UNIVERSITI PUTRA MALAYSIA

STABILITY OF THIN LIQUID FILM UNDER EFFECT OF APOLAR AND ELECTROSTATIC FORCES ON A HORIZONTAL PLANE

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for Degree of Master of Science

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DEDICATED

TO

My parents, brothers and sisters for their real help

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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The understanding of stability, dynamics and morphology of supported thin ($<100nm$) 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, and many other areas While the wetting of surface by large drops is relatively well understood, wetting characteristics of nanodrops and films have not been extensively studied In some applications like trickle bed reactors, thick coating, contact equipment for heat and mass transfer, and the like

Factors that would affect the total free excess energy (per unit area) of a thin film on a substrate include the film thickness, as well as the apolar and electrostatic spreading coefficients for the system The dynamics of the liquid film is formulated using the Navier-Stokes equations augmented by a body forces describing the apolar

and electrostatic interactions. The liquid film is assumed to be charge neutralized, nondraining, and laterally unbounded. A modified Navier-Stokes equation with associated boundary conditions is solved using a long wave approximation method to obtain a nonlinear equation of evolution of the film interface.

A nonlinear theory based upon the condition of infinitesimal perturbation on the film surface is derived to obtain the growth coefficient, dominant wavelength (i.e., wavelength corresponding to maximum growth coefficient of the surface instability) and the film rupture time.

Solution of the nonlinear partial differential equation for a wide range of the initial amplitude and wavelength is solved by using finite difference methods. The calculation domain is fixed on the interval $0 < X < 2\pi/\lambda$. The mesh size is taken sufficiently small so that space and time errors are negligible. The nonlinear algebraic equations obtained as a result of finite difference discretization are solved using efficient-numerical technique employing IMSL subroutine DNEQNJ.

The electrostatic force part is bigger in value than apolar, therefore it found that it plays the dominant role in characteristics 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. The linear theory may overestimate or underestimate the time of rupture by several orders of magnitude depending upon thin film parameters. Hence linear theory is inadequate to describe the stability characteristics of films and therefore, the need of a nonlinear approach to the study of thin film dynamics. The calculations indicated that the apolar and electrostatic forces can be solely responsible for the formation of flat film of $h_0 \cong 30\,nm$ in thickness. In this respect the proposed theory is consistent with the effect of apolar and electrostatic forces on thin liquid films on a horizontal plane.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

KESTABILAN SAPUT CECAIR NIPIS DI BAWAH KESAN DAYA APOLAR DAN ELETROSTATIK PADA SATU PERMUKAAN RATA

Oleh

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Kefahaman berkenaan kestabilan. Dinamik dan morfologi bagi cecair filem nipis ($<100nm$) dan titisan nano adalah mustahak dalam fenomena seperti perapungan, pelekatan cecair bendalir ke permukaan, kinetik dan termodinamik penanda filem dalam pembasahan, penukleusan heterogen, pendidihan/pemelewapan, pelbagai lapisan penjeraban/tekanan filem, ketidakstabilan filem biologi/membran, dan banyak bidang lain. Sementara pembasahan permukaan oleh titsan besar adalah mudah di fahami, pencirian pembasahan titsan nano dan filem belum dikaji secara intensif. Dalam beberapa penggunaan seperti reaktor lapisan cucur, bersalut tebal, peralatan sentuh bagi haba dan pemindahan jisim, dan sepertinya.

Filem berkenaan adalah dimodelkan sebagai dua dimensi cecair Newtonian ketumpatan tetap ρ dan kelikatan μ mengalir pada satah mendatar. Cecair filem ketebalan min h_0 adalah dianggap nipis cukup untuk mengabai kesan garaviti dan

terhad diatas oleh satu gas dan terlanjut secara sisi ke infinit (model dua-dimensi). Kemudian aliran seperti berikut boleh diwakili oleh satu persamaan dua-dimensi Navier-stokes dipasangkan dengan persamaan selanjar dan keadaan sempadan bersekutu. Sebutan daya badan dalam persamaan Navier-stokes adalah diubahsuai dengan memasukkan saling tindak antara molekul berlebihan (apolar dan daya elektrostatik) antara filem bendalir dan permukaan pepejal dipunyai daya apolar dan daya elektrostatik. Persamaan Navier-Stokes terkait dengan keadaan sempadan bersekutu adalah telah diselesaikan di bawah kaedah anggaran gelombang panjang untuk mendapat satu persamaan tidak linear bagi filem antara muka.

Satu teori tidak linear berdasarkan atas keadaan usikan sangat kecil ke atas permukaan filem adalah diterbitkan untuk mendapat pekali pertumbuhan, panjang gelombang berkaitan kepada pekali pertumbuhan maksimum bagi ketidakstabilan permukaan dan masa filem pecah.

Persamaan tidak linear bagi eolusi adalah diselesaikan secara berangka dalam bentuk konservatif sebagai sebahagian satu masalah nilai awal bagi keadaan sempadan berkata sempadan pada banjaran tertetap $0<X<2\pi/\lambda$, dimana λ adalah satu gelombang angka. Perbezaan tertengah dalam ruang dan peraturan takat tengah (crank-Nicholson) dalam masa digunakan. Saiz jejaring adalah diambil cukup kecil dengan itu ralat ruang dan ralat masa diabaikan. Persamaan algebra tidak linear diperolehi sebagai satu hasil pengdiskretan perbezaan terhingga adalah diselesaikan menggunakan teknik berangka cekap menggunakan IMSL subroutin DNEQNJ.

Bahagian daya elektrostatik adalah lebih besar dalam nilai, apolar, dengan itu kita dapati iaitu ia memainkan peranan penting dalam pencirian filem nipis dan kesan utama ke atas tingkahlaku tenaga bebas berlebihan, kadar tumbuh maksimum, gelombang neutral, gelombang nombor dominan, panjang gelombang. dominan dan masa pecah. Teori linear mungkin terlebih anggaran atau terkurang anggaran masa pecah oleh beberapa tertib magnitud bergantung atas parameter filem nipis. Dengan itu teori linear adalah tidak cukup untuk menghurai ciri kestabilan filem dan dengan itu, keperluan satu pendekatan tidak linear kepada kajian bagi dinamik filem nipis. Pengiraan menunjukkan daya apolar dan daya elektrostatik mungkin hanya bertanggungjawab bagi pembentukan filem flat no $h_0 \cong 30\,nm$ ketebalan. Dalam hal ini teori cadangan adalah konsisten dengan kesan daya apolar dan daya elektrostatik ke atas filem cecair nipis pada satu satah mendatar.

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LIST OF SYMBOLS

A	Area	m^2
A'	Hamakar constant	-
A'_{ij}	Hamakar constant for various binary interactions	-
Ca	Capillary number	-
d_0	Equilibrium separation distance between two bulks phase at contact	nm
$H(h)$	Thickness of thin film	nm
h_0	Mean thickness of thin film	nm
k	Debye length	nm
L	Distance from the surface	nm
L_0	Equilibrium distance	nm
$P(p)$	Hydrodynamic pressure inside the film	Kpa
P_0	Pressure in the film	Kpa
q	Nondimensional wavenumber (a small parameter) used for rescaling space and time coordinates	-
S^{LW}	apolar component of spreading coefficient of the film liquid	mJ/m^2
R	Radius of a sphere	cm
$T(t)$	Time coordinate	-
t_l	Rupture time from linear theory	sec
t_n	Rupture time from nonlinear theory	-
$U(u)$	x-Component of the velocity vector	- (m/s)

$W(w)$	z -Component of the velocity vector	- (m/s)
$X(x)$	Spatial coordinate in the longitude direction	- (m)
$Z(z)$	Spatial coordinate in the longitude direction	- (m)

Greek Symbols

σ	Surface tension	mJ/m^2
ε	Amplitude of perturbation	-
ψ	Electrical potential	mJ/m^2
φ	Dielectric constant	-
ξ,τ	Rescaled spatial and time coordinate for long wave approximation	-
λ	Wavenumber of perturbation	-
λ_m	Dominant wavenumber of perturbation	-
λ_{ml}	Nondimensional dominate wavenumber of perturbation	-
λ_n	Neutral wavenumber of perturbation	-
μ	Dynamic viscosity of film fluid	$g/cm.s$
ν	Kinematics viscosity of film fluid	$g/cm.s$
ρ	Density of the film fluid	g/cm^3
γ	Interfacial tension	mJ/m^2
γ^{LW}	The apolar surface tension component	mJ/m^2
γ_{ij}^{LW}	The apolar surface tension component between phases i and j	mJ/m^2
Ω	Magnitude of ion valence	-

ΔG	Excess free energy per unit area due to intermolecular interactions	mJ/m^2
ΔG^{EL}	The electrostatic component of free energy	mJ/m^2
ΔG^{LW}	The apolar component of free energy	mJ/m^2
ΔG^{LW}_{132C}	Free energy change in bringing two bluk material 1 and 2 from infinity to equilibrium separation distance, d_0 thickness of the thin film	mJ/m^2
ΔG_T	Total excess free energy per unit area due to intermolecular interactions	mJ/m^2
ΔP	Pressure difference causing the film to thin	kpa
Π	Disjoining pressure	kpa
Γ_m	Dominate wavelength from linear theory	-
Γ_n	Neutral wavelength from linear theory	-
ω	Disturbance growth coefficient	m^3/s
ω_m	Maximum disturbance the growth coefficient	m^3/s
ϕ	First derivative of the excess free energy, ΔG	mJ/m^2
ϕ_h	Second derivative of the excess free energy, ΔG	mJ/m^2