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Spreading, retraction and sustained oscillations of surfactant-laden lenses

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Workshop on Surfactant Driven Thin Films Flow
Fields Institute, Toronto, 24 February, 2012

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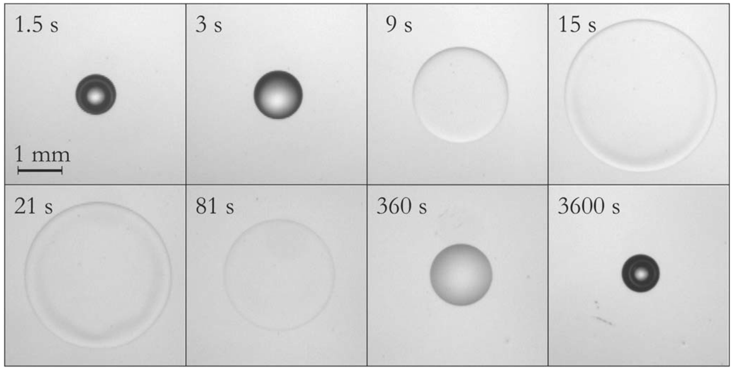
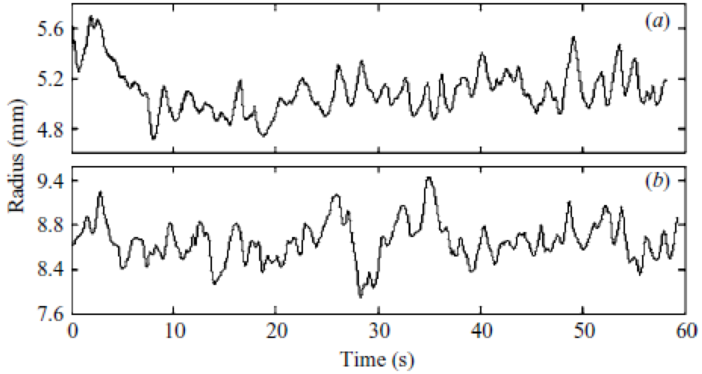
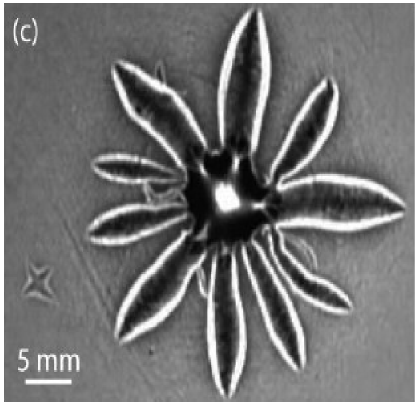
Motivation



Van Nierop et al. PoF 2006



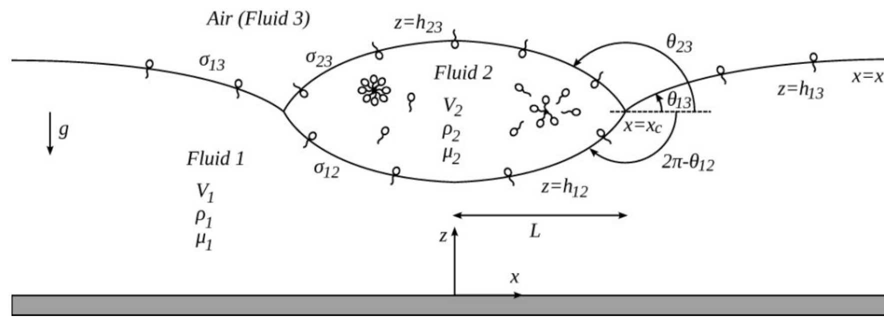
Stocker & Bush JFM 2007



Daniels et al. 2007

Formulation I

$$\varepsilon = V_2 / L^2 << 1$$



Surfactant transport and chemical kinetics

S_i = empty space at interface i

$$S_{23} + c_2^* \leftrightarrow c_{23}^* \qquad S_{12} + c_2^* \leftrightarrow c_{12}^* \qquad Nc_2^* \leftrightarrow m_2^*$$

$$S_{23} + c_{12}^* \leftrightarrow S_{12} + c_{23}^* \qquad S_{13} + c_{12}^* \leftrightarrow S_{12} + c_{13}^* \qquad S_{13} + c_{23}^* \leftrightarrow S_{23} + c_{13}^*$$

Approximations

- Lubrication theory
- Rapid vertical diffusion

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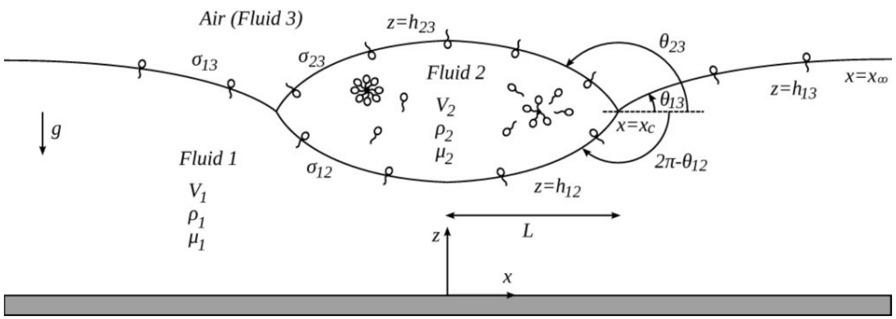
Formulation II



Governing Equations

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

$$h_{13,t} = -\left(\int_0^{h_{13}} u_1 dz \right)_x \qquad h_{23,t} = -\left(\int_0^{h_{12}} u_1 dz + \int_{h_{12}}^{h_{23}} u_2 dz \right)_x \qquad \text{where} \int u_i dz = f(h_i, \sigma_i)$$

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

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

J_i = sorption fluxes

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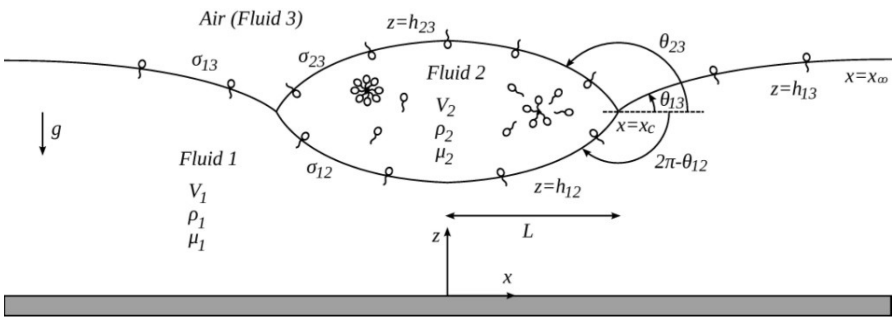
Formulation III

$$c_{12,t} + \left(u_{s,12} c_{12}\right)_x = \frac{c_{12,xx}}{Pe_{12}} + J_{c2c12}$$



$$c_{13,t} + \left(u_{s,13} c_{13}\right)_x = \frac{c_{13,xx}}{Pe_{13}} + J_{ev13}$$

$$c_{23,t} + \left(u_{s,23} c_{23}\right)_x = \frac{c_{23,xx}}{Pe_{23}} + J_{c2c23} + J_{ev23}$$

$J_i =$ sorption fluxes

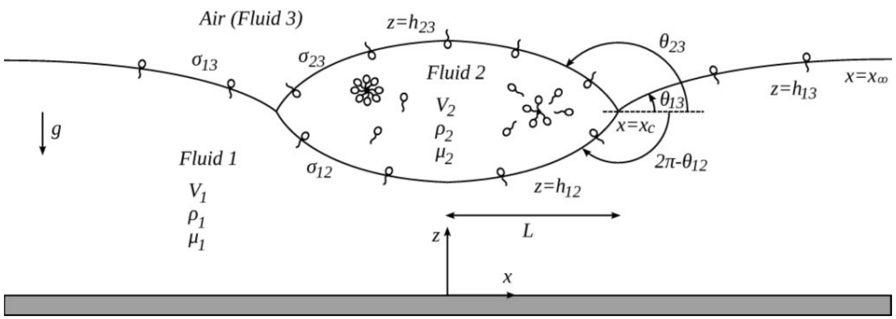
Equation of state

Sheludko 1967

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

$$\Sigma_i = \left(\sigma^*_{io} - \sigma^*_{im}\right)/\sigma^*_{im} \qquad \delta_i = \sigma^*_{im}/\sigma^*_{23m} \qquad i = 12,13,23$$

Formulation IV



Boundary Conditions

Contact line ($x = x_c$)

- $h_{12} = h_{13} = h_{23}$
- Force balance $h_{12,x} = h_{23,x} + f(\sigma_i)$ $h_{13,x} = h_{23,x} + g(\sigma_i)$
- Continuity of pressure $F(h_{i,xx}, \sigma_i) = 0$
- Mass conservation $2\int_0^{x_c} h_{12}dx + 2\int_{x_c}^{x_\infty} h_{13}dx = V_1$ $2\int_0^{x_c} (h_{23} - h_{12})dx = V_2$

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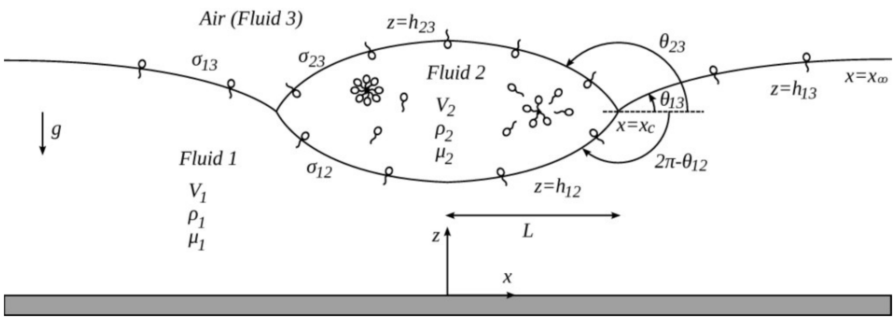
Formulation V

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

S : spreading parameter $\quad S = \sigma_{13} - \sigma_{12} - 1$

Clean fluid

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

$$\sigma_i = \frac{\sigma_i^* - \sigma_{im}^*}{\sigma_{io}^* - \sigma_{im}^*}$$

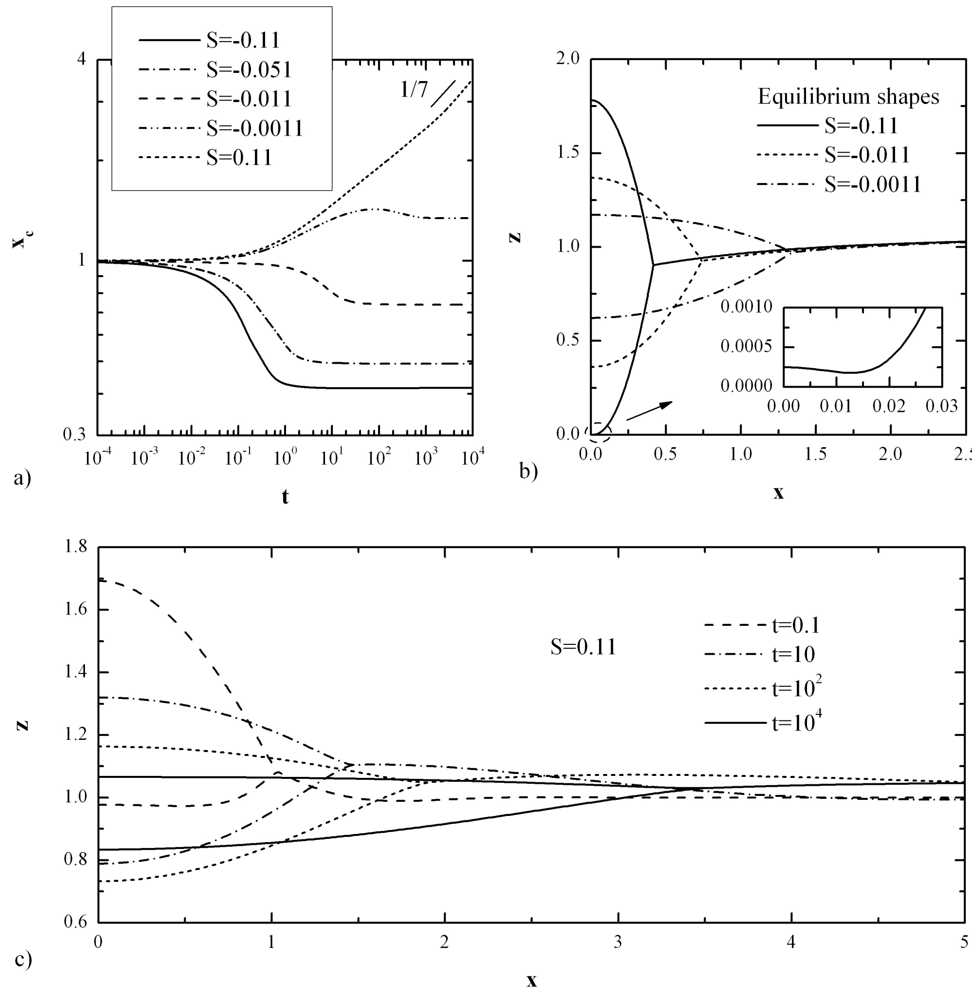
$$\rho = \frac{\rho_2^*}{\rho_1^*}$$

$$\mu = \frac{\mu_2^*}{\mu_1^*}$$

Joanny 1987

Fraaije and Cazabat 1989

$\Big\} \; x_c \sim t^{1/7}$



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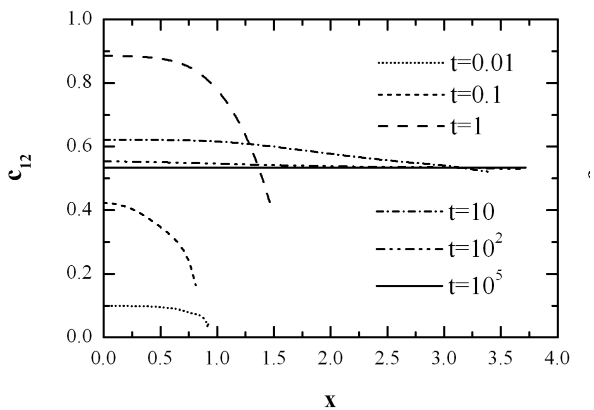
Results II

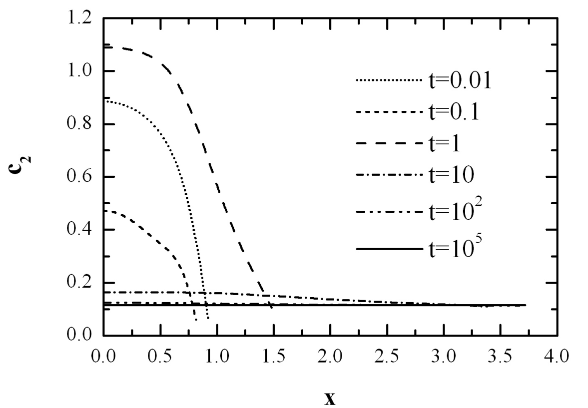
$$M = M^* / \left(V_2^* c_{cmc}^* \right) \qquad \Sigma_i = \left(\sigma_{io}^* - \sigma_{im}^* \right) / \sigma_{im}^* \qquad \delta_i = \sigma_{im}^* / \sigma_{23m}^*$$

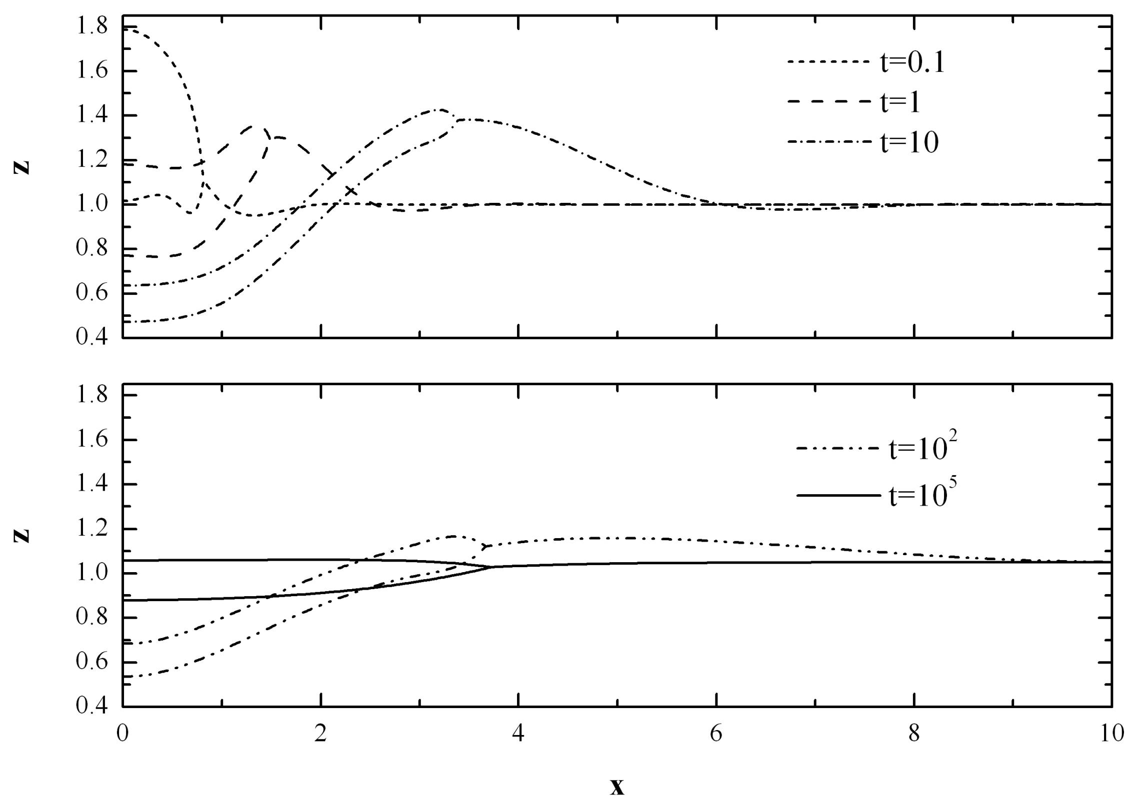
Surfactant-laden drop

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

$\Sigma_i=0.1$, $\rho=\mu=1$







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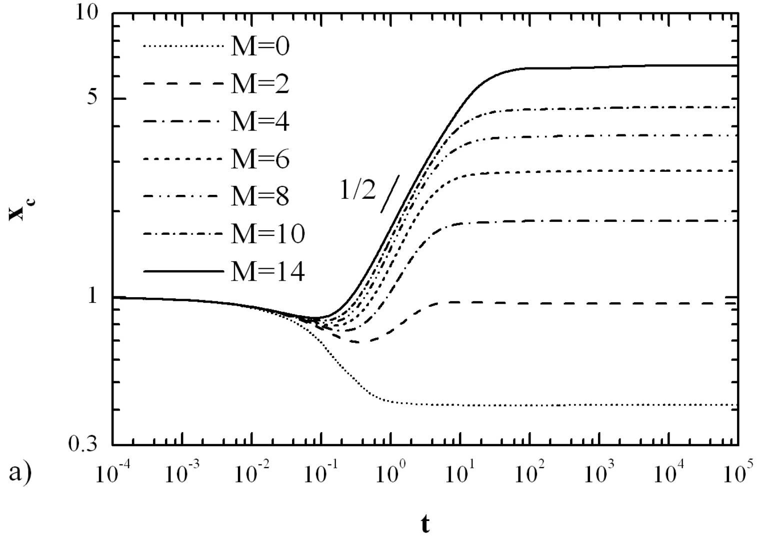
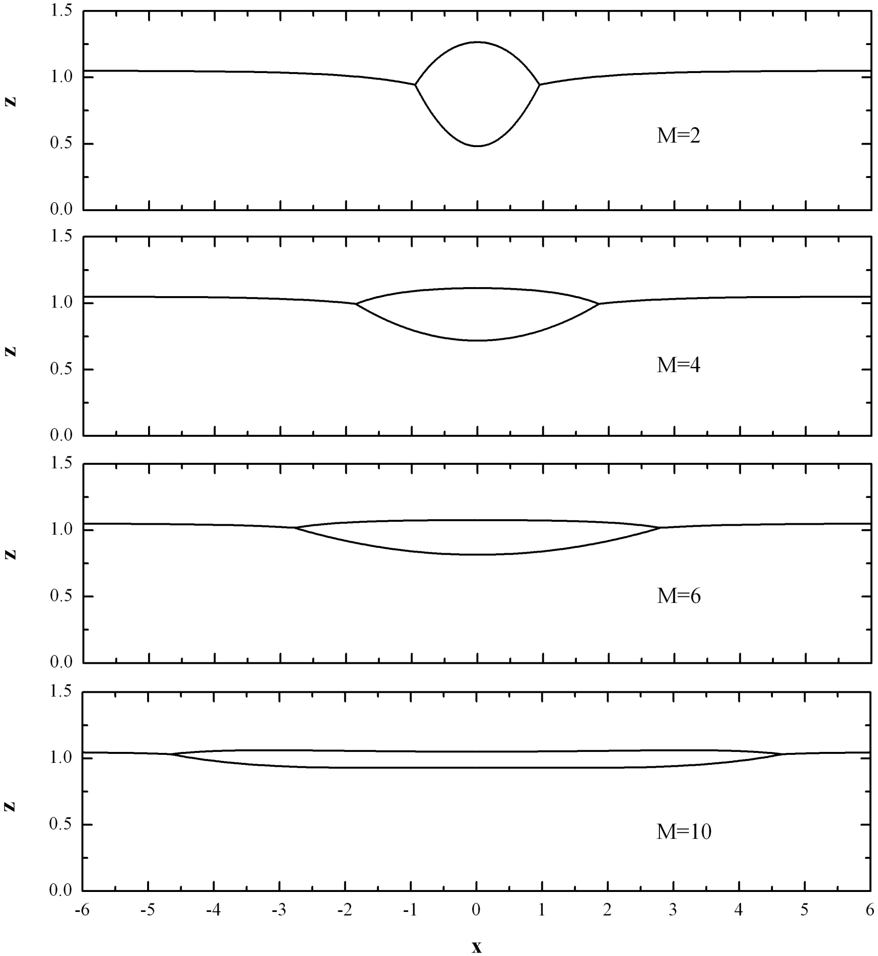
Results III

$$M = M^*/(V_2^* c_{cmc}^*) \qquad \Sigma_i = (\sigma_{io}^* - \sigma_{im}^*)/\sigma_{im}^* \qquad \delta_i = \sigma_{im}^*/\sigma_{23m}^*$$

Effect of M

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





Long time drop shapes, t=10

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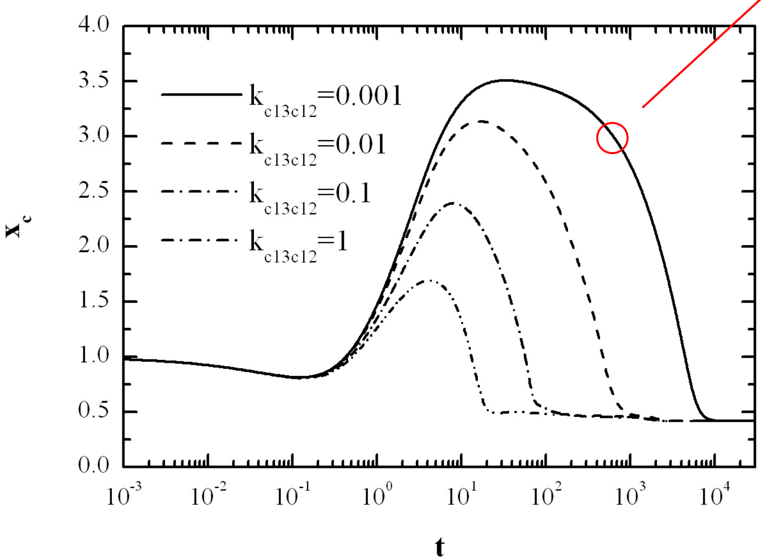
Results IV

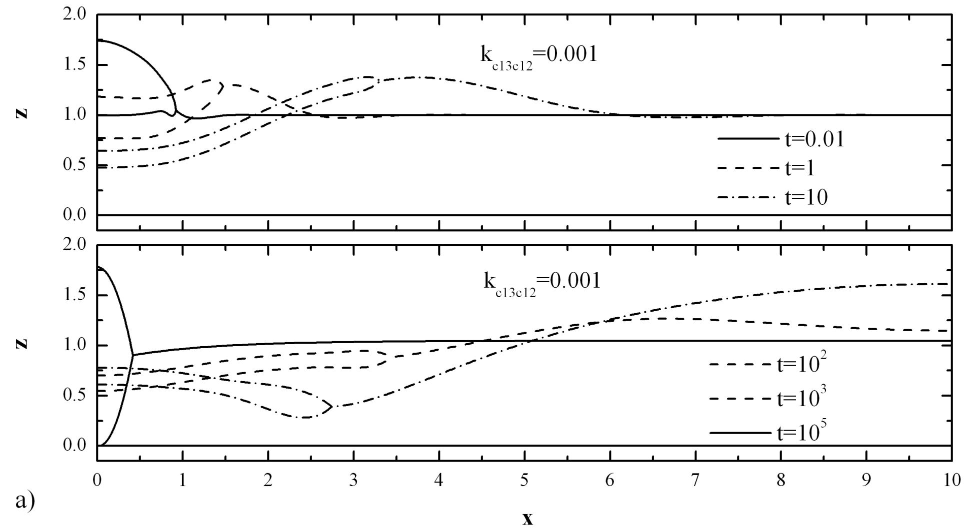
$$J_{c13c12} = k_{c13c12}\left[R_{c13c12}c_{13}\left(1 - c_{12}\right) - c_{12}\left(1 - c_{13}\right)\right]_{x = x_c}$$

Adsorption at the contact line

M=8, δ_{23}=1.9, δ_{12}=1, Σ_i=0.1

$$S_{13} + c_{12}^{*} \leftrightarrow S_{12} + c_{13}^{*}$$





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Results IV

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

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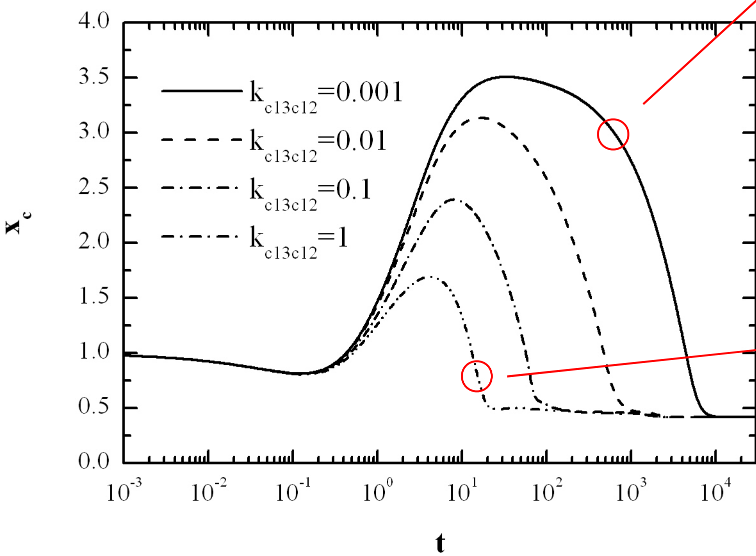
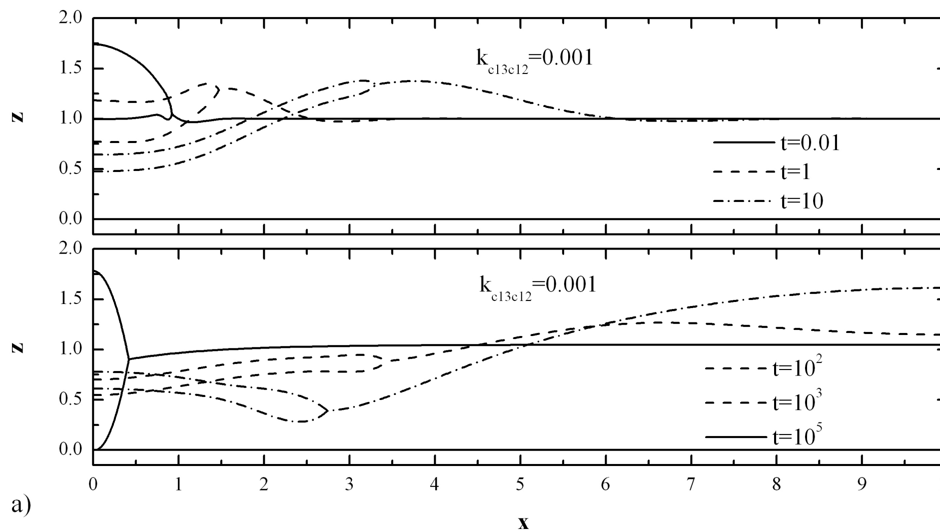
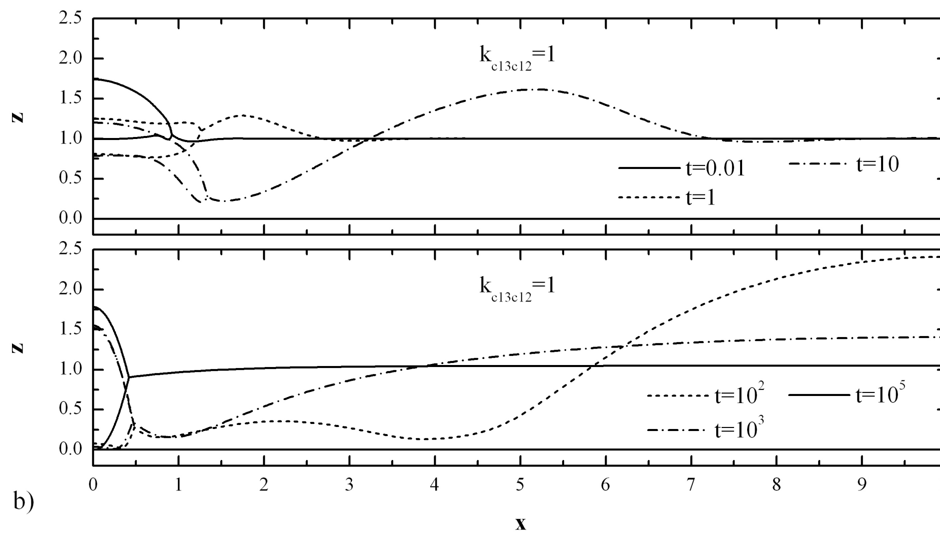




a)



b)

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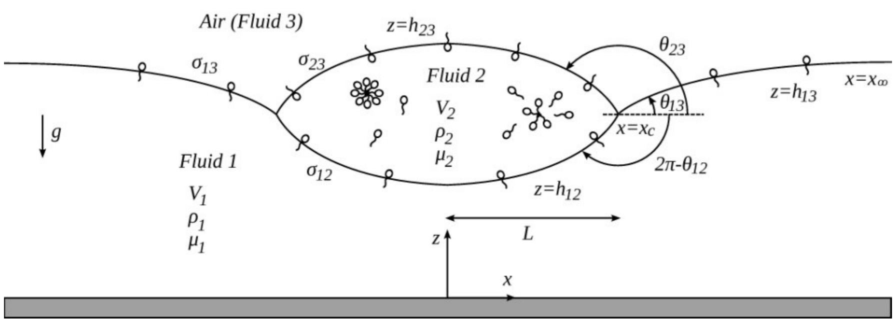
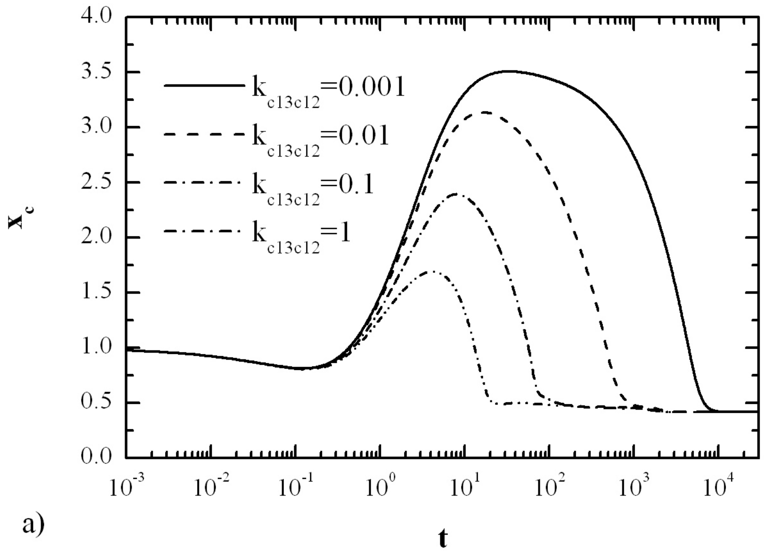
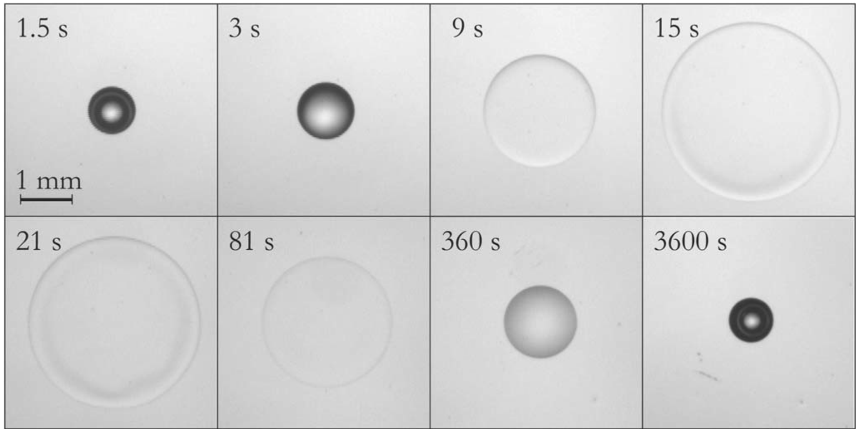
Results V



Oil water interface:

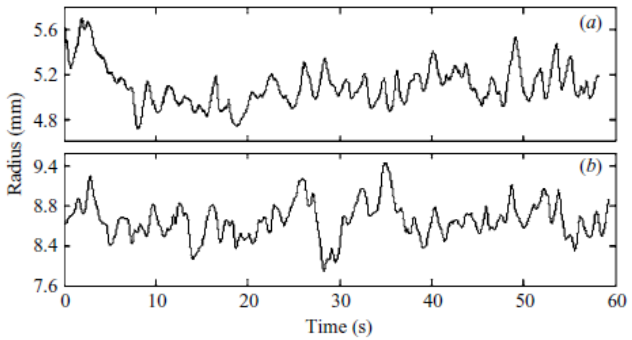
Oleic acid + NaOH $\rightarrow$ Na-oleate





Van Nierop et al. PoF 2006

Results VI



Stocker & Bush JFM 2007

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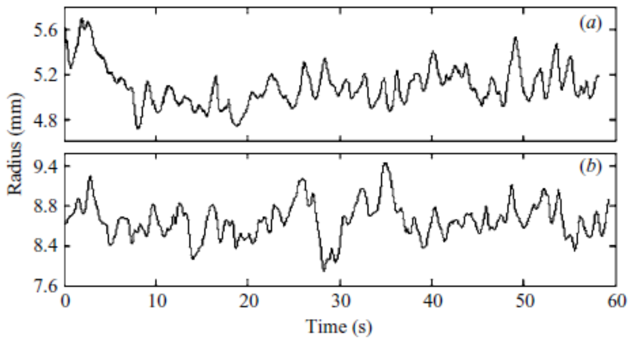
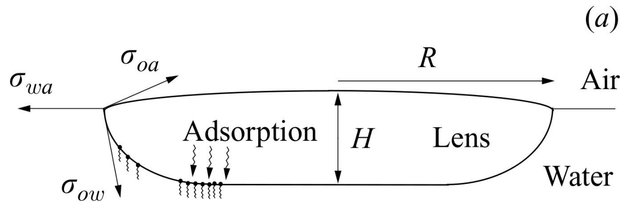
Results VI



Stocker & Bush JFM 2007



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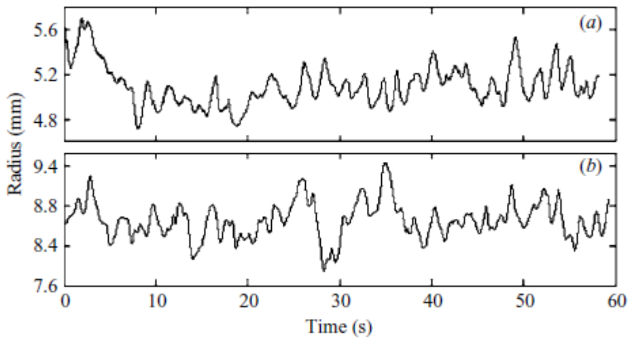
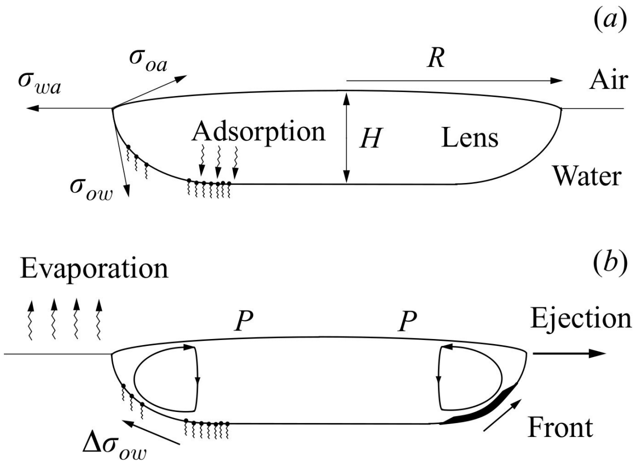
Results VI



Stocker & Bush JFM 2007



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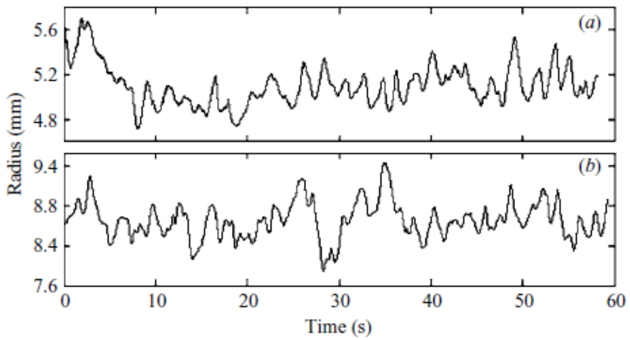
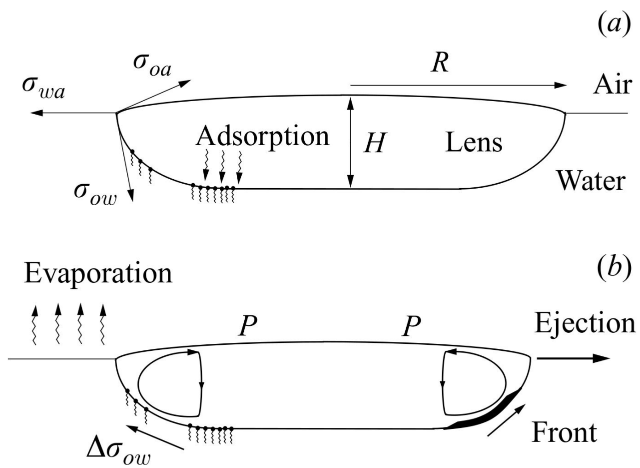
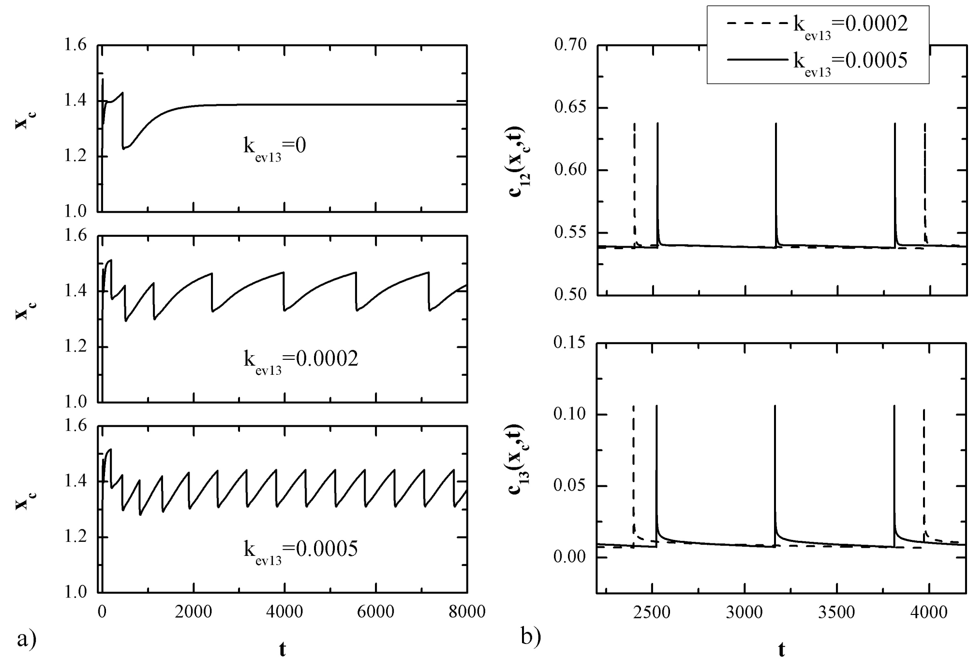
Results VI

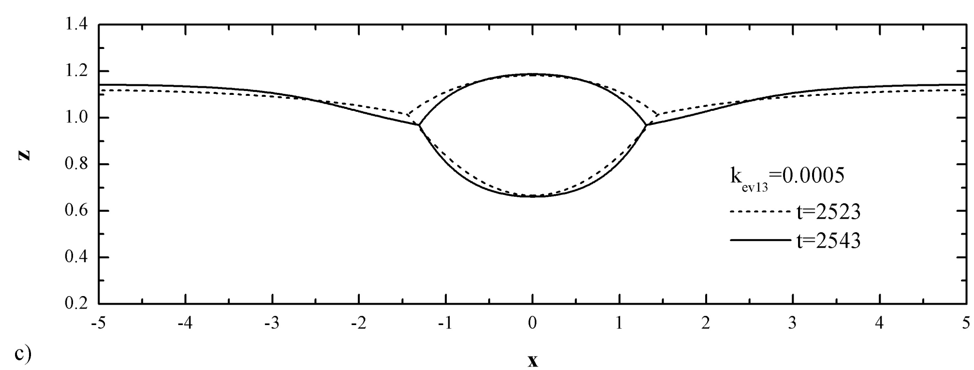
k_{ev13} = kinetic parameter for evaporation



Stocker & Bush JFM 2007







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Results VII

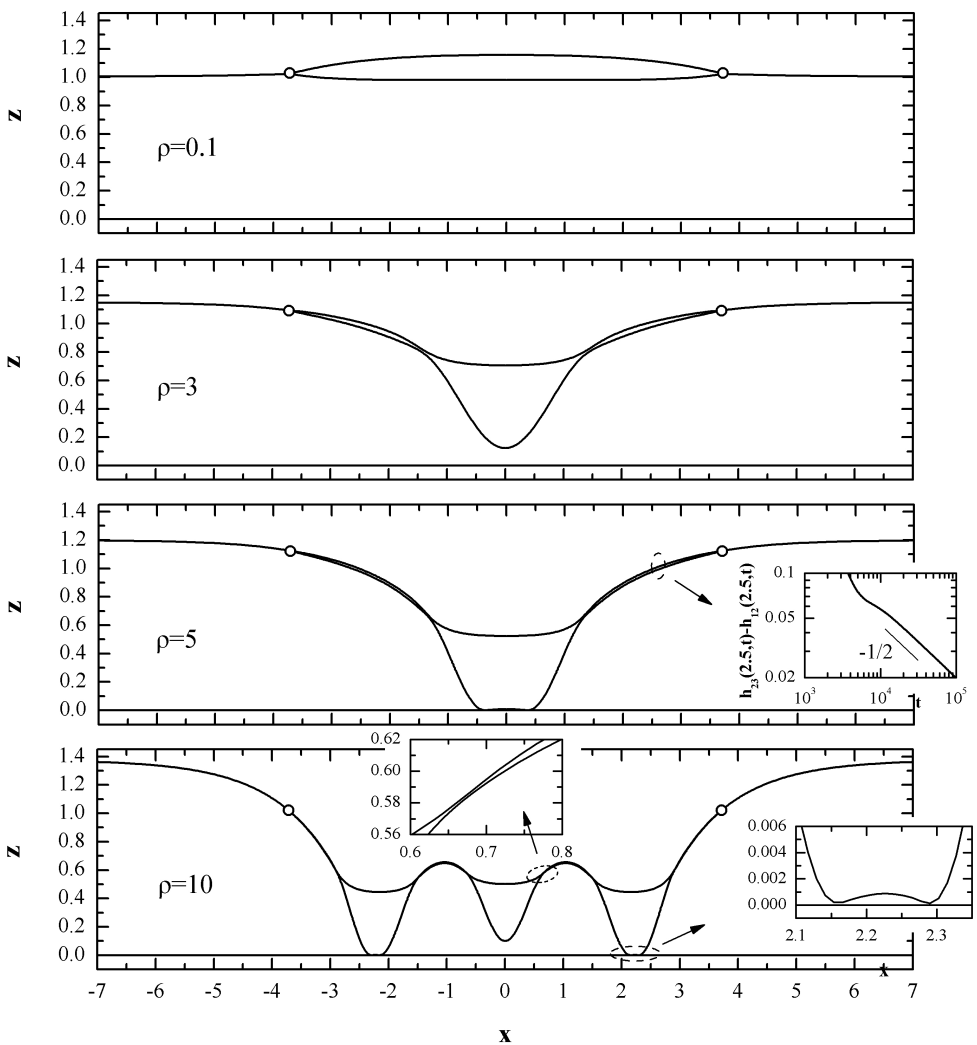
$$M = M^*/\left(V_2^* c_{cmc}^*\right) \qquad \Sigma_i = \left(\sigma_{io}^* - \sigma_{im}^*\right)/\sigma_{im}^* \qquad \delta_i = \sigma_{im}^*/\sigma_{23m}^*$$

Effect of density ratio, ρ

M=8, δ_{23}=1.9, δ_{12}=1, Σ_i=0.1

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

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



Conclusions

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.

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Thank you for your attention!