Numerical Simulation of Drop Coalescence in the Presence of Soluble Surfactant

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Contents

Introduction: Drop coalescence and applications; Effect of soluble surfactants.

Mathematical model:

- Simplifications;
- Hydrodynamic model - Stokes equations, lubrication approximation;
- Convection-diffusion equations in the phases and the interface.

Numerical method:

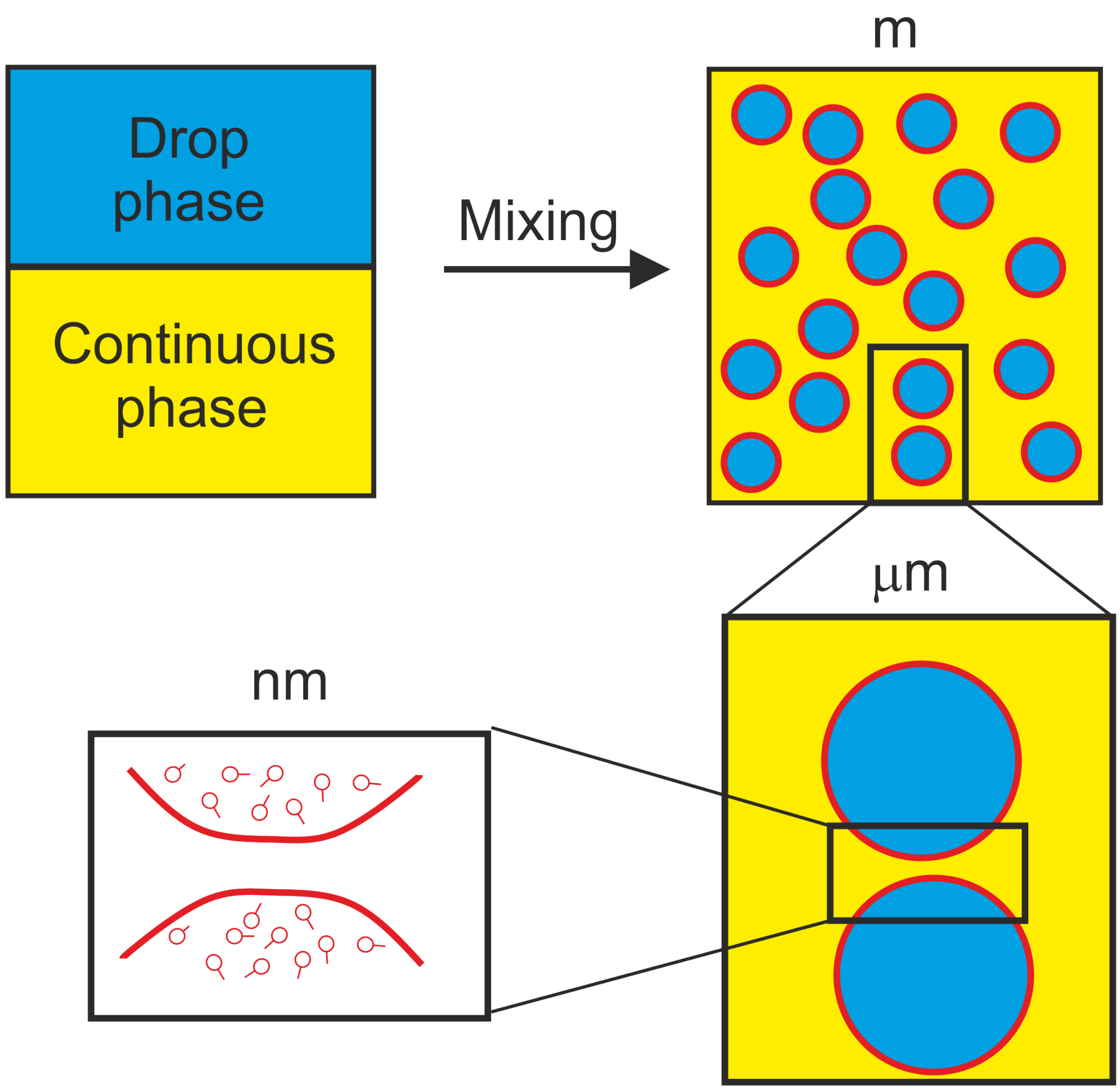
- Boundary Integral Method for the Stokes equations in the drops;
- Finite Difference Method for the flow in the film and the convection-diffusion equations.

Results

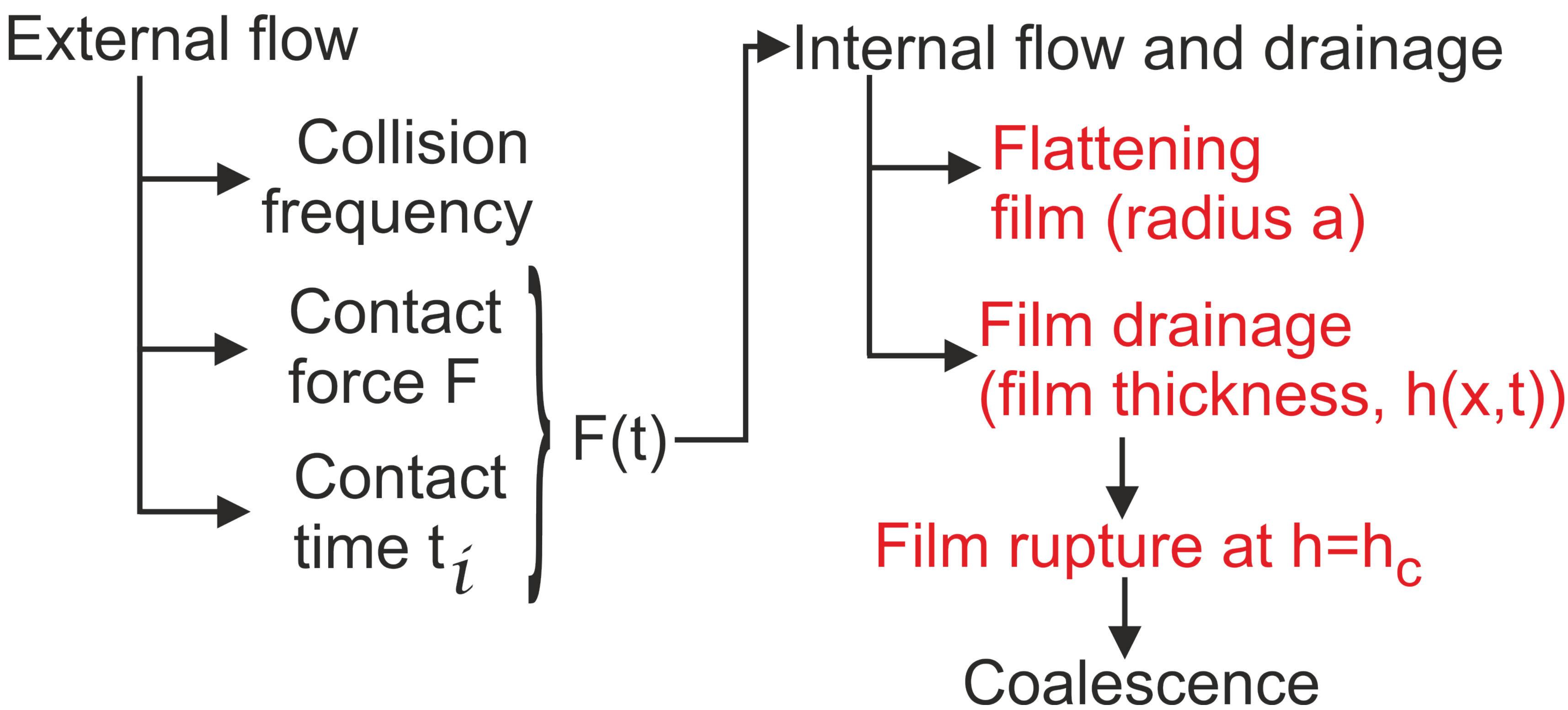
Conclusions; Future work

Introduction: Drop coalescence and applications

Applications of multiphase systems: Emulsions - Food; drugs; cosmetics; composite materials; chemicals; petroleum; etc.

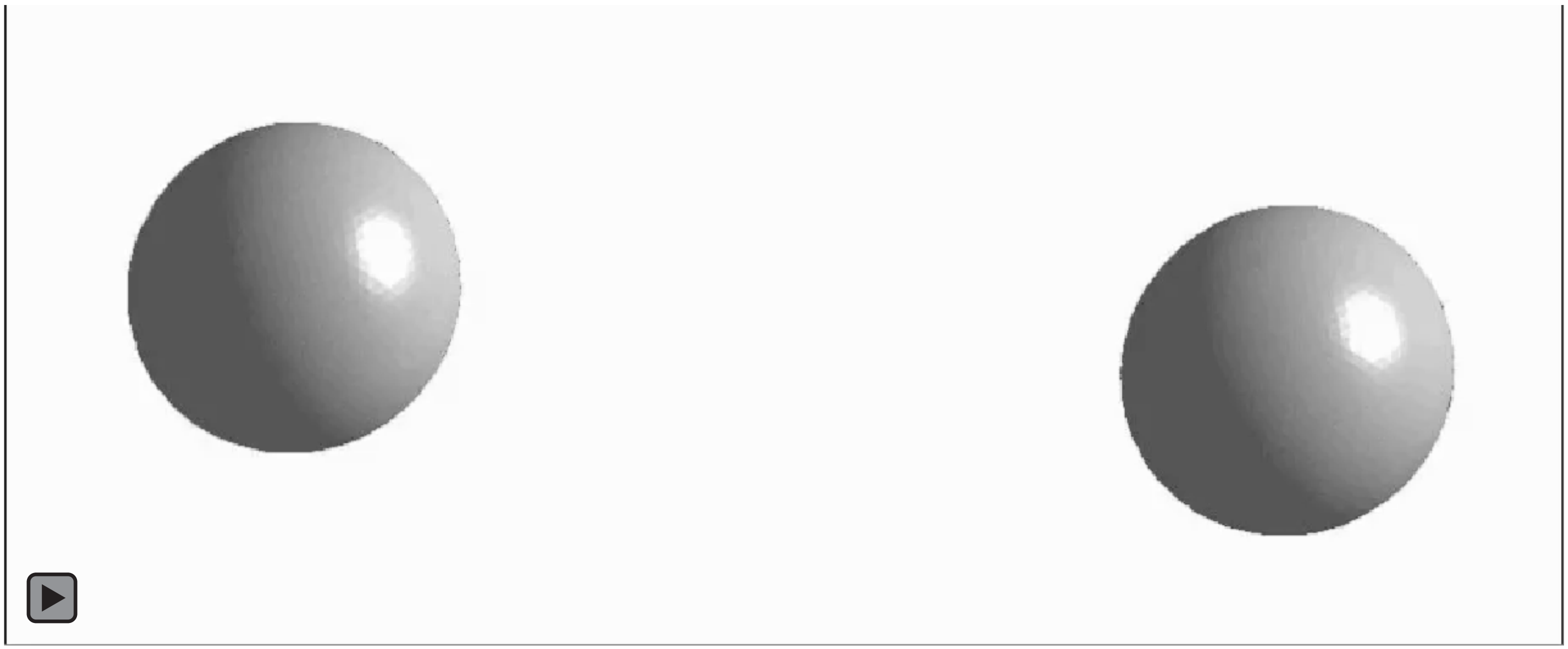


Introduction: Conceptual framework for coalescence modelling.

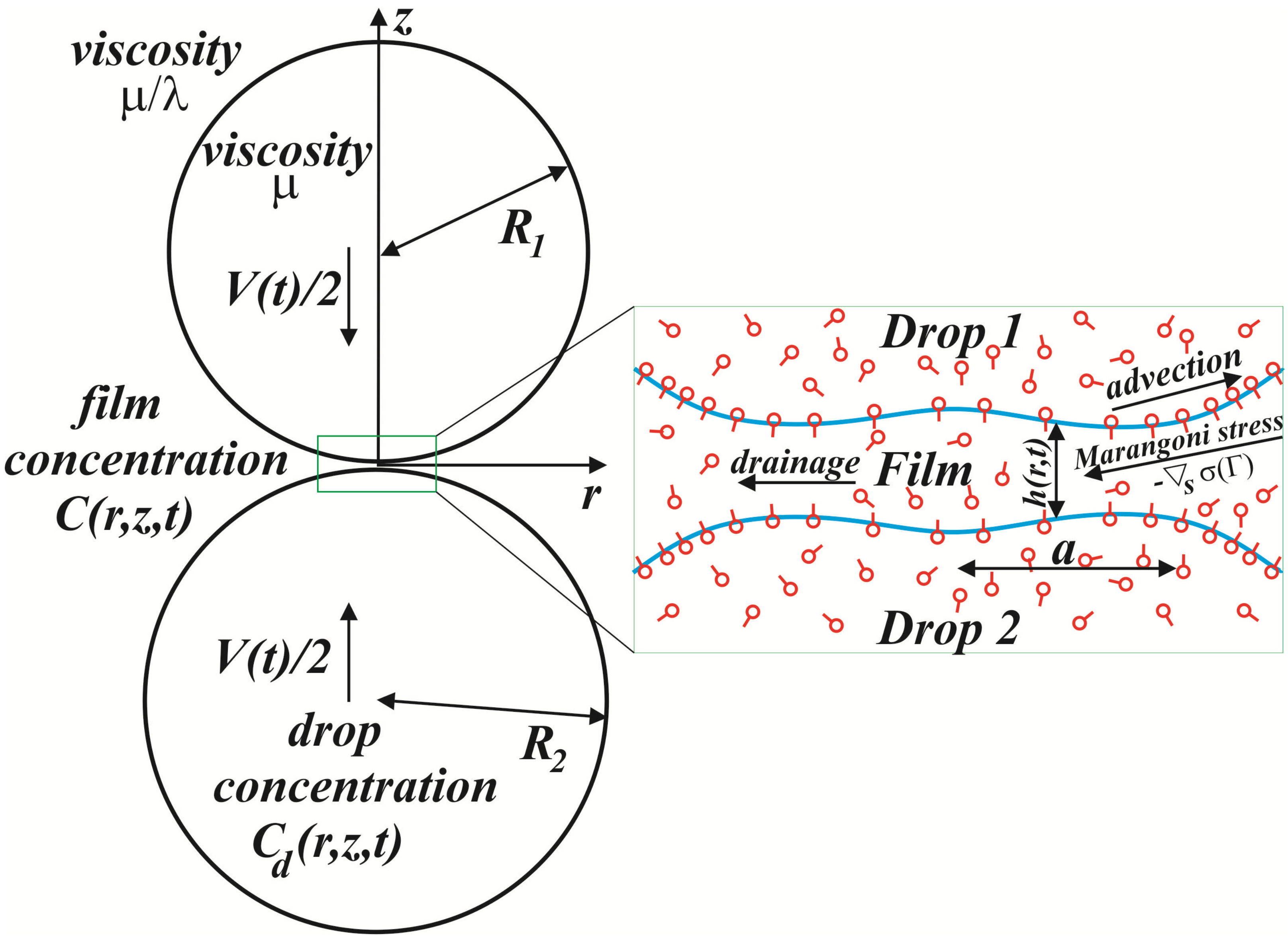


$$? \ t_i <> t_c \ ?; \quad t_c = t(h_{min} = h_c)$$

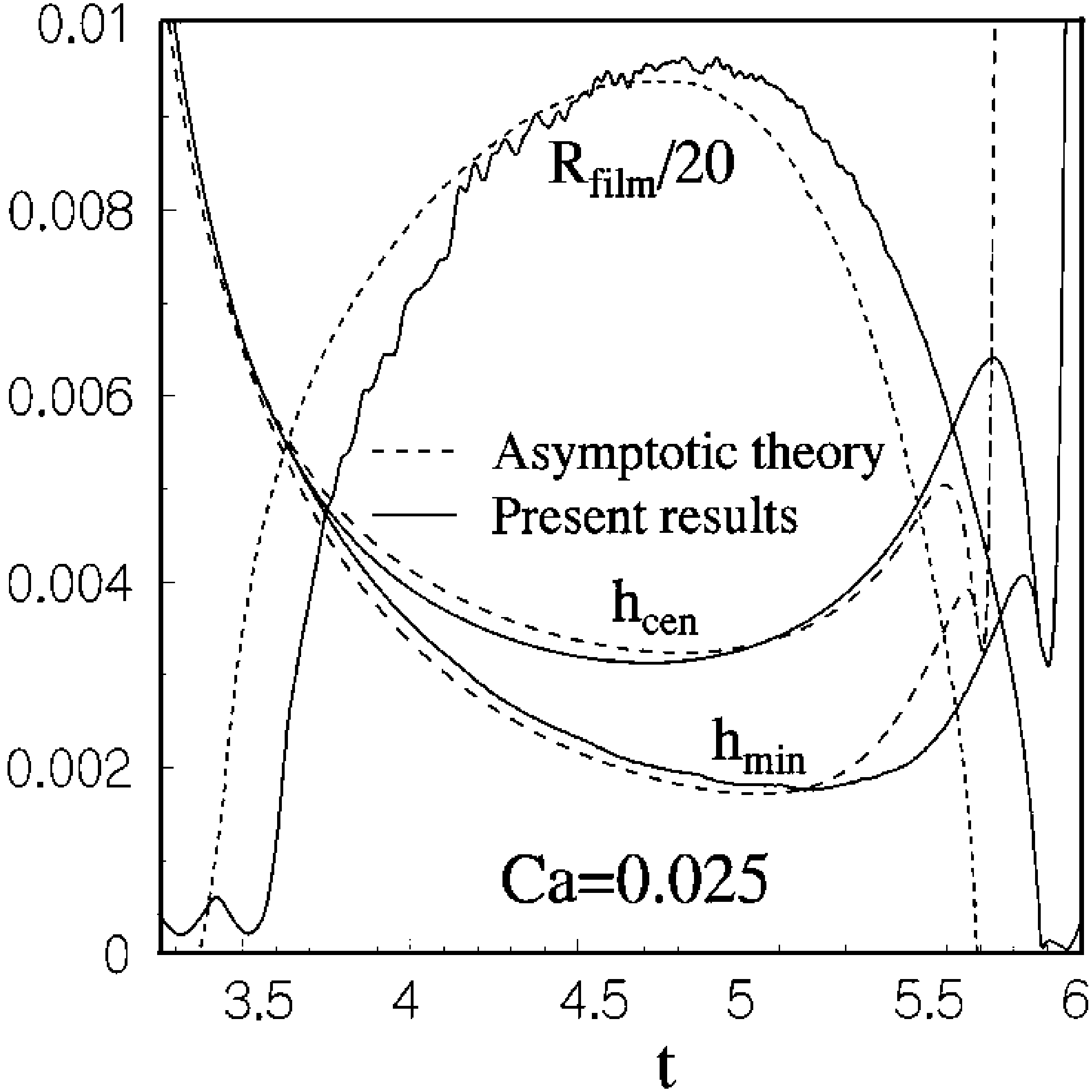
Drop-to-drop interaction in simple shear flow at $Ca = 0.25$



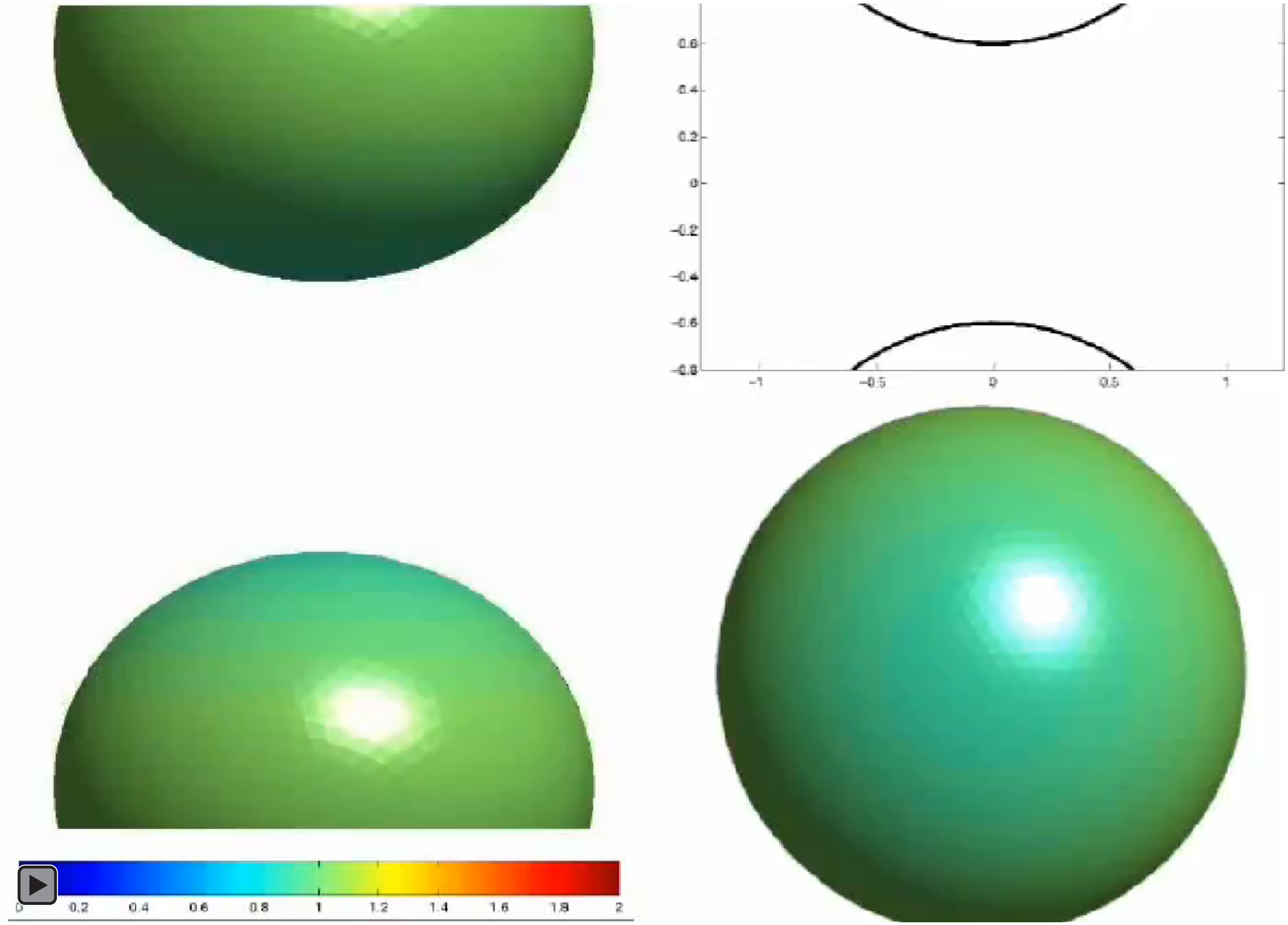
Schematic sketch of the problem



Comparison with 3D simulation in simple shear flow.



Head-on collision in axisymmetric compressional flow, insoluble surfactant.



Mathematical model: Hydrodynamic part.

In the drops:

$$\nabla \cdot v = 0; \quad -\nabla p_d + \nabla^2 v = 0; \quad \text{Stokes equations in the drops} \tag{1}$$

In the film (Lubrication equation):

$$\frac{\partial h}{\partial t} = -\frac{1}{r}\frac{\partial (rhu_u)}{\partial r} + \frac{1}{r}\frac{\lambda}{12}\frac{\partial}{\partial r}\left(h^3 r \frac{\partial p}{\partial r}\right); \quad u_r = u_u + \frac{\lambda}{2}\frac{\partial p}{\partial r}\left(z^2 - \left(\frac{h}{2}\right)^2\right) \tag{2}$$

$$p = 2 - \frac{1}{2}\left(\frac{\partial^2 h}{\partial r^2} + \frac{1}{r}\frac{\partial h}{\partial r}\right) + \frac{2A}{3h^3}; \tag{3}$$

$$2H = \frac{1}{B^3}\frac{\partial^2 S}{\partial r^2} + \frac{1}{rB}\frac{\partial S}{\partial r}; B = \sqrt{1 + \left(\frac{\partial S}{\partial r}\right)^2} \tag{4}$$

BC: $$-\frac{h}{2}\frac{\partial p}{\partial r} - \frac{\partial \Gamma}{\partial r} = \frac{1}{\lambda}\frac{\partial v_r}{\partial z}; \quad u_u = v_r; \quad \int_0^{r_\infty}\left(p - \frac{2A}{3h^3}\right) r dr = F(t) \tag{5}$$

Mathematical model: Surfactant transport - interface.

At the interface:

$$\frac{\partial \Gamma}{\partial t} + \frac{1}{r}\frac{\partial (r\Gamma u_u)}{\partial r} - \frac{1}{Pe_s r}\frac{\partial}{\partial r}\left(r\frac{\partial \Gamma}{\partial r}\right) = \frac{1}{Pe_d}\left(\frac{\partial C_d}{\partial z_d}\right)\Big|_{z_d=0} - \frac{1}{Pe}\left(\frac{\partial C}{\partial z}\right)\Big|_{z=h/2} \qquad (6)$$

with boundary conditions:

$$\left(\frac{\partial \Gamma}{\partial r}\right)_{r=0} = 0, \quad \left(\frac{\partial \Gamma}{\partial r}\right)_{r=r_l} = 0. \qquad (7)$$

Adsorption isoterms:

$$KC|_{z=h/2} = \Gamma = K_d C_d|_{z_d=0} \qquad (8)$$

Mathematical model: Surfactant transport - bulk.

In the film:

$$\frac{\partial C}{\partial t} + u_r \frac{\partial (C)}{\partial r} + u_z \frac{\partial C}{\partial z} = \frac{1}{Pe} \left(\frac{\partial^2 C}{\partial z^2} \right) \tag{9}$$

$$\left(\frac{\partial C}{\partial r} \right)_{r=0} = 0; \qquad \left(\frac{\partial C}{\partial r} \right)_{r=\infty} = 0 \tag{10}$$

In the drop:

$$\frac{\partial C_d}{\partial t} + (u_r)_d \frac{\partial (C_d)}{\partial r} + (u_z)_d \frac{\partial C_d}{\partial z_d} = \frac{1}{Pe_d} \left(\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_d}{\partial r} \right) + \frac{\partial^2 C_d}{\partial z_d^2} \right) \tag{11}$$

$$\left(\frac{\partial C_d}{\partial r} \right)_{r=0} = \left(\frac{\partial C_d}{\partial z_d} \right)_{z_d=\infty} = \left(\frac{\partial C_d}{\partial r} \right)_{r=\infty} = 0 \tag{12}$$

Mathematical model: Initial conditions.

For the film thickness:

$$h(r,t=0)) = h_{ini} + r^2, \tag{13}$$

For the solute distribution:

- initially uniform concentration only in the drops:

$$C_d(r,z_d,t=0) = 1 = \Gamma/K_d; \qquad C(r,z,t=0) = 0. \tag{14}$$

- initially uniform concentration only in the film:

$$C_d(r,z_d,t=0) = 0; \qquad C(r,z,t=0) = 1 = \Gamma/K. \tag{15}$$

Transformation and Parameters.

$$t^* = \frac{t\sigma_s a'}{R_{eq}\mu}; \; r^* = \frac{r}{R_{eq}a'}; \; z^* = \frac{z}{R_{eq}{a'}^2}; \; h^* = \frac{h}{R_{eq}{a'}^2};$$

$$u_r^* = \frac{u_r\mu}{\sigma_s {a'}^2}; \; u_z^* = \frac{u_z\mu}{\sigma_s {a'}^3};$$

$$z_d^* = \frac{z_d}{R_{eq}a'}; \; (u_r)_d^* = \frac{(u_r)_d\mu}{\sigma_s {a'}^2}; \; (u_z)_d^* = \frac{(u_z)_d\mu}{\sigma_s {a'}^2};$$

a' is the dimensionless radius of the film, $a' = a/R_{eq}$; $\quad R_{eq}^{-1} = \frac{1}{2}(R_1^{-1} + R_2^{-1})$.

Dimensionless groups:

$$\lambda^* = \lambda a'; \quad K^* = \frac{K}{R_{eq}a'^2}; \quad K_d^* = \frac{K_d}{R_{eq}}; \quad Pe_s^* = \frac{\sigma_s R_{eq} a'^3}{D_s\mu}; \quad Pe^* = \frac{\sigma_s R_{eq} a'^5}{D\mu};$$

$$Pe_d^* = \frac{\sigma_s R_{eq} a'^3}{D_d\mu}; \quad A^* = \frac{A}{4\pi\sigma_s R_{eq}^2 a'^2};$$

Numerical method: Hydrodynamic part in the drops.

BIM for the flow in the drops:

$$(u_r)_d(r, z_d) = \int_0^{r_l} \phi_1(r, r')\tau_d(r')\,dr', \quad (u_z)_d(r, z_d) = \int_0^{r_l} \phi_3(r, r')\tau_d(r')\,dr',$$

where

$$\begin{aligned}\phi_1(r, r') \quad &= \quad \frac{r'}{4\pi}\int_0^{2\pi}\left(\frac{2\cos\theta}{(r^2 + r'^2 - 2rr'\cos\theta + z^2)^{1/2}}\right. \\ &- \quad \left.\frac{z^2\cos\theta + rr'\sin^2\theta}{(r^2 + r'^2 - 2rr'\cos\theta + z^2)^{3/2}}\right)\,d\theta\end{aligned}$$

$$\phi_3(r, r') = \frac{r'}{4\pi}\int_0^{2\pi}\frac{(r\cos\theta - r')zr'\,d\theta}{(r^2 + r'^2 - 2rr'\cos\theta + z^2)^{3/2}}.$$

Numerical method: Hydrodynamic part in the film.

$$\frac{\partial h}{\partial t} = -\frac{1}{r}\frac{\partial (rhu_u)}{\partial r} + \frac{1}{r}\frac{\lambda}{12}\frac{\partial}{\partial r}\left(h^3 r \frac{\partial p}{\partial r}\right); \qquad p = 2 - \frac{1}{2}\left(\frac{\partial^2 h}{\partial r^2} + \frac{1}{r}\frac{\partial h}{\partial r}\right) + \frac{2A}{3h^3}$$

Forth-order nonlinear equation for $h(r,t)$ is solved by an Euler explicit scheme in time and a second order FD scheme on non-uniform mesh in space. Requirements for numerical stability:

$$(\Delta t)_I \leq const \cdot \min_j \left(\frac{\Delta r_j^3}{h_j^2}\right); \quad (\Delta t)_{II} \leq \frac{24}{\lambda} \cdot \min_j \left(\frac{\Delta r_j^4}{h_j^5}\right)$$

Adaptive mesh/step are used both for the time as well as space discretization: Δt of order $10^{-4} - 10^{-9}$; in the film region Δr and Δz of order 0.01

$$M = \frac{(\Delta t)_I}{(\Delta t)_{II}}; \qquad \Delta T = M \Delta t$$

Numerical method: Convection diffusion in the bulk phases.

The convection-diffusion equations for the surfactant concentration in the drop and in the film are solved by a second order FD approximation in r and z in combination of hybrid (implicit/explicit) time integration:

$$C(i,j,k+1) + \beta \Delta T \left[u_z \delta_z - \frac{1}{Pe} \delta_z^2 \right] C(i,j,k+1) = \tag{16}$$

$$C(i,j,k) - \Delta T u_r \delta_r C(i,j,k) + (\beta - 1) \Delta T \left[u_z \delta_z - \frac{1}{Pe} \delta_z^2 \right] C(i,j,k),$$

where δ_x and δ_x^2 are finite difference approximations for the first and second derivatives with respect to the variable x (x stands for r or z). Here five node discretization is used for the first and second derivatives in the r and z directions. Thus the second derivative is approximated as:

$$\frac{\partial^2 C(i,j,k)}{\partial z^2} \approx \delta_z^2 C(i,j,k) =$$

$$a_1.C(i,j-2,k) + a_2.C(i,j-1,k) + a_3.C(i,j,k) + a_4.C(i,j+1,k) + a_5.C(i,j+2,k),$$

with $a_1 = y_1, a_2 = y_2, a_3 = -(y_1 + y_2 + y_3 + y_4), a_4 = y_3, a_5 = y_4$, where the vector $\mathbf{y} = (y_1, y_2, y_3, y_4)^T$ is the solution of the algebraic system $\mathbf{E}\mathbf{y} = \mathbf{b}$, $\mathbf{b} = (0,2,0,0)^T$, $\Delta z_i = z_i - z_{i-1}$ and **E** is the matrix:

$$\begin{bmatrix} -(\Delta z_{i-1}+\Delta z_i) & -\Delta z_i & \Delta z_{i+1} & (\Delta z_{i+1}+\Delta z_{i+2}) \\ (\Delta z_{i-1}+\Delta z_i)^2 & (\Delta z_i)^2 & (\Delta z_{i+1})^2 & (\Delta z_{i+1}+\Delta z_{i+2})^2 \\ -(\Delta z_{i-1}+\Delta z_i)^3 & -(\Delta z_i)^3 & (\Delta z_{i+1})^3 & (\Delta z_{i+1}+\Delta z_{i+2})^3 \\ (\Delta z_{i-1}+\Delta z_i)^4 & (\Delta z_i)^4 & (\Delta z_{i+1})^4 & (\Delta z_{i+1}+\Delta z_{i+2})^4 \end{bmatrix}$$

The first derivative with respect to z is approximated as:

$$\frac{\partial C(i,j,k)}{\partial z} \approx \delta_z C(i,j,k) =$$

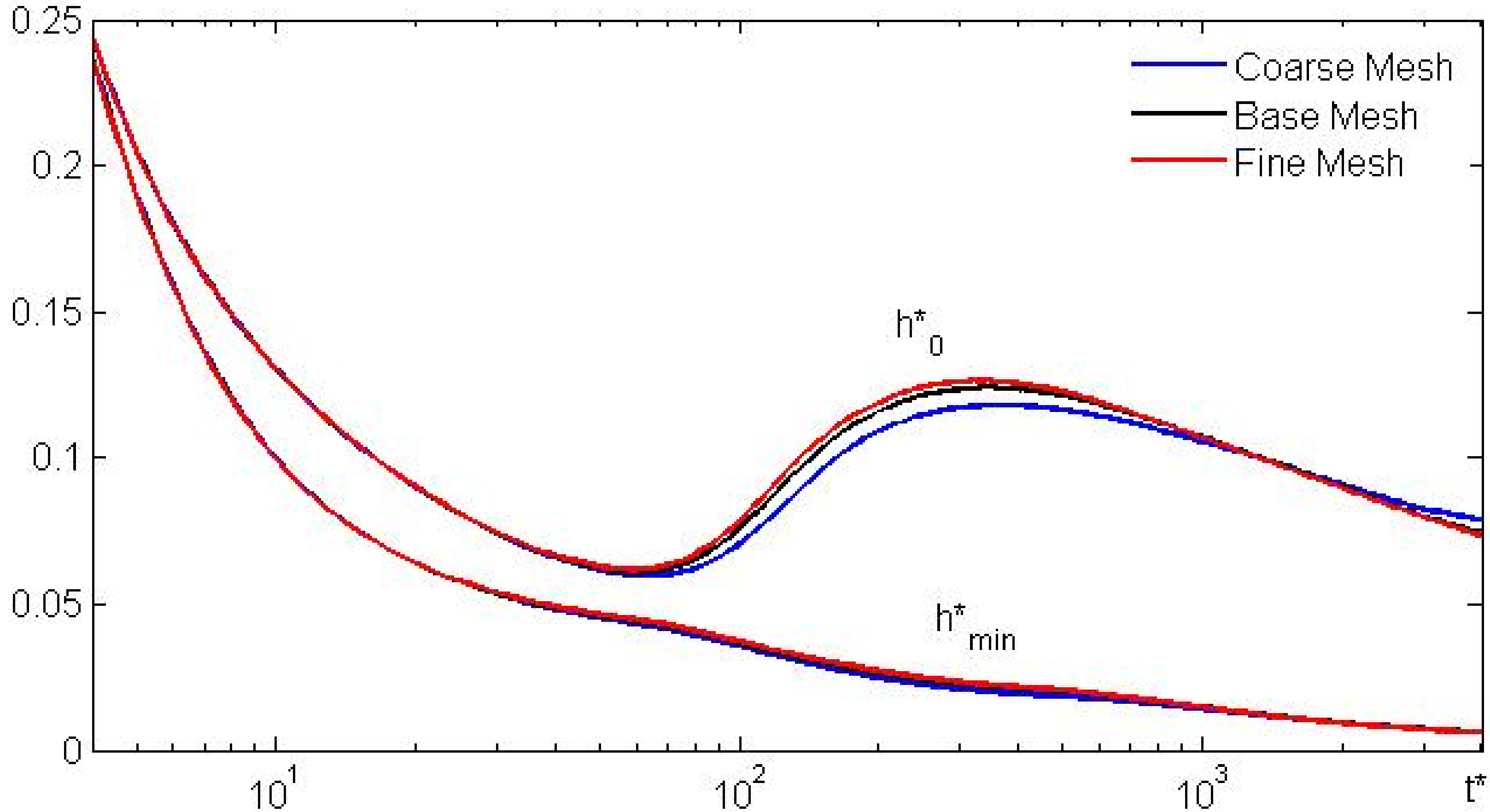
$$a_1.C(i,j-2,k)+a_2.C(i,j-1,k)+a_3.C(i,j,k)+a_4.C(i,j+1,k)+a_5.C(i,j+2,k),$$

with $a_1 = y_1, a_2 = -(y_1+y_2+y_3+y_4), a_3 = y_2, a_4 = y_3, a_5 = y_4$, where the vector $\mathbf{y}$ is the solution of the algebraic system $\mathbf{Ey} = \mathbf{b}$, here $\mathbf{b} = (1,0,0,0)^T$.

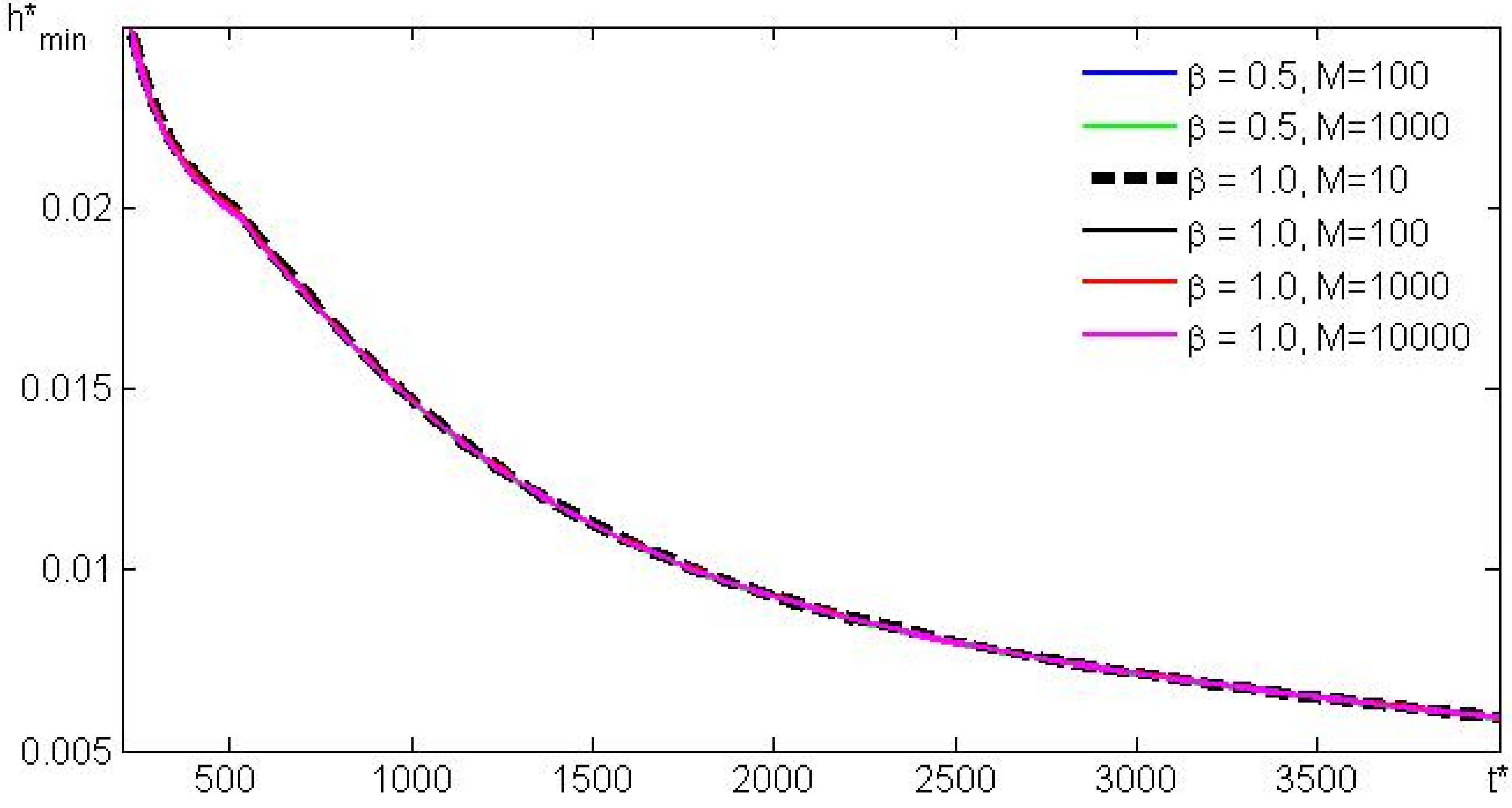
In order to approximate $\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_d}{\partial r}\right)$ on the left boundary $(r=0)$ we use

L'Hospital's Rule: $\lim\limits_{r\to 0}\dfrac{1}{r}\dfrac{\partial C_d}{\partial r} = \dfrac{\partial^2 C_d}{\partial r^2}$ and then natural symmetric boundary conditions are imposed.

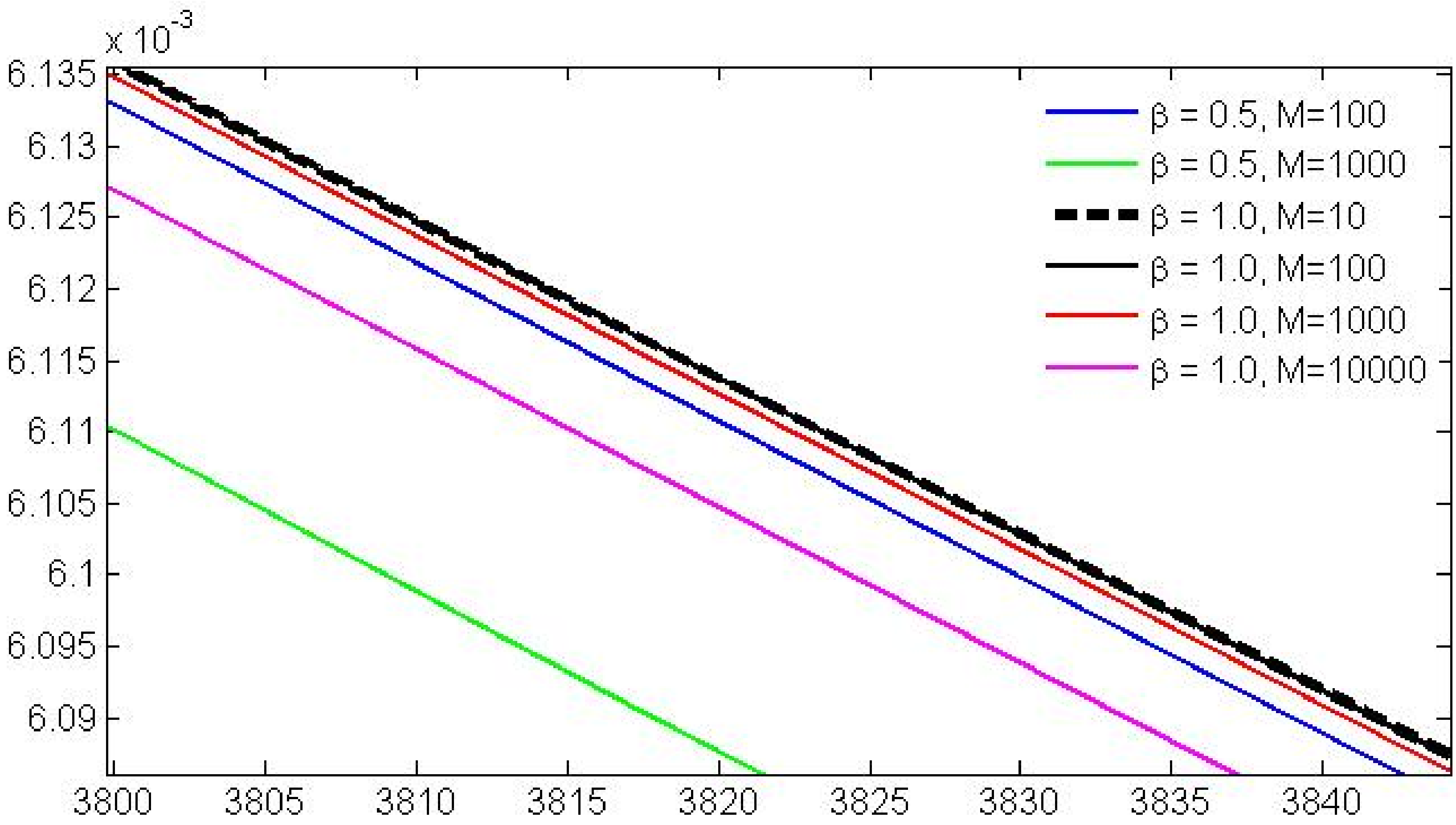
Numerical test: Space discretization.
The evolution of the film thickness for different meshes.



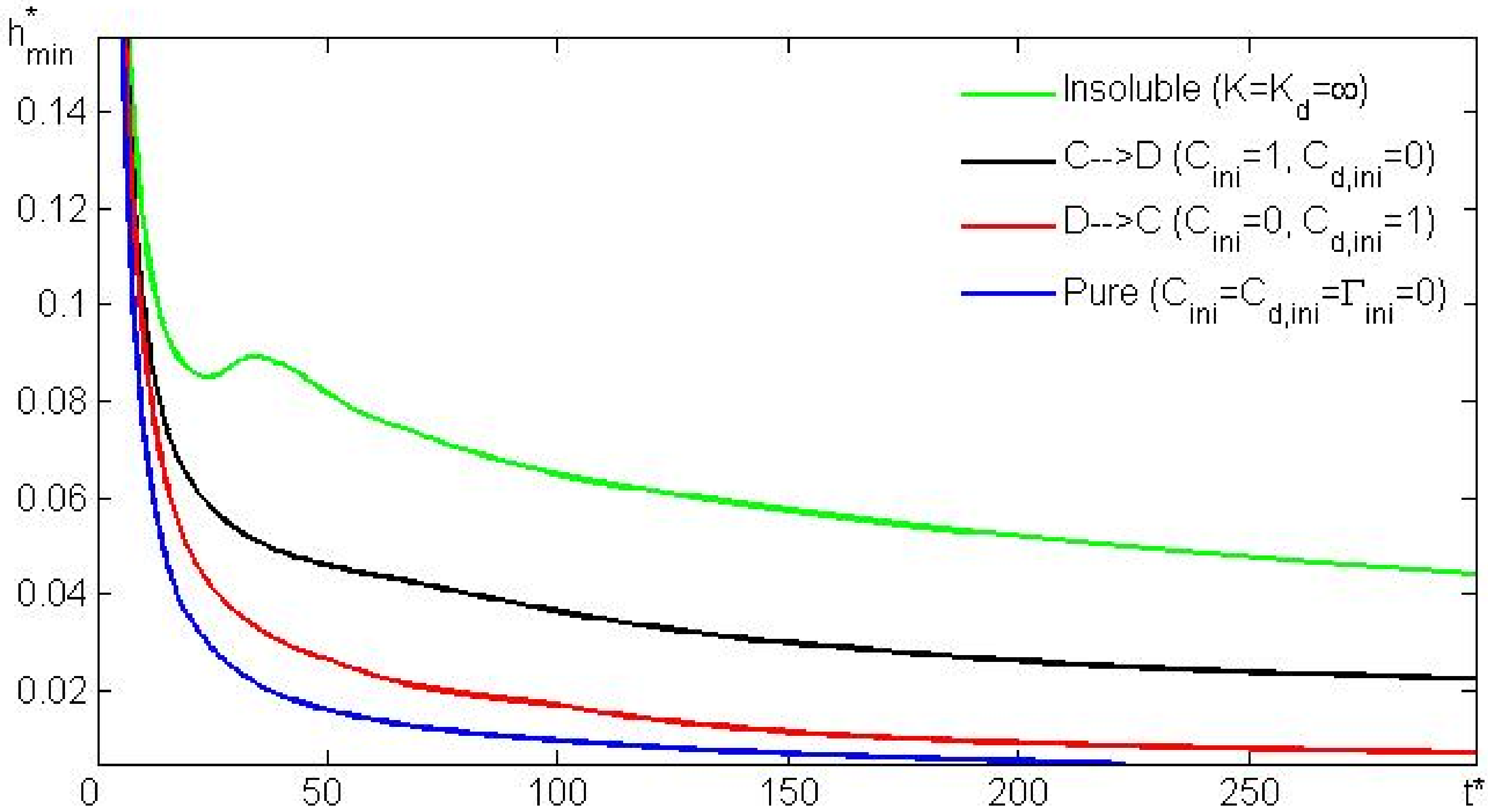
Numerical test: Time discretization. The evolution of the minimal film thickness for different time stepping methods.



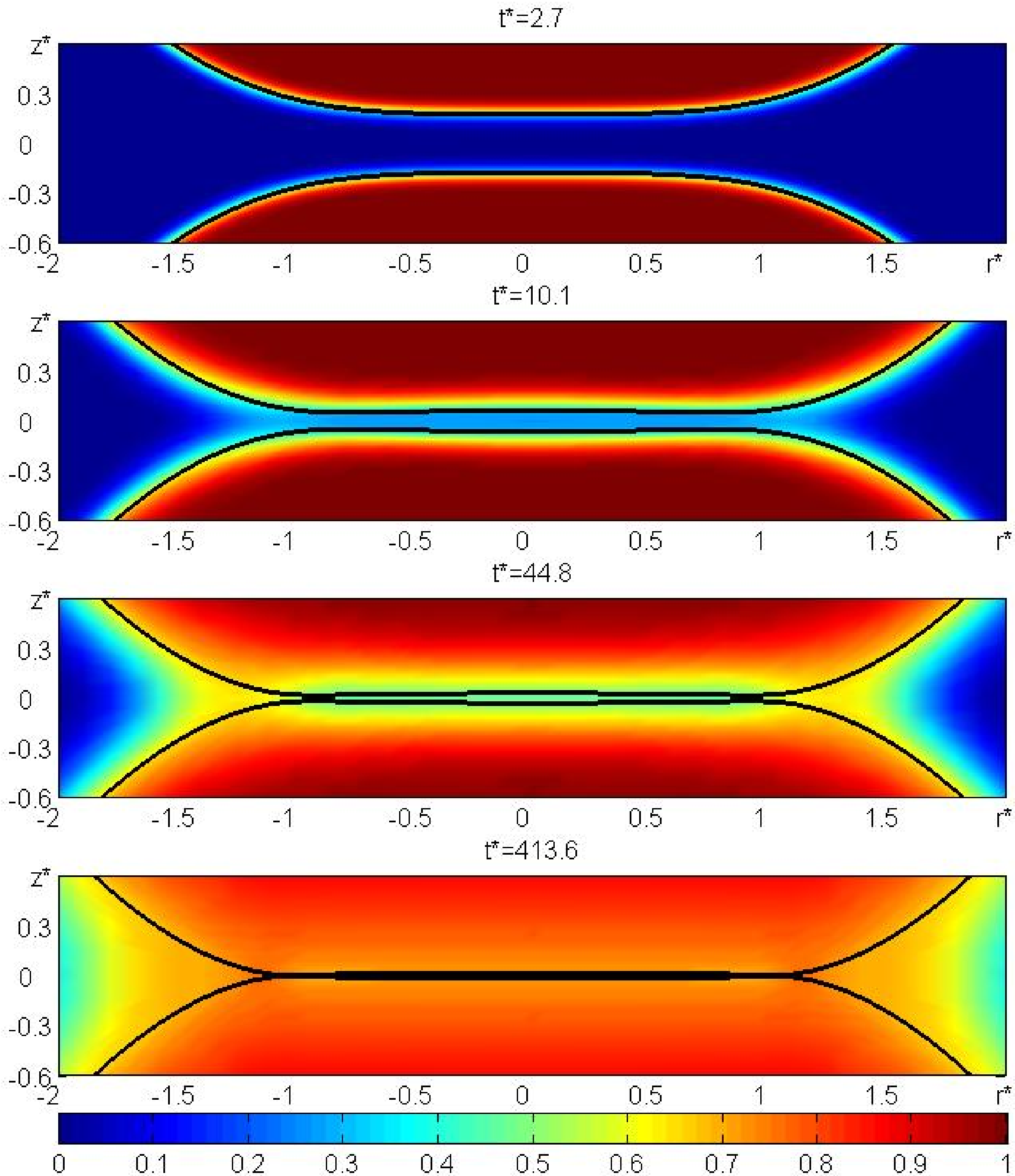
Numerical test: Time discretization. The evolution of the minimal film thickness for different time stepping methods - zoom.



The evolution of the minimal film thickness, h_{min} at $\lambda = 1;\ Pe_s = 10^5;\ Pe = Pe_d = 10^3;\ K = K_d = 0.2$

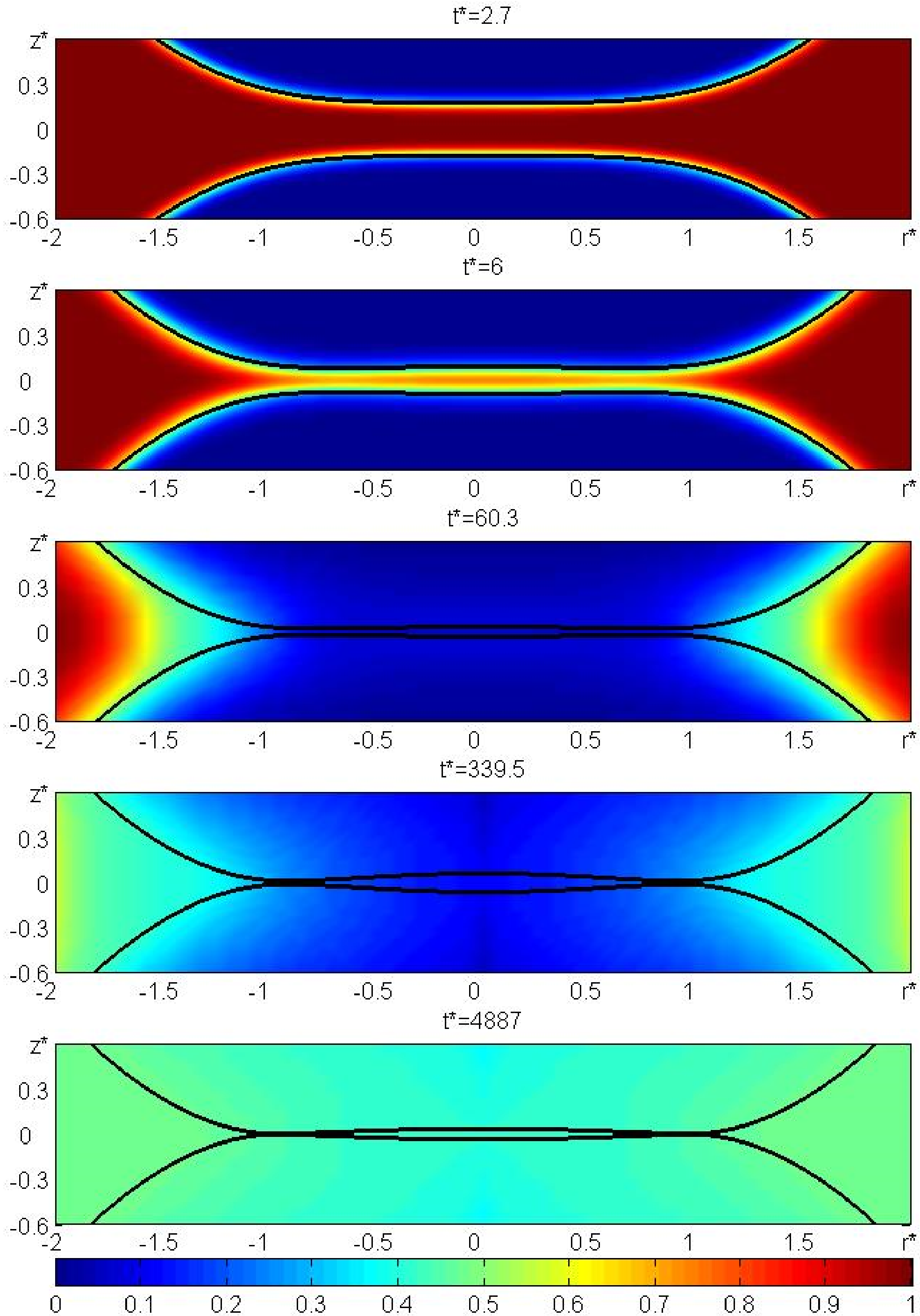


$D \to C$



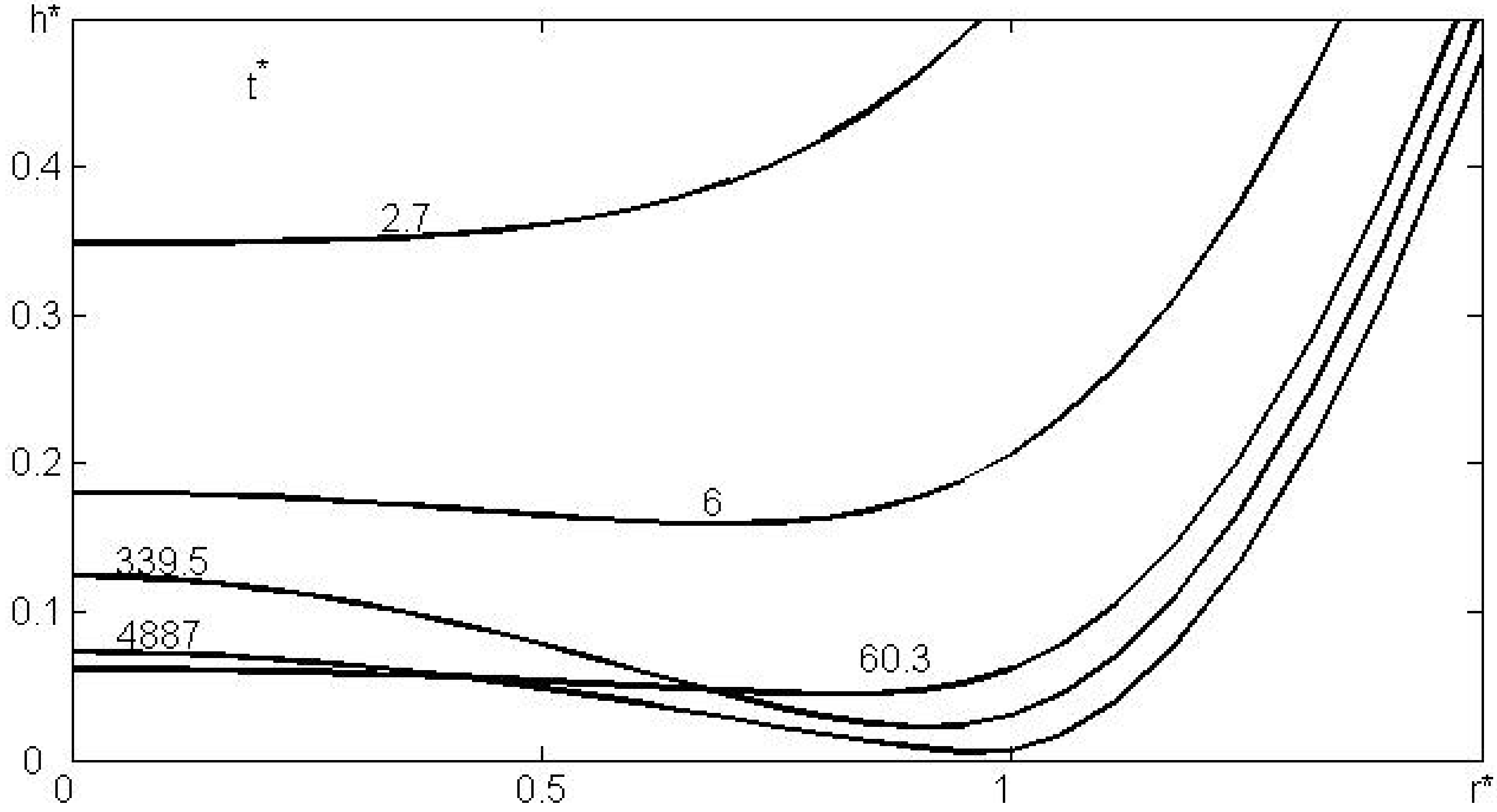
t*=2.7
z*
0.3
0
-0.3
-0.6
-2
-1.5
-1
-0.5
0
0.5
1
1.5
r*
t*=10.1
t*=44.8
t*=413.6
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

$C \to D$

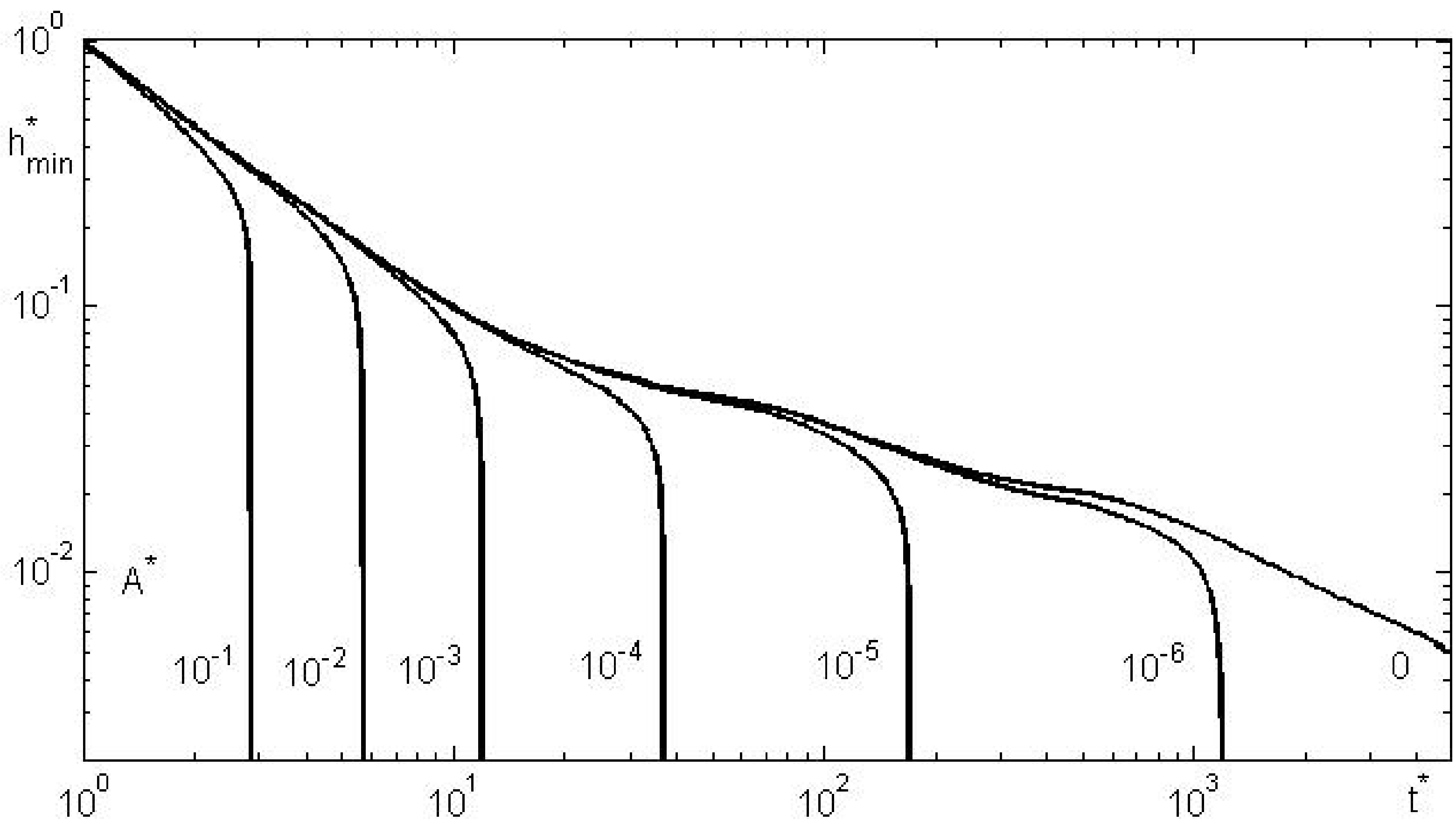


t*=2.7
t*=6
t*=60.3
t*=339.5
t*=4887
z*
r*
0.3
0
-0.3
-0.6
-2
-1.5
-1
-0.5
0
0.5
1
1.5
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

The evolution of the film thickness, h at $\lambda = 1;\ Pe_s = 10^5;\ Pe = Pe_d = 10^3;\ K = K_d = 0.2$, case $C \to D$



The effect of van der Waals forces, A, on the evolution of the minimal film thickness, h_{min}

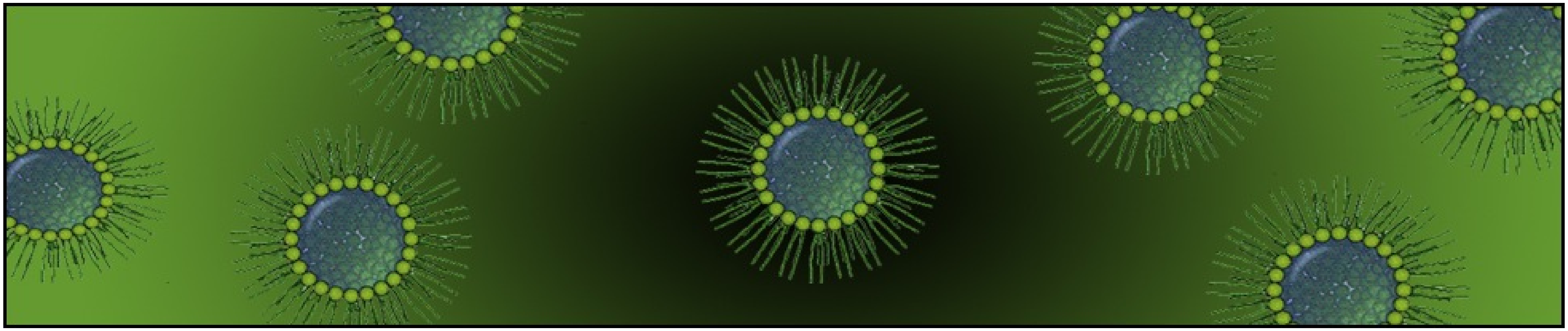


Future work:

- **Investigation of the effect of the parameters.**

- **Biosurfactants.**

Biosurfactants



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  - Cosmetics
  - Foods
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  - Natural Sophorolipids shown antimicrobial properties
  - Prevention of bio film build-up
- Fungicides as agro-active
  - Greenhouse trials performed
- Oil and gas
  - Proven surface cleaning and emulsification of crude oil
  - Crude oil emulsification

Thank you for your patience and attention!