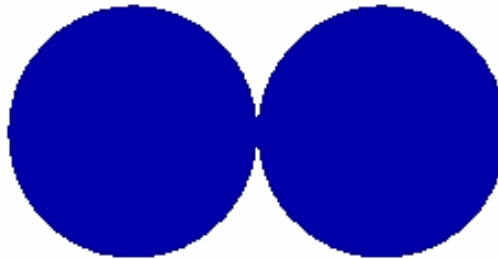

FLOW ASSURANCE: DROP COALESCENCE IN THE PRESENCE OF SURFACTANTS

Vishrut Garg and Osman A. Basaran

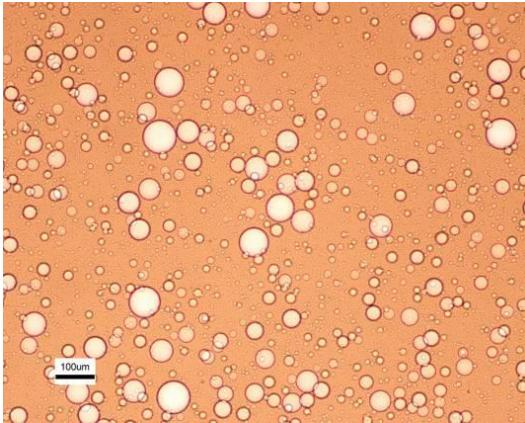
Davidson School of Chemical Engineering
Purdue University



*With special thanks to:
Krish Sambath (now at Chevron) and
Sumeet Thete (now at Air Products)*

10 May 2018

Emulsions



A fine dispersion of minute droplets of one liquid in another and in which the drop liquid is neither soluble nor miscible

Oil-in-water (O/W) emulsion

Food industry



O/W emulsion



W/O emulsion

Agriculture



Insecticides are prepared as oil-in-water (O/W) emulsions for cheap and effective application

Pharmaceuticals

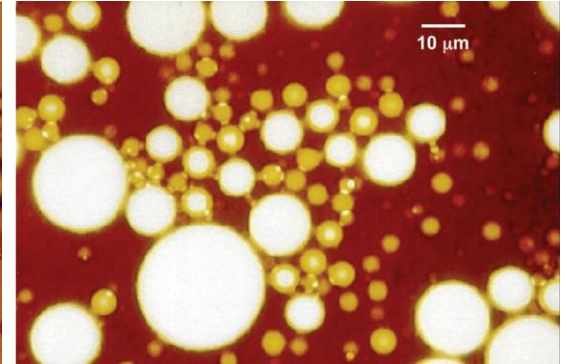
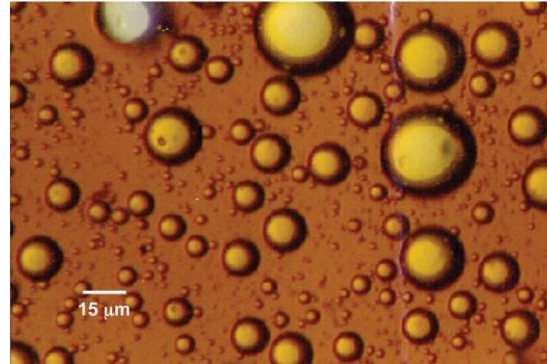


Ointments



Intravenous lipid emulsions

Emulsions in the oil and gas industry



Water-in-oil (W/O) emulsions are common in almost all phases of oil processing and production

- Water/brine is usually present during extraction or injected during enhanced oil recovery (EOR) and desalting
- Agitation due to flow through pumps, chokes, valves and other surface equipment leads to formation emulsions
- The presence of emulsifying agents is crucial for the formation of these emulsions. Some of these occur naturally (such as asphaltenes) but others are also added during extraction (e.g. anti-corrosion chemicals)

Emulsions: assurance and safety concerns



- Emulsions can “sit” in oil-water separators for inordinately long times
 - Emulsions always have higher viscosity than clean oil and cause flow assurance problems
 - Presence of salts and sediments in the aqueous phase during transport of emulsions can lead to corrosion and scaling in equipment
 - Inefficient separation of emulsions can lead to release of oil droplets mixed in wastewater discharged into the environment
 - Excessive utilization of demulsifiers can pose environmental risks
 - Emulsions formed in oil spills/pipeline failures persist for long periods and are difficult to cleanup
-

Separation of emulsions via coalescence

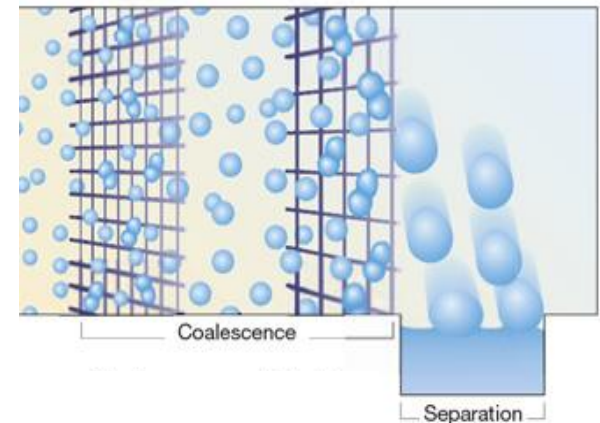
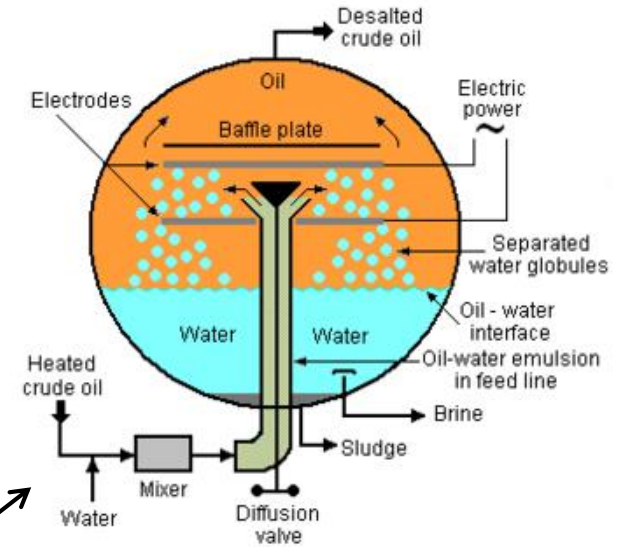


**Thin film drains,
ruptures, and leads
to coalescence of
two drops**

Applications in:

Crude oil desalters

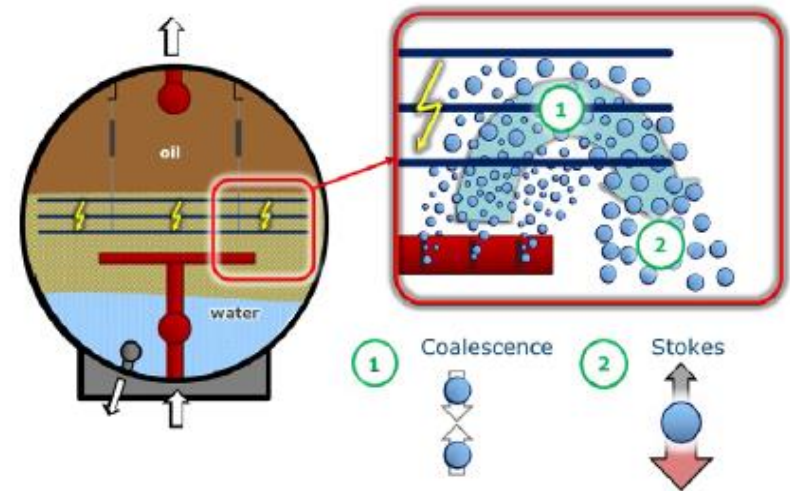
Coalescers for L/L
extraction



Process Description

Frames builds on its vast experience in coalescer engineering, enabling us to give our clients a competitive advantage when it comes to cleaning crude oil. By efficiently and effectively removing undesirable water and salts, our clients are able to increase the quality of their crude oil, cut their transport costs and protect their downstream processes and equipment.

Removal of water and contaminants generally comprises two steps: dehydration and desalting. Frames coalescers are designed for both steps, and are applied in upstream as well as downstream applications. In oilfields, the emphasis is generally on a combination of dehydration and desalting, whereas in refineries the focus is primarily on desalting.



Working principle of coalescence (1) and separation (2) inside Electrostatic Coalescer

Population balances

- Population balances are used to determine evolution of drop sizes or drop size distributions in coalescers using semi-empirical models for collision rates of drops and coalescence probabilities
- The time evolution of number of drops of size i per unit volume (n_i) in a given coalescer is given by:

$$\frac{dn_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} J_{i-j,j} - \sum_{j=1}^n J_{i,j}$$

where J_{ij} is the the rate of collision per unit volume of drops of size i with drops of size j

$$J_{i,j} = n_i n_j \pi (a_i + a_j)^2 V_{ij} e_{ij}$$

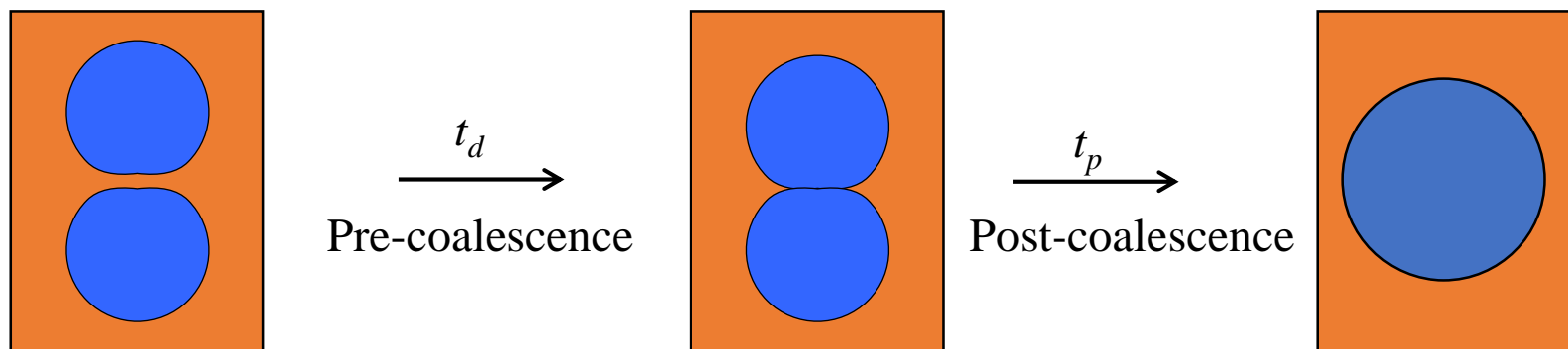
a_i - Characteristic radius for drop of size i

V_{ij} - Relative velocity of the two drops

Collision efficiency

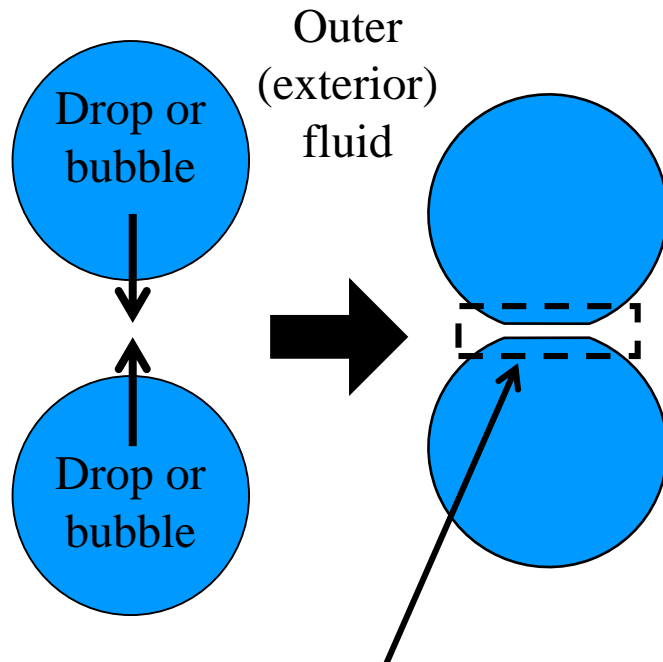
Single coalescence events

- Collision efficiency (e_{ij}) is the ratio of the actual collision rate to that for drop coalescence in the presence of gravity alone
- Analysis of local dynamics of two drop interactions using simulation or computational analysis provides accurate estimates for the collision efficiency as compared to semi-empirical models
- **These results can be fed back into population balance models to make engineering calculations and aid coalesce design**
- Key parameter of single coalescence events is the drainage time (t_d)



Two distinct coalescence problems

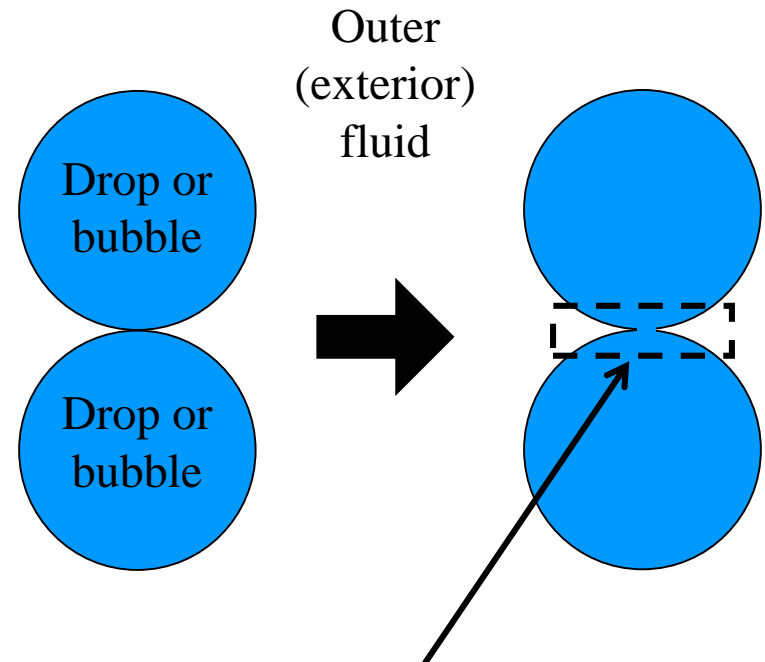
Pre-coalescence problem



Thin film/sheet (that has to rupture for coalescence to occur)

Singularity at the end of the process

Post-coalescence problem

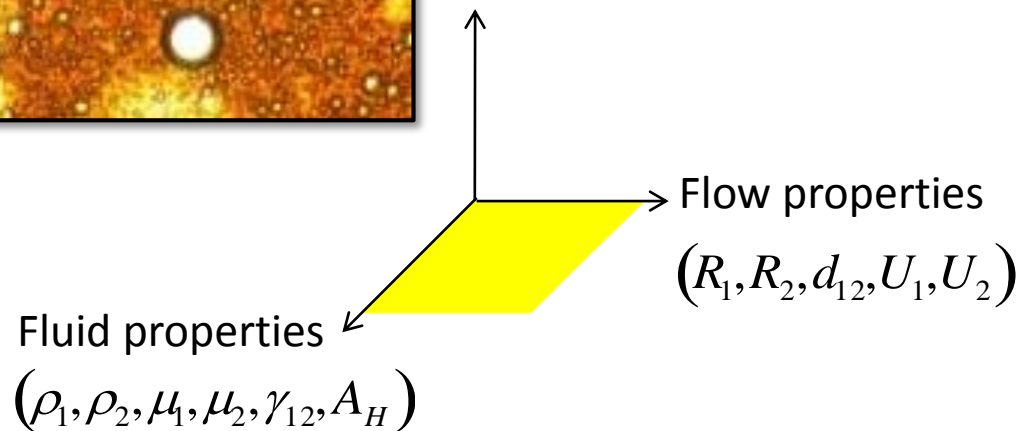
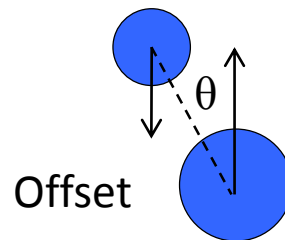
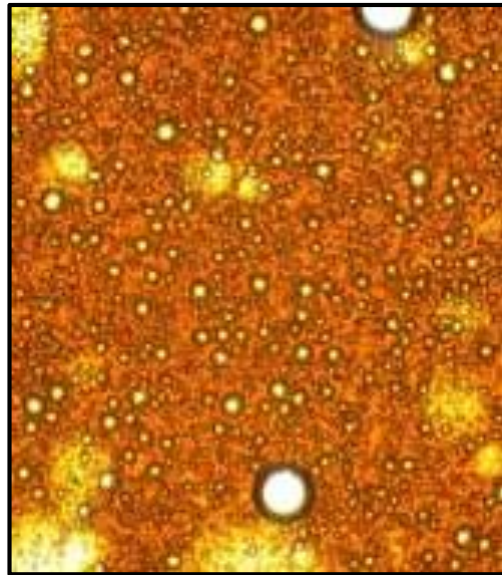


Thin film/sheet with a growing hole (or a growing bridge that connects the two drops/bubbles)

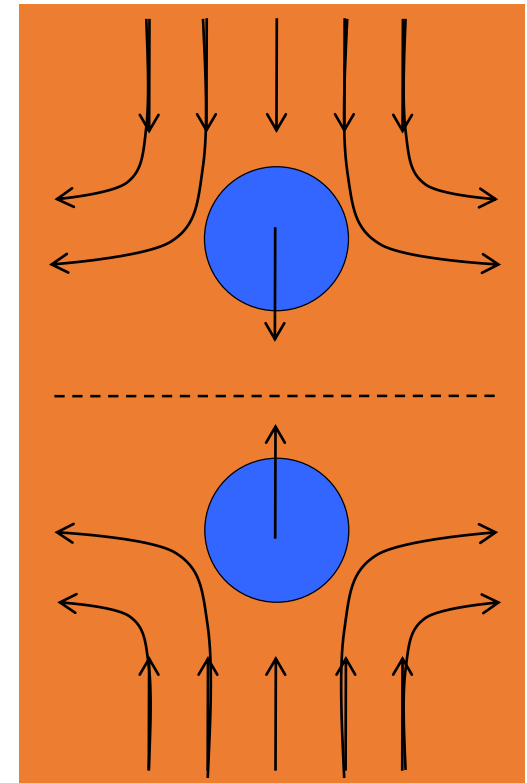
Singularity at the beginning of the process

Fluid dynamics of drop pairs: Pre-coalescence problem

Water drops in oil or oil drops in water



Two drops of equal size
colliding head on



Common features of all the flow assurance problems under consideration

Breakup and coalescence problems all involve:

- Hydrodynamic singularities (technical name: **finite time singularities**)
- **Free surface flows** involving **topological changes**
- Disparate length scales (**multi-scale physics**), e.g. if the initial drop size is 1 mm and at “breakup” the thread radius is 10 nm (the limit of continuum mechanics), *length scales differing by 5 orders of magnitude or a factor of 10^5 must be resolved in a single simulation!!! (Commercial codes/diffuse interface methods can barely do 2 orders.)*

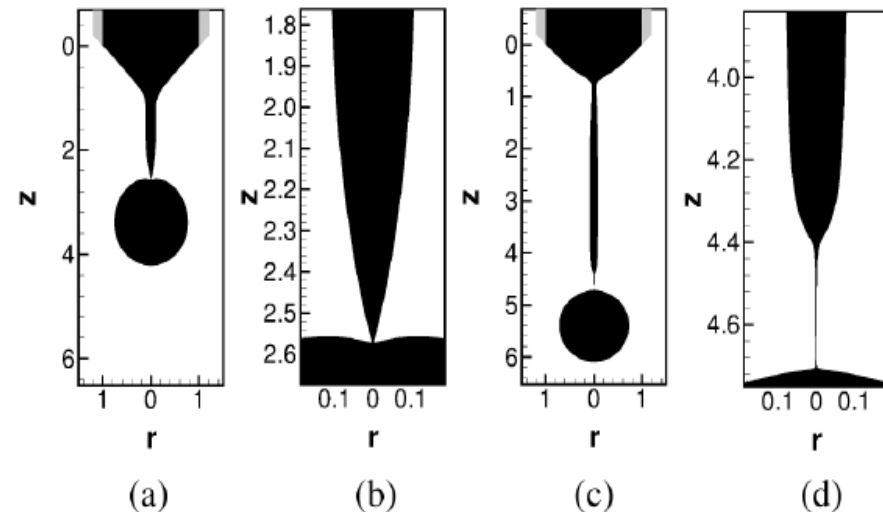


FIG. 1. Computed shapes of water, (a),(b), and 83% glycerol, (c),(d), drops at the incipience of pinch-off. Here (a) and (c) show the global shapes and (b) and (d) show their blowups in the vicinity of h_{\min} . For the water drop, $h_{\min} = 2 \times 10^{-3}$, and for the 83% glycerol drop, $h_{\min} = 1 \times 10^{-3}$.

Previous works

All the best studies are restricted to creeping/Stokes flow, i.e. $Re=0$.



❖ R.H. Davis and co-workers (1990 – 1997)

- Lubrication approximation
- Scaling theory

❖ L.G. Leal and co-workers (2001 – present)

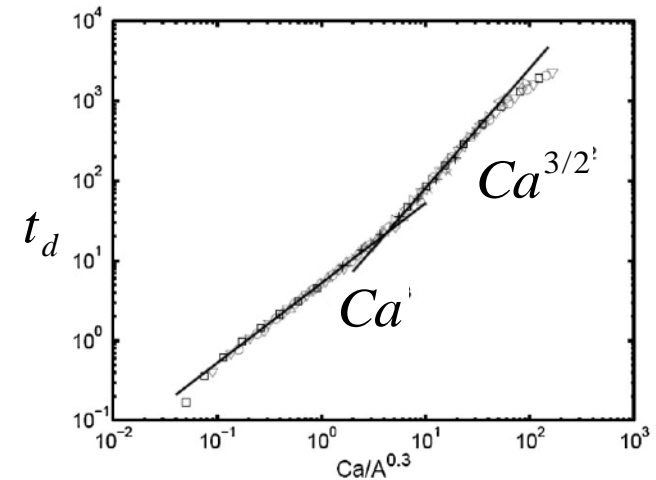
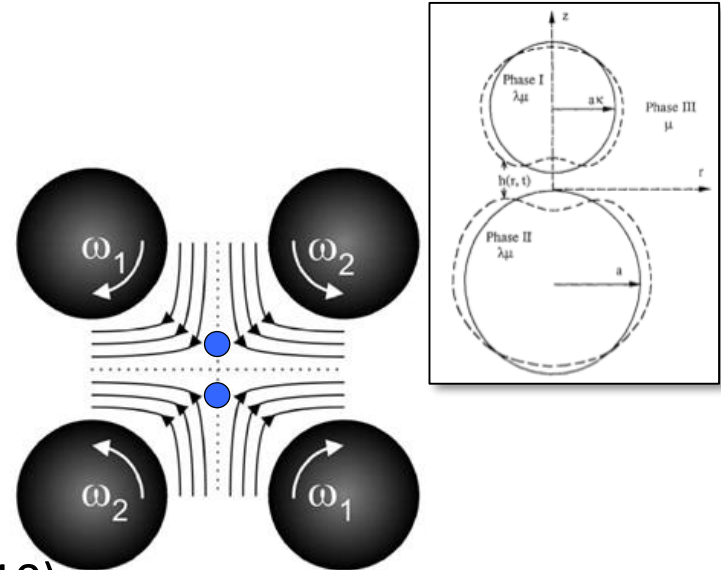
- Experiments using Taylor's four roll mill
- Boundary integral (BI) simulations
- Scaling theory

❖ M. Loewenberg and co-workers (2004 – 2010)

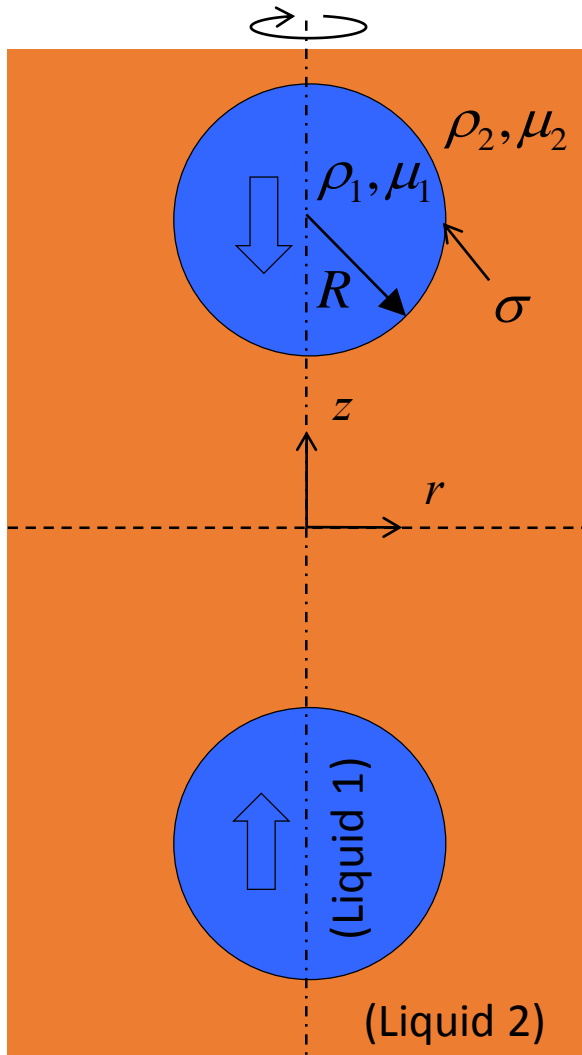
- BI sims (role of internal flows in arresting drop coalescence)

❖ H. Meijer and co-workers (2006 – present)

- Boundary integral simulations
- Scaling theory



Problem setup



Imposed bi-axial extensional flow } $\mathbf{u}_0(\mathbf{x}) = G \left(\frac{r}{2} \mathbf{e}_r - z \mathbf{e}_z \right)$

Key Dimensionless groups:

$$Ca = \frac{GR\mu_2}{\sigma}$$

Capillary number or viscous / surface tension force

$$A^* = \frac{A_H}{6\pi\sigma R^2}$$

Van der Waals force / Surface tension force

$$m_i = \mu_i / \mu_1 \quad i=1,2$$

Viscosity ratio

$$d_i = \rho_i / \rho_1$$

Density ratio

$$Oh = \frac{\mu_1}{(\rho_1 R \sigma)^{1/2}}$$

Ohnesorge number or dimensionless viscosity

$$Re = \frac{GR^2 \rho_2}{\mu_2} = \frac{Ca d_2}{(m_2 Oh)^2}$$

1 mm water drops in oil

10^{-4} to 0.1

10^{-13}

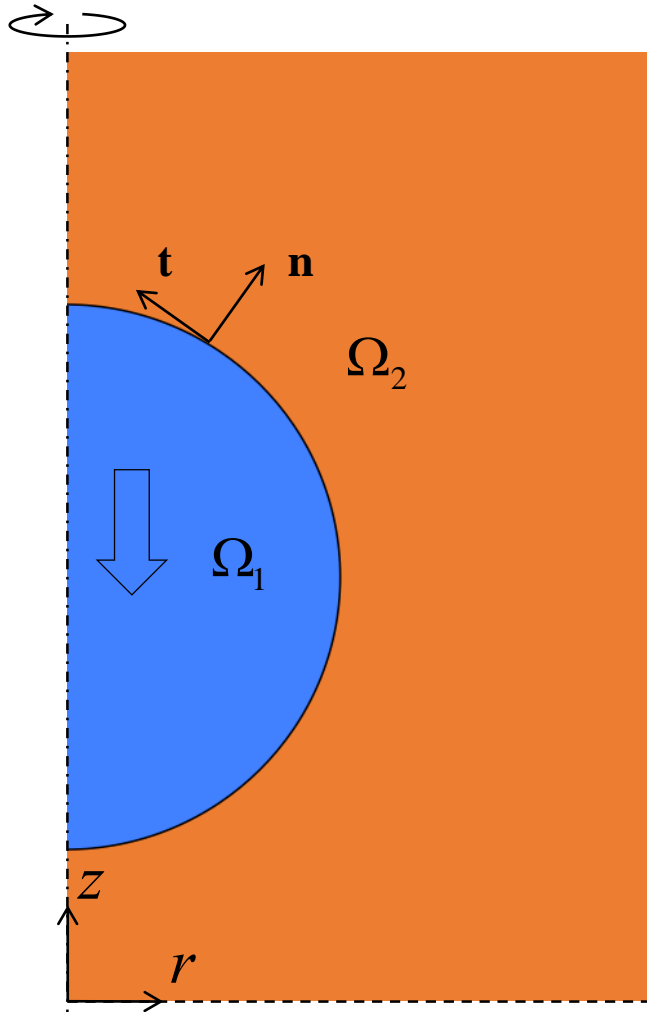
10

0.9

0.006

0.01 to 10

Mathematical formulation



Navier-Stokes system:

$$\left. \begin{aligned} \nabla \cdot \mathbf{v}_i &= 0 \\ d_i \left(\frac{\partial \mathbf{v}_i}{\partial t} + \mathbf{v}_i \cdot \nabla \mathbf{v}_i \right) &= \nabla \cdot \mathbf{T}_i \end{aligned} \right\} \Omega_1 \cup \Omega_2$$

$$\text{where } \mathbf{T}_i = -p_i \mathbf{I} + m_i Oh \left((\nabla \mathbf{v}_i) + (\nabla \mathbf{v}_i)^T \right)$$

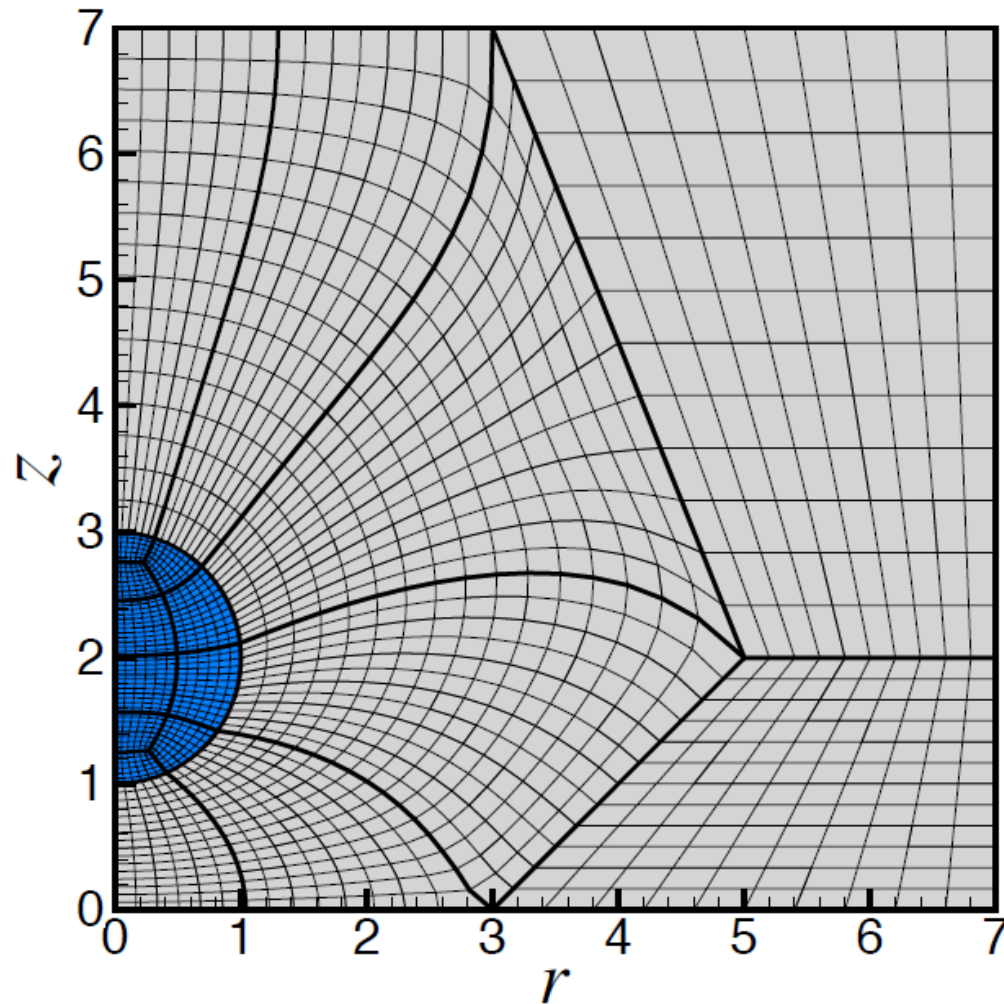
Boundary conditions:

$$\left. \begin{aligned} \mathbf{n} \cdot (\mathbf{v}_i - \mathbf{v}_{s,i}) &= 0 \\ \mathbf{n} \cdot [\mathbf{T}_i]_1 &= \left(2H - \frac{A^*}{h(\mathbf{x})^3} \right) \mathbf{n} \end{aligned} \right\} \partial \Omega_{1-2}$$

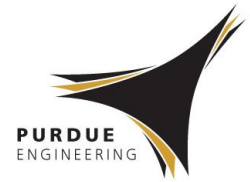
where $h(\mathbf{x})$ – vertical separation
between drops' interfaces

For typical liquids, $A_H = 10^{-21}$ to $10^{-18} J$

Elliptic mesh generation

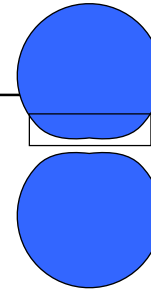
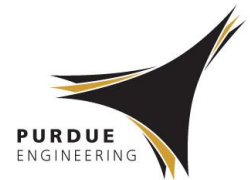


Different non-dimensionalizations

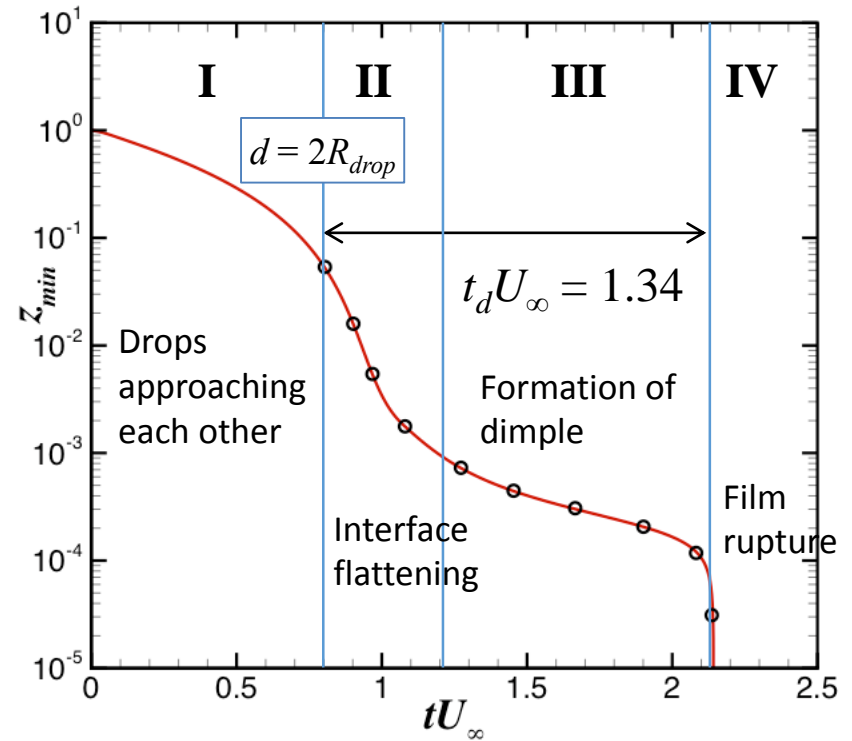
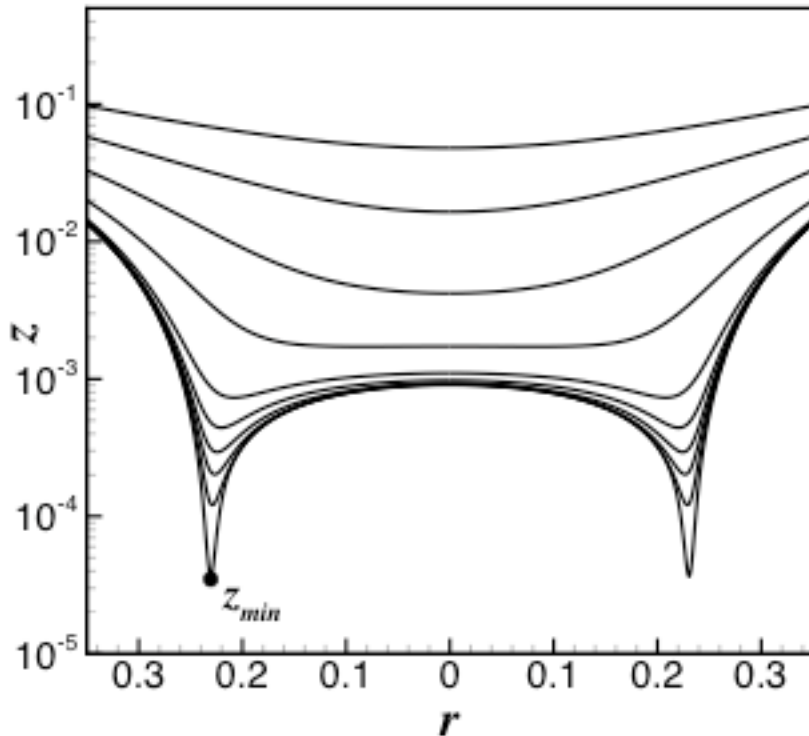


- Dimensionless external or approach velocity driving the two drops together: $U_{\infty} = G \sqrt{\rho_1 R^3 / \sigma}$
← Inertial-capillary (Rayleigh) time
- Ca is velocity made dimensionless with viscous-capillary time and U_{∞} is that using inertial-capillary time
- Note that $Ca = m_2 Oh U_{\infty}$. In Stokes flow, $Oh \rightarrow \infty$ but $U_{\infty} \rightarrow 0$ so that Ca is finite
- Thus, one possible set of dimensionless groups is: Oh, m_2, d_2, Ca, A^* (Stokes limit is obtained by setting $Oh^{-1} = 0$ and dropping d_2 from the list of dimensionless parameters)
- A second set of candidate dimensionless groups is: $Oh, m_2, d_2, U_{\infty}, A^*$ (used in the remainder of the talk)

Final stages of film drainage



$$Oh = 0.1, \quad m_2 = 5.3, \quad d_2 = 1.1, \quad U_\infty = 0.0285, \quad A^* = 5 \times 10^{-11}$$

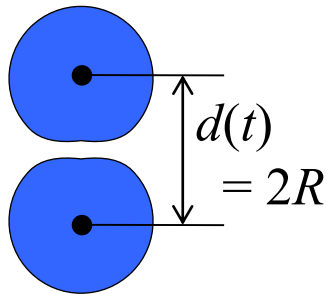


❖ Experimentally measured **drainage time** for 27 μm sized poly-butylene drops coalescing in silicone oil (Yoon *et al.* 2007) } : $t_d U_\infty \approx 1.32$

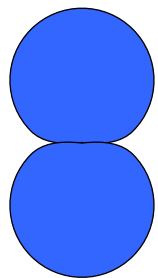
Impact on drainage time

Defined as:

Beginning at

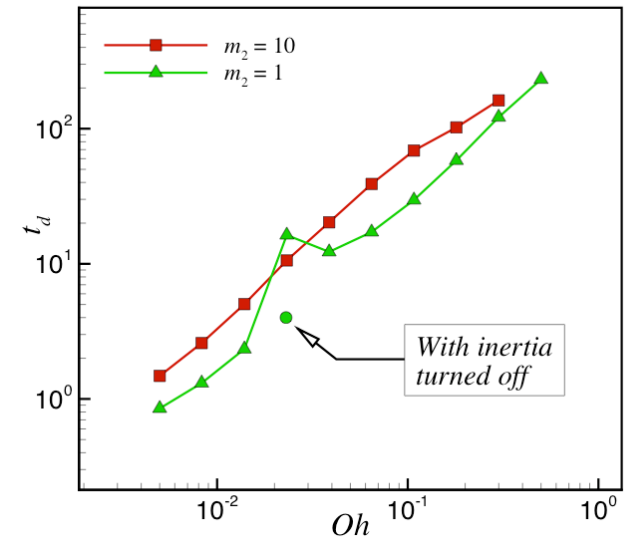
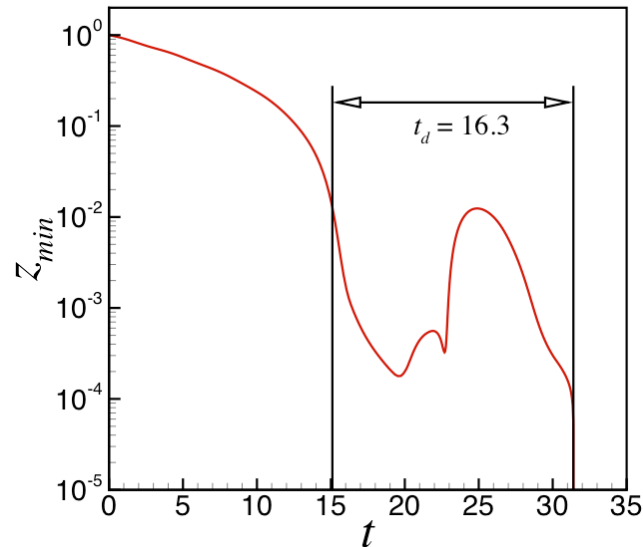


Ending with



Coalescence

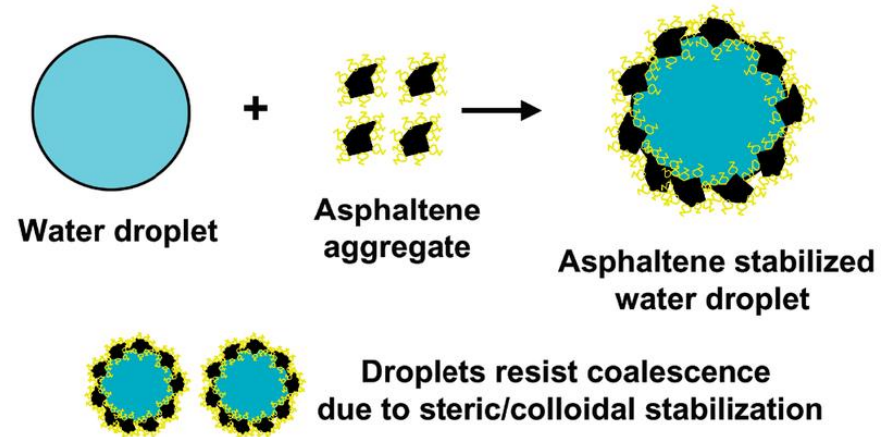
$$Oh = 0.023, U_\infty = 0.05, d_2 = 1, m_2 = 1, A^* = 10^{-10}$$



- *Inertia* causes the droplets to rebound on first approach at intermediate values of Oh resulting in the non-monotonic variation of drainage time with Oh
- Accurate prediction/knowledge of drainage time is essential if the results of simulations are to be used in engineering calculations (e.g. population balances) and in engineering design

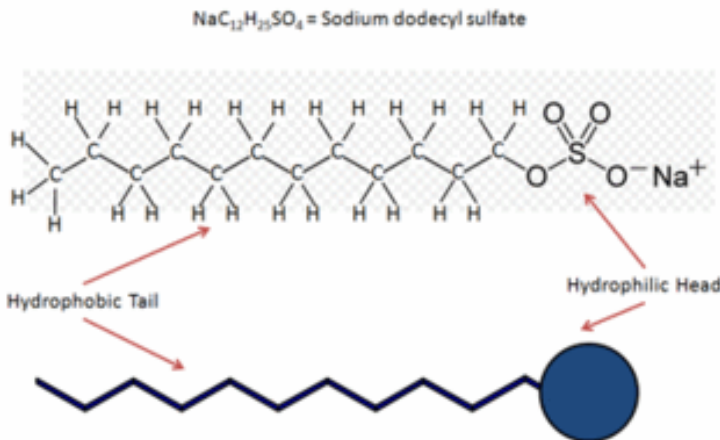
Emulsifiers are surface-active agents

- Naturally occurring asphaltenes and resins in crude oil reservoirs are surface-active agents that reduce the interfacial tension at water-oil interfaces
- Enhanced oil recovery (EOR) operations involve injection of surfactants in order to reduce the interfacial tension and free oil films from pore walls



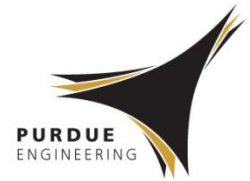
Asphaltenes are naturally occurring emulsifiers

Presence of these surfactants complicates separation procedures as they tend to stabilize the emulsions!



SDS – A common surfactant injected during EOR operations

Modeling surfactant-laden flows



- Surfactant effects are accounted for by means of two additional equations

Surfactant transport equation
for surfactant concentration (Γ)

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\mathbf{v} \Gamma) = \frac{1}{Pe} \nabla_s^2 \Gamma \quad \Gamma(t = 0) = \Gamma_0$$

Szyszkowski equation
for local surface tension (σ)

$$\sigma = 1 + \beta \ln(1 - \Gamma)$$

Initial surfactant loading

- Surfactant effects are accounted for by means of two additional equations

Surfactant transport equation
for surfactant concentration (Γ)

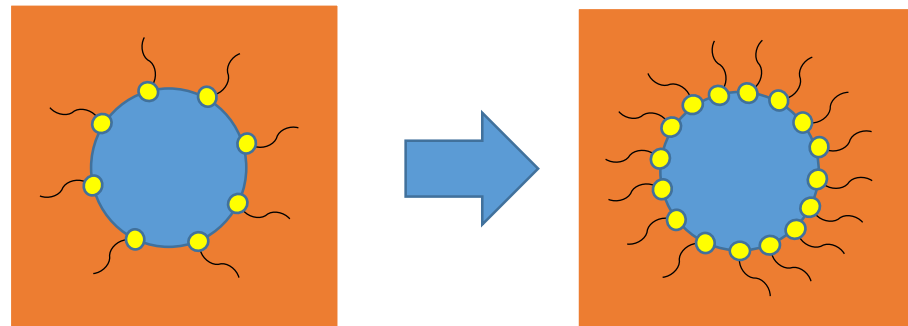
$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\mathbf{v} \Gamma) = \frac{1}{Pe} \nabla_s^2 \Gamma \quad \Gamma(t = 0) = \Gamma_0$$

Szyszkowski equation
for local surface tension (σ)
$$\sigma = 1 + \beta \ln(1 - \Gamma)$$

Three additional parameters

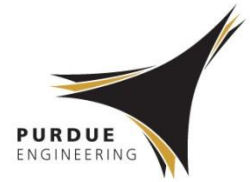
1. Initial surfactant loading (Γ_0)

Amount of surfactant initially present in the system. It is typically some fraction of maximum packing concentration



Increasing Γ_0

Surfactant strength parameter



- Surfactant effects are accounted for by means of two additional equations

Surfactant transport equation
for surfactant concentration (Γ)

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\mathbf{v}\Gamma) = \frac{1}{Pe} \nabla_s^2 \Gamma \quad \Gamma(t=0) = \Gamma_0$$

Szyszkowski equation
for local surface tension (σ)

$$\sigma = 1 + \beta \ln(1 - \Gamma)$$

Three additional parameters

2. Surfactant strength parameter (β)

Governs the extent to which local interfacial tension is reduced from the interfacial tension of pure liquid (σ_p)

$$\beta = \frac{\Gamma_m R_g T}{\sigma_p}$$

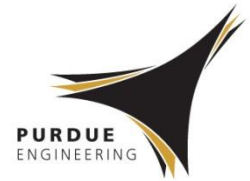
Γ_m Maximum packing concentration

R_g Gas constant

T Temperature

σ_p Interfacial tension of pure liquid

Interface (or surface) Peclet number



- Surfactant effects are accounted for by means of two additional equations

Surfactant transport equation
for surfactant concentration (Γ)

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\mathbf{v}\Gamma) = \frac{1}{Pe} \nabla_s^2 \Gamma \quad \Gamma(t=0) = \Gamma_0$$

Szyszkowski equation
for local surface tension (σ)

$$\sigma = 1 + \beta \ln(1 - \Gamma)$$

Three additional parameters

3. Interface Peclet number (Pe)

Ratio of convective transport of surfactants along the surface to diffusive transport. Values are typically large, i.e. $O(100)$ to $O(10^5)$.

$$Pe = \sqrt{\frac{R\sigma_p}{\rho_1 D_s^2}}$$

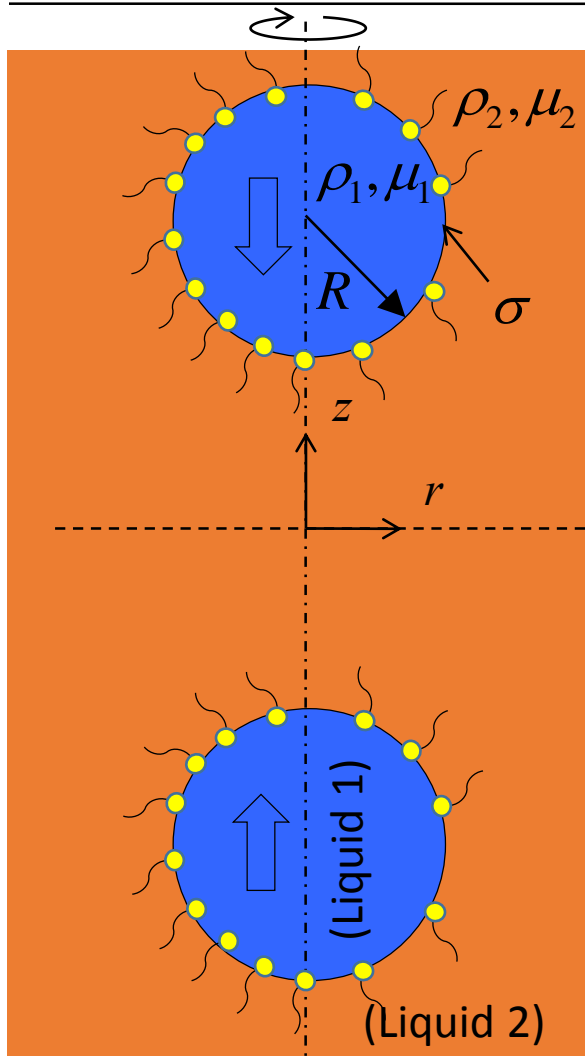
R Drop radius

D_s Surface diffusivity

ρ_1 Density of inner liquid

σ_p Interfacial tension of pure liquid

Problem setup

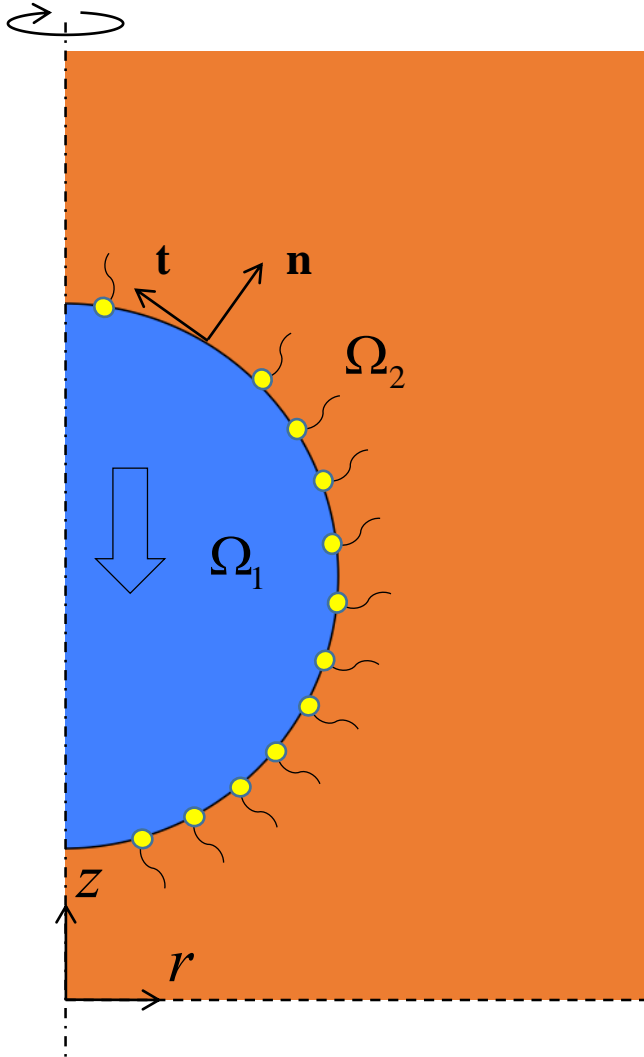


Imposed bi-axial extensional flow } $\mathbf{u}_0(\mathbf{x}) = G \left(\frac{r}{2} \mathbf{e}_r - z \mathbf{e}_z \right)$

Key Dimensionless groups:

		1 mm water drops in oil
$Oh = \frac{\mu_1}{(\rho_1 R \sigma_p)^{1/2}}$	Ohnesorge number or dimensionless viscosity	0.006
$A^* = \frac{A_H}{6\pi\sigma_p R^2}$	Van der Waals force Surface tension force	10^{-13}
$m_i = \mu_i / \mu_1$ <small>$i=1,2$</small>	Viscosity ratio	10
$d_i = \rho_i / \rho_1$	Density ratio	0.9
Γ_0	Initial surfactant loading	0 (0.1)
$\beta = \frac{\Gamma_m R_g T}{\sigma_p}$	Surfactant strength parameter	0.3
$Pe = \sqrt{\frac{R\sigma_p}{\rho_1 D_s^2}}$	Surface Peclet number	1000

Mathematical formulation



Navier-Stokes system:

$$\left. \begin{aligned} \nabla \cdot \mathbf{v}_i &= 0 \\ d_i \left(\frac{\partial \mathbf{v}_i}{\partial t} + \mathbf{v}_i \cdot \nabla \mathbf{v}_i \right) &= \nabla \cdot \mathbf{T}_i \end{aligned} \right\} \Omega_1 \cup \Omega_2$$

Boundary conditions:

$$\left. \begin{aligned} \mathbf{n} \cdot (\mathbf{v}_i - \mathbf{v}_{s,i}) &= 0 \quad \text{Marangoni stress} \\ \mathbf{n} \cdot [\mathbf{T}_i]_1^2 &= \left(2H - \frac{A^*}{h(\mathbf{x})^3} \right) \mathbf{n} + \nabla_s \sigma \end{aligned} \right\} \partial\Omega_{1-2}$$

Surfactant transport equation

$$\frac{\partial \Gamma}{\partial t} + \nabla_s \cdot (\mathbf{v} \Gamma) = \frac{1}{Pe} \nabla_s^2 \Gamma$$

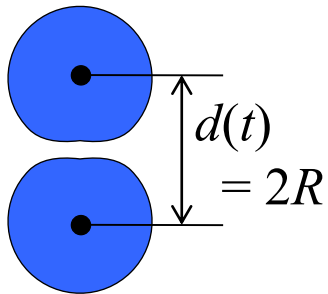
Szyzscowski equation

$$\sigma = 1 + \beta \ln(1 - \Gamma)$$

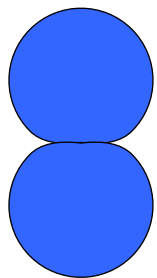
Impact on drainage time

t_d Defined as:

Beginning at

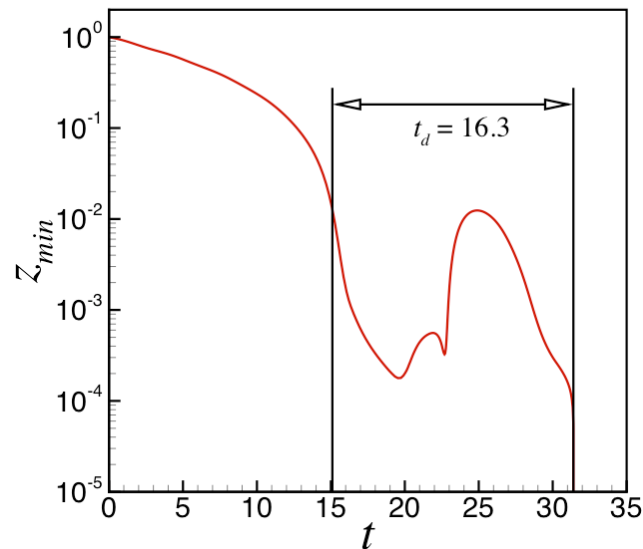


Ending with

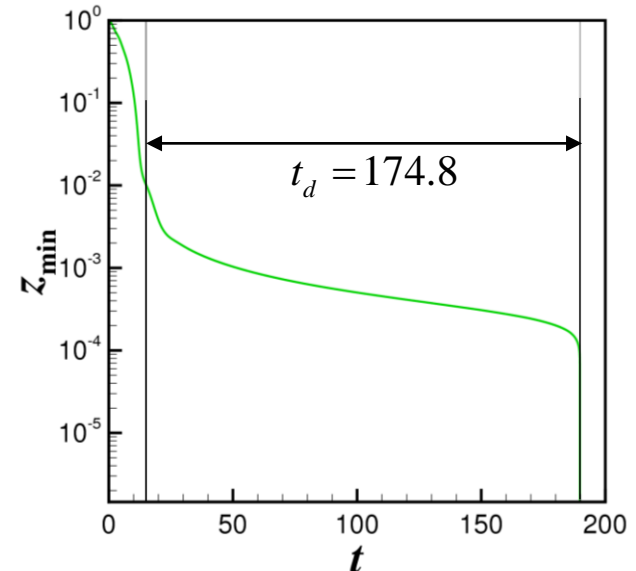


Coalescence

$$Oh = 0.023, U_\infty = 0.05, d_2 = 1, m_2 = 1, A^* = 10^{-10}$$



No surfactant



Surfactant present

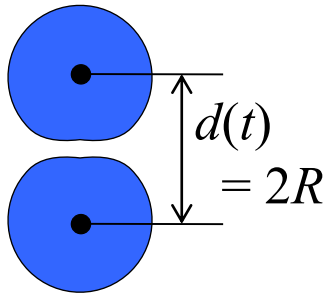
$$\Gamma_0 = 0.3, \beta = 0.3, Pe = 1000$$

- Drainage time *increases by more than 10 times* when surfactant is present while all other parameters are kept constant
- Rebound phenomena **absent** when surfactants are added

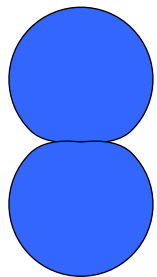
Effect of initial loading (Γ_0)

t_d Defined as:

Beginning at



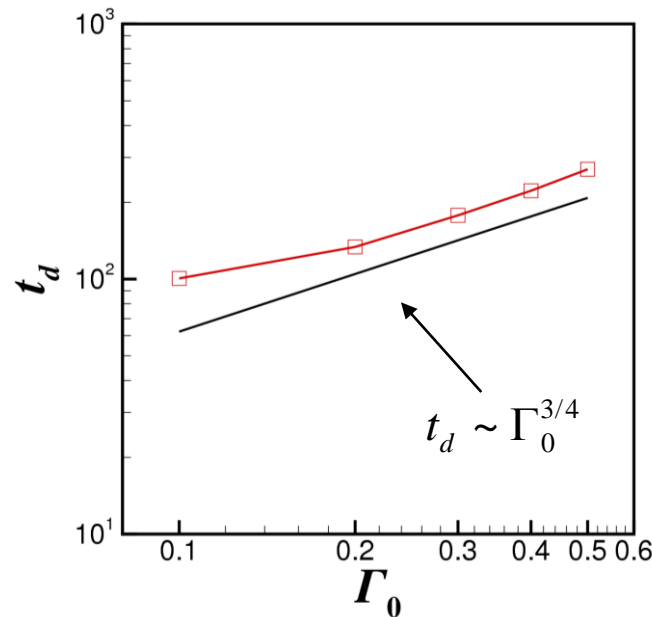
Ending with



Coalescence

$$Oh = 0.023, U_\infty = 0.05, d_2 = 1, m_2 = 1, A^* = 10^{-10}$$

$$\beta = 0.3, Pe = 1000$$



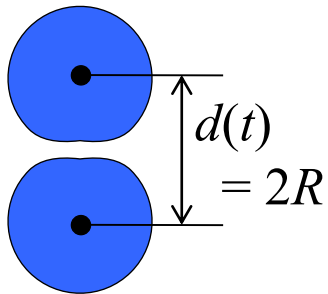
- Drainage time **increases** as more surfactant is initially loaded
- Variation of drainage time with initial loading given by **power-law expression**:

$$t_d \sim \Gamma_0^{3/4}$$

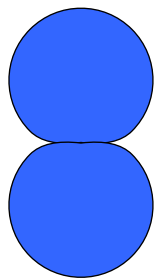
Effect of initial loading (Γ_0)

t_d Defined as:

Beginning at



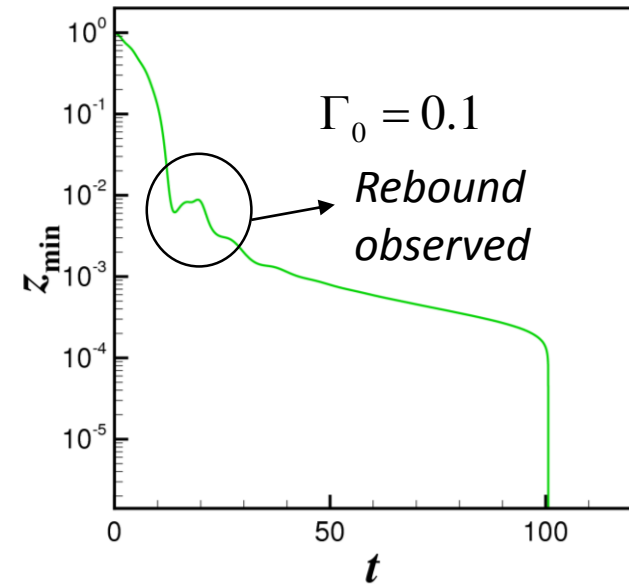
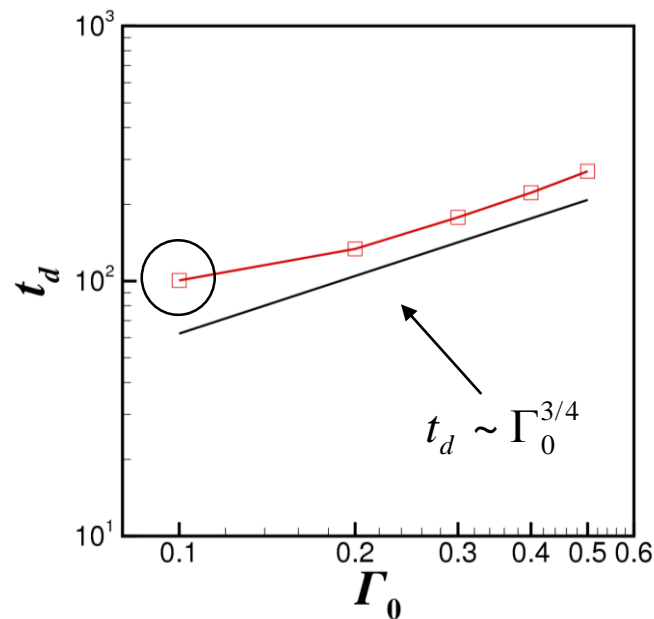
Ending with



Coalescence

$$Oh = 0.023, U_\infty = 0.05, d_2 = 1, m_2 = 1, A^* = 10^{-10}$$

$$\beta = 0.3, Pe = 1000$$



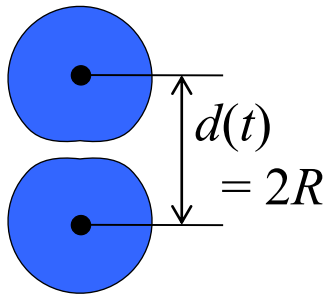
- Deviation from power-law relationship for $\Gamma_0 = 0.1$ related to rebound phenomenon

$$t_d \sim \Gamma_0^{3/4}$$

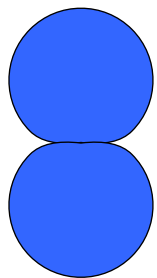
Effect of initial loading (Γ_0)

t_d Defined as:

Beginning at



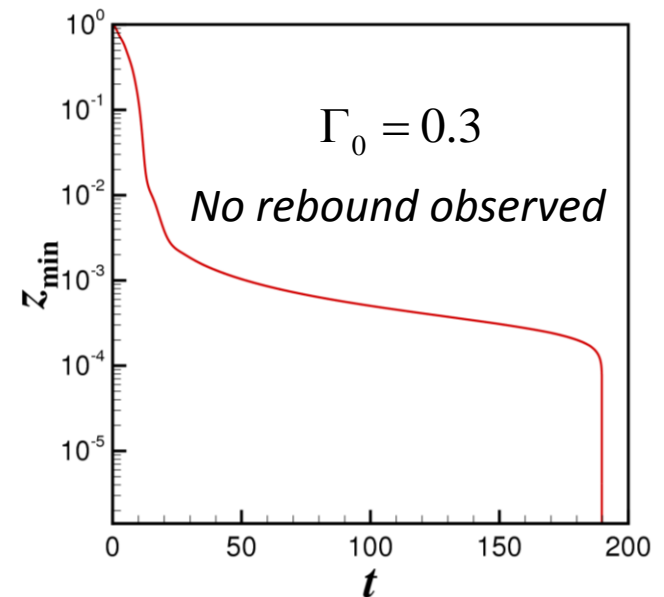
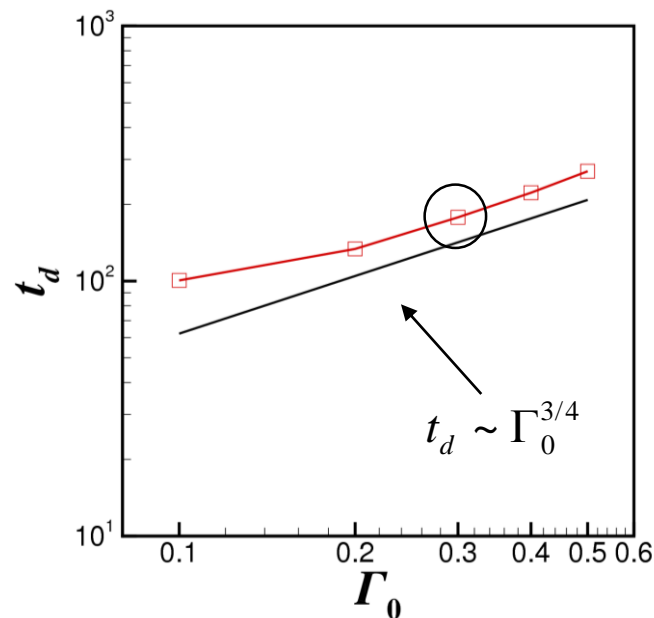
Ending with



Coalescence

$$Oh = 0.023, U_\infty = 0.05, d_2 = 1, m_2 = 1, A^* = 10^{-10}$$

$$\beta = 0.3, Pe = 1000$$



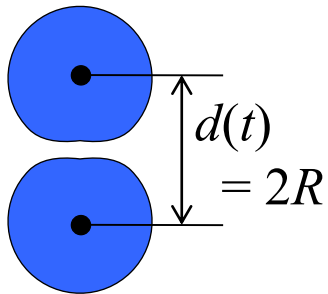
- For larger values of Γ_0 no rebound is observed and the drainage time follows the power-law dependence given by:

$$t_d \sim \Gamma_0^{3/4}$$

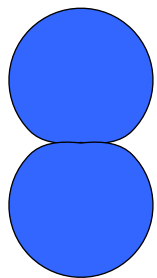
Effect of initial loading (Γ_0)

t_d Defined as:

Beginning at



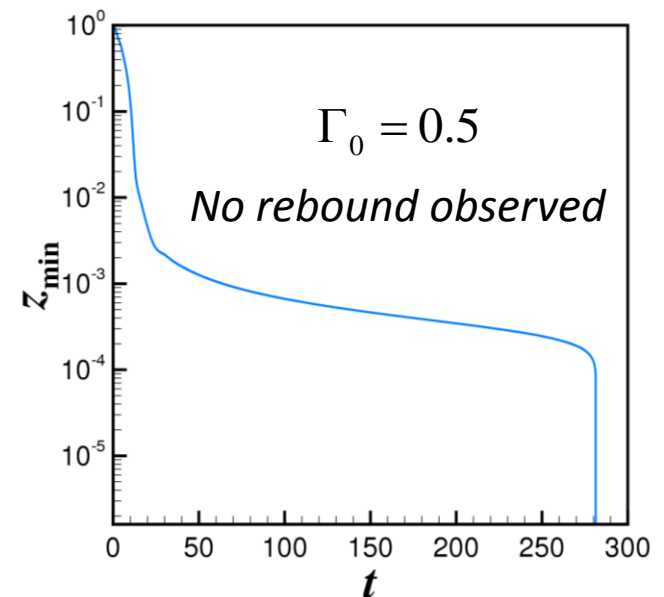
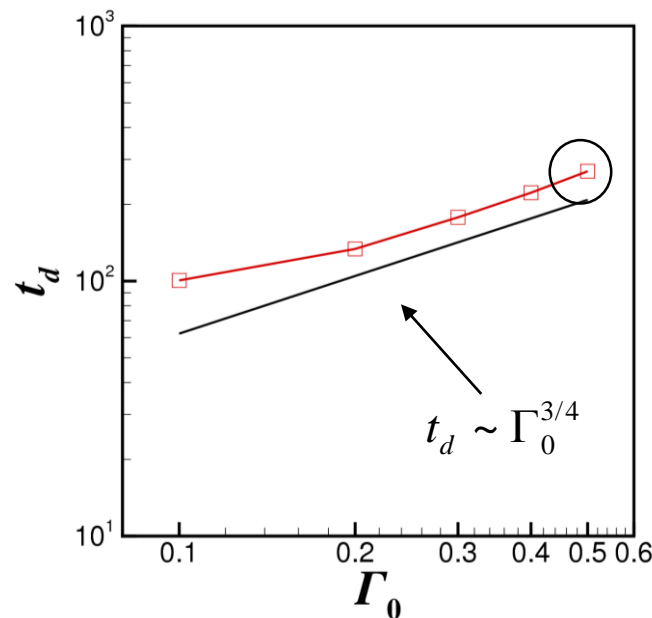
Ending with



Coalescence

$$Oh = 0.023, U_\infty = 0.05, d_2 = 1, m_2 = 1, A^* = 10^{-10}$$

$$\beta = 0.3, Pe = 1000$$



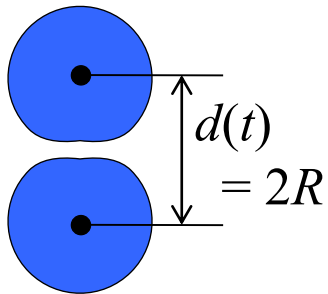
- For larger values of Γ_0 no rebound is observed and the drainage time follows the power-law dependence given by:

$$t_d \sim \Gamma_0^{3/4}$$

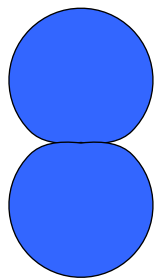
Effect of strength parameter (β)

t_d Defined as:

Beginning at



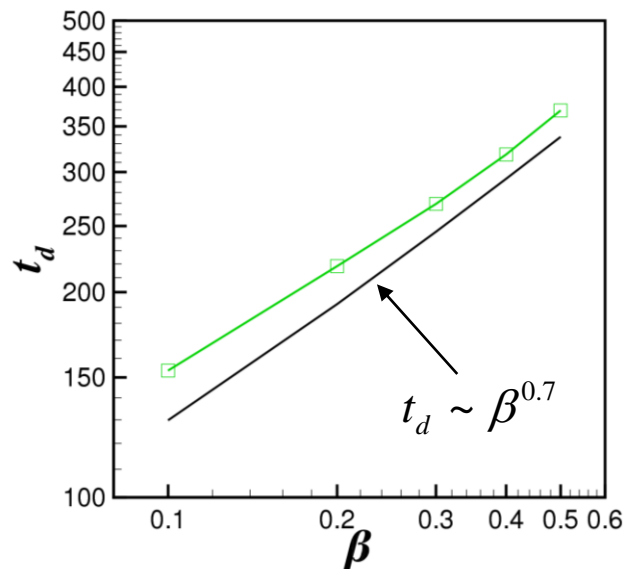
Ending with



Coalescence

$$Oh = 0.023, U_\infty = 0.05, d_2 = 1, m_2 = 1, A^* = 10^{-10}$$

$$\Gamma_0 = 0.5, Pe = 1000$$



- Increasing β leads to an increase in drainage time, with the variation given by the power-law expression

$$t_d \sim \beta^{0.7}$$

- This expression also captures the variation of drainage time with system temperature, since:

$$\beta = \frac{\Gamma_m R_g T}{\sigma_p}$$

Conclusions and future work



- High-accuracy, high-resolution simulations for pure liquids have revealed and quantified unexpected role of inertia on drainage and coalescence times in drop coalescence as a function of Ohnesorge number
- Our simulations have revealed that drainage times increase by ten times or more in the presence of surfactants, and we have quantified the dependence of drainage times on initial surfactant loading (Γ_0) and the surfactant strength parameter (β)
- Future work will involve exploring the parameter space in greater detail and studying the impact of the interface Peclet number (Pe)
- Further study is need to establish the mechanism of surfactant laden drop coalescence and, in particular, to clarify the role Marangoni forces play in increasing film drainage times
- Future work will also include extending the present approach to situations in which surfactants are soluble in the bulk fluids

