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LINEAR STABILITY OF THIN LIQUID FILM ON SOLID SURFACE UNDER EFFECT OF APOLAR AND ELECTROSTATIC FORCES

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Abstract. The stability of thin liquid film on solid surface under apolar and electrostatic forces is investigated. The flow was represented by a two-dimensional Navier-Stokes equation coupled with continuity equation and associated boundary conditions. The film is modeled as a two-dimensional Newtonian liquid of constant density, ρ and viscosity, μ flowing on a horizontal plane. The liquid film of mean thickness, h_0 is assumed to be thin enough to neglect the gravitational effect and bounded above by a passive gas and laterally extends to infinity (two-dimensional model). The body force term in the Navier-Stokes equation is modified by the inclusion of excess intermolecular interactions (apolar and electrostatic forces) between fluid film and the solid surface owing to apolar and electrostatic forces. The modified Navier-Stokes equation with associated boundary conditions is solved under long wave approximation method to obtain a nonlinear equation of evolution of the film interface. The results indicated that the behavior of the growth rate (Figure 2(a) and 2(b)) is a wave reducing in size and gradually disappearing altogether, whereas the value of growth rate starts at negative values and then increases gradually until it reaches the highest point, after which it decrease gradually until it disappears with increase in film thickness to reach stabilization which equals zero. This situation occurs when the film thickness is ≤ 30 *nm*, after the thickness of the film equals to 30 *nm*, it is noted that there is no effect on growth rate, so it can be interpreted that the effect of apolar and electrostatic forces occurs only when the thickness of thin film ≤ 30 *nm*. Thus, it can be noted that any increase in the value of the wavenumber leads to a decrease in the value of growth rate. Therefore, it can be established that the relationship between wavenumber and growth rate is proportional.

Keywords: Apolar force, electrostatic force, linear stability, growth rate, thin film rupture

Abstrak. Kestabilan lapisan tipis cecair pada permukaan pepejal di bawah kuasa kutub dan elektrostatik dikaji. Aliran ditunjukkan oleh persamaan *Navier-Stokes* dua dimensi dipasangkan dengan persamaan penerusan serta digabungkan dengan garisan sempadan. Lapisan tipis adalah dimodelkan sebagai cecair *Newtonian* dua dimensi ketumpatan, ρ dan kelikatan, μ mengalir pada permukaan mendatar. Lapisan tebal purata, h_0 adalah dianggap cukup tebal untuk mengabaikan kesan graviti dan dihadkan oleh gas pasif serta ditambah pada sisinya kepada infiniti (model dua dimensi). Kuasa jasad pada persamaan *Navier-Stokes* telah diubahsuai dengan mengambil kira interaksi di antara (kuasa kutub dan elektrostatik) lapisan cecair dengan permukaan pepejal disebabkan oleh kuasa kutub dan elektrostatik. Pengubahsuaian persamaan *Navier-Stokes* dengan gabungan garisan sempadan diselesaikan dengan menggunakan persamaan panjang gelombang untuk mendapatkan persamaan tidak lurus evolusi permukaan-permukaan lapisan. Bahagian kuasa

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elektrostatik adalah lebih besar dalam nilai kuasa kutub dan berpengaruh terhadap sifat lapisan tipis serta kesan utama pada sifat-sifat tenaga bebas berlebihan, kadar penambahan, kadar penambahan maksimum, nombor gelombang natural, nombor gelombang berpengaruh dan masa pecahan. Maka, teori linear adalah kurang menunjukkan sifat-sifat kestabilan lapisan. Pengiraan menunjukkan bahawa kuasa kutub dan elektrostatik hanya boleh digunakan untuk penghasilan lapisan mendatar dengan ketebalan $h_0 \leq 30$ *nm*. Teori ini adalah konsisten dengan kuasa kutub dan elektrostatik terhadap lapisan tipis cecair pada permukaan mendatar.

Kata kunci: Kuasa kutub, kuasa elektrostatik, kestabilan linear, kadar penambahan, pecahan lapisan tipis

1.0 INTRODUCTION

The stability of thin liquid films plays an important role in chemical engineering as it allows the modeling of various disperse systems. These include free aqueous films as models for foams, a film of one liquid in another as a model for emulsion and thin liquid film between solids as a model for colloidal suspensions. From its formation, the aqueous film gradually becomes thinner; either it reaches a stable thickness or ruptures. The latter case is caused by the undamped growth of fluctuations at the film surfaces [1]. The understanding of stability, dynamics and morphology of supported thin (< 100 *nm*) liquid films and nanodrops are important in phenomena like flotation, adhesion of fluid particles to surfaces, kinetics and thermodynamics of precursor films in wetting, heterogeneous nucleation, film boiling/condensation, multilayer adsorption/film pressure, instability of biological films/membranes, among others. While the wetting of surface by large drops is relatively well understood, wetting characteristics of nanodrops and films have not been extensively studied, some applications like trickle bed reactors, thick coating, contact equipments for heat and mass transfer, and the like. The study of thin films phenomena has been motivated both by their scientific and industrial applications. For instance, thin liquid films sandwiched between two fluids, between two solids, and between a fluid and solid surfaces are encountered in several industrial and biological systems [2]. The drainage and instability of liquid films between two fluids control the coalescence and lifetimes of foams and emulsions. Additionally, the films between two solids are important in flocculation and coagulation in solid-liquid dispersions, and in attachment of particles to surfaces [3]. In some cases like trickle bed reactor, thick coating, contact equipment for heat and mass transfer, etc., initially thicker films can become thinner (≤ 100 *nm*) due to drainage, evaporation, etc., and the intermolecular interaction can eventually engender dry spots [4, 5]. Thin liquid films have been the objects of many investigations, and model studies, which are difficult to realize with real dispersion systems, are carried out with thin liquid films. In this way, phenomena that are connected with the type and distribution of the surfactants on the interface and affect the hydrodynamic behavior and interactions in thin liquid films and their stability are studied [6].

This study aims at examining linear effects in stability of thin film. It thus extends the work of Ruckenstein and Jain [7], Williams and Davis [8], Burelbach *et al.* [9] and Jameel and Sharma [10] to include the effect of the electrostatic and apolar forces on the stability of the thin liquid film on solid surface.

2.0 FORMULATION

Two-dimensional fluid motion in thin film (Figure 1) is governed by the Navier-Stokes equations with the inclusion of excess body forces derived from apolar (Lifshitz-van der Waals) and electrostatic (electrical double layer) intermolecular interactions. The equations of motion and associated boundary conditions at the free surface are simplified considerably whenever the film deformation occurs on a length scale that is large compared to the film thickness. The long wavelength reduction procedure [11, 12], when applied to a laterally unbounded, pure thin film resting on a substrate, gives the following leading order nonlinear equation of evolution for the film thickness, $h(x,t)$ [8, 13, 14]:

$$h_t + \frac{1}{3\mu}\left[h^3\left(\gamma_{23}h_{xxx} - \phi_x\right)\right]_x = 0 \tag{1}$$

where subscripts t, x, μ and γ_{23} are time, lateral space coordinate, film viscosity, and film surface tension respectively, ϕ denotes the excess potential energy per unit volume of the film due to intermolecular interactions. Equation (1) is a fourth order nonlinear equation which may be solved for the film profile, $h(x,t)$ if the appropriate form of excess free energy for the film is known and is obtained when viscosity of the bounding fluid is small compared to the viscosity of the film (e.g., gas-film interface). The same form of the equation (with numerical constant 3 replaced by 12) is also obtained if the bounding fluid has a high viscosity [13].

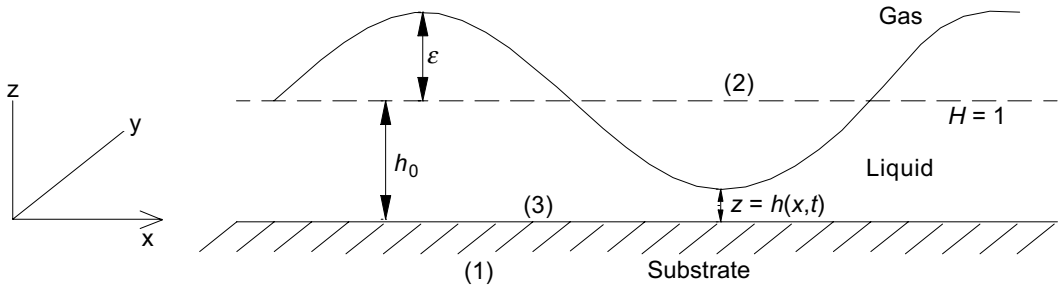


Figure 1 Schematic presentation of interfacial instability of thin fluid, 3 bounded by a substrate, 1 and a semi-infinite fluid, 2

The total excess free energy of interaction (per unit area) of two electrically neutral pure bulk phases (1 and 2) separated by a film of fluid 3 is the sum of apolar $\Delta G^{LW}(h)$ and electrostatic $\Delta G^{EL}(h)$ excess energies of interactions [15]:

$$\Delta G_T(h) = \Delta G^{LW}(h) + \Delta G^{EL}(h) \tag{2}$$

The excess free energy due to apolar force may be expressed in terms of macroscopic parameter of wetting the separation coefficient due to apolar interactions [16]:

$$\Delta G^{LW} = S^{LW}\left(\frac{d_0^2}{h^2}\right) \tag{3}$$

where S^{LW} is the apolar component of spreading coefficient and d_0 is the equilibrium separation distance between two bulks phase at contact. The equilibrium distance between Kihara shells of the molecules is found to be 0.158 *nm* [17, 18].

The excess free energy due to electrostatic force is found by Miller [19]:

$$\Delta G^{EL}(h) = \frac{\varphi k \psi_0^2}{4\pi}\left[1 - \tanh\left(kh/2\right)\right] \tag{4}$$

where φ is the dielectric constant, for water, $\varphi = 80$; k is the Debye length, $k^{-1} = 1$ *nm* [19] and ψ_0 is the electrical potential, $\psi_0 =$ (0 to 200) *mv* [20].

Now, replacing Equations (3) and (4) into Equation (2):

$$\Delta G_T(h) = S^{LW}\left(\frac{d_0^2}{h^2}\right) + \frac{\varphi k \psi_0^2}{4\pi}\left[1 - \tanh\left(\frac{kh}{2}\right)\right] \tag{5}$$

The second derivative of Equation (5) is:

$$\phi_h = \frac{\partial^2 \Delta G_T}{\partial h^2} = 6S^{LW}\left(\frac{d_0^2}{h^4}\right) + \frac{\varphi k \psi_0^2}{4\pi}\left[1 + \frac{k^2}{2}\sec h^2\left(\frac{kh}{2}\right)\tanh\left(\frac{kh}{2}\right)\right] \tag{6}$$

Equation (1) can be rearranged as:

$$h_t + \frac{1}{3\mu}\left[\gamma_{23} h_{xxx} h^3 - h_x h^3 \left\{\left(\frac{6d_0^2 S^{LW}}{h^4}\right) + \frac{\varphi k \psi_0^2}{4\pi}\left(1 + \frac{k^2}{2}\sec h^2\left(\frac{kh}{2}\right)\tanh\left(\frac{kh}{2}\right)\right)\right\}\right]_x = 0 \tag{7}$$

2.1 Linear Stability Analysis

The initial (short time) evolution of the film profile is adequately described by linearized equation (about the trivial state) whenever the amplitude of initial disturbance is much smaller than the mean film thickness. Linearization of the general equation of evolution in dimensional form, Equation (1) around the mean film thickness, $h = 1$, leads to the following solution [8]:

$$h(x,t) = h_0 \exp(\omega t + \lambda x) \tag{8}$$

where ω is the disturbance growth rate and λ is the wavenumber. Substituting Equation (8) into Equation (1) yield the characteristic equation:

$$\omega = \left[\phi_{h_0} - \gamma_{23}\lambda^2\right] \times \frac{h_0^3 \lambda^2}{3\mu} \tag{9}$$

The small disturbance will grow if $\omega > 0$ and will decay if $\omega < 0$. It is obvious from Equation (9) that for $\phi_{h_0} > \gamma_{23}\lambda^2$, the growth coefficient is positive real quantity as λ is always positive. In this case, any imposed disturbances are attenuated and a stable planar film is eventually formed. On the other hand, the film becomes unstable, for $\phi_{h_0} < \gamma_{23}\lambda^2$ and $\lambda < \lambda_n$, where λ_n is a cut-off wavenumber corresponding to a neutrally stable system, i.e. $\omega = 0$. The neutrally stable wave has a wavenumber, λ_n given by:

$$\lambda_n^2 = \left[\frac{\phi_{h_0}}{\gamma_{23}}\right] > 0 \tag{10}$$

where the maximum growth rate, ω_m of the linear wave occurs for the dominant wavenumber, λ_m which is obtained by setting $\frac{\partial \omega}{\partial \lambda} = 0$ in Equation (9):

$$\lambda_m^2 = \left[\frac{\phi_{h_0}}{2\gamma_{23}}\right] \tag{11}$$

and

$$\omega_m = \frac{h_0^3 \lambda_m^4 \gamma_{23}}{3\mu} \tag{12}$$

Thus, the linear theory predicts unhindered growth of surface deformation ($\omega > 0$) up to the point of film rupture whenever the condition is satisfied and $0 < \lambda < \lambda_n$. However, in reality, the linear theory can predict neither the time scale on which instability evolves, nor the eventual fate of the growing deformations when the

(repulsive) nonlinear interactions become important in Equation (1). The growth of instability may lead either to true rupture (but on a time scale different from that predicted by the linear theory), or to a complex time stationary shape for the film. In essence, the linear theory assumes a constant force during all stages of film deformation, whereas in reality, thinner and thicker portions of the film encounter different (nonlinear) force fields as perturbations grow [16].

The total force may even reverse its sign over a part of the film. In order to assess the role of nonlinearities, we may take the linear theory seriously up to the point of film breakup, and determine a time of rupture by setting $h = 0$ at $\sin \lambda x = -1$ in Equation (13) [21]:

$$h = 1 + \varepsilon_0 \sin \lambda x e^{\omega t} \tag{13}$$

This gives a linear estimate for the time of film rupture for a disturbance of wave λ:

$$t_1 = \frac{1}{\omega(\lambda)} \ln \frac{1}{\varepsilon} \tag{14}$$

The shortest time of rupture from the linear theory is clearly obtained for the dominant wave, $\lambda = \lambda_m$.

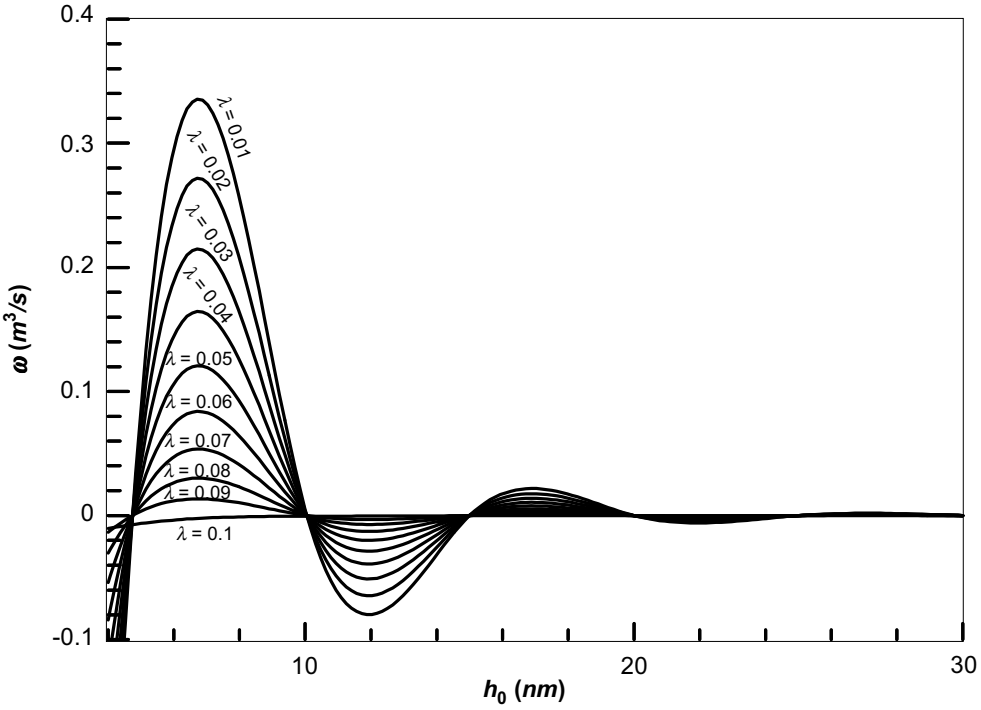
2.2 Results from Linear Theory

It can be noted from Equation (9) that the growth rate depends on the thickness of the film, h_0 and wavenumber, λ. Since the value of the electrostatic which term in Equation (6) is electrostatic force is much larger than the apolar term, it has the main effect on the behavior of the disturbance growth rate, ω.

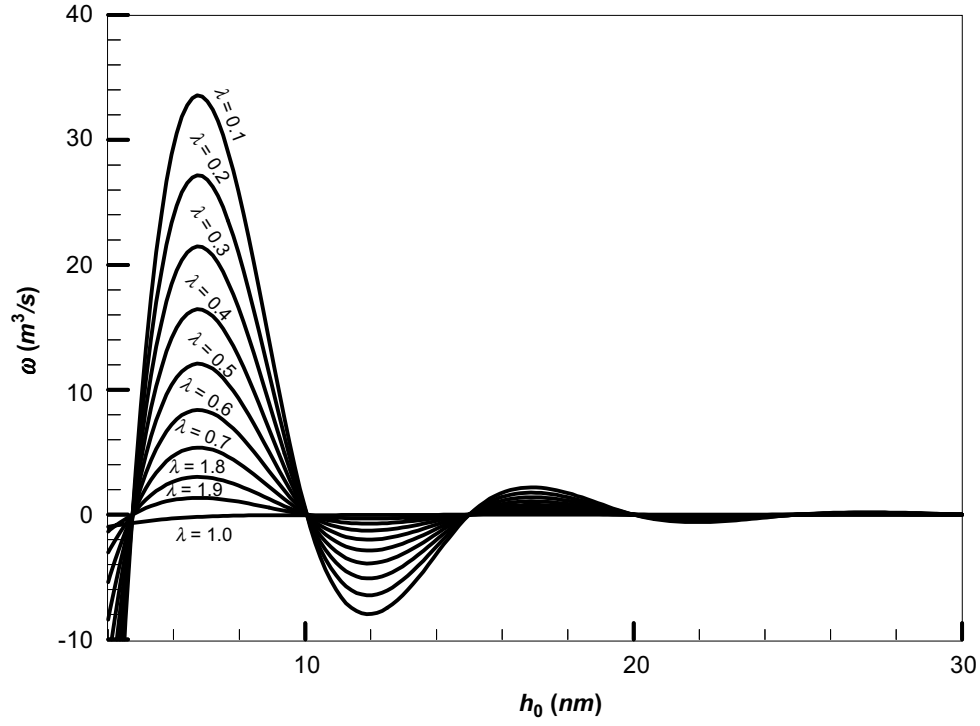
Figure 2 (a) and (b) presents the relationship between ω and h_0 as a function of λ. It is noted that the waves reduce in magnitude as λ increases. It is observed that the value of ω starts at a negative value and then increases gradually until it reaches the maximum, after which it decreases gradually and eventually approaching zero when h_0 is sufficiently large, i.e. $h_0 \leq 30\ nm$. Therefore, the effect of apolar and electrostatic forces are only significant when the thickness of thin film $\leq 30\ nm$.

Figure 3 (a) and (b) presents the relationship between wavelength, λ and growth rate, ω as a function of h_0 for λ = (0.01 to 1.0). It can be noted that an increase in the value of λ leads to a decrease in the value of ω.

From Equation (9), it can therefore be established that ω is proportional to λ. So it can be concluded that ω increases when the wavelength decreases until the value of the growth rate reaches to nearly zero at $h_0 = 30\ nm$. For h_0 larger than 30 nm, the effect of disturbance is found to be negligible.

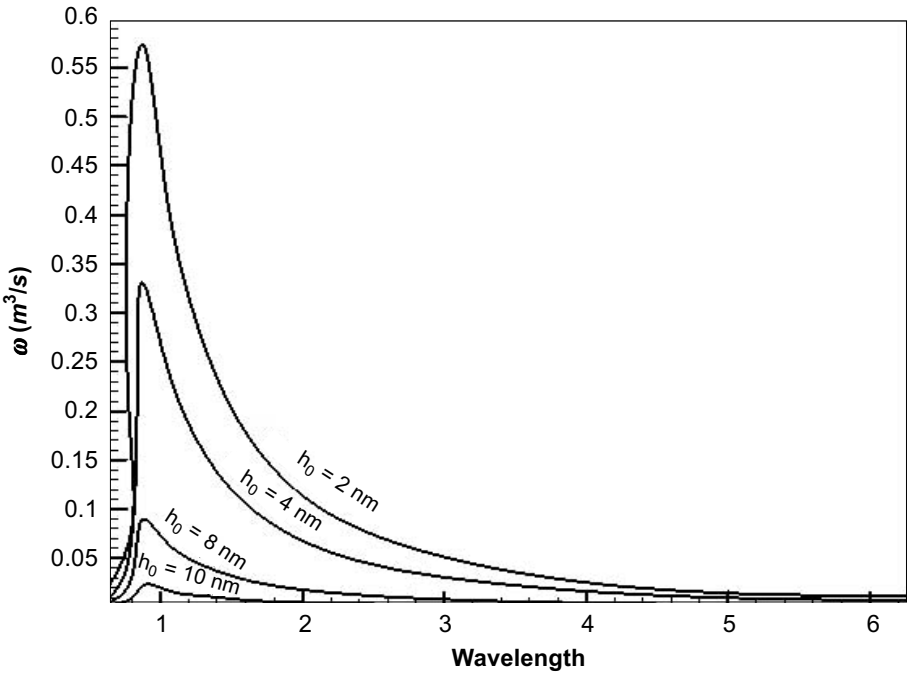


(a)

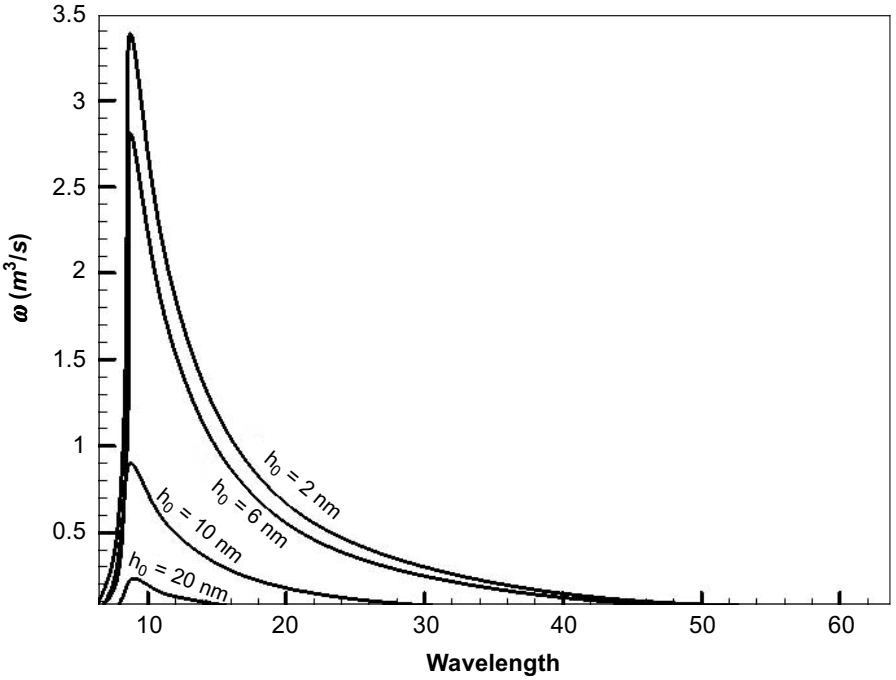


(b)

Figure 2 (a) – (b) Growth rate as a function of h_0 at λ = (0.1 to 1.0) from linear theory



(a)



(b)

Figure 3(a) – (b) Growth rate as a function of wavelength at $h_0 \leq 30\ nm$ and λ = (0.1 to 1.0) from linear theory

3.0 CONCLUSION

The stability of thin liquid film on solid surface under the effect of apolar and electrostatic forces are investigated. The motion in the film is represented by two-dimensional Navier-Stokes equation and associated boundary condition, which are later simplified under long wave approximation, (i.e. surface disturbance evolves on a length scale much longer than the film thickness). In this study, the Navier -Stokes equation is modified by inclusion of excess intermolecular interactions between film fluid and the solid surface into the body force term. However, the body force due to apolar and electrostatic forces becomes insignificant as the mean film thickness is larger than 30 nm. For mean film thickness less than 30 nm, the disturbance growth rate is proportional to the wavenumber.

NOMENCLATURES

h_0	mean thickness of the film
d_0	equilibrium separation distance
ΔG^{EL}	excess free energy due to electrostatic
ΔG^{LW}	excess free energy due to apolar force
ΔG_T	total excess free energy due to intermolecular interactions
S^{LW}	apolar component of spreading coefficient
k	Debye length
t_1	rupture time from linear theory

Greek Letters

ε_0	initial amplitude of perturbation
ε	amplitude of perturbation
φ	dielectric constant
γ_{23}	surface tension
μ	dynamic viscosity
λ	wavenumber of perturbation
λ_m	dominant wavenumber of perturbation
λ_n	neutral wavenumber of perturbation
ϕ_h	second derivative of the excess free energy, ΔG
ω	disturbance growth coefficient
ω_m	maximum disturbance the growth coefficient

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