasing the slip length at the surface. The slip length is generally defined as an extrapolated distance relative to the substrate where the tangential velocity component vanishes. Schnell (1956) obtained a small but measurable slip length in water flowing over glass treated with a water-repellent silane vapor for capillary tubes of various diameters. Churaev et al. (1984) also reported the slippage of water and mercury in thin quartz capillaries (smaller than 1 mm in radius) treated with silane vapor. Recent experiments on the flow properties of water near a hydrophobic surface are discussed in Vinogradova (1999). Lauga et al. [chapter 19 of Tropea et al. (2007)] provide an overview of the experimental, numerical, and theoretical investigations on the slip length of liquid flows on hydrophobic surfaces and the different experimental methods that have been used to measure slip in Newtonian liquids. The experimental results of Watanabe and Udagawa (1999) have shown that a significant drag reduction can be achieved for water laminar flows down a cylindrical pipe treated with hydrophobic silica.

The studies mentioned above constructed hydrophobic substrates by coating the substrate with a water-repellent vapor or a chemical solution. Another method to achieve hydrophobicity is to use structured surfaces, i.e., a solid with a roughness of the order of micro-nanometers that has cavities or grooves filled with gas. Structured surfaces have superhydrophobic or ultrahydrophobic properties and have been the main method for increasing the slip length in fluids since the gas-filled cavities provide no-shear segments (segments with perfect slip). The review of Rothstein (2010) discusses the theoretical and experimental studies that use structured surfaces for producing significant drag reduction in both laminar and turbulent pressure-driven flows. This review mentions that structuring can be used to enhance mixing in laminar flows and enhance the slip in diffusion-osmotic flows.
For pressure-driven flows, Ou and Rothstein (2005) fabricated ultrahydrophobic surfaces with precise patterns of micrometer-sized ridges and experimentally found a maximum slip velocity of nearly 20 mm per second at the center of the water-gas interface. They also showed that slip along the no-shear segments is the primary mechanism responsible for the drag reduction observed in flows over ultrahydrophobic surfaces. Cottin-Bizzone et al. (2004) investigated the effects of surface heterogeneity on liquid flow slippage by considering molecular dynamics simulations and continuum hydrodynamics; they estimated effective slip lengths for different microscopic slip lengths and no-shear strip widths.

Teo and Khoo (2009) obtained analytical solutions for a pressure-driven Stokes flow through microchannels employing superhydrophobic surfaces with alternating microgrooves (gas-filled cavities) and solid segments (or ribs) patterned on one or both channel walls where the grooves, are parallel and perpendicular to the flow direction. They determined that the effective slip length increases with the shear-free fraction, and that for a fixed shear fraction, the normalized slip length is higher for longitudinal grooves which is consistent with the results of Sbragaglia and Prosperetti (2003). Lauga and Stone (2003) analytically solved the Stokes flow problem of a pressure-driven flow in
a cylindrical pipe for two different configurations of zero shear strips and evaluated the effective slip length as the relative width of the no-shear stress region increases. Ybert et al. (2007) obtained scaling laws for the effective slip at the superhydrophobic surface in terms of the roughness length scale, depth of the grooves, and fraction of the no-shear region, compared them to numerical results in various geometries, and predicted that slip lengths of up to 100 mm can be achieved for an optimized patterned surface. The numerical simulations of Cheng et al. (2009) extended the validity of the scaling laws of Ybert et al. (2007) to high Reynolds numbers and to other geometries, such as arrays of posts and poles. They showed that channel wall confinement effects increase the effective slip length for square posts and longitudinal grooves and decrease the effective slip length for square holes and transverse grooves.

Based on the studies we reviewed, it is clear that in pressure-driven flows the slip length is increased significantly with the introduction of structuring. It is also known that electrokinetic and electroosmotic effects provide an enhancement of transport rates compared to pressure-driven flows and allow one to maintain relatively high transport rates at decreasing length scales, even if there is no slip at the solid substrate. Squires (2008) considered electrokinetic flows over inhomogeneously slipping and inhomogeneously charged surfaces. He concluded that electroosmotic flows with uniformly charged surfaces show a macroscopic slip length enhancement, while surfaces whose slip regions are uncharged (as it usually happens at an air-water interface) show no enhancement due to slip. Zhao (2010) conducted numerical simulations of electroosmotic flows over a periodically striped superhydrophobic surface and showed that this surface has a larger effective Navier slip length than a smooth surface. He concluded that an electroosmotic flow can be enhanced only when the liquid-gas interface is charged and when there is an appropriate zeta potential at the surface that does not reduce the tangential component of the electric field. By analyzing the electroosmotic mobility and its relation to the hydrodynamic slippage, Bahga et al. (2010) showed that a significantly enhanced electroosmotic flow is possible only with charged liquid-gas interfaces and that the electroosmotic mobility for an uncharged liquid-gas interface is the same as for a homogeneous no-slip solid substrate, i.e., there is no flow enhancement due to the slip regions.

All of the previous studies on electroosmotic flows over a superhydrophobic surface have shown that the slippage is significant only when the liquid-gas interfaces are charged. Steffes et al. (2012) propose that electric charges at liquid-gas interfaces can be controlled by adding complementary electrodes within the structure to attract ions from the bulk liquid to the interface. In this theoretical study, the additional charge leads to a moderate enhancement of the electroosmotic flow if the cavity medium is air, but to a significant enhancement if the cavity has high relative electric permittivity, e.g., if it is filled with transformer oil.

A necessary condition for the efficient microscale transport of bubbles or drops in microscale fluid systems is that the bubble or drop does not get attached to the solid substrate. Hence it is necessary to analyze the stability of thin liquid films and the conditions of film rupture. The studies of Ajaev (2013), Burelbach et al. (1988), Craster and Matar (2009), Oron et al. (1997), and Williams and Davis (1982) discuss thin-film rupture on flat solid substrates. The stability of thin films on structured surfaces is still an active area of research. Previous works of Ajaev et al. (2011), Davalos-Orozco (2007), Kabova et al. (2006), Kargupta and Shama (2002), Sharma et al. (2003), and Thiele et al. (2003) have developed a general framework for numerical studies of film stability on structured, smoothly deformed, or chemically patterned surfaces. Ajaev et al. (2011) investigated film rupture on a structured surface under the action of London-van der Waals forces. They considered periodic transverse grooves and took into account the effect of slip due to the presence of no-shear regions at the liquid-gas interfaces. They showed that structuring destabilizes the film by increasing the growth rate of the fastest growing instability and that film rupture is accelerated and is also possible for films that are stable on a flat solid substrate. The stability theory for van der Waals thin-film rupture on structured surfaces is further verified in Ajaev et al. (2012). Numerical simulations based on Fourier discretization are used to show that the thin film eventually ruptures for any small random perturbation to the initial liquid profile.

The limitations of a numerical approach include a high computational cost, large computational domains, and interpolation errors. An alternative is the application of Floquet theory [discussed, e.g., in Chapt. 2 of Chicone (2006)] to obtain analytical stability criteria for Stokes flows. Floquet theory has been used in fluid dynamics to analyze the stability of time-periodic flows (Davis, 1976) and to find steady-state solutions of partial differential equations with periodic varying coefficients (Patterson and Bailey, 2010). Trifonov (2007) conducted a theoretical analysis of the stability of a gravity-driven flow down a corrugated surface, and they showed that for moderate Reynolds numbers the surface has a stabilizing effect for certain corrugation parameters. D’Alessio et al. (2009) also analyzed the stability...
of a thin film on corrugated substrates and verified the analytical predictions by performing numerical simulations for the evolution of the perturbed equilibrium flow. Kao et al. (2006) analyzed the stability and rupture of thin liquid films on chemically patterned solid substrates and performed a nonlinear stability analysis to determine film profiles, growth rates, and rupture times.

Ajaev et al. (2013) studied the stability of liquid films on structured surfaces for van der Waals dispersion forces and compared the analytical results obtained by the use of Floquet theory with the numerical results of Ajaev et al. (2012). Furthermore, they solved the full Stokes stability model and showed that the lubrication-type approximation is justified for a range of film thicknesses smaller than the characteristic wavelength of the instability.

The objective of the present paper is to investigate the stability of an electrolyte film on a charged structured surface. In Sec. 2, we describe the general dimensional model and the interfacial boundary conditions. In Sec. 3, we obtain the system of lubrication-type equations that allows us to derive the film thickness evolution equation of Sec. 4. In Sec. 5, we describe the application of Floquet theory to analyze the stability of a film on a structured surface and compare it with the stability of an electrolyte film on a flat solid surface. In Sec. 6, we make further comparisons between both cases by performing nonlinear simulations of the film thickness evolution equation.

2. FORMULATION

The geometry of the problem is illustrated in Fig. 1. The liquid film is in contact with a surface structured by an array of parallel grooves. The grooves of the surface are filled with gas so that the liquid does not enter the grooves. At the bottom, the liquid is thus bounded by the structured surface which consists of segments corresponding to the solid and the liquid-gas menisci segments. The dimensional groove length is denoted by $w^*$ and the dimensional distance between the grooves by $l^*$. The top liquid-gas interface of the film is described by the function $y^* = h^*(x^*, t^*)$.

The general dimensional model for the electrolyte film is the following:

$$\frac{\rho D u^*}{D t^*} = \nabla^* \cdot (T^f + T^e)$$

(1)

$$\nabla^* \cdot u^* = 0$$

(2)

$$\nabla^* h^* = \lambda^2 \frac{\psi^*}{D^2}$$

(3)

$$\vec{E}^* = -\nabla^* \psi^*$$

(4)

![Sketch of a liquid film on a structured surface.](image)

FIG. 1: Sketch of a liquid film on a structured surface.
The fluid stress tensor $T^f$ is
\begin{equation}
T^f = p^* I + \frac{1}{2} \mu \left( \nabla^* \tilde{u}^* + \nabla^* \tilde{u}^{*T} \right) \tag{5}
\end{equation}
and the electrostatic effects are included in the Maxwell stress tensor $T^e$,
\begin{equation}
T^e = \varepsilon \left( \tilde{E}^* \tilde{E}^* - \frac{1}{2} \left| \tilde{E}^* \right|^2 I \right) \tag{6}
\end{equation}
where $p^*$ is the dimensional pressure, $\tilde{E}^*$ is the dimensional electric field, and $I$ is the identity matrix.

The electrostatic potential of the electrolyte film satisfies the Debye-Hückel Eq. (3). The Debye length or screening length denoted by $\lambda_D$ corresponds to an electrolyte film with $N$ different types of ions of valencies $z_j$ and bulk concentrations $n_j$ ($j = 1, 2, \cdots, N$).
\begin{equation}
\lambda_D = \sqrt{\frac{\varepsilon k_B T^*}{e^2 \sum_{j=1}^{N} n_j z_j^2}} \tag{7}
\end{equation}
At the liquid-gas interface $y^* = h^*(x^*, t^*)$, we apply the constant surface charge density condition (8), the tangential stress condition (9), and the normal stress condition (10).
\begin{equation}
\psi^*_{y^*} = \frac{1}{\varepsilon} q_2^* \tag{8}
\end{equation}
\begin{equation}
\| \tilde{n} \cdot \left( T^f + T^e \right) \cdot \tilde{t} \| = 0 \tag{9}
\end{equation}
\begin{equation}
\| \tilde{n} \cdot \left( T^f + T^e \right) \cdot \tilde{n} \| = \sigma K^* \tag{10}
\end{equation}
The double bars $\| (\circ) \|$ denote the jump across the liquid-gas interface, i.e., $(\circ)_{\text{gas}} - (\circ)_{\text{liquid}}$.

Additionally, we have a standard kinematic boundary condition.
\begin{equation}
h^*_{x^*} + u^* h^*_{x^*} = v^* \tag{11}
\end{equation}
At the structured surface $y^* = 0$, we have a no-penetration boundary condition (12), a constant surface charge density condition (13), and a tangential stress condition (14) that incorporates a Navier slip length for the no-shear segments:
\begin{equation}
v^* = 0 \tag{12}
\end{equation}
\begin{equation}
\psi^*_{y^*} = -\frac{1}{\varepsilon} q_1^* \tag{13}
\end{equation}
\begin{equation}
\mu u^* = \beta^*(x^*) \| \tilde{n} \cdot \left( T^f + T^e \right) \cdot \tilde{t} \| \tag{14}
\end{equation}
where $\beta^*(x^*)$ is the dimensional Navier slip length along the structured surface. If the Navier slip length is zero, the tangential stress condition (14) reduces to a no-slip condition, which is often the case for a solid surface with no hydrophobic properties. As the Navier slip length increases, the tangential stress condition (14) converges to the tangential stress condition (9) obtained for the top liquid-gas interface.

In our model we assume that the liquid-gas interface at the structured surface is flat. If the size of the groove between the structured surface is sufficiently small, the liquid does not enter the groove due to surface tension effects. Ybert et al. (2007) examined the influence of the meniscus curvature in the groove and found that the shape of the meniscus has a minimal influence on the flow in the liquid phase.
3. LUBRICATION MODEL

Following the standard lubrication-type approach (Ajaev, 2012), applicable for the scale of interface deformations being much larger than the film thickness, and neglecting the effects of gravity, we introduce vertical and horizontal length scales defined by \( d \) and \( \text{Ca}^{-1/3}d \), respectively, where \( \text{Ca} = \mu U/\sigma \) is the capillary number based on the velocity scale defined below in Eq. (16). We can use the linearized Grahame equation (Grahame, 1947) to obtain a characteristic electrostatic potential \( \Psi \) that relates the electrostatic potential to the constant surface charge density at the structured surface.

\[
\Psi = \frac{q^* \lambda_D}{\epsilon} \quad (15)
\]

The velocity and pressure scales,

\[
U = \left( \frac{\epsilon d}{\mu \sigma^{1/2}} \frac{\Psi^*}{\lambda_D^3} \right)^{3/2} \quad (16)
\]

\[
P = \frac{\epsilon \Psi^*}{\lambda_D} \quad (17)
\]

are obtained by considering the balance between the electrostatic, capillary, and viscous contributions in the film through a dimensional analysis of the general model (1).

The dimensional horizontal and vertical velocity components, \( u^* \) and \( v^* \), the pressure \( p^* \), and time \( t^* \) can now be used to define the corresponding nondimensional variables according to

\[
u = \frac{u^*}{U} \quad (18)
\]

\[
v = \frac{v^*}{\text{Ca}^{1/3} U} \quad (19)
\]

\[
p = \frac{p^*}{P} \quad (20)
\]

\[
\psi = \frac{\psi^*}{\Psi} \quad (21)
\]

\[
t = \frac{U t^*}{3d \text{Ca}^{-1/3}} \quad (22)
\]

The scale for \( v \) is chosen such that the nondimensional equation of continuity has the standard form and the time scale is based on the kinematic boundary condition at the interface.

The complete dimensionless Stokes model, with the dimensionless variables defined in Eqs. (18)–(22), is

\[
p_x - \psi \psi_{xx} = \text{Ca}^{2/3} u_{xx} + u_{yy} \quad (23)
\]

\[
p_y - \psi \psi_y = \text{Ca}^{2/3} \left( \text{Ca}^{2/3} v_{xx} + v_{yy} \right) \quad (24)
\]

\[
u_x + v_y = 0 \quad (25)
\]

\[
\text{Ca}^{2/3} \psi_{xx} + \psi_{yy} = \kappa^2 \psi \quad (26)
\]

where \( \kappa \) is the film thickness scaled by the Debye length,

\[
\kappa = \frac{d}{\lambda_D} \quad (27)
\]
At the liquid-gas interface, the dimensionless tangential condition (28) and normal stress condition (29) are

\[
\left(1 + \frac{Ca^{2/3}h_x^2}{\kappa^2}\right) \left(u_y + Ca^{2/3}v_x\right) + 2Ca^{2/3}(v_y - u_x) + \frac{1 + Ca^{2/3}h_x^2}{\kappa^2}\psi_x\psi_y - \frac{h_x}{\kappa^2} \left(\psi_y + Ca^{2/3}\psi_x^2\right) = 0 \tag{28}
\]

\[
\left(1 + \frac{Ca^{2/3}h_x^2}{\kappa^2}\right)(p_o - p) + 2Ca^{2/3}(v_y + Ca^{2/3}h_x^2u_x) + \frac{1}{2\kappa^2} \left[\psi_y^2 - Ca^{2/3}\psi_x^2\right] = \frac{h_{xx}}{\left(1 + Ca^{2/3}h_x^2\right)^{1/2}} \tag{29}
\]

At the liquid-gas interface \(y = h\), we also have a dimensionless kinematic boundary condition (30) and a constant surface charge density condition (30),

\[
h_t + 3(\mu h_x - v) = 0 \tag{30}
\]

\[
\psi|_{y=h} = \kappa \hat{q} \tag{31}
\]

where \(\hat{q} = q^2 / q_1^2\) is the ratio of the dimensional constant surface charge densities of Eqs. (8) and (13).

At the structured surface \(y = 0\), we have a dimensionless no-penetration condition (32), a constant surface charge density condition (33), and a dimensionless tangential stress condition (34):

\[
u = 0 \tag{32}
\]

\[
\psi|_{y=0} = -\kappa \tag{33}
\]

\[
\frac{\mu}{\beta(x)} = \left(1 + \frac{Ca^{2/3}h_x^2}{\kappa^2}\right) \left(u_y + Ca^{2/3}v_x\right) + 2Ca^{2/3}(v_y - u_x) + \frac{1 + Ca^{2/3}h_x^2}{\kappa^2}\psi_x\psi_y - \frac{h_x}{\kappa^2} \left(\psi_y^2 + Ca^{2/3}\psi_x^2\right) \tag{34}
\]

For a small capillary number \(Ca = \mu U / \sigma \ll 1\), we can neglect the higher order terms of the dimensionless Stokes model (23)–(26) and we can simplify considerably the dimensionless boundary conditions (28)–(34) at both interfaces.

The dimensionless Stokes model simplifies to the following lubrication-type model:

\[
p_x - \psi \psi_x = u_{yy} \tag{35}
\]

\[
p_y - \psi \psi_y = 0 \tag{36}
\]

\[
u_x + v_y = 0 \tag{37}
\]

\[
\psi_{yy} = \kappa^2 \psi \tag{38}
\]

At the liquid-gas interface, the dimensionless liquid shear stress and normal stress conditions simplify to

\[
u_y|_{y=h} = -\hat{q} \left(\frac{\hat{q} h + \psi}{\kappa}\right)|_{x=h} \tag{39}
\]

\[
p - p_o = -h_{xx} + \frac{\hat{q}^2}{2} \tag{40}
\]

while the dimensionless kinematic boundary condition (30) and the no-penetration boundary condition (32) remain unchanged.

At the structured surface \(y = 0\), we have a dimensionless Navier slip condition that takes into account the effects of the tangential electric field.

\[
u|_{y=0} = \beta(x) \left[u_y + \left(h + \frac{\psi}{\kappa}\right)\right]|_{y=0} \tag{41}
\]
The electrostatic potential of the electrolyte film satisfies the Debye–Hückel equation (38) with the constant surface charge density conditions (31) and (33). The potential everywhere in the field is
\[
\psi = \frac{\cosh \kappa (h - y) + \hat{q} \cosh \kappa y}{\sinh (\kappa h)}
\] (42)

while the derivative of the potential with respect to the film interface, denoted by \(\psi_h\), is
\[
\psi_h = \kappa \frac{\sinh \kappa (h - y) \sinh \kappa h - \cosh \kappa h [\cosh \kappa (h - y) + \hat{q} \cosh \kappa y]}{\sinh^2 (\kappa h)}
\] (43)

To simplify the notation, we use the differentiation chain rule to rewrite the dimensionless liquid shear stress condition (39) and the dimensionless Navier slip condition (41) as
\[
u_x = -\hat{q}_y (\hat{q} + \kappa^{-1} \psi_{h2})
\] (44)

\[
u = \beta (x) \left[ \nu_y + \left( \frac{1 + \psi_{h1}}{\kappa} \right) h_x \right]
\] (45)

where the variables \(\psi_{h2}\) and \(\psi_{h1}\) are the derivatives of the potential with respect to the film interface evaluated at the liquid-gas interface \(y = h\) and structured surface \(y = 0\), respectively.

\[
\psi_{h2} = \psi_h \bigg|_{y=h} = -\kappa \cosh \kappa h \left( 1 + \hat{q} \cosh \kappa h \right) \sinh^2 (\kappa h)
\] (46)

\[
\psi_{h1} = \psi_h \bigg|_{y=0} = -\kappa \frac{1 + \hat{q} \cosh \kappa h}{\sinh^2 (\kappa h)}
\] (47)

4. FILM THICKNESS EVOLUTION EQUATION

We integrate Eq. (35) and use the liquid shear stress equation, Eq. (44), to obtain
\[
u_y = (p_x - \psi \psi_x) (y - h) - \hat{q}_x (\hat{q} + \kappa^{-1} \psi_{h2})
\] (48)

and we use the normal stress condition (40) to rewrite Eq. (48) as
\[
u_y = -\left( h_{xx} + \frac{1}{2} \psi_x^2 \right)_x (y - h) - \hat{q}_x (\hat{q} + \kappa^{-1} \psi_{h2})
\] (49)

By integrating Eq. (49) and using the Navier slip condition (45), we obtain the horizontal velocity profile.
\[
u = -\frac{1}{2} \left( h_{xx} + \frac{1}{2} \psi_x^2 \right)_x (y^2 - 2yh) - \hat{q}_x (\hat{q} + \kappa^{-1} \psi_{h2})
\] (50)

By substituting the flow rate Eq. (51),
\[
\bar{u} = \frac{1}{3} h^3 \left( h_{xx} + \frac{1}{2} \psi_x^2 \right)_x - \frac{1}{2} \hat{q}_x h_x (\hat{q} + \frac{\psi_{h2}}{\kappa})
\] (51)
into the kinematic boundary condition (30), we obtain a dimensionless evolution equation for the film thickness:

\[ h_t + h^3(h_{xx} + \frac{1}{2} \psi^2)_x - 3\frac{\hat{q}}{k} h^2 h_x(\hat{q} + \frac{1}{k} \psi_{h2})_x + 3 \left[ \beta(x) h \left( h_{xx} + \frac{1}{2} \psi^2 \right)_x \right. \\
\left. + h_x \left[ 1 - \hat{q}^2 + \frac{\psi_{h1}}{k} - \frac{\hat{q}\psi_{h2}}{k} \right] \right]_x = 0 \]  

(52)

where \( \psi_2 \) is the electrostatic potential Eq. (42) at the liquid-gas interface \( y = h \).

Note that the first term describes the effects of the electrostatic component of disjoining pressure and the effects of the liquid shear stress, while the second term describes the effects of the Navier slip length. The evolution equation (52) for the structured case reduces to the solid surface model found in Ketelaar and Ajaev (2014) if there is no slip \( \beta(x) = 0 \). In this model it was found that film rupture in finite time is expected if the double layers overlap significantly.

5. LINEAR STABILITY ANALYSIS

For the structured surface model, the constant thickness solution \( h = 1 \) is a solution to the evolution Eq. (52). If we consider a small perturbation to this solution \( h = 1 + \zeta(x) \) we obtain the following linearized interface equation:

\[ \zeta_t + \left[ \zeta_{xxx} + \zeta_x \left( \psi_2 \psi_{2h} \right) \left( \hat{q} + \frac{\psi_{h2}}{k} \right) \right]_x \]

\[ + 3 \left[ \beta(x) \left[ \zeta_{xxx} + \zeta_x \left( \psi_2 \psi_{2h} + 1 - \hat{q}^2 + \frac{\psi_{h1}}{k} - \frac{\hat{q}\psi_{h2}}{k} \right) \right] \right]_x = 0 \]  

(53)

where \( \psi_{2h} \) is the derivative of the potential at the liquid-gas interface with respect to the film thickness evaluated at \( h = 1 \).

\[ \psi_{2h} = -\kappa \frac{\cosh \kappa + \hat{q}}{\sinh^2 \kappa} \]  

(54)

For the linearized model, the potential at each of the interfaces is evaluated at \( h = 1 \). Note that this linearized interface shape equation (53) is no longer a constant-coefficient equation; hence, we cannot obtain a dispersion relation using the standard normal mode analysis that can be used for the solid surface case. Also note that when there is zero slip at the structured surface, \( \beta = 0 \), we get the linearized interface equation of the solid surface case, as discussed in Ketelaar and Ajaev (2014).

We are going to use Floquet theory to analyze the stability of the linearized interface shape equation (53). The classical Floquet theory, which can be found in chapter 2 of Chicone (2006), studies the solution of the following time-dependent homogeneous linear system of differential equations with periodic coefficients:

\[ \tilde{\zeta}_x = A(x)\tilde{\zeta} \]  

(55)

where \( \tilde{\zeta} \) is a vector function of space, and \( A(x) \) is a matrix function whose entries are \( L \)-periodic functions of \( x \).

The main result of Floquet’s theorem considers the change of coordinates \( \tilde{\zeta} = P(x)\tilde{y} \) to transform a periodic coefficient linear system to a real constant coefficient linear system \( \tilde{y} = By \). The fundamental solution for the periodic differential equation (55) is

\[ \tilde{\zeta}_x = M(x)e^{Bx} \]  

(56)

where \( M(x) \) is an \( L \)-periodic matrix, and \( B \) is a matrix independent of space.

If \( \mu_f \) is a characteristic exponent for the homogeneous linear periodic differential equation (55), then \( \mu_f \) is an eigenvalue of the matrix \( B \). The periodic-coefficient linear system has a nontrivial complex solution of the form

\[ \tilde{\zeta}(x) = m(x)e^{\mu_f x} \]  

(57)

where \( m(x) \) is an \( L \)-periodic function.
Studies of stability of time-periodic flows often rely on Floquet theory, as discussed in the review of Davis (1976). However, Floquet theory can also be used to find solutions of partial differential equations with periodic spatial variations of the coefficients. In fluid mechanics, Trifonov (2007) and D’Alessio et al. (2009) used Floquet theory to study gravity-driven flows on inclined solid surfaces that have periodic spatial variations. An application of Floquet theory to analyze the stability of a film under the action of van der Waals dispersion forces on structured surfaces can be found in Ajaev et al. (2013).

The linearized interface shape equation is a partial differential equation with \( L \)-periodic coefficients on the horizontal scale. Using the application of Floquet theory, the solutions of Eq. (53) can be written in the form \( \zeta = e^{\gamma t} \hat{\zeta} (x) \).

The conditions of instability can be determined by analyzing the following time-independent equation for the spatial perturbation \( \hat{\zeta} \):

\[
\gamma \hat{\zeta} + \left\{ \hat{\zeta}_{xxx} + \hat{\zeta}_x \left[ \psi_2 \psi_{2h} - \frac{3}{2} \hat{q} \left( \hat{q} + \frac{\psi_{h2}}{\kappa} \right) \right] \right\}_x + 3 \left\{ \hat{\zeta}_{xxx} + \hat{\zeta}_x \left[ \psi_2 \psi_{2h} + 1 - \hat{q}^2 + \frac{\psi_{h1}}{\kappa} - \frac{\psi_{h2}}{\kappa} \right] \right\}_x = 0 \tag{58}
\]

It is helpful if we consider a new perturbation function \( \eta(x) \) such that \( \eta_x = \hat{\zeta} \). Then we can integrate Eq. (58) in \( x \) to obtain the following fourth-order differential equation:

\[
\gamma \eta + \eta_{xxxx} + \eta_{xx} \left[ \psi_2 \psi_{2h} - \frac{3}{2} \hat{q} \left( \hat{q} + \frac{\psi_{h2}}{\kappa} \right) \right] + 3 \beta(x) \left[ \eta_{xxx} + \eta_{xx} \left( \psi_2 \psi_{2h} + 1 - \hat{q}^2 + \frac{\psi_{h1}}{\kappa} - \frac{\psi_{h2}}{\kappa} \right) \right] = 0 \tag{59}
\]

Since the Navier slip length depends on the horizontal length, we need to consider a functional dependence for the Navier slip length at the structured surface. Usually we have a no-slip boundary condition \( u = 0 \) at the solid segments of the surface, while we have a constant Navier slip length (denoted by \( \beta_o \)) at the groove segments of the surface; hence we can consider the square wave function \( f(x) \)

\[
f(x) = \begin{cases} 
0, & -l < x < 0 \\
1, & 0 \leq x \leq w 
\end{cases} \tag{60}
\]

to represent the Navier slip condition in the structured surface as a piecewise constant function, i.e.,

\[
\beta(x) = \beta_o f(x) \tag{61}
\]

Floquet theory allows us to consider only one period of the structure \(-l < x \leq w\) to analyze the stability of the film on the entire structure. On the left side of the domain, \((-l < x < 0)\), we have the solid case \([f(x) = 0]\), and a solution denoted by \( \eta_L \); while on the right side of the domain, \((0 < x < w)\), we have the groove \([f(x) = 1]\) and a solution denoted by \( \eta_R \).

If we consider the different cases of Eq. (59) by using Eq. (61) for the Navier slip condition, we get the following constant coefficient fourth-order differential equations:
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\[ \eta^{(4)}_L + G_L \eta''_L + \gamma \eta_L = 0 \]  
\[ \eta^{(4)}_R + G_R \eta''_R + \gamma \eta_R = 0 \]  
\[ \gamma_R = \gamma (1 + 3 \beta_o)^{-1} \]  
\[ G_L = \psi_2 \psi_{2h} - \frac{3}{2} \left( \frac{\hat{q}^2 + \frac{\psi_{h2}}{\kappa}}{1 + 3 \beta_o} \right) \]  
\[ G_R = \psi_2 \psi_{2h} - \frac{3\hat{q} \left( \frac{\psi_{h2}}{\kappa} \right)}{2(1 + 3 \beta_o)} + 3 \beta_o \left( \frac{1 - \hat{q}^2 + \frac{\psi_{h1}}{\kappa} - \frac{\hat{q} \psi_{h2}}{\kappa}}{1 + 3 \beta_o} \right) \]  

The solution of each of the differential equations (62) and (63) is a combination of exponentials

\[ \eta_L = a_1 e^{r_1 x} + a_2 e^{r_2 x} + a_3 e^{r_3 x} + a_4 e^{r_4 x} \]  
\[ \eta_R = a_5 e^{r_5 x} + a_6 e^{r_6 x} + a_7 e^{r_7 x} + a_8 e^{r_8 x} \]  

with the characteristic roots

\[ r_{1,2,3,4} = \pm \sqrt{0.5} \sqrt{-G_L \pm \sqrt{G_L^2 - 4\gamma}} \]  
\[ r_{5,6,7,8} = \pm \sqrt{0.5} \sqrt{-G_R \pm \sqrt{G_R^2 - 4\gamma_R}} \]  

We use the condition that the solution of Eq. (59) and its derivatives have to be continuous

\[ \eta_L(0) = \eta_R(0), \quad \eta'_L(0) = \eta'_R(0) \]  
\[ \eta''_L(0) = \eta''_R(0), \quad \eta'''_L(0) = \eta'''_R(0) \]  

to obtain the first four equations for the eight unknown constants, \( a_n \).

According to Floquet theory (Chicone, 2006) the solution of the differential Eq. (59) has to be of the form

\[ \eta = e^{ikx} g(x) \]  

where \( g(x) \) is a complex function with period equal to \( l + w \) and \( k \) is the wave number. To obtain the other four equations for the unknown constants \( a_n \), we use the following conditions of periodicity of \( g(x) \) and its derivatives:

\[ g(-l) = g(w), \quad g'(-l) = g'(w) \]  
\[ g''(-l) = g''(w), \quad g'''(-l) = g'''(w) \]  

Based on the solution of \( \eta \) in Eq. (73), the complex periodic function \( g(x) \) is rewritten in terms of the solutions at the left and right domains

\[ g(x) = \begin{cases} e^{-ikx} \eta_L(x), & -l < x < 0 \\ e^{-ikx} \eta_R(x), & 0 \leq x \leq w \end{cases} \]  

If we combine this formula with Eqs. (67) and (68), the periodicity conditions (74)–(75) can be expressed in terms of the constants \( a_n \). By using the continuity conditions (71)–(72) and the periodicity conditions (74)–(75), we obtain the following system of equations for the arbitrary constants:

\[ R(i\kappa, \gamma) a = 0 \]
where the components of the matrix $R$ are the following:

$$R_{mn} = \begin{cases} 
    r_m^{n-1}, & m \leq 4, n \leq 4 \\
    -r_m^{n-1}, & m \leq 4, n > 4 \\
    (r_n - ik)^{m-1}e^{ikr_n}, & m > 4, n \leq 4 \\
    -(r_n - ik)^{m-1}e^{ikw}, & m > 4, n > 4
\end{cases}$$  \quad (78)

The condition for having nontrivial solutions of the homogeneous linear system (77) is that the matrix $R$ is singular,

$$\text{det}R(i\kappa, \gamma) = 0$$  \quad (79)

which allows us to obtain an implicit but analytic dispersion relation between the wave number $\kappa$ and its growth rate $\gamma$.

We introduce the groove length fraction, denoted by $\delta = w/(l + w)$, as is usually done in several studies of flows on structured surfaces (Ajaev et al., 2011; Bahga et al., 2010; Lauga and Stone, 2003; Teo and Khoo, 2009; Vinogradova and Belayev, 2011), then our stability results depend on $\beta_o$, $\delta$, and $l$. For thin films, the distance between the grooves is small, since the period of the structure is small compared to the characteristic wavelength of the instability. In all of our stability results we found that the effect of the distance between the grooves is insignificant on the growth rates if it is less than order unity. In all of the results of this section we are using $l = 0.5$. We found that the Navier slip length $\beta_o$ and the groove fraction $\delta = 0.5$ are the most significant variables in determining the growth rate of the instability.

First, we are going to consider the effect of the Navier slip on the stability of the film. Initially, we are going to assume that the groove and the solid segments have the same fraction, i.e., $\delta = 0.5$. The plots in Fig. 2 show that an increase in the Navier slip destabilizes the film. This means that as we increase the Navier slip, the growth rate of the instability, denoted by $\gamma$, increases for any wave number. The maximum growth rate, denoted as $\gamma_{\text{max}}$, is the most relevant measure of the instability in the studies mentioned above and in many practical applications. The plots in Fig. 2 show that the maximum growth rate $\gamma_{\text{max}}$ increases significantly as we increase the Navier slip length.

Even though our domain includes wave numbers that are higher than order unity (as can be seen in the dispersion curves of Fig. 2), we will proceed to discuss why the use of the lubrication approximation is still valid in our model.

\begin{center}
\textbf{FIG. 2:} Dispersion curves for $\hat{q} = -2$, $\kappa = 0.5$, and $\delta = 0.5$, and different Navier slip lengths $\beta_o$.
\end{center}
Our condition of a small capillary number is equivalent to the condition that the vertical length scale is much smaller than the horizontal length scale (which includes an array of structured segments). We are using the approach of Ajaev et al. (2012, 2013) and Burelbach et al. (1988), that uses a different scaling than the approach of Dávalos-Orozco (2007), by scaling in terms of the film thickness instead of the wavelength of the perturbation: with our scaling approach we can observe wave numbers of order unity or higher. Moreover, Sec. IV of Ajaev et al. (2012) verified the validity of the lubrication approximation by performing the stability analysis for the full Stokes model.

In the absence of the liquid shear stresses, i.e., \( \hat{q} = 0 \), the model of Eq. (53) reduces to a model similar to the van der Waals model on structured surfaces found in Ajaev et al. (2011), with the only difference that we have an electrostatic disjoining pressure instead of a van der Waals pressure term. In both van der Waals and the electrostatic models, the growth factor increases as the Navier slip length increases. Even when we consider the effect of the liquid shear stress, which stabilizes the film as discussed in Ketelaar and Ajaev (2014), the net effect is that the instability rate increases, i.e., the destabilizing Navier slip length effect is more predominant than the stabilizing liquid shear stress effect.

We determine the effects of the groove length fraction on the stability of the film by fixing the Navier slip and the surface charge densities. The plots in Fig. 3 show that if we increase the groove length fraction \( \delta \), the growth rate of the instability increases for every wave number. This means that an increase in the groove size also destabilizes the film; we obtained similar results for different choices of Navier slip lengths and surface charge densities. Notice that an increase in the groove length fraction does not increase the maximum growth rate as significantly as an increase in the Navier slip length does.

6. NONLINEAR STABILITY ANALYSIS

We solved the full nonlinear equation (52) numerically using the method, of lines with time stepping by Gear’s BDF method as implemented in Matlab, with \( \psi_{h,2} \) from (46) and \( \psi_{h,1} \) from (47). The size of the computational domain \( L \) is dictated by the wavelength of the fastest-growing perturbation: we choose \( L = \pi/k_{\text{max}} \), where \( k_{\text{max}} \) is the wave number with the maximum growth rate obtained from the dispersion analysis of Sec. 5. We have the following symmetric boundary conditions:

![FIG. 3: Dispersion curves for \( \hat{q} = -2 \), \( \kappa = 0.5 \), \( \beta_o = 0.2 \), and different groove length fractions \( \delta \).]
\begin{align}
  h_x(0, t) &= h_x(L, t) = 0, \\ 
  h_{xxx}(0, t) &= h_{xxx}(L, t) = 0, 
\end{align}
(80)

and the initial perturbation is sinusoidal, i.e.,

\[ h(x, 0) = 1 - \zeta_o \cos (k_{\text{max}} x) \]
(82)

The square wave function \( f(x) \) in the slip length Eq. (61) is approximated with the following smooth distribution (Gel’fand and Shilov, 1964):

\[ f(x) = \int_{-\infty}^{\infty} S(\tilde{x}) \omega(x - \tilde{x}) d\tilde{x} \]
(83)

where

\[
\omega(x) = \begin{cases} 
  C_\epsilon e^{-x^2/(\epsilon^2 - x^2)}, & |x| \leq \epsilon \\
  0, & |x| > \epsilon 
\end{cases}
\]
(84)

Note that this function is infinitely differentiable and equal to zero outside of the interval \([x - \epsilon, x + \epsilon]\). The constant \( C_\epsilon \) is chosen so that the integral of \( \omega(x) \) is equal to unity.

The plots in Fig. 4 show snapshots of the interface evolution at different times for \( \hat{q} = -2, \kappa = 0.5, \delta = 0.5, \) and a dimensionless Navier slip length of \( \beta_o = 0.1 \). With the choice of the initial condition Eq. (82), the minimum film thickness is reached at the origin \( x = 0 \). Notice that film thinning tends to speed up at later times. Since we are assuming that the film does not penetrate the grooves, which is the case for a superhydrophobic surface in the Cassie state, the liquid-gas interface at the structure surface is flat with no meniscus curvature and we do not have the possibility of a resonant effect due to the periodic properties of the wall, as found in Dávalos-Orozco (2007). There is the possibility of a resonant effect if we take into account the effect of the meniscus deformation, but it is beyond the present scope of this study.

![Fig. 4: Snapshots of the interface evolution for \( \hat{q} = -2, \kappa = 0.5, \delta = 0.5, \) and \( \beta_o = 0.1 \).](image-url)
In order to better visualize the film rupture, we can plot the minimum film thickness as a function of time and compare this result with the minimum film thickness for a film on a solid surface. The plots in Fig. 5 for \( \hat{q} = -2 \) and \( \kappa = 0.5 \) show that both the solid model (solid line) and the structured model (dot-dashed line) predict film rupture in finite time in a manner similar to the case of van der Waals driven rupture on solid surfaces (Burelbach et al., 1998) and structured surfaces (Ajaev et al., 2011), where film rupture speeds up considerably near the rupture time.

We notice that introduction of structuring accelerates rupture, which is consistent with the linear stability results of Sec. 5. We observed a similar behavior for different surface charge densities, Navier slip lengths, and groove length fractions, as can be seen in Figs. 6 and 7. We also increased the size of the computational domain to observe if the

**FIG. 5:** Minimum film thickness comparison between a solid surface (solid line) and a structured surface (dashed line) for \( \hat{q} = -2, \kappa = 0.5, \delta = 0.5, \) and \( \beta_o = 0.1. \)

**FIG. 6:** Minimum film thickness evolution for \( \hat{q} = -2, \kappa = 0.5, \) and \( \delta = 0.5, \) and different Navier slip lengths.
FIG. 7: Minimum film thickness evolution for ∇ = −2, κ = 0.5, and β = 0.1, and different groove fractions δ.

number of periodic structures inside of the computational domain affected the rupture times. We observed insignificant differences in the rupture times, which further validates the use of the lubrication-type approach and the Floquet theory analysis of only one period of the structure.

The plots in Fig. 6 show the evolution of the scaled minimum thickness for different Navier slip lengths. These results show that film rupture accelerates as we increase the Navier slip length, which is consistent with the increasing rates of instability observed in the plots of Fig. 2. The additional advantage of the nonlinear simulations is that we are able to observe film rupture in finite time and show how the nonlinearities of the interface shape Eq. (52) and accelerate rupture.

The plots in Fig. 7 show the evolution of the scaled minimum thickness for different groove length fractions. The nonlinear simulations also predict that an increase in the groove length fraction accelerates the rate of thinning, which is qualitatively consistent with the linear stability results of Fig. 3. Initially, there are significant differences for small groove length fractions, as can be seen between δ = 0.1 and δ = 0.3, but the differences become smaller as we increase the groove length fraction and become insignificant past the groove length fraction δ = 0.6. As we increase the groove length fraction, there is the possibility that film rupture accelerates if the liquid penetrates the groove so in this study we limit the groove length fraction to δ ≤ 0.6.

7. CONCLUSIONS

We used a lubrication-type approach to derive an interface evolution equation for a thin film on an electrically charged structured surface. In this model it is important to consider boundary conditions that take into account the effects of the liquid shear stresses across each of the liquid-gas interfaces and the effect of the Navier slip length between the different segments of the structured surface. We considered the linear and nonlinear stability of thin electrolyte films on a structured surface. The spatial periodicity of the Navier slip length allows us to apply Floquet theory, leading to implicit but analytical stability criteria.

The linear stability results show that the introduction of structuring increases the rate of the instability, for any Navier slip length and any groove length fraction. An increase in the Navier slip enhances the flow rate due to slippage and thus increases the maximum growth rate of the instability. An increase in the groove length also increases the
growth rate of the instability but the effects become insignificant for larger groove length fractions. We also found that the dimensionless distance between the grooves has an insignificant effect on the growth rates if it is less than order unity.

A comparison of the nonlinear simulations between the solid surface model and the structured surface model shows that the introduction of structuring accelerates the rate of thinning, which is consistent with the linear stability results. A direct comparison between the solid surface model and the structured surface model shows that both models predict rupture in finite time, but structuring significantly decreases the rupture times. The nonlinear simulations predict that either an increase in the Navier slip length or an increase in the groove length fraction decreases the rupture times. Initially, there are significant differences in the computed rupture times for small groove length fractions, but these differences become insignificant past the groove length fraction $\delta = 0.6$.

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REFERENCES


