

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

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Abstract. The total excess free energy per unit area (ΔG) of a pure, uncharged thin film on a support is solely derived from the *apolar* (*Lifshitz - van der Waals*) and *polar* (*acid-base*) intermolecular interactions. Polar interactions are variously described as the hydration pressure, hydrophobic interaction and acid base interaction. The total free excess energy (per unit area) of a thin film on a substrate depends on the film thickness, and the apolar and polar spreading coefficients for the system. The film is modelled 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 gravity 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 polar forces) between fluid film and the solid surface owing to apolar and polar 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 apolar and polar forces were found to play the dominant role in characteristic of thin films and the main effect on the behavior of the excess free energy, growth rate, maximum growth rate, neutral wave, dominant wavenumber, dominant wavelength and rupture time. Hence, the linear theory is inadequate to describe the stability characteristics of films.

Keywords: Apolar force, polar force, linear stability, growth rate, rupture time

Abstrak. Tenaga lebihan bebas Gibb per unit luas (ΔG) bagi suatu saput nipis yang tulen, tanpa cas pada satu sokongan hanya diterbitkan daripada interaksi antara molekul *apolar* (*Lifshitz - van der Waals*) dan *polar* (*acid-bes*). Interaksi polar dapat dinyatakan secara berasingan sebagai tekanan penghidratan, interaksi hidrofobik dan interkasi asid-bes. Jumlah tenaga lebihan bebas Gibb per unit luas (ΔG) bagi satu saput nipis pada satu lapisan bergantung kepada ketebalan saput, dan angkali penyebaran apolar dan polar untuk sistem tersebut. Saput dimodelkan sebagai cecair Newtonian 2-dimensi dengan ketumpatan tetap, ρ , dan kelikatan, μ , mengalir di atas satu permukaan mengufuk. Ketebalan purata saput cecair, h_0 , dianggapkan cukup nipis supaya kesan graviti boleh diabaikan dan melambung atas oleh gas pasif dan menyambung secara lateral hingga infiniti (Model dua-dimensi). Daya badan yang disebut dalam persamaan *Navier-Stokes* adalah diubahsuaikan oleh kandungan interaksi antara molekul lebihan (daya apolar dan polar) antara saput bendalir dan permukaan pepejal bergantung kepada daya-daya apolar and polar. Persamaan *Navier-Stokes* telah diubahsuai dengan keadaan sempadan berkaitan diselesaikan bawah kaedah pendekatan gelombang panjang untuk memperolehi persamaan perkembangan tak-linear bagi saput antara permukaan. Daya apolar dan polar telah didapati memainkan peranan pencirian atas saput nipis dan kesan utama pada sifat tenaga lebihan bebas, kadar penubuhan, kadar penubuhan maksimum, gelombang neutral, nombor

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gelombang yang dominan, jarak gelombang dominan dan masa memecah. Oleh demikian, teori linear adalah kurang sesuai untuk menyatakan kestabilan pencirian selaput.

Kata kunci: Daya apolar, daya polar, kestabilan linear, kadar pertumbuhan, masa memecah

1.0 INTRODUCTION

The study of ultrathin ($\leq 100 \text{ nm}$) fluid films has become more and more important and popular recently since it is frequently applied in mechanical, chemical, biomedical engineering, and high-tech processing among other applications as they allow the modelling 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 until reaching a stable thickness or until rupturing. This latter case is caused by the undamped growth of fluctuations at the film surfaces [1]. A film is simply a layer of material and while the term 'thin' is imprecise, it is generally used to describe a layer of thickness of less than about $1 \mu\text{m}$. The study of thin films of solid materials is old by modern standards, but recent years have seen a burgeoning of activity, which has now become so great that the subject is a major component of today's physics of solid state. A thin film, being simply a thin slice from a material, has all the properties of that material, albeit modified by the special way in which it has, been made and by the fact that it has a very large ratio of surface to volume. Interest in thin films arises because of the range of uses and applications that they offer [2]. For extremely thin films of thickness, *i.e.*, less than $50 \mu\text{m}$, the free surface becomes unstable and deforms when the force per unit volume; *i.e.*, the second derivative of the total free energy with respect to the film thickness, becomes negative [3,4]. The total excess free energy of a pure, un-charged thin film on a support is solely derived from the apolar and polar intermolecular interactions. The polar interactions [5,6] have been variously described as the hydration pressure, hydrophobic interactions, hydrogen bonding, acid base interactions [6,7] among others, and are clearly important for films of polar liquids (*e.g.*, water) bounded by apolar or polar media. Polar interactions may be quantified by direct force measurements [5,8], or by more facile measurements of macroscopic parameters such as Interfacial tensions and equilibrium contact angles [5,7], all of which are rather profoundly affected by the polar interactions. Since the free energy of a thin film is but a remnant of the interfacial energy between bulk phases, stability of a thin film is also altered by the energy of polar interactions [9]. Previous investigations of thin film stability have largely focused on the role of apolar (Lifshitz van der Waals) forces, which always engender a true rupture of the film [4, 10] whenever the effective Hamaker constant is positive, *i.e.*, the apolar (LW) component of the spreading coefficient (S^{LW}) is negative. These conditions also ensure that the second derivative of the free energy (force per unit volume) is negative for all film thickness. However, as is shown later, the system

consisting of substrate, film and bounding fluid are completely apolar only when the film is fluid and at least one of the bounding media is apolar (*e.g.*, hydrocarbon films bounded by a gas), in which case the polar component of the spreading coefficient vanishes. It is only in this particular case that the total free energy of the system is derived from the sum of apolar interactions. Based on the linear stability analysis of Navier Stokes equations for the thin film, we have recently derived conditions for the initial growth of infinitesimal perturbations in the apolar and polar systems [11]. 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 [12].

The present work aims at examining linear effects in stability of thin film. This study extends the work of Ruckenstein & Jain [13], Williams and Davis [10], Burelbach *et al.*, [14] and Jameel and Sharma [15] to include the effect of the apolar and polar forces on the stability of the thin liquid film on solid surface.

2.0 MODEL

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 and polar 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 [16,17], 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, $h(x, t)$ [10,17,18]:

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

where subscripts denote differentiation; t, x, μ and γ_{23} are denoted as time, lateral space coordinate, film viscosity, and film surface tension respectively and ϕ is denote

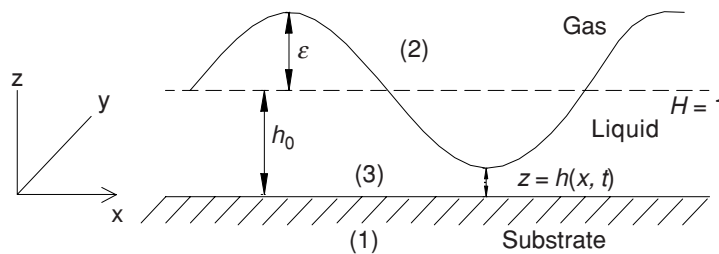


Figure 1 Schematic presentation of interfacial instability of thin fluid, 3 bounded by a substrate, 1 and a semi-infinite fluid, 2.

to the excess potential energy per unit volume of the film due to intermolecular interactions. Equation (1) is a fourth order nonlinear equation which is solved for the film profile, $h(x, t)$, if the appropriate form of excess free energy for the film is known, is obtained when the 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 being replaced by 12) is also obtained if the bounding fluid has a large viscosity [19].

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 polar $\Delta G^P(h)$ excess energies of interactions [20]:

$$\Delta G_T(h) = \Delta G^{LW}(h) + \Delta G^P(h) \quad (2)$$

The excess free energy due to apolar force expressed in terms of macroscopic parameter of wetting the separation coefficient due to apolar interactions [15, 20]:

$$\Delta G^{LW} = S^{LW} (d_0^2 / h^2) \quad (3)$$

where (S^{LW}) is the apolar component of spreading coefficient and d_0 is equilibrium separation distance between two bulks phase at contact. The equilibrium distance between Kihara shells of the molecules is given as 0.158 nm [21,22].

The excess free energy due to polar force is given as [20]:

$$\Delta G^P(h) = S^P \exp[(d_0 - h) / l_0] \quad (4)$$

where (S^P) , the polar component of spreading coefficient and l_0 , is correlation (decay) length for the polar fluid. l_0 for water lies in the range $(0.2 \text{ to } 1.2) \text{ nm}$, with the best estimate of about 0.4 nm [23].

By replacing Equation (3) and Equation (4) into Equation (2); total excess energy of interaction per unit area is given as:

$$\Delta G_T(h) = S^{LW} (d_0^2 / h^2) + S^P \exp[(d_0 - h) / l_0] \quad (5)$$

The second derivative of Equation (5) is:

$$\phi_h = (\partial^2 \Delta G / \partial h^2) = 6S^{LW} (d_0^2 / h^4) + (S^P / l_0^2) \exp[(d_0 - h) / l_0] \quad (6)$$

Now, Equation (1) can be rearranged as:

$$h_t + (1/3\mu) [\gamma_{23} h_{xxx} h^3 - h_x h^3 \{ (6d_0^2 S^{LW} / h^4) + (S^P / l_0^2) \exp[(d_0 - h) / l_0] \}]_x = 0 \quad (7)$$

Where the x-component of the body force, ϕ_x is evaluated as $\phi_h h_x$ where ϕ_h is the second derivative of the surface free energy due to intermolecular interactions [20].

3.0 METHOD OF SOLUTION

3.1 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, [10]:

$$h(x, t) = h_0 + h_1(x, t) \quad (8)$$

$$h_1(x, t) = \varepsilon \sin \lambda x e^{\omega t} \quad (9a)$$

$$h_1 t = \varepsilon \omega \sin \lambda x e^{\omega t} \quad (9b)$$

$$h_1 x = \varepsilon \lambda e^{\omega t} \cos \lambda x \quad (9c)$$

$$h_1 xx = -\varepsilon \lambda^2 e^{\omega t} \sin \lambda x \quad (9d)$$

$$h_1 xxx = -\varepsilon \lambda^3 e^{\omega t} \cos \lambda x \quad (9e)$$

$$h_1 xxxx = -\varepsilon \lambda^4 e^{\omega t} \sin \lambda x \quad (9f)$$

Here, ω is the disturbance growth rate, λ , is the wavenumber and ε , is the dimensional amplitude disturbance. Equation (1) can be rewritten as:

$$\frac{\partial(h_0 + h_1)}{\partial t} + \frac{1}{3\mu} \left[(h_0^3 + 3h_0^2 h_1 + 3h_0 h_1^2 + h_1^3) \left\{ \frac{\partial^3(h_0 + h_1) \gamma_{23}}{\partial x^3} - \frac{\partial(h_0 + h_1)}{\partial x} \frac{\partial \phi}{\partial(h_0 + h_1)} \right\} \right] = 0$$

$$\frac{\partial h_1}{\partial t} + \frac{1}{3\mu} \left[\gamma_{23} h_0^3 \frac{\partial^3 h_1}{\partial x^3} - h_0^3 \frac{\partial h_1}{\partial x} \frac{\partial \phi}{\partial h_0} \right] = 0$$

$$h_1 + \frac{1}{3\mu} \left[\gamma_{23} h_0^3 h_{1xxxx} - h_0^3 h_{1x} \phi_{h_0} \right] = 0 \quad (10)$$

If we substitute Equation (9a–9f) into Equation (10), we obtain the characteristic equation:

$$\omega = - \left[\phi_{h_0} + \gamma_{23} \lambda^2 \right] \times \frac{h_0^3 \lambda^2}{3\mu} \quad (11)$$

Small disturbance grow if $\omega > 0$ and decay if $\omega < 0$. Hence, it is obvious from Equation (11) that whenever $(\phi_{h_0}) > 0$, *i.e.*, the force field is purely repulsive, the growth coefficient is negative and real quantity as (λ) is always positive. In this case, any imposed disturbances are attenuated and a stable planar film is eventually formed. Therefore, the film becomes unstable, *viz.*, $\omega < 0$ any when (ϕ_{h_0}) (force per unit volume) $> \gamma_{23} \lambda^2$.

The linear theory predicts unhindered growth of surface deformation ($\omega > 0$) up to the point of film rupture whenever condition is satisfied. 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 predicated 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. 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 $\lambda x = -1$ in equation below [15]:

$$h = 1 + \varepsilon_0 \sin \lambda x e^{\omega t} \quad (12)$$

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

$$t_i = \frac{1}{\omega(\lambda)} \ln \frac{1}{\varepsilon} \quad (13)$$

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

4.0 RESULTS AND DISCUSSION

It is obvious from Equation (11) that the growth rate (ω) depends on the thickness of the film (h_0), wavenumber (λ) and excess free energy (ϕ_{h_0}). The linear theory predicts that the growth rate can only appear if the second derivative of the free energy with respect to film thickness, (ϕ_h) evaluated at the mean film thickness, (h_0) is negative. The function $(\partial^2 \Delta G / \partial h^2) = \phi_h(h)$ (Equation (6)), displays five qualitatively distinct shapes depending upon the sign and magnitude of (S^{LW}) and (S^p). The growth rates of various models are illustrated in relation to film thickness, (h_0) in Figures (2) to (11) for cases when $\lambda = (0.02 \text{ to } 0.1)$ and $\lambda = (0.2 \text{ to } 1.0)$. The growth rate in the Figures (2) to (5) are positive, hence the film is stable, since the values of components of free energy and are negative and the growth rate in the Figures (6) to (11) are negative, hence the film is unstable and the values of components of free energy (S^{LW}) and (S^p) are positive. It is clearly seen from these figures, the values of the growth rate are too small, which means that the rupture time in case of thin film with apolar and polar forces will take a longer time to occur.

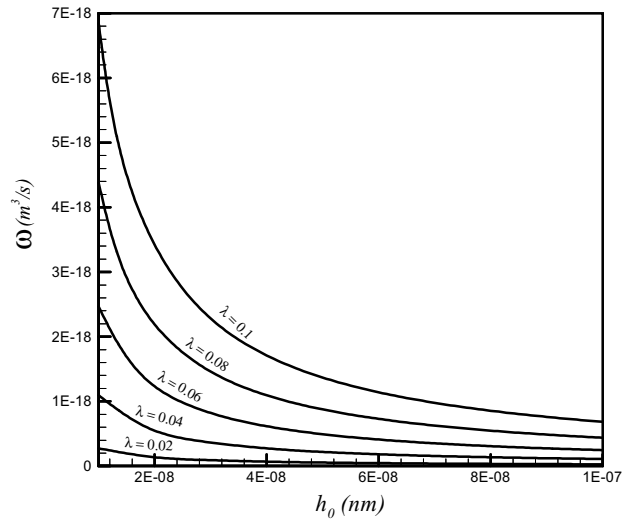


Figure 2 Growth rate as a function of h_0 at $\lambda = (0.02 - 0.1)$ from linear theory. For S^{LW} and $S^\phi = -100 \text{ mJ/m}^2$.

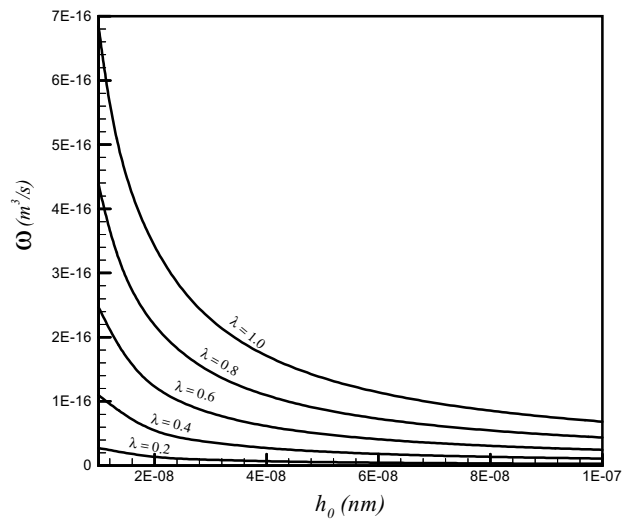


Figure 3 Growth rate as a function of h_0 at $\lambda = (0.2 - 1.0)$ from linear theory. For S^{LW} and $S^\phi = -100 \text{ mJ/m}^2$.

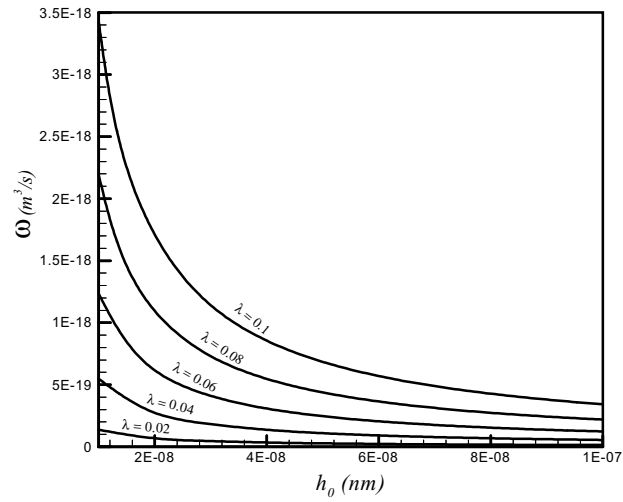


Figure 4 Growth rate as a function of h_0 at $\lambda = (0.02 - 0.1)$ from linear theory. For S^{LW} and $S^\phi = -50 \text{ mJ/m}^2$.

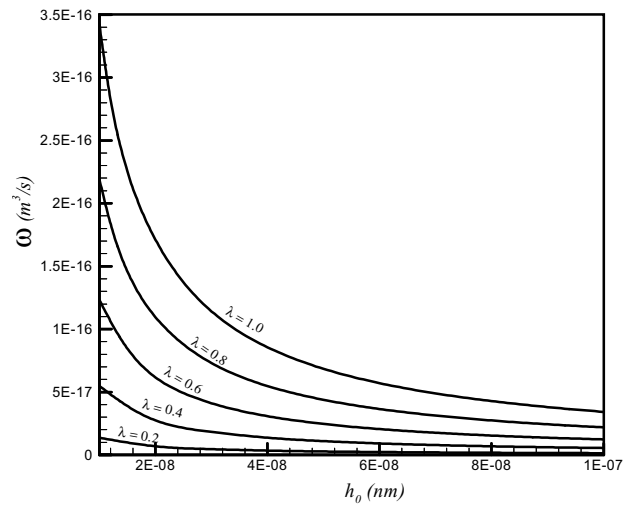


Figure 5 Growth rate as a function of h_0 at $\lambda = (0.2 - 1.0)$ from linear theory. For S^{LW} and $S^\phi = -50 \text{ mJ/m}^2$.

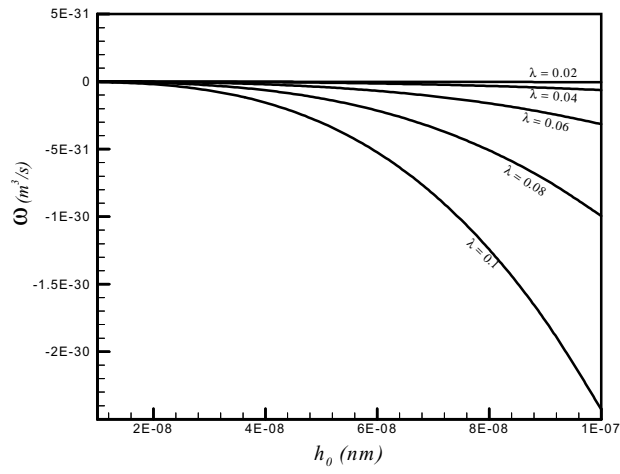


Figure 6 Growth rate as a function of h_0 at $\lambda = (0.02 - 0.1)$ from linear theory. For S^{LW} and $S^\phi = 0 \text{ mJ/m}^2$.

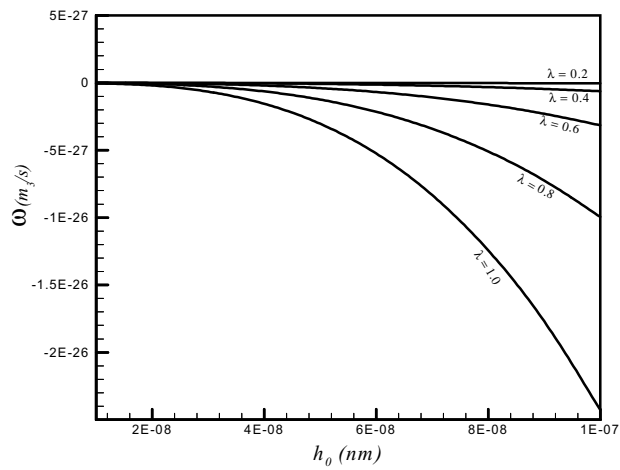


Figure 7 Growth rate as a function of h_0 at $\lambda = (0.2 - 1.0)$ from linear theory. For S^{LW} and $S^\phi = 0 \text{ mJ/m}^2$.

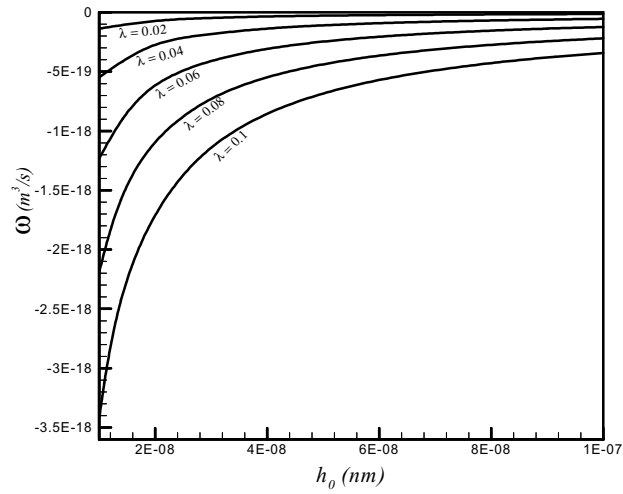


Figure 8 Growth rate as a function of h_0 at $\lambda = (0.02 - 0.1)$ from linear theory. For S^{LW} and $S^\phi = 50 \text{ mJ/m}^2$.

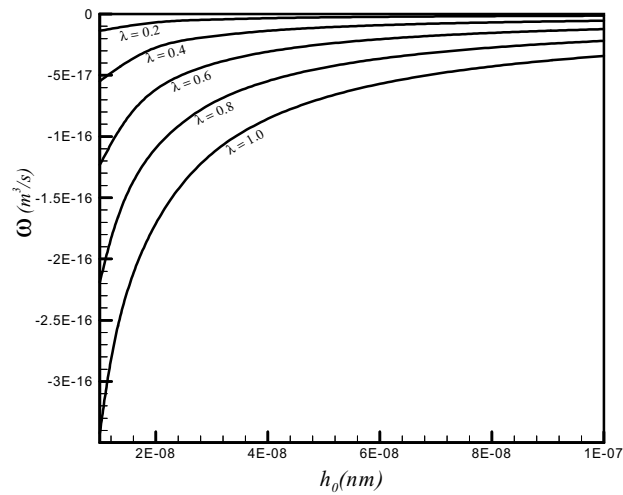


Figure 9 Growth rate as a function of h_0 at $\lambda = (0.2 - 1.0)$ from linear theory. For S^{LW} and $S^\phi = 50 \text{ mJ/m}^2$.

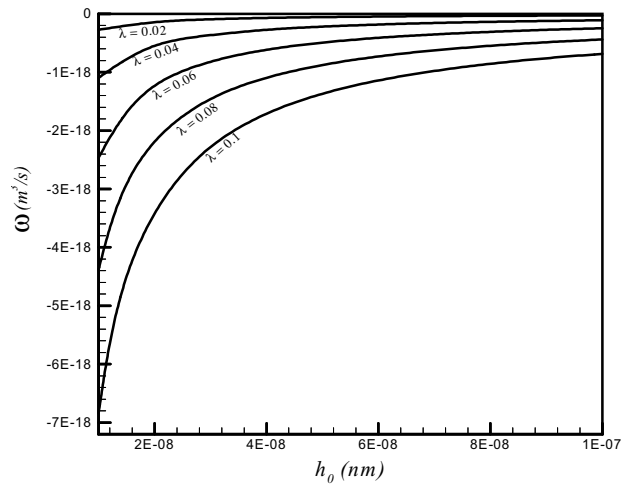


Figure 10 Growth rate as a function of h_0 at $\lambda = (0.02 - 0.1)$ from linear theory. For S^{LW} and $S^\phi = 100 \text{ mJ/m}^2$.

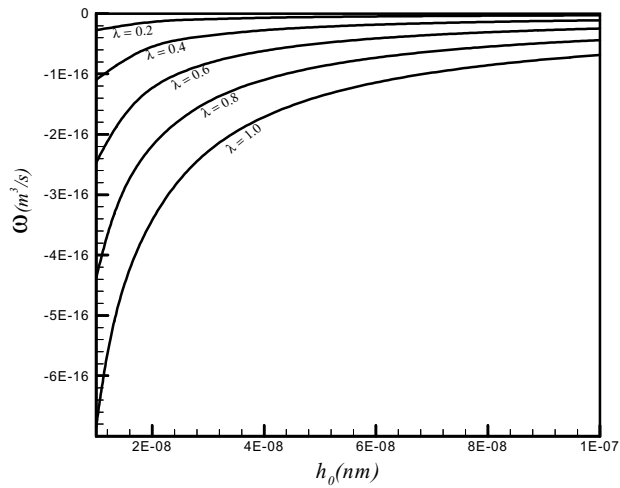


Figure 11 Growth rate as a function of h_0 at $\lambda = (0.2 - 1.0)$ from linear theory. For S^{LW} and $S^\phi = 100 \text{ mJ/m}^2$.

5.0 CONCLUSION

The stability of thin liquid film ($h_0 \leq 100 \text{ nm}$) is correlated to the macroscopic parameters of wetting, by both the apolar and polar free energy components. The apolar and polar free energy components (per unit area) of a thin film on a substrate depend on the film thickness, and the apolar and polar components of spreading coefficient for the system. The free interface of the film becomes unstable and deforms when the growth rate is negative. The stable film will only be formed if both the apolar, (S^{LW}) and the polar, (S^p) components of free energy are in negatives values. The small growth rate indicates that the rupture time may be not appear or will take longer time to happen. In this present case, a small growth rate was found in thin film.

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