Interfacial Phenomena in a Thin Film

MOTIVATION

- Interfacial phenomena involve the study of
  - Capillary forces
  - Marangoni stresses (flow due to surface tension gradient)
  - Liquid/Vapor Interfacial Phase-Change
  - Intermolecular forces (van der Waals interactions, etc.)
- These concepts are important in explaining fundamental phenomena like spreading, coating, adsorption, stability, pattern formation, evaporation, condensation, etc.

MOTIVATION : APPLICATIONS

1. Miniature Heat Pipes
   Passive fluid flow and phase-change heat transfer (evaporation and condensation)

2. Surfactant adhesion/spreading
   Spreading of surfactant containing drops

3. MEMS/Microfluidics
   Fluid flow and phase-change in micro-channels, droplets

4. Micro-electronics
   Stability of thin solid films on Si, adhesive properties of thin porous films for spin coating applications etc.

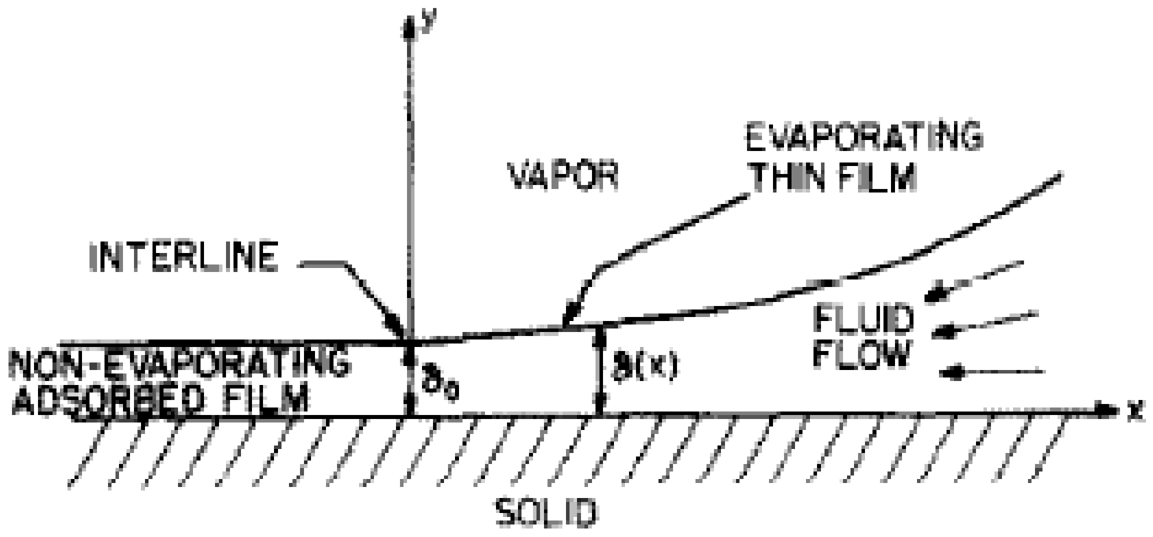
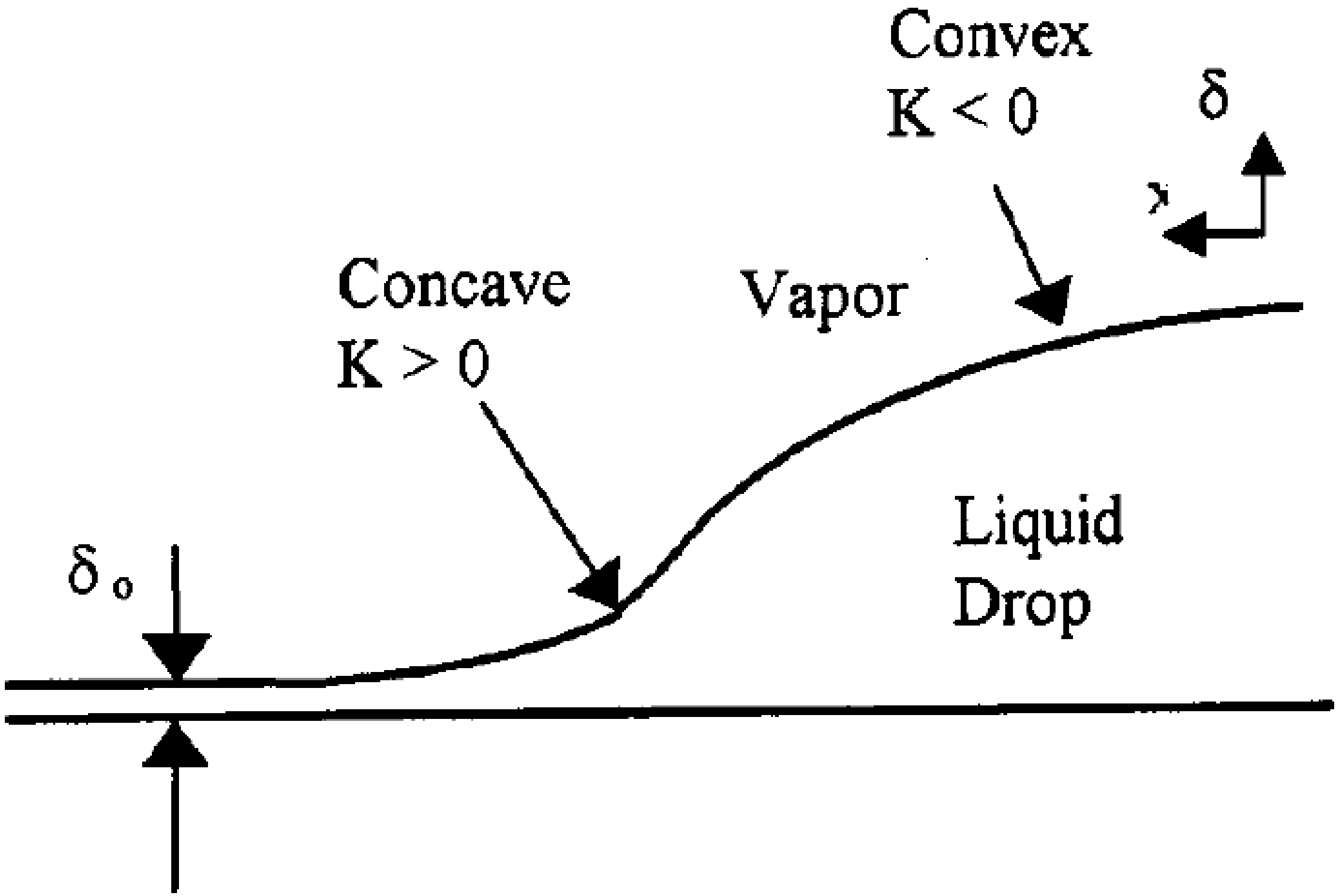


FIG. 1. Interline junction of vapor, adsorbed evaporating thin film and adsorbed non-evaporating thin film.

The heat transfer and other transport phenomena in the **contact line** (interline) region, where the liquid, vapor and the solid are in close proximity, are important in many technologically important processes, e.g., rewetting of a hot spot.



Schematic drawing of the measured interfacial profile of a condensing drop

INTRODUCTION

Capillary Pressure : $\sigma_{l\,v}\,K$

K is the curvature,
+ve for a concave surface,
-ve for a convex surface

Disjoining pressure :

$$\Pi = \frac{-\bar{A}}{\delta^3} \quad ; \quad \delta < 20nm$$

$$= -\frac{B}{\delta^4} \quad ; \quad \delta > 20nm$$

$\bar{A}$ is the modified Hamaker constant,
B is the dispersion constant

They are negative for a wetting system

Capillary and disjoining pressures are functions of the thickness profile.

Augmented Young-Laplace equation

$$\Delta P = P_l - P_V = -\sigma K - \prod$$

where P_v is the vapor pressure, P_l is the pressure inside the liquid, K is the curvature of the liquid–vapor interface, σ is the surface tension, and δ is the film thickness of the liquid.

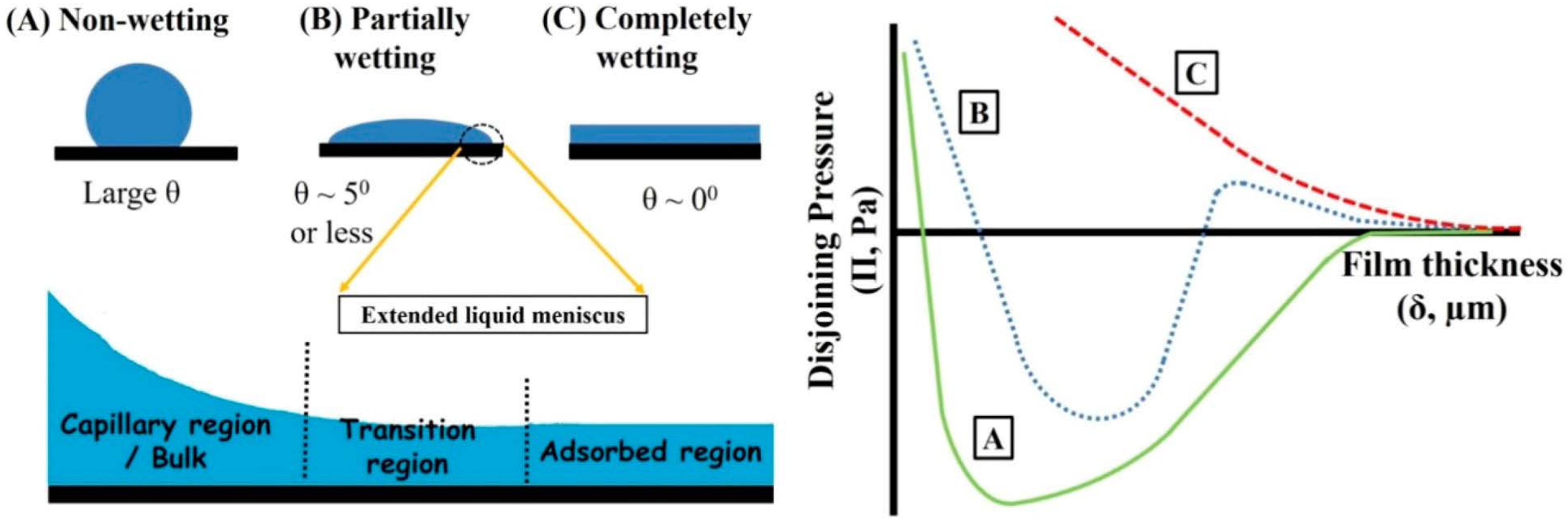
The second term on the right-hand side of the equation signifies the van der Waals interactions and is defined as[49]

$$\frac{\partial \Delta G^{vdw}}{\partial \delta} = \frac{A}{6\pi\delta^3} = -\Pi,$$

Where ΔG^{vdw} is the excess interfacial free energy per unit area due to the van der Waals interactions. The symbol A is the Hamaker constant

A negative value of the Hamaker constant (van der Waals interaction) signifies that a thin film in the microscopic region, with a thickness of that studied herein, will be stable and will reduce the free energy of the system.

We use the sign convention that a negative Hamaker constant and a positive disjoining pressure (Π) represent a system showing a stable, adsorbed wetting film.



(i) (ii)

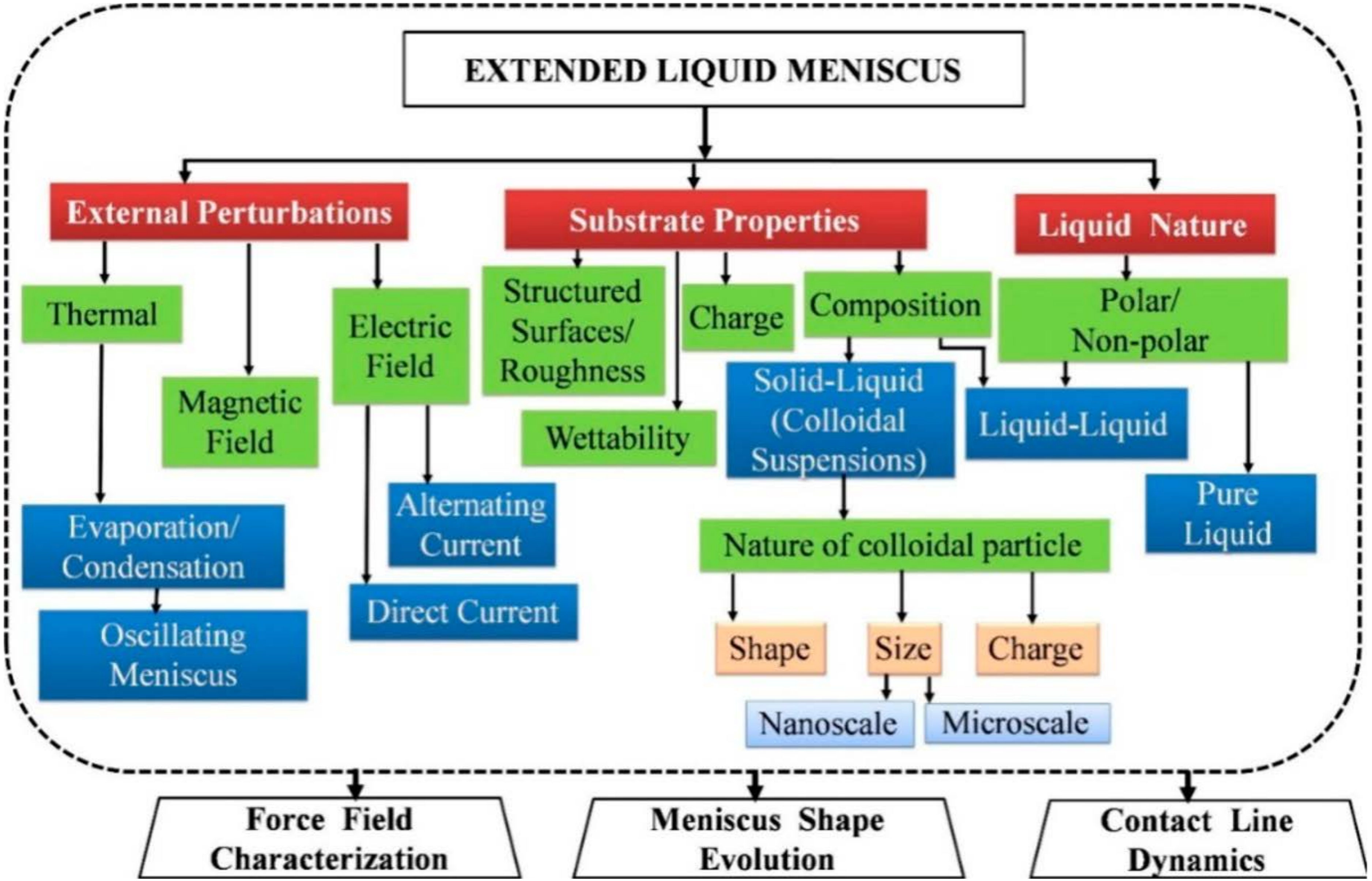
Classification of **(i)** wetting scenarios based on the magnitudes of the contact angles (θ) as nonwetting, partially wetting, and completely wetting films. The extended meniscus region can be observed for the partially wetting and wetting films and can be divided into three spatial regions in decreasing order of film thickness as the capillary region, transition region, and adsorbed region.

(ii) Disjoining pressure isotherms for (A) nonwetting, (B) partially wetting, and (C) complete wetting.

The Hamaker constant, A, for two phases, 1 and 2, interacting across a medium 3 can be expressed in terms of the refractive indices and the dielectric constants of the three phases.

$$A = \frac{3}{4}kT\left(\frac{\varepsilon_1-\varepsilon_3}{\varepsilon_1+\varepsilon_3}\right)\left(\frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3}\right)+\frac{3h\nu_e}{8\sqrt{2}}\frac{(n_1^2-n_3^2)(n_2^2-n_3^2)}{(n_1^2+n_3^2)^{1/2}(n_2^2+n_3^2)^{1/2}\{(n_1^2+n_3^2)^{1/2}+(n_2^2+n_3^2)^{1/2}\}},$$

where ε is the static dielectric constant, k is the Boltzmann's constant, h is the Planck's constant, ν_e is the plasma frequency of the free electron gas and n is the refractive index.



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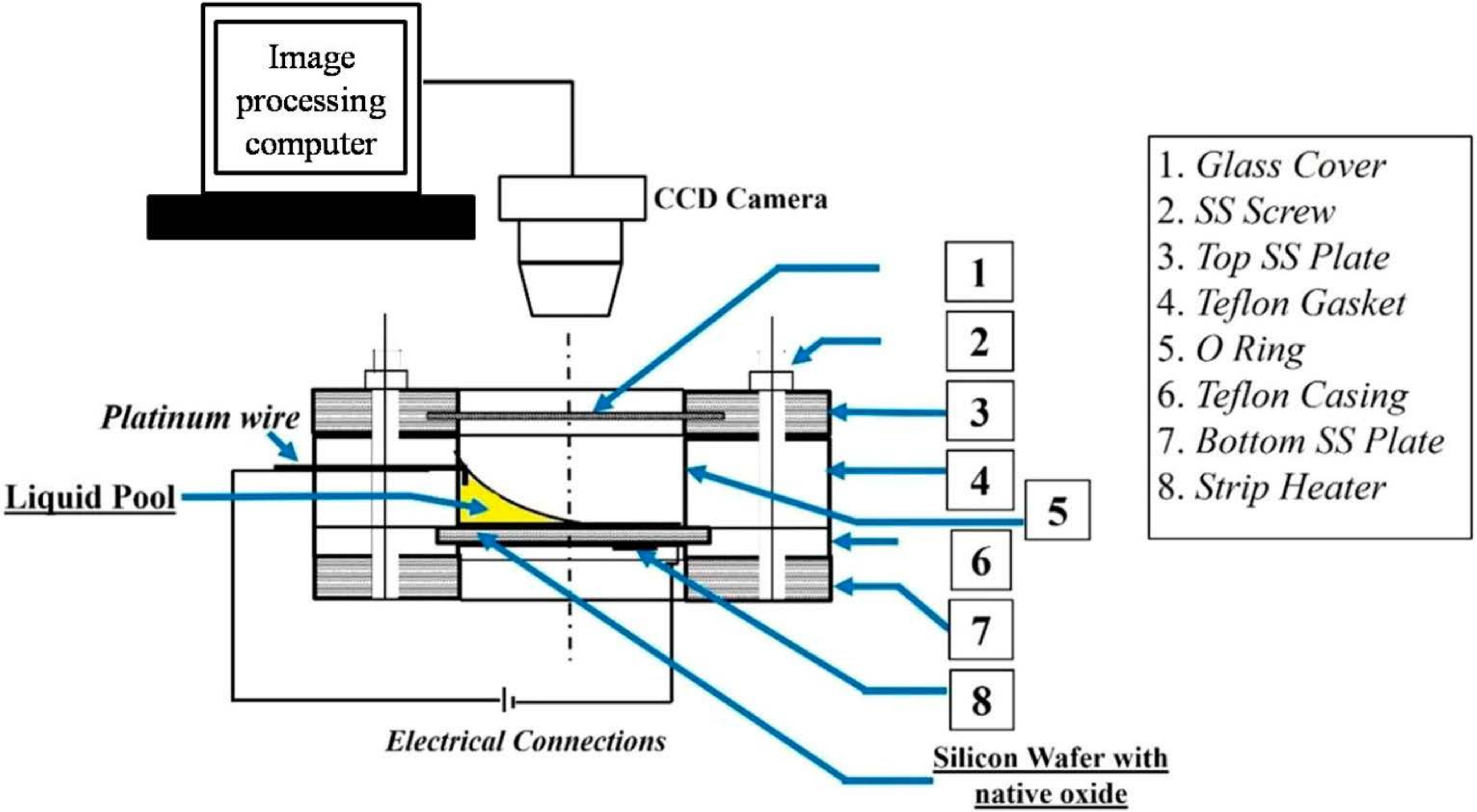
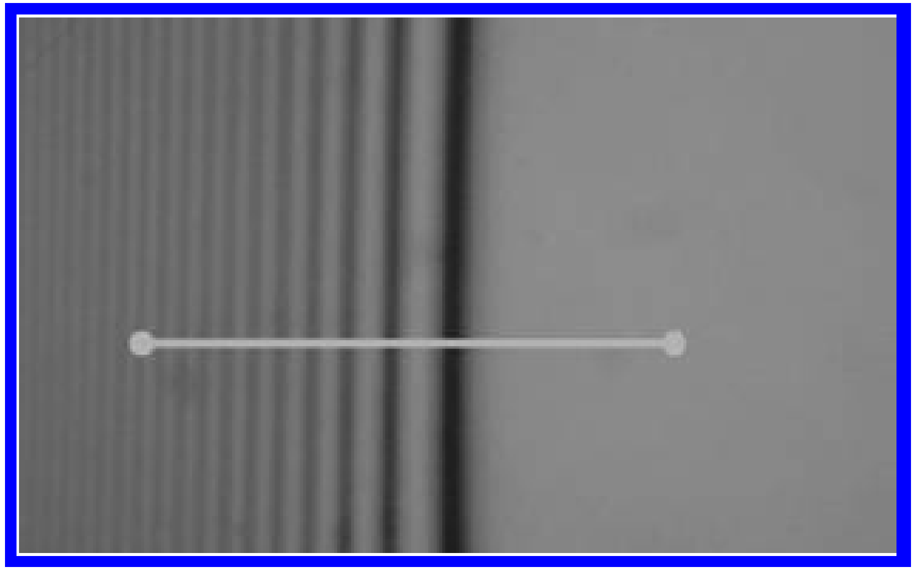


Schematic of the experimental setup.



Typical interference pattern observed for heptane on glass

Langmuir **2007**, *23*, 1234−1241

Image digitization → Assignment of Gray value → Determination of Relative Gray value

$$\bar{G}(x) = \frac{G(x) - G_{\min}(x)}{G_{\max}(x) - G_{\min}(x)}$$

$$RL = \bar{G}(x)[RL_{\max} - RL_{\min}] + RL_{\min}$$

$$\left.\begin{aligned} \theta_l &= \frac{2\pi\delta n_l}{\lambda}; \alpha = r_1^2 + r_2^2; \\ r_1 &= \frac{n_l - n_v}{n_l + n_v}; \beta = 2r_1 r_2; \\ r_2 &= \frac{n_s - n_l}{n_l + n_s}; \kappa = 1 + r_1^2 r_2^2 \end{aligned}\right] RL = \frac{\alpha + \beta\cos 2\theta_l}{\kappa + \beta\cos 2\theta_l} = f(\delta)$$

→ Evaluation of Film Thickness, δ → Evaluation of Slope → Evaluation of Film Curvature, K

Algorithm for thin film thickness and curvature evaluation, where the different notations have the following meanings: G, gray value; $\bar{G}$, relative gray value; RL, reflectivity; δ, film thickness; K, curvature; nl, nv, and ns, refractive indices of the liquid, vapor, and solid, respectively; λ, wavelength of the monochromatic light used for illumination.

Force field characterization model

$$\prod + \sigma K - \rho_l \, g \, H = 0$$

Force balance at equilibrium

$$\prod(\text{Disjoining Pressure}) = \frac{-B}{\delta^n}$$

Disjoining pressure

$$\Delta P = P_l - P_V = -\sigma K - \prod$$

Augmented Y-L equation

$$\sigma K - \frac{B}{\delta^4} = \sigma K_\infty \qquad Q = 0$$

Isothermal condition, K_∞ is the curvature of the capillary meniscus

$$\sigma \frac{d^2\delta}{dx^2} - \frac{B}{\delta^4} = \sigma K_\infty$$

Using simplified form of curvature

Non-dimensionalization

$$\eta = \frac{\delta}{\delta_0} \qquad Z = x\left(\frac{K_\infty}{\delta_0}\right)^{1/2}$$

$$\frac{\mathrm{d}^2\eta}{\mathrm{d}Z^2} + \left(\frac{-B}{\sigma K_\infty \delta_0{}^4}\right)\frac{1}{\eta^4} = 1.$$

Parameter, α, defined as

$$\alpha^4 = \frac{-B}{\sigma K_\infty \delta_0{}^4}$$

α is a measure of the deviation of a specific meniscus from the equilibrium conditions, α = 1 at equilibrium

$$\left(\frac{\mathrm{d}\eta}{\mathrm{d}Z}\right)^2 = 2\eta + \frac{2}{3}\frac{\alpha^4}{\eta^3} + C_1$$

BC $\eta = \alpha,\ \mathrm{d}\eta/\mathrm{d}Z = 0,$

Slope of a curved thin film can be obtained accurately using Y-L eqn.

$$\frac{\mathrm{d}\delta}{\mathrm{d}x} = -(K_\infty \delta_0)^{1/2}\sqrt{2\eta + \frac{2}{3}\frac{\alpha^4}{\eta^3} - \frac{8}{3}\alpha}$$

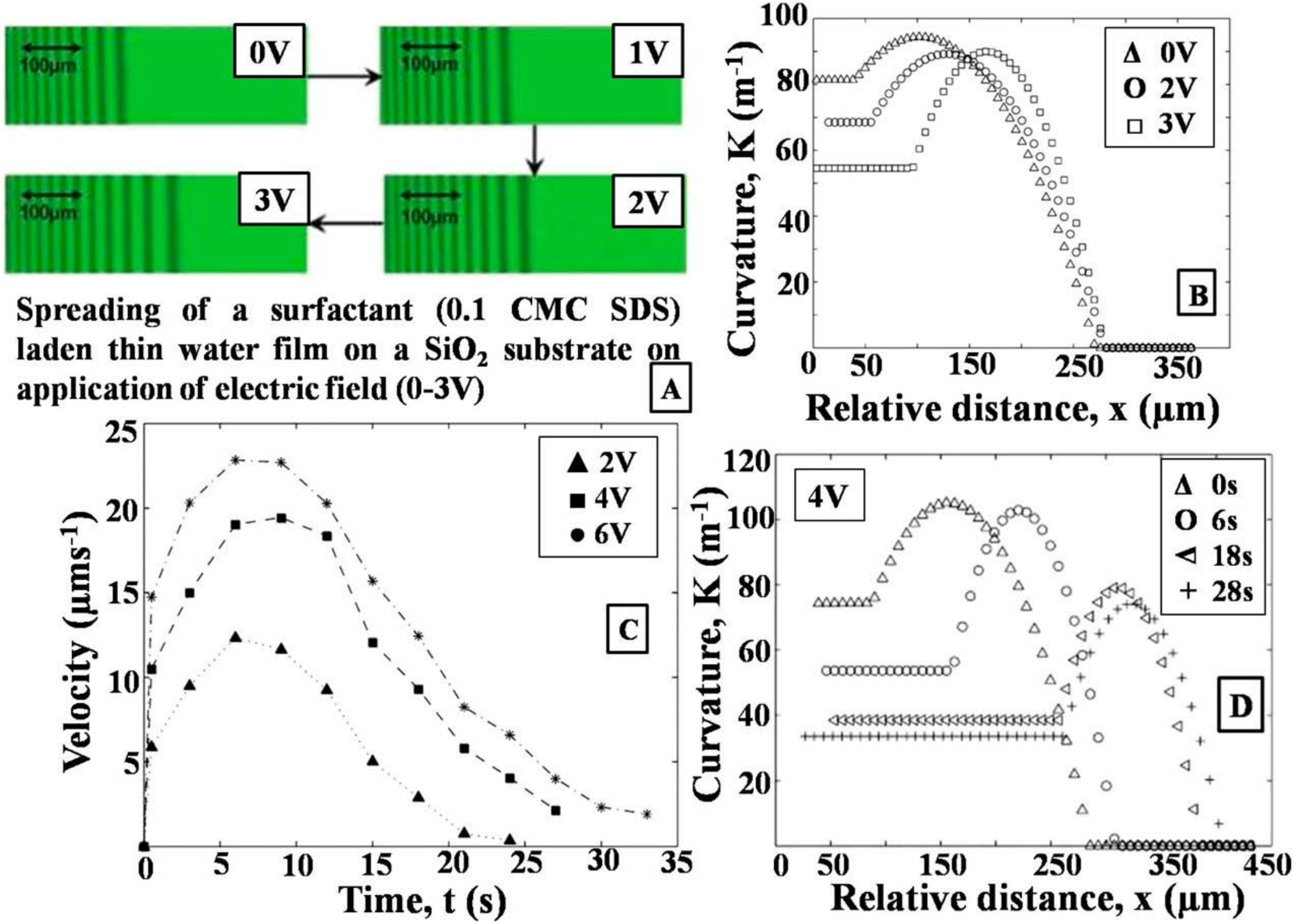
IN-SITU evaluation of B

Langmuir **2007,** *23,* 1234−1241

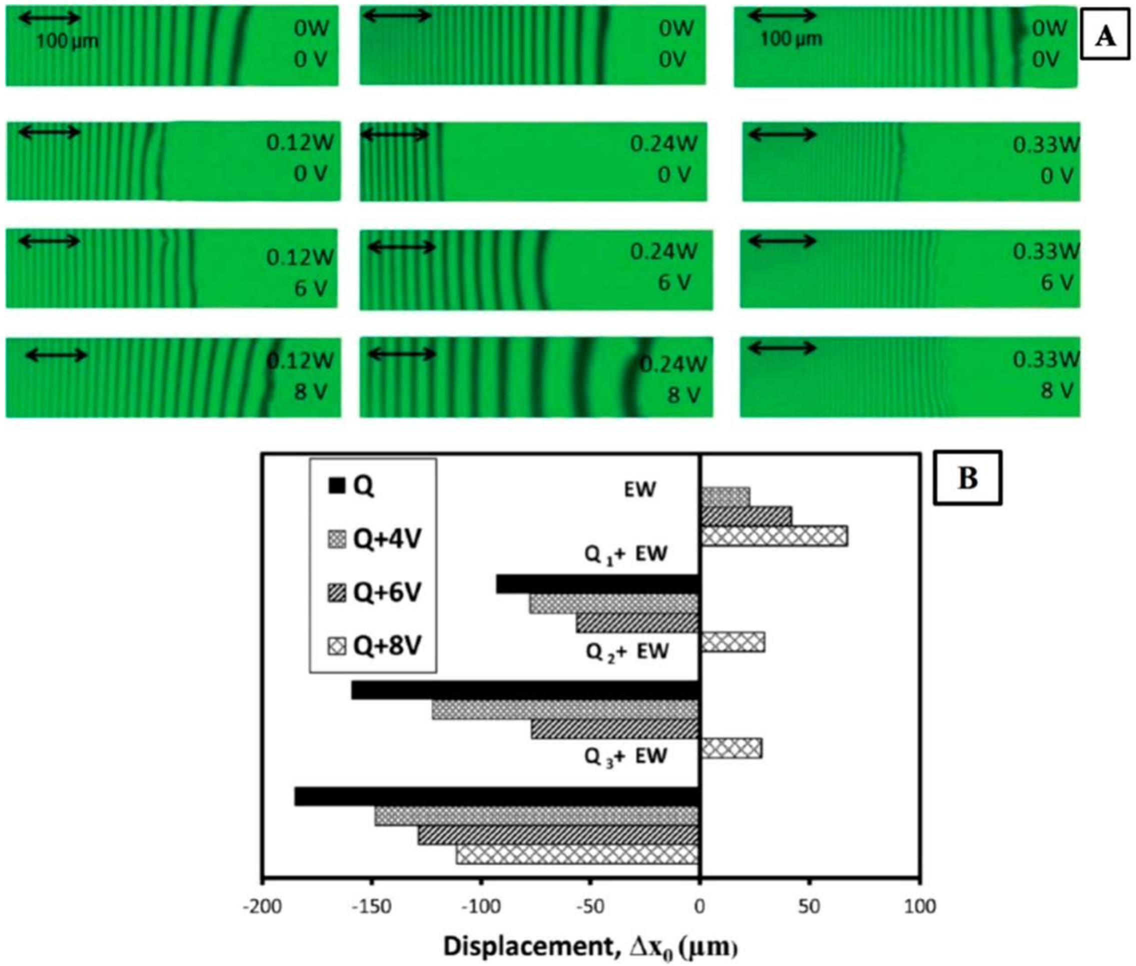
Variation of Capillary Pressure and Suction Potential for an Extended Meniscus Subjected to Thermal Perturbations

	δ_0 (m^{-1})	B/δ_0^4 (Pa)	K_∞ (m^{-1})	σK_∞ (Pa)	α
near equilib.	3.39×10^{-8}	8.02	392.62	7.90	1.004
evaporation	1.2 × 10–8	4.00	452.03	9.10	0.814
condensation	3.9 × 10–8	5.57	258.77	5.21	1.017

Electric Field Enhanced Spreading of Thin Liquid Films

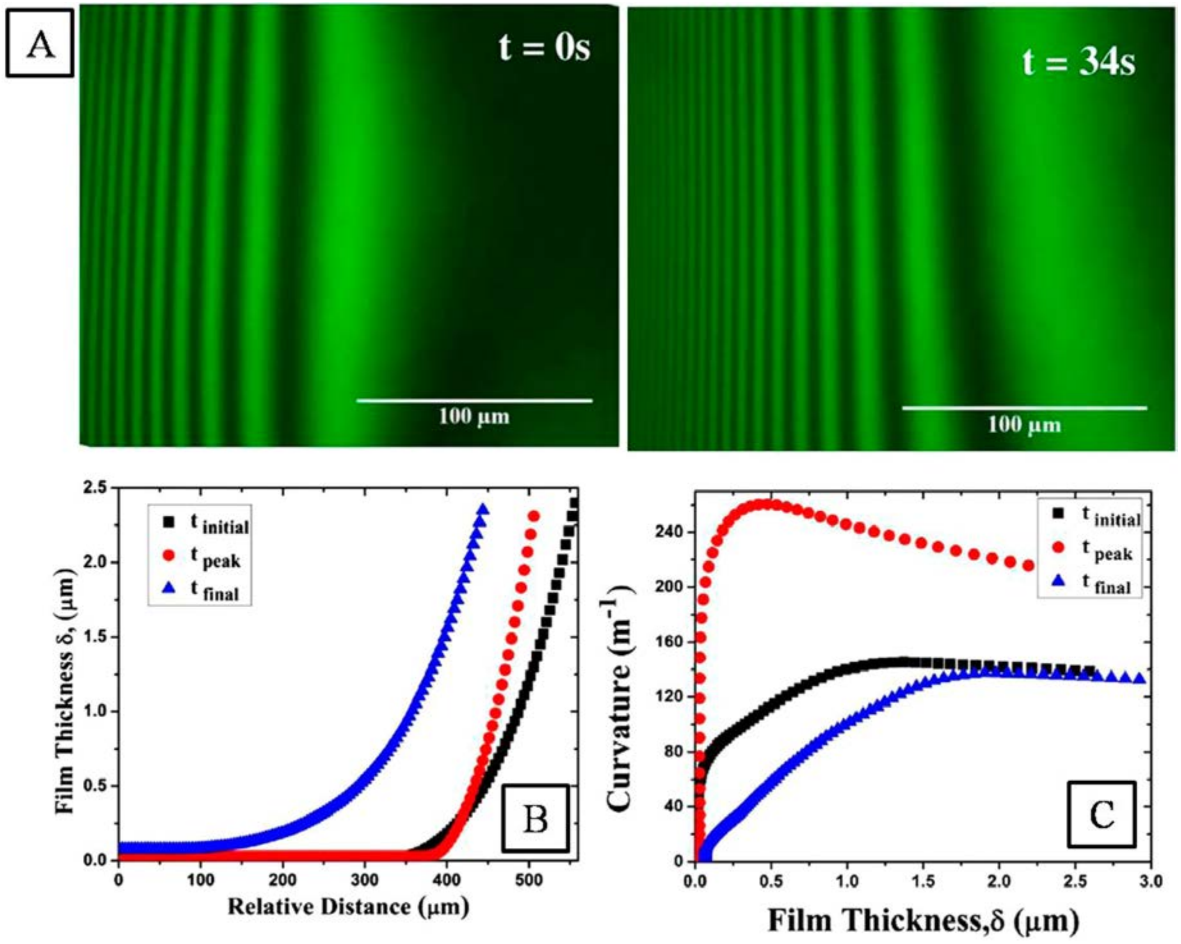


(A) Experimentally observed increase in fringe spacing with an increase in applied voltage and (B) the corresponding decrease in the capillary region curvature, (C) an enhancement in the contact line spreading velocity with increasing driving force (applied voltage), and (D) a dynamic reduction in the capillary end curvature of a liquid meniscus at a specific applied voltage (4 V).



Interferometric images showing the recession during the evaporation of the liquid meniscus countered by the advancement of the meniscus upon application of an electric field. (B) Displacement of the meniscus with increasing voltage at specific heat loads, Q_1 = 0.12 W, Q_2 = 0.24 W, and Q_3 = 0.33 W. The vertical line at $\Delta x_0 = 0$ indicates the reference meniscus position in the absence of an applied electric field and heat flux.

Magnetic Field Enhanced Spreading of Thin Liquid Films



(A) Image sequence depicting the thin film on exposure to a magnetic field at the initial (t = 0 s) and final (t = 34 s) instants. (B) Spatiotemporal behavior of the thin film thickness when subjected to magnetic field. (C) Variation in film curvature in the presence of a magnetic field with film thickness.

Using the lubrication approximation, the governing equation for liquid flow inside a thin film could be modified so as to include the body force (magnetic force) term and is given as

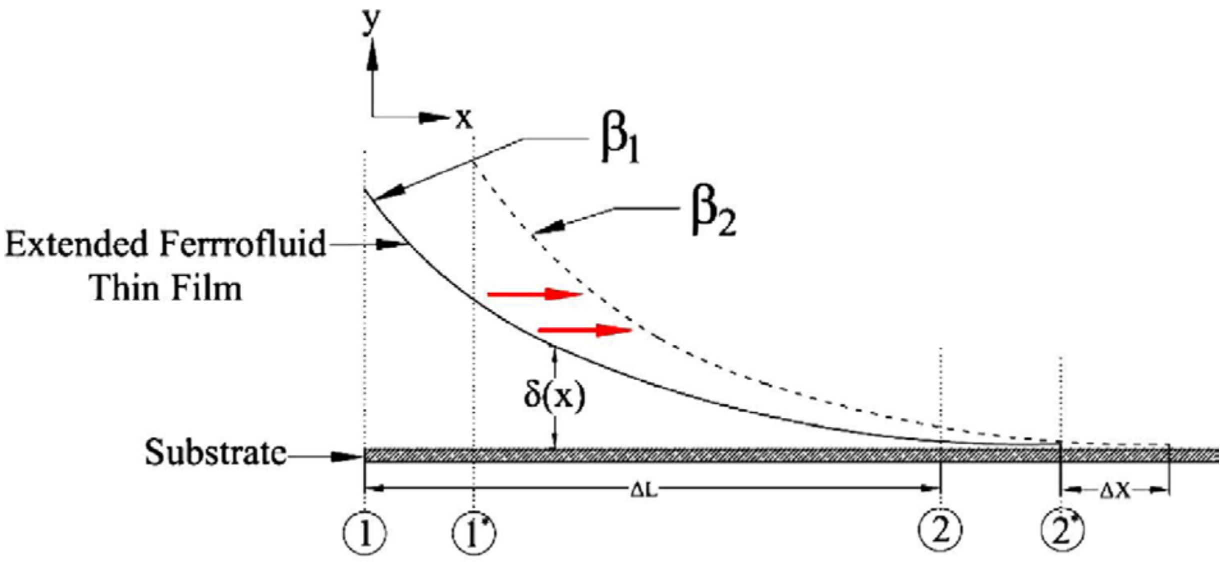
$$\frac{dp_l}{dx} = \mu \frac{d^2 u(x)}{dy^2} + \beta$$

Where, μ denotes the viscosity of the liquid and β denotes the net magnetic force per unit volume.

Integrating the above equation with the appropriate boundary conditions (no slip at the wall and no shear at the interface), the average velocity is obtained as

$$u_{avg} = \frac{1}{\mu\delta}\int_0^{\delta}\left[\left(\frac{dp_l}{dx}\right) - \beta\right]\left(\frac{y^2}{2} - \delta y\right)dy = -\frac{\delta^2}{3\mu}\left[\left(\frac{dp_l}{dx}\right) - \beta\right]$$

where, δ represents the film thickness at a specific location (along the x-direction)



The control volume in the present case represents the expanse between the two regions of the extended meniscus, one region with an almost constant curvature K_∞ (the capillary region, point 1 in the figure and the other region, close to the contact line (point 2) Hence, the modified expression for the average velocity could be represented as

$$u_{avg} = -\frac{\delta^2}{3\mu}\left(\frac{P_{l_1} - P_{l_2}}{\Delta L} - \beta\right)$$

$$u_{avg} = -\frac{\delta^2}{3\mu}\left(\frac{P_{l_1} - P_{l_2}}{\Delta L} - \beta\right)$$

The pressure jump across the liquid-vapor interface at any given instance of time can be approximated at the two ends of the film as

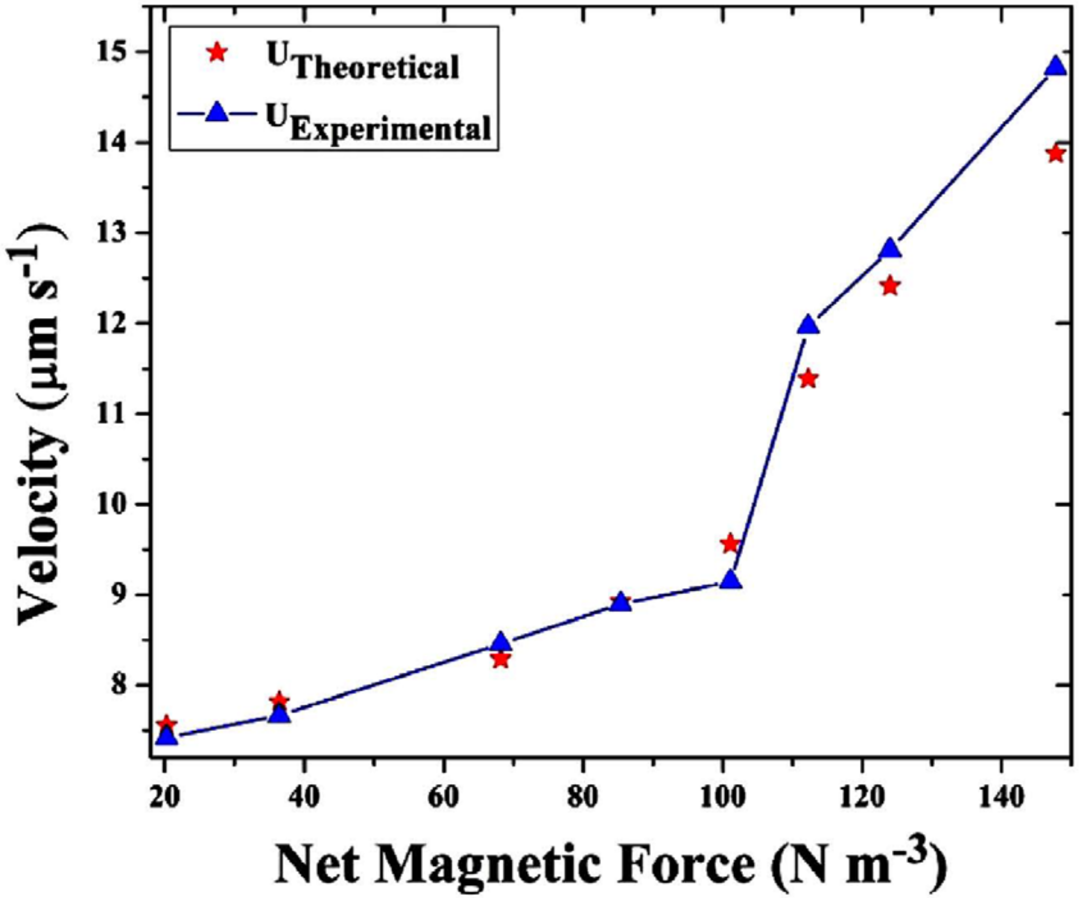
$$P_{l_1} - P_v = -\sigma K_{\mathrm{inf}}$$

$$P_{l_2} - P_v = -\Pi$$

$$\Delta P = P_{l_2} - P_{l_1} = -\Pi + \sigma K_{\mathrm{inf}}$$

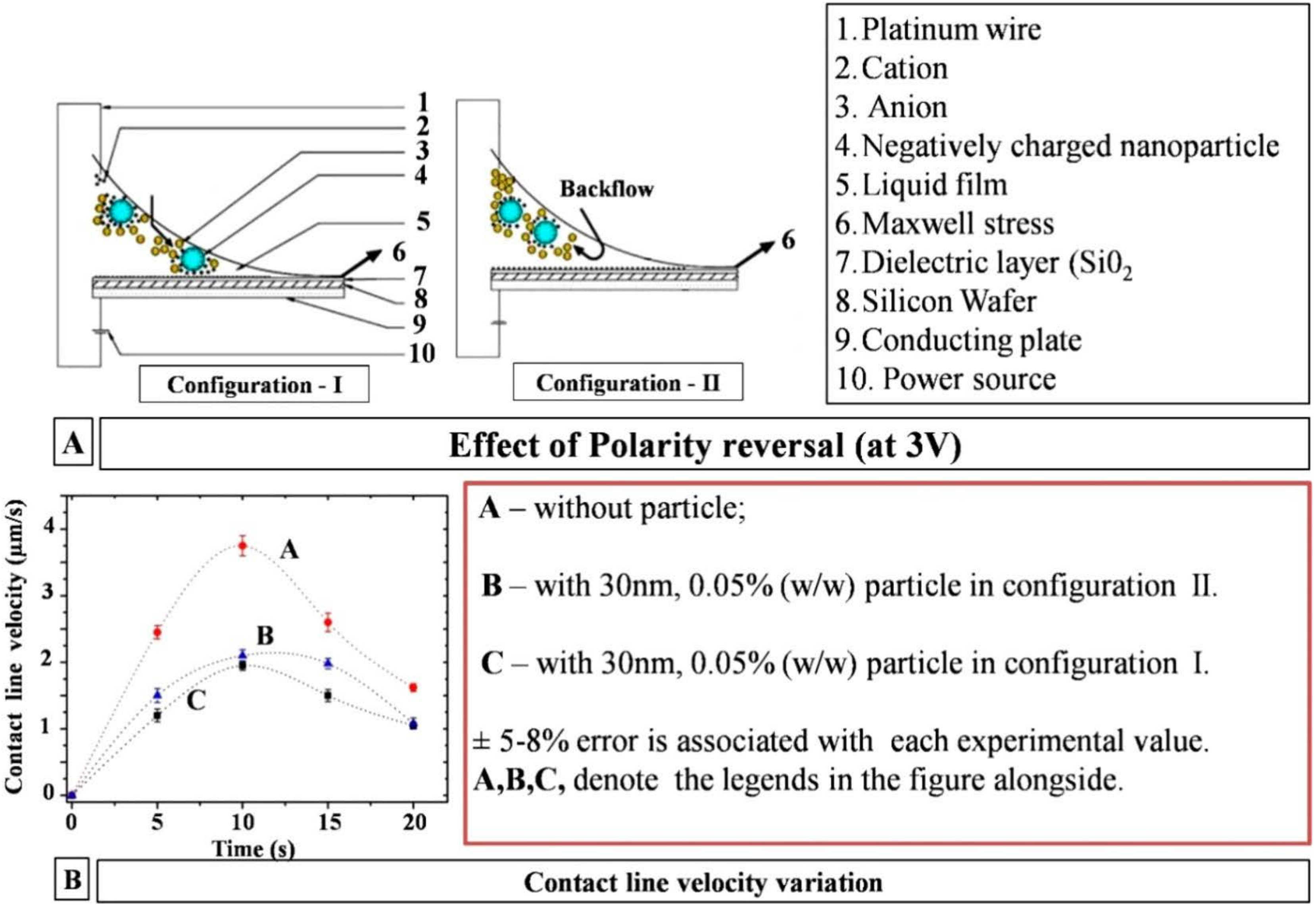
Therefore

$$u_{avg} = -\frac{\delta^2}{3\mu}\left(\frac{\Pi - \sigma K_{\mathrm{inf}}}{\Delta L} + \beta\right)$$

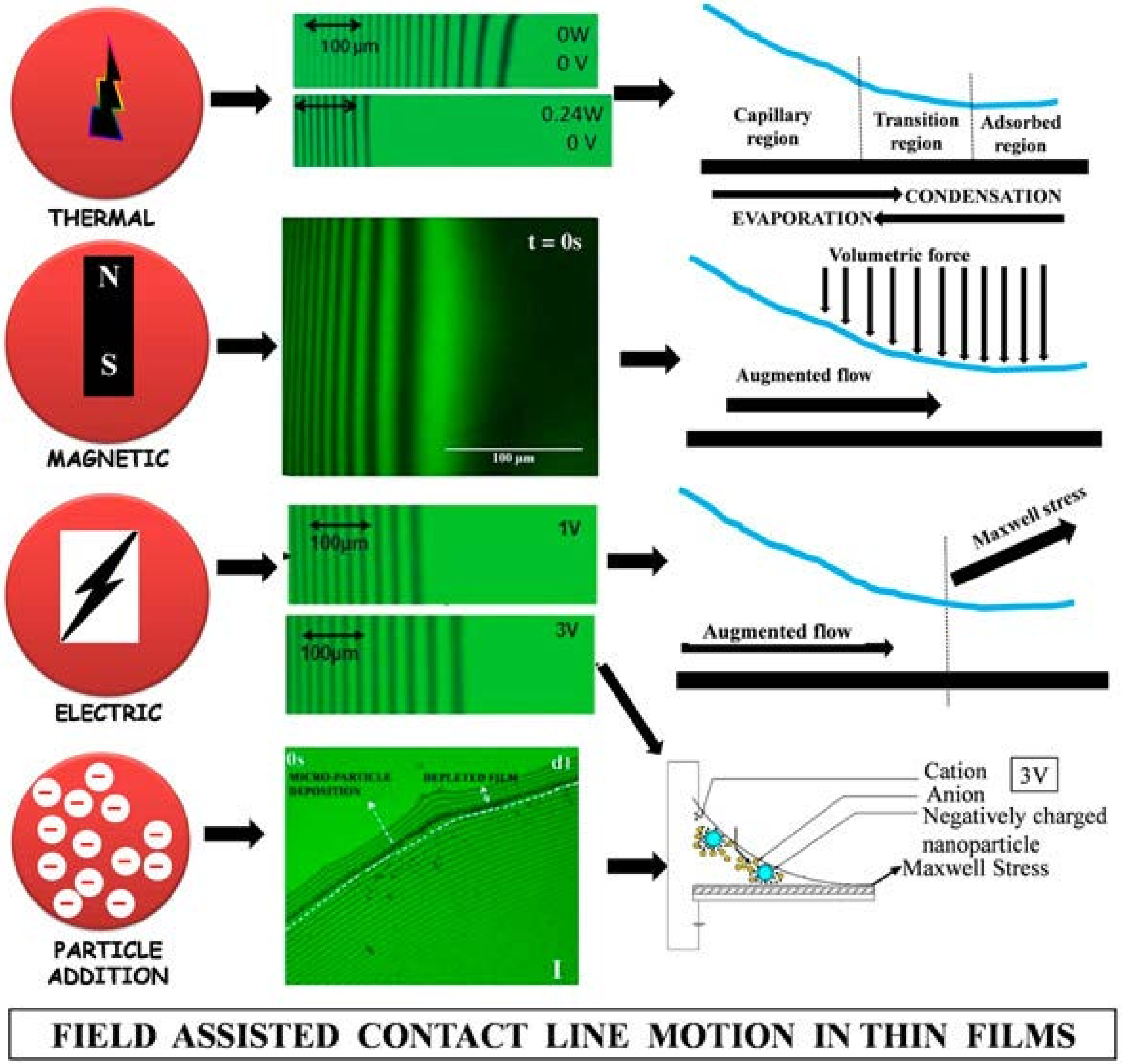


$$u_{avg} = -\frac{\delta^2}{3\mu}\left(\frac{\Pi - \sigma K_{\inf}}{\Delta L} + \beta\right)$$

Effect of Polarity of Suspended NP on the Spreading of Thin Liquid Films



(A) Configuration of the electrowetting setup for studying the effect of the reversal of electrode polarity. (B) Contact line velocity variation in the presence of nanoparticles (30 nm in diameter, carboxylate-modified, 0.05% w/w) and an electric field.


THERMAL
100μm
0W
0 V
0.24W
0 V
Capillary region
Transition region
Adsorbed region
CONDENSATION
EVAPORATION
MAGNETIC
N
S
t = 0s
100 μm
Volumetric force
Augmented flow
ELECTRIC
100μm
1V
100μm
3V
Maxwell stress
Augmented flow
PARTICLE ADDITION
0s
MICRO-PARTICLE DEPOSITION
DEPLETED FILM
I
Cation
Anion
3V
Negatively charged nanoparticle
Maxwell Stress
FIELD ASSISTED CONTACT LINE MOTION IN THIN FILMS