Spreading, retraction and sustained oscillations of surfactant-laden lenses

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Motivation

Van Nierop et al. PoF 2006

Daniels et al. 2007

Stocker & Bush JFM 2007
**Formulation I**

\[ \varepsilon = \frac{V_2}{L^2} \ll 1 \]

**Surfactant transport and chemical kinetics**

\[ S_{23} + c_2^* \leftrightarrow c_{23}^* \]
\[ S_{12} + c_2^* \leftrightarrow c_{12}^* \]
\[ S_{23} + c_{12}^* \leftrightarrow S_{12} + c_{23}^* \]
\[ S_{13} + c_{12}^* \leftrightarrow S_{12} + c_{13}^* \]
\[ S_{13} + c_{23}^* \leftrightarrow S_{23} + c_{13}^* \]

**Approximations**

- Lubrication theory
- Rapid vertical diffusion

\[ S_i = \text{empty space at interface } i \]
Formulation II

Governing Equations

\[ h_{12,t} = -\left( \int_0^{h_{12}} u_1 dz \right)_x \]

\[ h_{13,t} = -\left( \int_0^{h_{13}} u_1 dz \right)_x \]

\[ h_{23,t} = -\left( \int_0^{h_{12}} u_1 dz + \int_{h_{12}}^{h_{23}} u_2 dz \right)_x \]

where \[ \int u_i dz = f(h_i, \sigma_i) \]

\[ c_{2,t} + \frac{c_{2,x}}{h_{23} - h_{12}} \int_{h_{12}}^{h_{23}} u_2 dz = \left[ \frac{(h_{23} - h_{12})c_{2,x}}{(h_{23} - h_{12})Pe_{c2}} \right]_x - \frac{\beta_{c2c12}}{h_{23} - h_{12}} J_{c2c12} - \frac{\beta_{c2c23}}{h_{23} - h_{12}} J_{c2c23} - J_2 \]

\[ m_{2,t} + \frac{m_{2,x}}{h_{23} - h_{12}} \int_{h_{12}}^{h_{23}} u_2 dz = \left[ \frac{(h_{23} - h_{12})m_{2,x}}{(h_{23} - h_{12})Pe_{m2}} \right]_x + J_2 \]

\[ J_i = \text{sorption fluxes} \]
Formulation III

\[ c_{12,t} + (u_{x,12}c_{12})_x = \frac{c_{12,xx}}{Pe_{12}} + J_{c2c12} \]

\[ c_{13,t} + (u_{x,13}c_{13})_x = \frac{c_{13,xx}}{Pe_{13}} + J_{ev13} \]

\[ c_{23,t} + (u_{x,23}c_{23})_x = \frac{c_{23,xx}}{Pe_{23}} + J_{c2c23} + J_{ev23} \]

\[ J_i = \text{sorption fluxes} \]

Equation of state

Sheludko 1967

\[ \sigma_i = \left( 1 + \frac{1}{\Sigma_i} \right) \left( 1 + c_i \left( \left( 1 + \Sigma_i \right)^{1/3} - 1 \right) \right)^{-3} \]

\[ \Sigma_i = \frac{(\sigma^*_{io} - \sigma^*_{im})}{\sigma^*_{im}} \]

\[ \delta_i = \frac{\sigma^*_{im}}{\sigma^*_{23m}} \]

\[ i = 12, 13, 23 \]
Formulation IV

Boundary Conditions

Contact line ($x = x_c$)

- $h_{12} = h_{13} = h_{23}$

- Force balance
  
  \[ h_{12,x} = h_{23,x} + f(\sigma_i) \quad h_{13,x} = h_{23,x} + g(\sigma_i) \]

- Continuity of pressure
  
  \[ F(h_{i,x}, \sigma_i) = 0 \]

- Mass conservation
  
  \[ 2\int_{0}^{x_c} h_{12} \, dx + 2\int_{x_c}^{x} h_{13} \, dx = V_1 \quad 2\int_{0}^{x_c} (h_{23} - h_{12}) \, dx = V_2 \]
Boundary Conditions

Contact line \((x = x_c)\)

\[
\left. \frac{c_{23,x}}{Pe_{23}} \right|_{x=x_c} = \beta_{c12c23} J_{c12c23} + \beta_{c13c23} J_{c13c23}
\]

\[
\left. \frac{c_{12,x}}{Pe_{12}} \right|_{x=x_c} = \beta_{c13c12} J_{c13c12} + J_{c12c23}
\]

\[
\left. \frac{c_{13,x}}{Pe_{13}} \right|_{x=x_c} = J_{c13c12} + J_{c13c23}
\]
Results I

Clean fluid

$\sigma_{12} = 1, \rho = 1, \mu = 1$

$\sigma_i = \frac{\sigma^*_{i} - \sigma^*_{im}}{\sigma^*_{io} - \sigma^*_{im}}$

$\rho = \frac{\rho^*_2}{\rho^*_1}$

$\mu = \frac{\mu^*_2}{\mu^*_1}$

$X_c \sim t^{1/7}$

Joanny 1987
Fraaije and Cazabat 1989

$S :$ spreading parameter

$S = \sigma_{13} - \sigma_{12} - 1$
Results II

Surfactant-laden drop

$M=8$, $\delta_{23}=1.9$, $\delta_{12}=1$,  
$\Sigma_i=0.1$, $\rho=\mu=1$

\[ M = \frac{M^*}{(V_2^* c_{cmc}^*)} \quad \Sigma_i = \frac{(\sigma_{io}^* - \sigma_{im}^*)}{\sigma_{im}^*} \quad \delta_i = \frac{\sigma_{im}^*}{\sigma_{23m}^*} \]
Results III

Effect of $M$

$\delta_{23}=1.9$, $\delta_{12}=1$, $\Sigma_i=0.1$

Long time drop shapes, $t=10^5$
Results IV

Adsorption at the contact line

\[ M = 8, \delta_{23} = 1.9, \delta_{12} = 1, \Sigma_i = 0.1 \]

\[ S_{13} + c_{12}^* \leftrightarrow S_{12} + c_{13}^* \]

\[ J_{c13c12} = k_{c13c12} \left[ R_{c13c12} c_{13} (1 - c_{12}) - c_{12} (1 - c_{13}) \right]_{x=x_c} \]
Results IV

Adsorption at the contact line

\[ M = 8, \delta_{23} = 1.9, \delta_{12} = 1, \Sigma_i = 0.1 \]

\[ S_{13} + c_{12}^* \leftrightarrow S_{12} + c_{13}^* \]

\[ J_{c_{13}c_{12}} = k_{c_{13}c_{12}} \left[ R_{c_{13}c_{12}} c_{13} (1 - c_{12}) - c_{12} (1 - c_{13}) \right]_{x = x_c} \]
Results V

Oil water interface:

Oleic acid + NaOH $\rightarrow$ Na-oleate

Van Nierop et al. PoF 2006
Results VI

Stocker & Bush JFM 2007
Results VI

Stocker & Bush JFM 2007
Results VI

Stocker & Bush JFM 2007

(a) Adsorption

(b) Evaporation
$k_{ev13} = \text{kinetic parameter for evaporation}$
Results VII

Effect of density ratio, $\rho$

$M=8$, $\delta_{23}=1.9$, $\delta_{12}=1$, $\Sigma=0.1$

$$\rho = \frac{\rho_2^*}{\rho_1^*}$$

Long time drop shapes, $t=10$

$$M = \frac{M^*}{\left(V_2^* c_{cmc}^*\right)} \quad \Sigma_i = \frac{(\sigma_{io}^* - \sigma_{im}^*)}{\sigma_{im}^*} \quad \delta_i = \frac{\sigma_{im}^*}{\sigma_{23m}^*}$$
We have studied the spreading of surfactant-laden drops on thin layers of another liquid. The presence of Marangoni stresses gives rise to very rich dynamics which may include:

- Spreading until the drop reaches equilibrium \((S < 0)\).
- Continuous spreading \((S > 0)\)
- Spreading followed by retraction.
- Self-sustained oscillations.
Thank you for your attention!