EMULSIFICATION IN TURBULENT FLOW

A. GOAL AND PROBLEMS

1. REFERENCES

H = Hinze, J. O. Turbulence, McGraw-Hill, New York, 1975.

TL = Tennekes, H; Lumley J. L.; A first course in turbulence, The MIT Press, Cambridge, 1972

B = Batchelor, G. K *The theory of homogeneous turbulence*, Cambridge, 1953.

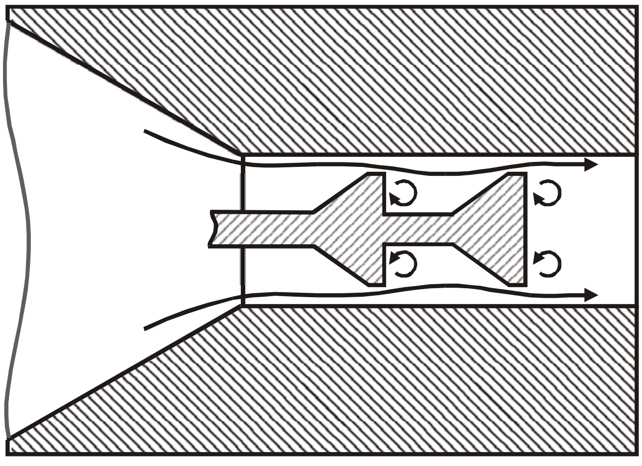
L = Levich, V. G. Physicochemical Hydrodynamics, Prentice Hall, Englewood Cliffs, New Jersey, 1962.

T = Coulaloglou, C. A.; Tavlarides, L.L Description of interaction processes in agitated liquid-liquid dispersions. *Chemical Engineering Science* **1977**, *32*, 1289.

P = Princen, H. M. The equilibrium shape of interfaces, drops, and bubbles. In *Surface and Colloid Science*, Matijevic, E. Ed.; Wiley, New York, 1969, Vol. 2, p. 1.

2. NARROW SLIT HOMOGENIZER

$$\varepsilon = \frac{p\,Q}{V_S} = \frac{(\Delta u)^3}{L}$$



- **Isotropic turbulence (chaotic and non-directional)**

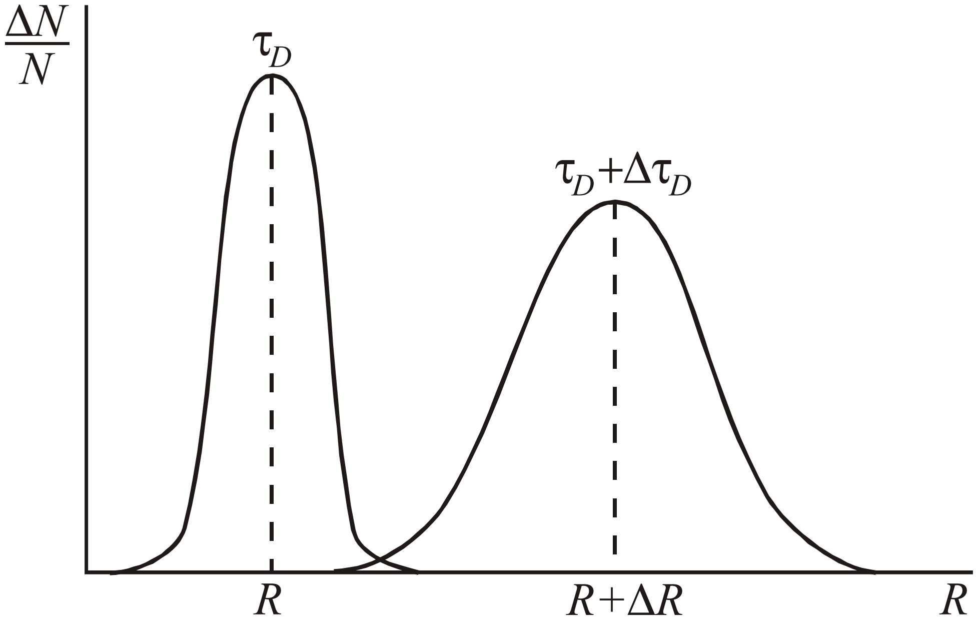
3. OVERALL GOAL

(1) Drop size distribution vs. stirring (ε), interfacial tension (σ), viscosity ratio (η_d/η_c) and drop life-time (τ_D) (surfactant adsorption Γ and distribution).

(2) Phase inversion

4. IMMEDIATE GOAL

- **Understand the emulsification mechanism**.
- **Describe quantitavely <u>variations</u> of drop size ΔR vs. variation of life time $\Delta\tau_D$ due to surfactants.**



5. APPROACH

Grasp the main factors and the overall scheme

(a) Account for polydispersity by considering discrete set of sizes

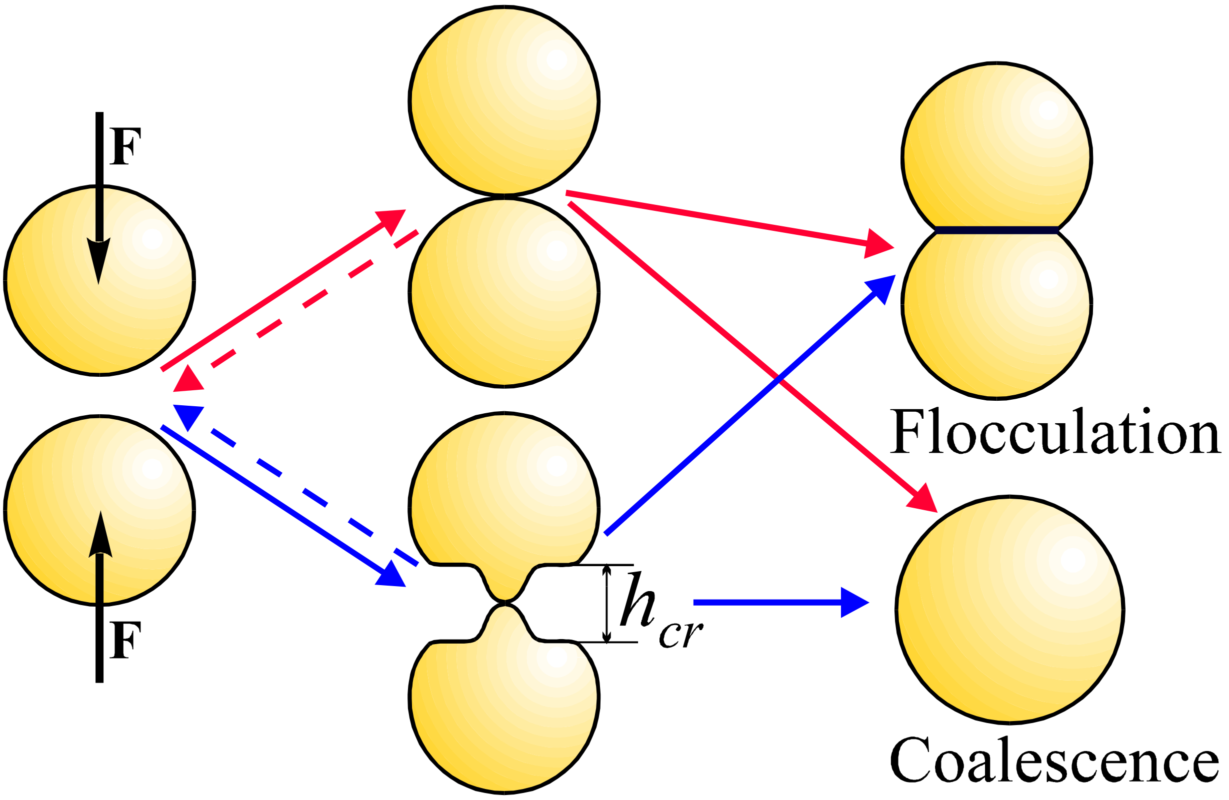
(b) Neglect dependence of rate constants on size

(c) Assume that drops split always on two equal size drops

(d) Assume that only equal size drops coalesce

B. DROPS AND FILMS

1. MAIN EVENTS DURING FLOCCULATION OR COALESCENCE

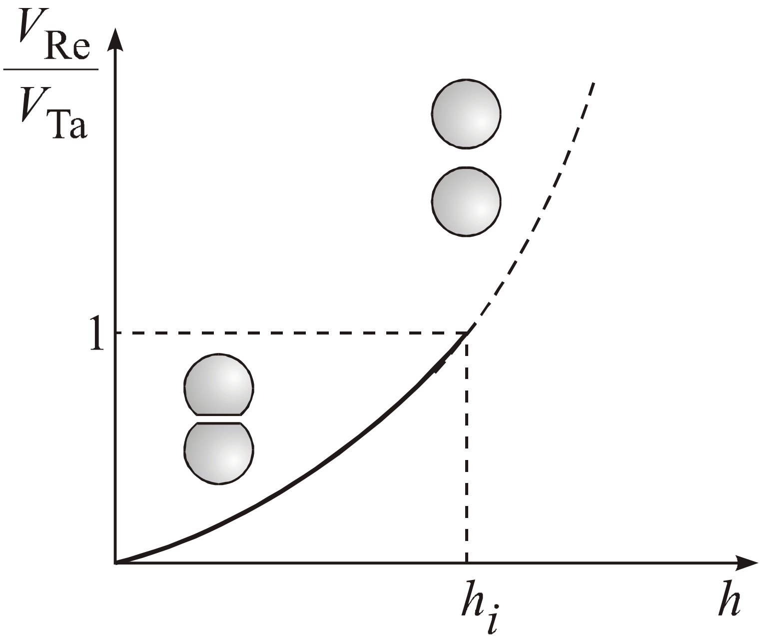


F = Driving Force (Buoyancy $F = \frac{4}{3}\pi R_d^3 \Delta\rho g$, Brownian, Turbulent, Surface Interactions)

Main parameters

- **Drop Shape**
- **Life Time, τ** $\boxed{\tau = \int_{h_{init}}^{h_{cr}} \frac{dh}{V} \propto \frac{1}{V}}$
- **Rate of Thinning, V** $V = -\frac{dh}{dt}$;
- **Critical Thickness of Rupture, h_{cr}**
- **Interfacial Mobility (Surfactant)**

2. TRANSITION SPHERE - FILM



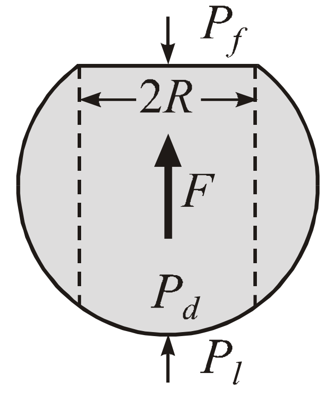
$$\frac{V_{\mathrm{Re}}}{V_{\mathrm{Ta}}} = \left(\frac{2\pi\sigma}{F}\right)^2 h^2$$

Inversion (Film Formation) Thickness, h_i:

$$\frac{V_{\mathrm{Re}}}{V_{\mathrm{Ta}}} = 1 \;\Rightarrow\; \boxed{h_i = \frac{F}{2\pi\sigma}}$$

- **Inversion at the same dissipation of energy**

3. FILM RADIUS



$$\left(P_f - P_l\right)\pi R^2 = F$$

$$P_f = P_d = P_l + \frac{2\sigma}{R_c}$$

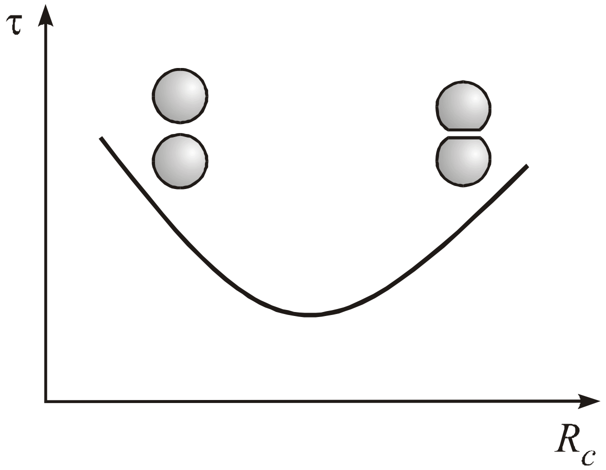
$$\pi R^2 \frac{2\sigma}{R_c} = F \qquad \boxed{R^2 = \frac{F R_c}{2\pi\sigma}}$$

$$F = \frac{4}{3}\pi\Delta\rho\, g\, R_c^3$$

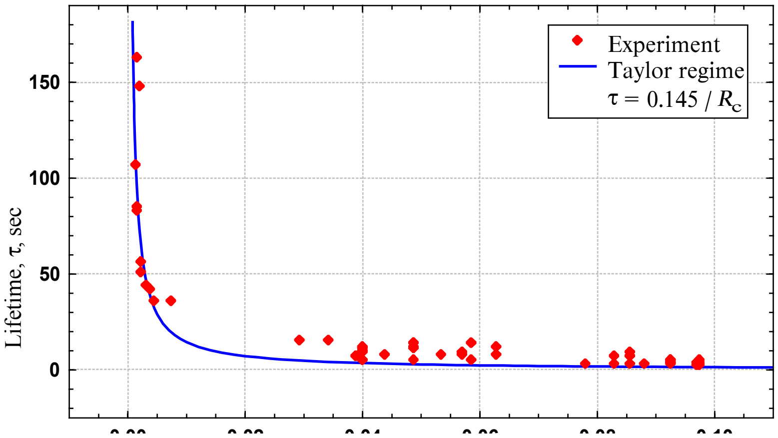
4. LIFE TIME OF DROPS DRIVEN BY BUOYANCY

$$\tau = \int_{h_{\text{in}}}^{h_{\text{final}}} \frac{d\,h}{V} \sim \frac{1}{V}$$

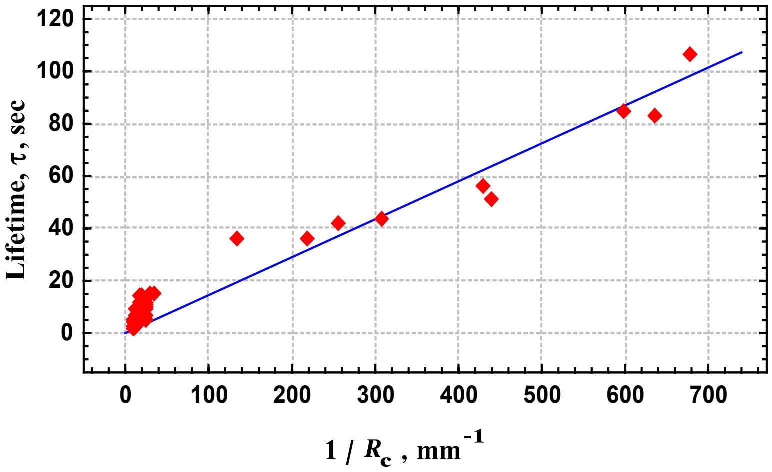
$$V_{\text{Ta}} = \frac{2}{3\pi\eta}\,\frac{h\,F}{R_c^2} \sim R_c \qquad\qquad V_{\text{Re}} = \frac{2\left(2\pi\sigma\right)^2}{3\pi\eta}\,\frac{h^3}{F\,R_c^2} \sim \frac{1}{R_c^5}$$



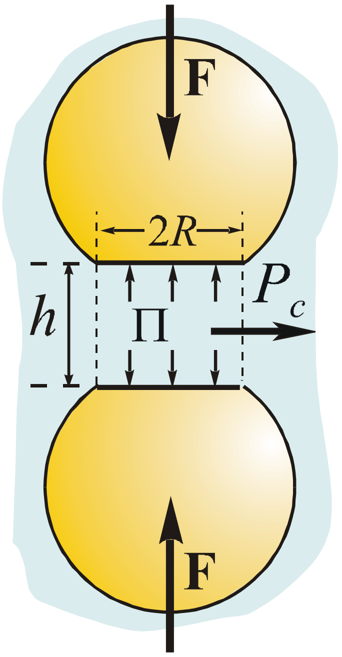
- **Increasing drop radius increases the driving force but thereby increases also the film radius, thus decreasing the drainage rate and increasing life time.**

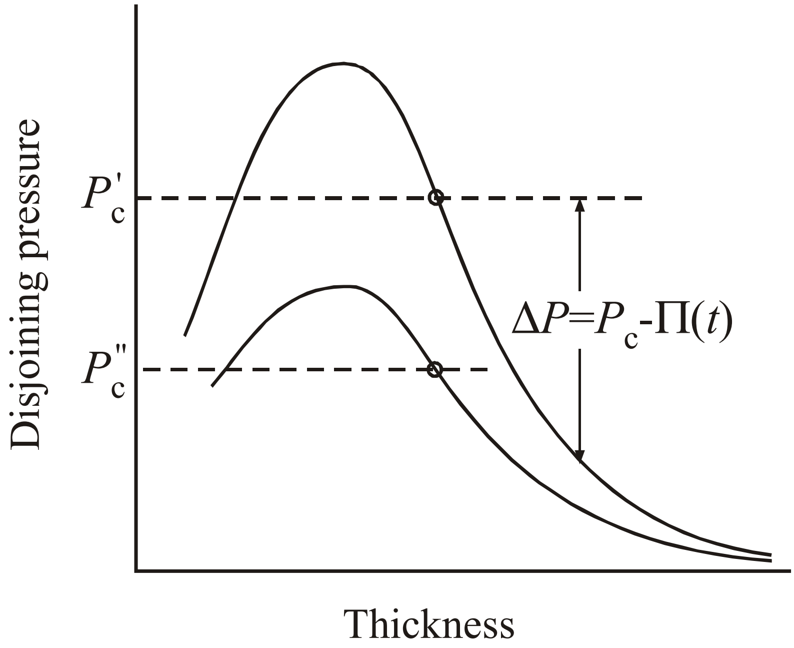


Small drops (no film)



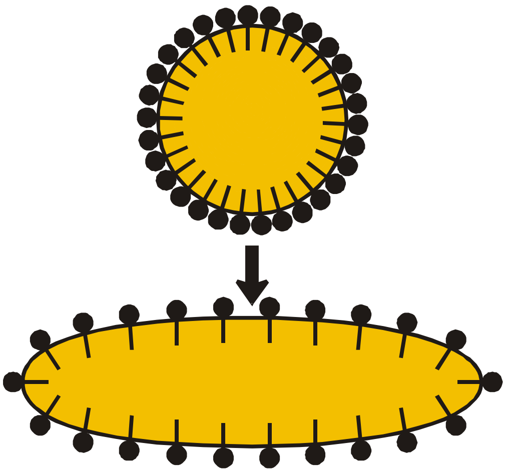
5. ROLE OF THE ADSORPTION

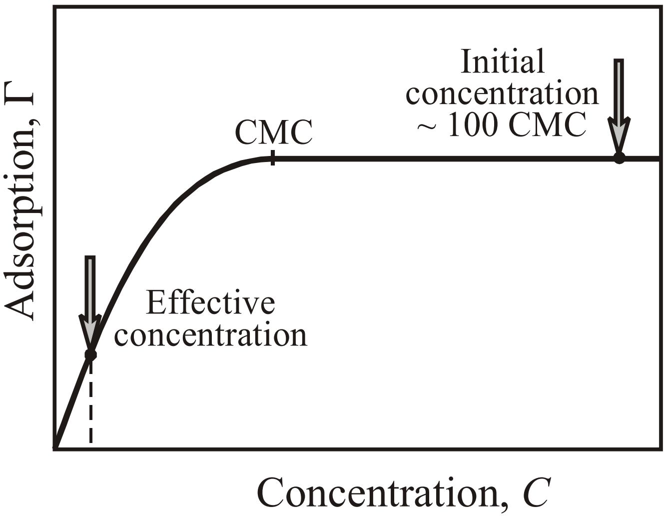




$$\Delta P = \frac{2\sigma}{R_d} - \Pi$$

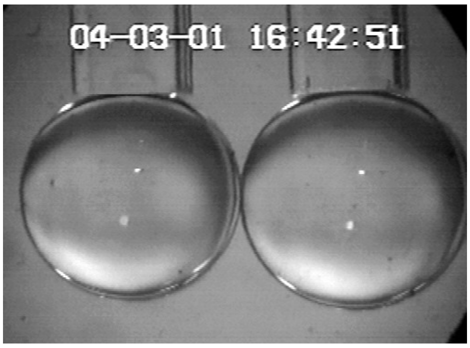
$$\Pi = -\frac{A}{6\pi h^3} + B e^{-\kappa h}$$

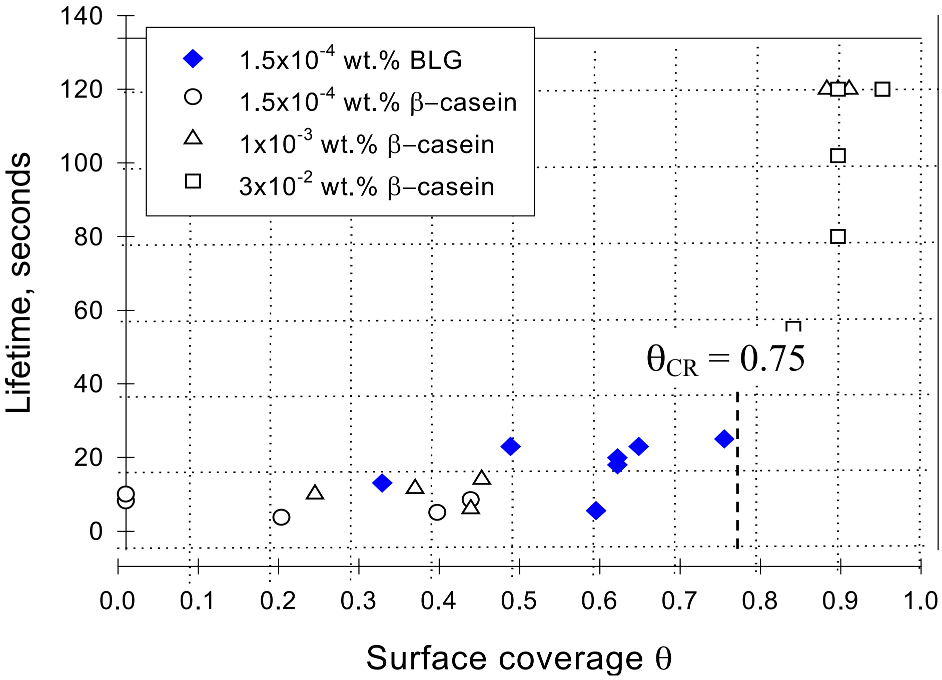




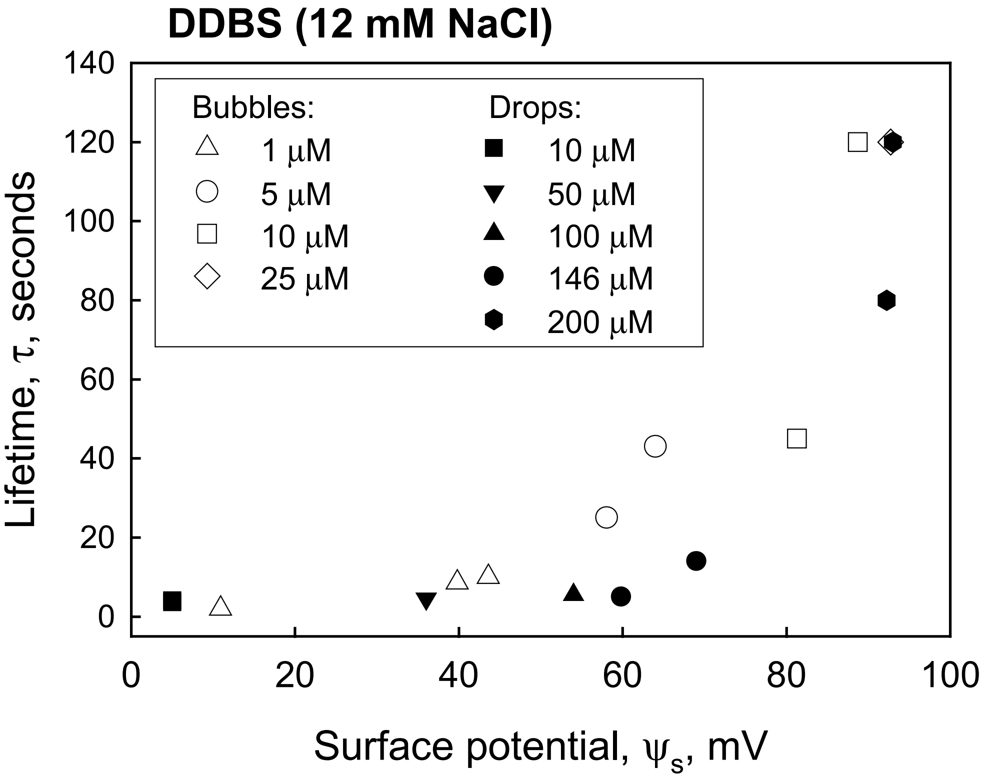
- **The effective concentration is much lower than the real bulk concentration.**

Colliding Drop Technique





- **Variation of <u>bulk concentration</u>, *C*, and <u>surface age</u>, t_W.**
- **Both lead to change of Γ.**



- **For DDBS there is a rather sharp transition between unstable and stable films, depending on the surface potential.**
- **The bubbles are stable with surface potential higher than ψ_S^{th} =70 – 80 mV.**

6. DRAINAGE RATE AND LIFE TIME OF THIN FILMS

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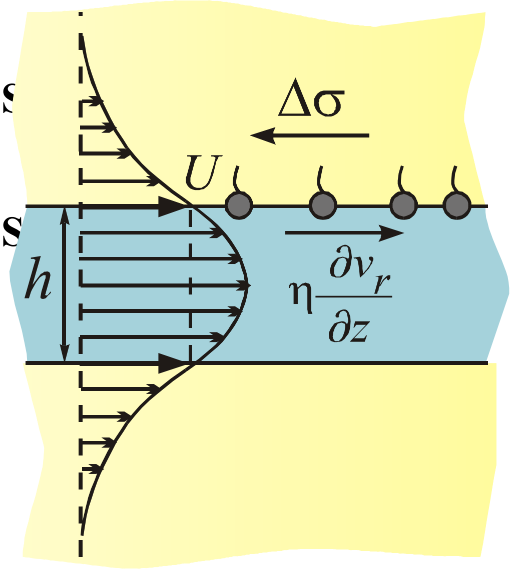
- S



Convection + Diffusion = 0

Shear = Elastic + Viscous

$$\boxed{\frac{V}{V_{\mathrm{Re}}} = 1 + \frac{h_S}{h}} \qquad V_{\mathrm{Re}} = \frac{2h^3\,\Delta P}{3\eta R^2} \qquad h_S = \frac{6\eta D_S}{\Gamma k T}$$

$$\tau = \frac{3\eta R^2}{2P_C h_{cr}^2}\left(x - x^2 \ln\frac{1+x}{x}\right); \qquad x = h_{cr}/h_S$$

- with $\theta = 0.1$, $h_S = 300$ nm – strong surface mobility
- with $h_{cr} = 40$ nm, $\tau = 21$ s

- **Role of the surface viscosity**

$$\frac{\text{Surface viscosity}}{\text{Surface elasticity}} \sim \frac{\eta_S h_S}{\eta R^2}$$

- **The <u>true</u> surface viscosity, η_S, can play a role only for small films and mobile surfaces when $h_S >> h$, but then $\eta_S \approx 0$.**
- **For dense monolayers $h_S \sim 0.5 \div 1$ nm - the surface mobility is not important.**

Interfacial Viscosity

$$\eta \frac{\partial v_r}{\partial z} = \frac{\partial \sigma}{\partial \Gamma} \frac{\partial \Gamma}{\partial r} + \eta_S \frac{\partial^2 v_r}{\partial r^2}$$

$$\frac{\text{Elastic}}{\text{Viscous}} \sim \frac{\partial \sigma / \partial r}{\eta_S \left(\partial^2 v_r / \partial r^2 \right)} \sim \frac{E_G / D_S}{\eta_S / R^2} \frac{\eta}{\eta} \sim \frac{\eta R^2}{\eta_S h_S}$$

- **Surface viscosity is coupled with surface mobility (through h_S) and can play a role ONLY for mobile surfaces.**
- **But then the TRUE surface viscosity is small.**
- **Even for small films (R = 10 μm) and mobile surfaces (h_S = 10 nm) the effect of surface viscosity is comparable to surface elasticity only if $\eta_S > 0.1$ sp.**

Apparent Dilatational Viscosity

$$\frac{h_S}{h} \sim \frac{\eta D_S}{h E_G} \frac{R^2}{R^2} \sim \frac{\eta R^2}{h \eta_d^{app}} \, ; \qquad \boxed{\eta_d^{app} = E_G \frac{R^2}{D_S} = E_G \, t_{diff}}$$

- **The apparent surface viscosity is due to dissipation through diffusion and is NOT related to intermolecular interaction**
- **η_d^{app} depends on the film radius, i.e. it is NOT a property of the adsorbed layer and CANNOT be directly measured in a separate experiment.**
- **It is extremely high even at low concentration:**

$$\eta_d^{app} \sim 1 \frac{\left(10^{-3}\right)^2}{10^{-5}} \sim 0.1 \text{ sp}$$

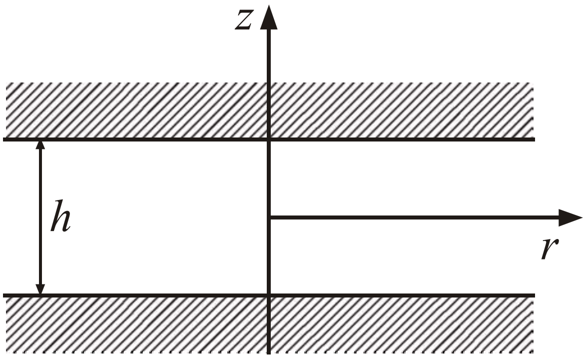
7. BASIC EQUATIONS FOR FILM DRAINAGE

Lubrication

$$\frac{\partial p}{\partial r} = \eta \, \frac{\partial^2 v_r}{dz^2}$$

$$\frac{\partial p}{\partial z} = 0$$

$$\frac{\partial v_r}{\partial r} + \frac{\partial v_z}{\partial z} = 0$$



Boundary Condition at $z = \pm h/2$

$$v_r = U \qquad v_z = -\frac{V}{2} = \frac{1}{2}\,\frac{dh}{dt}$$

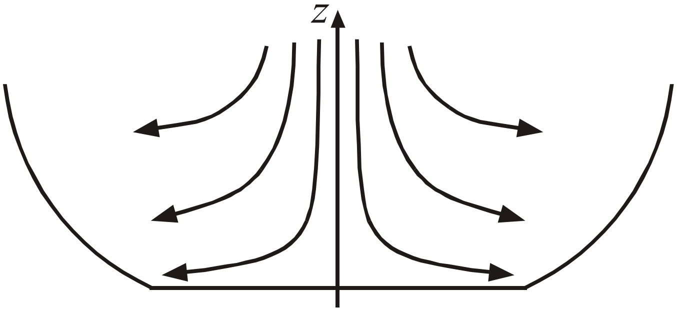
$$\eta\,\frac{\partial v_r}{\partial z} = \frac{\partial \sigma}{\partial r} + \eta_S\,\frac{\partial^2 v_r}{\partial r^2}$$

$$\Gamma_0\,\frac{\partial U}{\partial r} - D_S\,\frac{\partial^2 \Gamma}{\partial r^2} = -D\,\frac{\partial c}{\partial z}$$

$$c = C_0(r) + C_1\,\frac{z^2}{R^2}$$

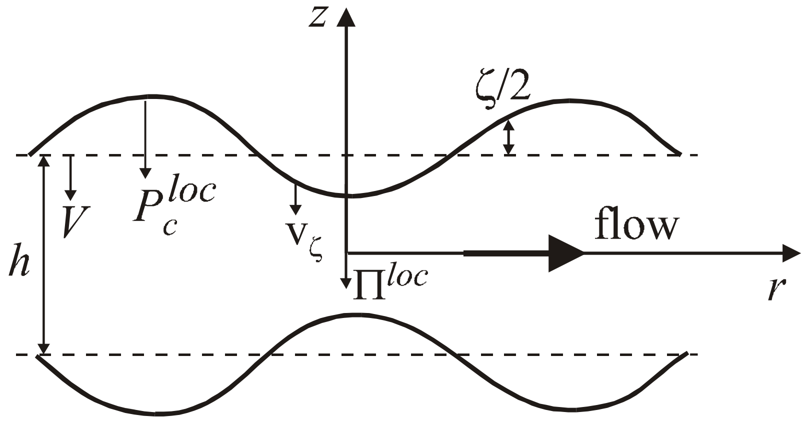
$$F = 2\pi \int_0^{R_F} (p - p_0)\, r\, dr$$

Emulsions



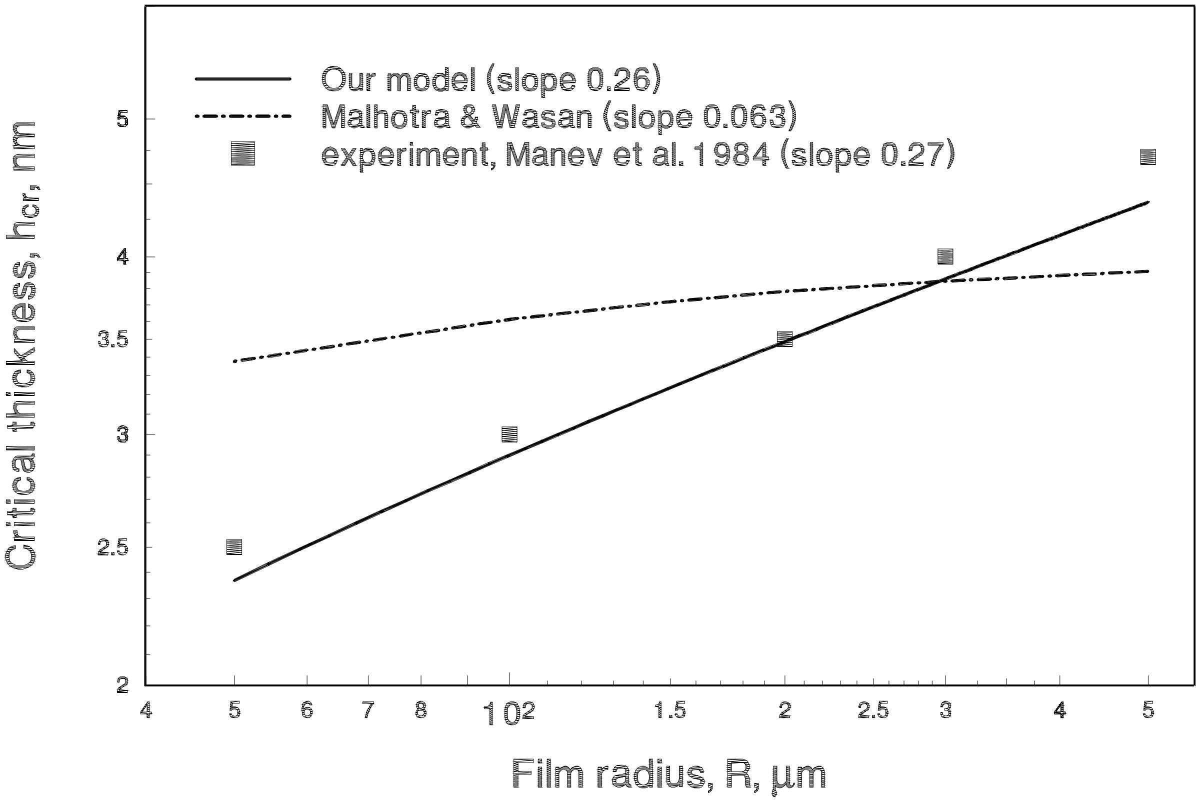
$$\rho v_r\,\frac{\partial v_r}{\partial r} = \eta\left(\frac{\partial^2 v_r}{\partial r^2} + \frac{\partial^2 v_r}{\partial z^2}\right)$$

8. RUPTURE OF THINNING FILMS



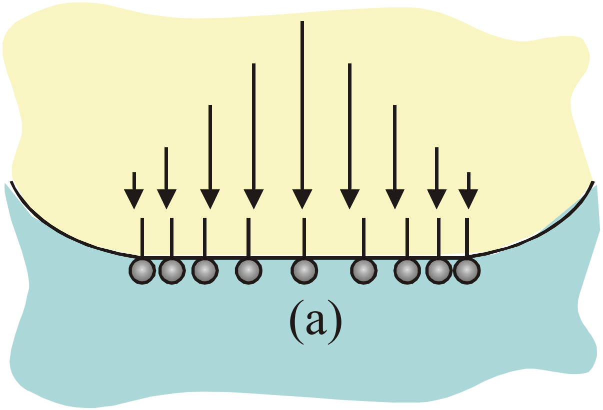
Wave pressure:

$$P_w = P_{pl} + \Pi'(h)\,\zeta + \frac{\sigma}{2}\,\zeta''$$



9. EMULSION FILMS SURFACTANT IN THE DROP PHASE (SYSTEM II)

Uniform Distribution of the Surfactant on the Film Surface

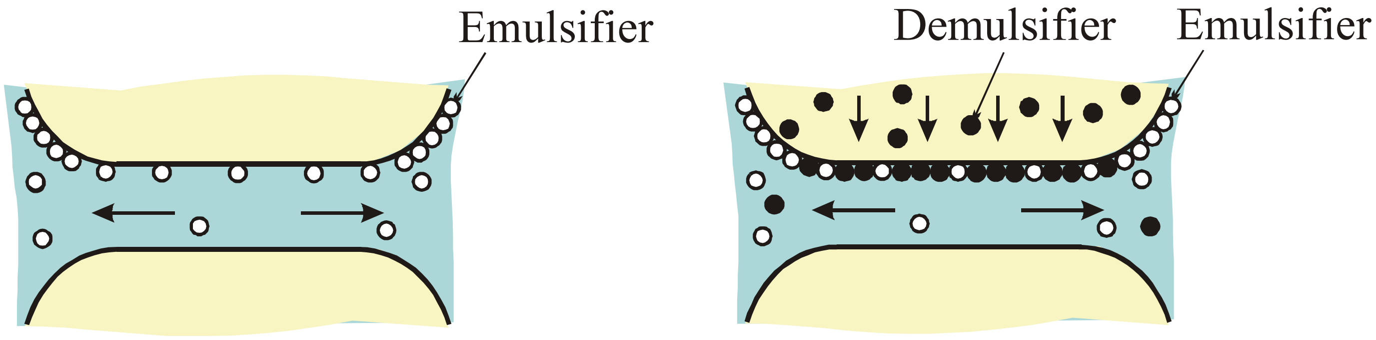


$$\Delta\Gamma = 0 \quad \Rightarrow \quad \Delta\sigma = E_G \frac{\Delta\Gamma}{\Gamma} = 0$$

$$\Rightarrow \quad \boxed{V_{\mathrm{II}} = V_{pure} >> V_{\mathrm{Re}}}$$

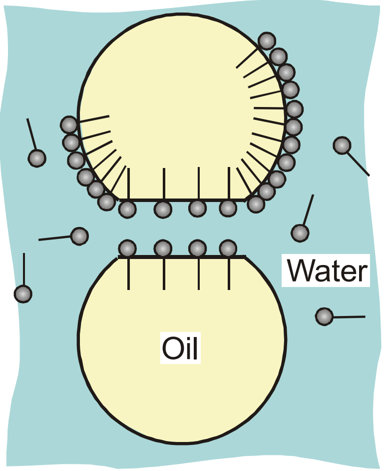
- The surfactant has no effect on the rate of thinning.

Chemical Demulsification

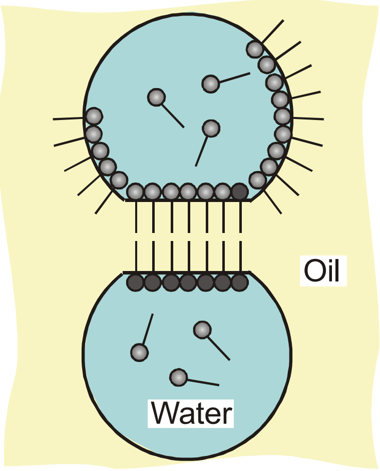


- The demulsifier fills in the spaces between the adsorbed emulsifier molecules damps the interfacial tension gradient Δσ and increases many times the rate of thinning and coalescence.

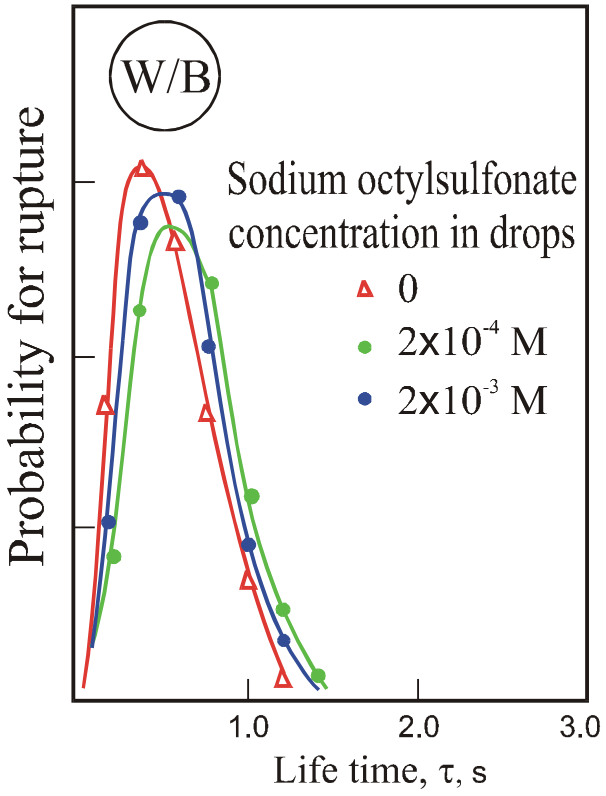
Comparison of the Life Times of Systems I and II



System I



System II

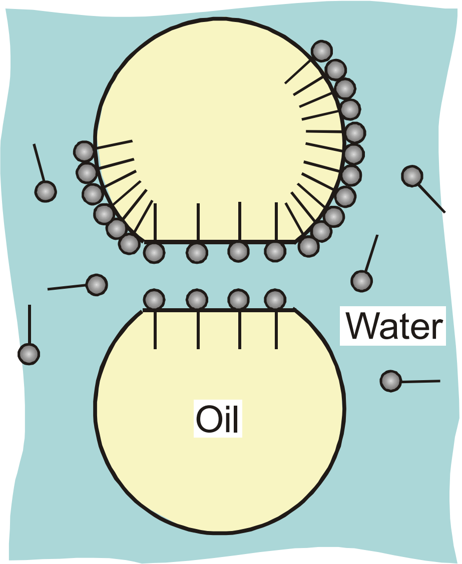


$$\tau = -\int_{\infty}^{h_{cr}} \frac{d\,h}{V}$$

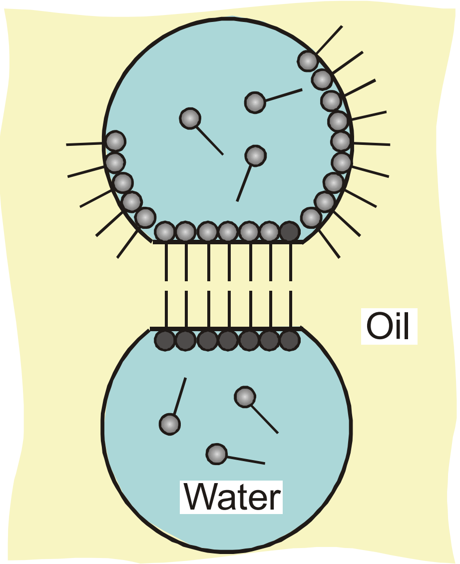
$$\frac{\tau_{\mathrm{O/W}}}{\tau_{\mathrm{W/O}}} \sim \frac{V_{\mathrm{W/O}}}{V_{\mathrm{O/W}}} \approx \frac{V_{pure}}{V_{\mathrm{Re}}} = 100 \div 1000 \qquad \tau_{\mathrm{W/O}} = 0.3\ \mathrm{s};\ \ \tau_{\mathrm{O/W}} = 35\ \mathrm{s}$$

- **The ONLY DIFFERENCE between the two systems is the SURFACTANT LOCATION.**
- **The surfactant concentration does not affect the life time of the emulsion W/O (system II).**

10. GENERALIZED BANCROFT RULE



System I



System II

$$\tau \sim \frac{1}{V}; \qquad V = \left(1 + \frac{h_S}{h}\right) V_{Re} \sim \frac{P_c - \Pi}{E_G}$$

$$\frac{\tau_{\mathrm{W/O}}}{\tau_{\mathrm{O/W}}} \approx \underbrace{\frac{8 \times 10^{-5}}{E_G}}_{\text{HYDRODYNAMICS}} \times \underbrace{\frac{P_c - \Pi_{\mathrm{O/W}}}{\left(P_c - \Pi_{\mathrm{W/O}}\right)^{2/3}}}_{\text{INTERACTION}}$$

- **If Π in both phases is zero, $\tau_{\mathrm{W/O}} << \tau_{\mathrm{O/W}}$ and the emulsion O/W (THE ONE WITH SURFACTANT IN THE CONTINUOUS PHASE) will survive – BNACROFT'S RULE.**
- **The surface interaction can play a decisive role through Π: If $\Pi_{\mathrm{W/O}} = P_c$ (but $\Pi_{\mathrm{O/W}} < P_c$), $\tau_{\mathrm{W/O}}/\tau_{\mathrm{O/W}} \to \infty$, emulsion W/O becomes *thermodymamically* stable and will survive in spite of the prediction of Bancroft's rule.**

C. DROP SIZE DISTRIBUTION

1. ISOTROPIC TURBULENCE (KOLMOGOROV)

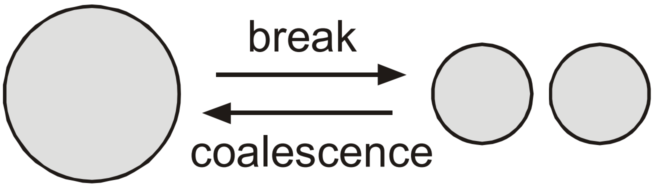
ε - rate of energy dissipation per unit mass

$$\rho\varepsilon \ \frac{1}{\tau}\rho u^2 \sim \frac{\rho u^2}{l/u} \sim \frac{\rho u^3}{l}$$

$$\boxed{u^2 \sim \varepsilon^{2/3}\, l^{2/3}; \quad p_0 \sim \rho u^2}$$

2. PRESENT THEORIES (STEADY DISTRIBUTION)

$$\left.\frac{\Delta N}{\Delta t}\right|_{\text{break}} = \left.\frac{\Delta N}{\Delta t}\right|_{\text{coalesce}}$$



$$\boxed{\Delta N_{\text{br}} = \frac{N_{\text{br}}}{\tau_{\text{br}}} = \frac{N_{\text{br}}}{\tau_{\text{br}}}\, e^{-\frac{E_\sigma}{E}}}$$

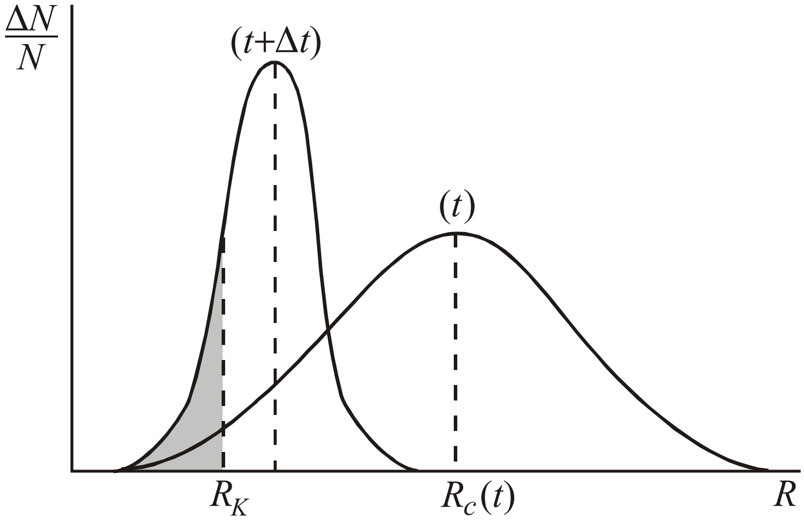
$$E_\sigma \sim \sigma d^2; \quad \overline{E} \sim \rho d^3 u^2; \quad \tau_{\text{br}} \sim d/u$$

$$\left.\frac{\Delta N}{\Delta t}\right|_{\text{coalesce}} = \underbrace{\left(u\, d^2\, N^2\right)}_{\text{coll. frequency}} \times \underbrace{\left(e^{-\tau_{\text{eife}}/\tau_{\text{contact}}}\right)}_{\text{efficiency}}$$

$$\tau_{\text{contact}} \sim d/u; \qquad N \sim \Phi/d^3$$

$$\boxed{\frac{\sigma}{\varepsilon^{2/3}} = -\ln\Phi\, d^{4/3} + \tau_{\text{eife}}\ \frac{d}{\varepsilon^{1/2}}}$$

3. APPROXIMATION OF $\Delta N/N$ BY δ - FUNCTION



$$\frac{dN(R,t)}{N(t)} = \sqrt{\frac{\alpha}{\pi}}\, e^{-\alpha(R-R_c)^2}\; dR \qquad \boxed{\alpha = \alpha(t)}$$

- **Kolmogorov's drops become important at longer times**

$$N_K(t) = \int_0^{R_K} dN(R,t)$$

Since

$$\int \frac{dN}{N} = \int f(R)\,dR = 1$$

one can set

$$\frac{dN}{N} = \frac{1}{a}\,\delta\left(\frac{R-R_c}{a}\right)dR \qquad a = \sqrt{\frac{\pi}{\alpha}}$$

- **This reduces most equations to the monodisperse case, including those for coalescence rate:**

$$V_{\text{coal}} \sim \int dN_R\, dN_{R'} \sim N(R_c)^2$$

- **Justifies assumptions (b) and (d).**
- **Fails at $R_c \gtrsim R_K$ (small drops).**
- **Works better when coalescence is present.**

D. TURBULENT PRESSURE AND DROP SHAPE

- **Eddies are NOT molecules**

[TL] Correlation coefficients $= \begin{cases} 10^{-6} & \text{for molecules} \\ 0.5\text{-}1 & \text{for eddies} \end{cases}$

(H., p. 310) **For large Reynolds numbers and small distance, *r*, the pressure gradient does NOT depend on time**

$$\left(p_A - p_B\right)^2 = 4A^2 \rho^2 \left(\varepsilon r\right)^{4/3}$$

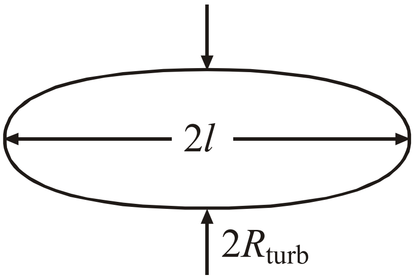
$$\overline{\Delta p} \sim \sqrt{\overline{(\Delta p)^2}} \sim 2A\rho\left(\varepsilon r\right)^{2/3}$$

$$\overline{p}(r) = \overline{p}(0) + \overline{\Delta p}$$

- **Laplace equation [P]**

Outside pressure $p = p(r)$, inside pressure p_{in} = const.

$p(r) - p_{\text{in}} = \sigma \times (\text{curvature})$ → “Equilibrium” shape of stable drops.

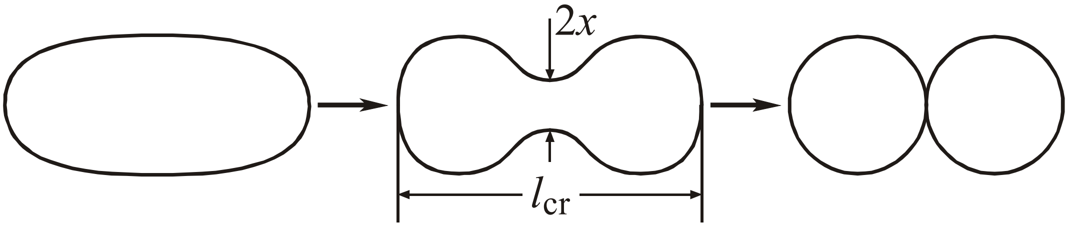


- **Under dynamic conditions – inside pressure is replaced by the viscous normal stress p_{nn}.**
- **Possible role of time and temporal pressure fluctuations**
  (a) Through the time dependence of the velocity correlation function $Q_{pp}(r, t)$ (H, p. 308 Eqs. (3.298), (3.296)).
  (b) Through the time spectra and distribution functions (TL, p. 274 and Chapter 6).

E. DROP BREAKAGE

1. CRITICAL (KOLMOGOROV) SIZE, R_K

If $\Delta p(r) > \sigma / R$



- **Find local capillary pressure $P_c(x)$.**
- **Determine l_{cr} from drop volume and the maximum P_c:**

$$\frac{\partial P_c(x)}{\partial x} = 0$$

- **Determine the drop radius R_K, at which the maximum in P_c disappears – this will give a generalized form of Kolmogorov size with numerical coefficient:**

$$R_K \sim \sigma^{0.6}\, \varepsilon^{-0.4}\, \rho^{-0.6}$$

2. BREAKAGE TIME, τ_B

- **Time needed for deformation from sphere to breakage at l_{cr}**

$$\rho \frac{\partial v}{\partial t} = -\frac{\partial p}{\partial r} + \eta \frac{\partial^2 v}{\partial r^2}$$

- **Scalling**

$$t \sim \tau \left(= \tau^B\right) \qquad r \sim l \qquad v \sim l / \tau \qquad p \sim \sigma / R$$

- **Inertia regime**

$$\rho \frac{\partial v}{\partial t} \sim \frac{\partial p}{\partial r}$$

$$\rho \frac{l/\tau}{\tau} \sim \frac{\sigma/R}{l}$$

$$\boxed{\tau_{\text{in}} \sim \left(\frac{\rho l^2 R}{\sigma}\right)^{1/2} \sim \left(\frac{\rho}{\sigma}\right)^{1/2} R^{3/2}}$$

- **Viscous regime**

$$\frac{\partial p}{\partial r} \sim \eta \frac{\partial^2 v}{\partial r^2}$$

$$\frac{\sigma/R}{l} \sim \eta \frac{l/\tau}{l^2}$$

$$\boxed{\tau_{\text{visc}} \sim \frac{\eta}{\sigma} R}$$

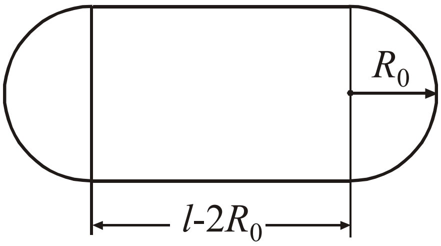
- **Limiting radius between the two regimes**

$$Re = \frac{\rho(\partial v/\partial t)}{\eta\left(\partial^2 v/\partial r^2\right)} \sim \frac{\rho\left(l/\tau^2\right)}{\eta\left(l/\tau l^2\right)} \sim \frac{\rho l^2}{\eta\tau}$$

From $Re = 1$ and τ_{visc} (or τ_{in})

$$\left(\frac{l^2}{R}\right)_{\text{lim}} = \frac{\eta^2}{\rho\sigma} \rightarrow \boxed{R_{\text{lim}} \sim \frac{\eta^2}{\rho\sigma}}$$

- **Rayleigh instability – only inertia regime** (Shih-I Pai, Fluid dynamics of jets, § 1.9)



- Determine R_0 and l from the conservation of volume
- Critical wave with length $\lambda_{cr} \approx (l\text{-}2R_0)_{cr} = 2\pi R_0$

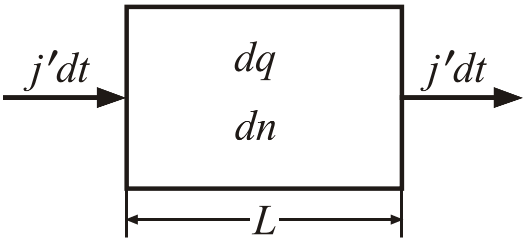
$$\frac{1}{\tau_{\mathrm{Ray}}^2} = \frac{\sigma}{\rho R_0^3} \frac{i x J_0'(i x)}{J_0(i x)} \left(1 - x^2\right); \qquad \left(x = k R_0\right)$$

$$\tau \sim \left(\frac{\rho}{\sigma}\right)^{1/2} R_0^{3/2}$$

- Formally coincides with the previous result but with different quantities.
- The total breakage time is obtained by adding to τ_{Ray} the time for expansion to length l.

- **<u>Goal</u> – Solve Stokes equation inside the drop with Laplace equation at least for small deformations (from sphere and/or cylinder) to obtain dynamic shape and breakage time <u>with numerical coefficients</u>.**

F. GENERAL KINETIC SCHEME



- **“Convective diffusion“ in time ”space”**

$$S\left(j_i' - j_i'\right)dt + L\,S\,dq = dn_i$$

n_i an N_i= total number and concentration of i – drops
j = flux = N_iV
N_{if} = const – concentration of i-drops in the feed
V = linear velocity
dq_i = production of i per unit volume in the element
θ = L/V = residence time in the element

$$\frac{j\,S}{L\,S} = \frac{N_i\,V}{L} = \frac{N_i}{\theta}$$

$$\boxed{\frac{dN_i}{dt} = \frac{N_i^f - N_i}{\theta} + \frac{dq_i}{dt}}$$

- **Source terms**

$$dq_i = dq_i^{\text{break}} + dq_i^{\text{coal}}$$

G. KINETIC SCHEME WITH ONLY BREAKAGE

1. MAIN ASSUMPTIONS

- **Drops break in half, forming two smaller drops**

$$v_i = \frac{v_1}{2^{i-1}} \qquad R_i = \left(\frac{R_1}{2^{i-1}}\right)^{1/3}$$

- **Drops with size smaller than Kolmogorov's ($R_i \leq R_K$) do not break.**
- **The rate constant are assumed eventually independent of R_i ($k_i = k$).**
- **Since $\tau_i^B = a\,R_i$ $\left(\text{or } B\,R_i^{3/2}\right)$, all $N_i(t)$ drops break simultaneously after time τ_i^B.**

$$\boxed{N_i\left(t+\tau_i^B\right)=0}$$

$$N_i\left(t+\tau_i^B\right)=N_i(t)+\frac{\partial N_i}{\partial t}\,\tau_i^B=0$$

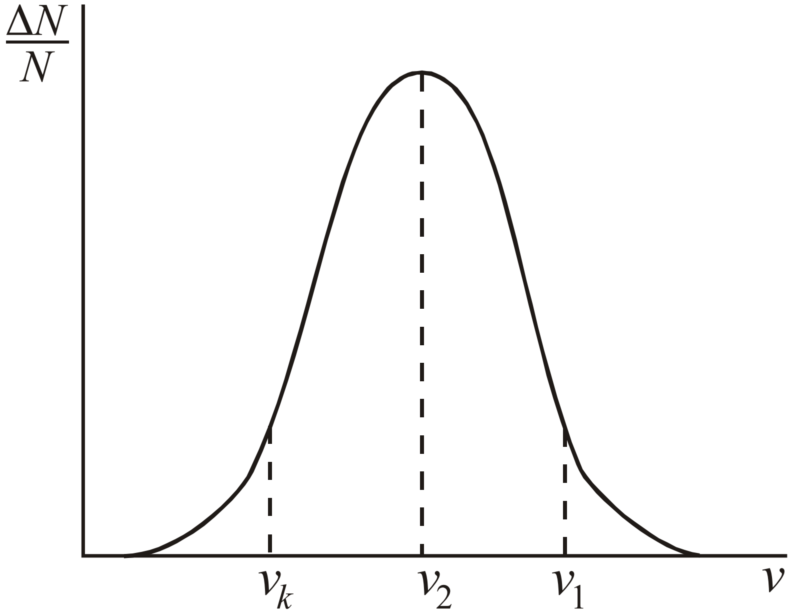
$$\boxed{\frac{\partial N_i}{\partial t}=-\frac{1}{\tau_i^B}\,N_i=-k_i^B\,N_i} \qquad \boxed{k_i^B=\frac{1}{\tau_i^B}}$$

- **τ_i^B depends weakly on v_i and is assumed constant, τ^B.**

$$\tau_i^B = a\,R_i = a\left(\frac{3}{4\pi}\right)^{1/3}\frac{v_1^{1/3}}{2^{\frac{i-1}{3}}}$$

$$\frac{\tau_{i+1}}{\tau_i}=2^{-\frac{1}{3}}=0.8$$

2. THREE-SIZE SYSTEM



v_1 = initial
$v_3 = v_k$

- **Assume that $k_1^B = k_2^B = k^B$. Dubious approximation even for a monodisperse emulsion, since N and thereby R and τ^B changes with t, so that τ^B and k^B must depend at least on $R_c(t)$.**

$$\frac{dN_1}{dt} = -k^B N_1$$

$$\frac{dN_2}{dt} = 2k^B N_1 - k^B N_2$$

$$\frac{dN_k}{dt} = 2k^B N_2$$

$$\boxed{\frac{dN}{dt} = k^B \left(N_1 + N_2\right) = k^B \left(N - N_k\right)} \qquad N = N_1 + N_2 + N_k$$

- **The process stops at $R = R_K$ (N=N_k).**

- **N_k can be determined from the volume fraction Φ:**

$$\Phi = \sum_{1}^{k} N_i\, v_i = v_1 \sum_{1}^{k} N_1 / 2^{i-1}$$

$$2^{1-k}\ \frac{dN_k}{dt} = -\sum_{i=1}^{k-1} 2^{i-1}\ \frac{dN_i}{dt}$$

- **At short times ($kt = X \ll 1$) $N_k \ll N$ and**

$$\ln Y = X \qquad \left(Y = N / N_0\right)$$

- **Exact solution:**

$$Y_1 = e^{-X}\,; \quad Y_2 = 2\,X\,e^{-X}\,; \quad Y_k = 4\left\lfloor 1-(1+X)e^{-X}\right\rfloor$$

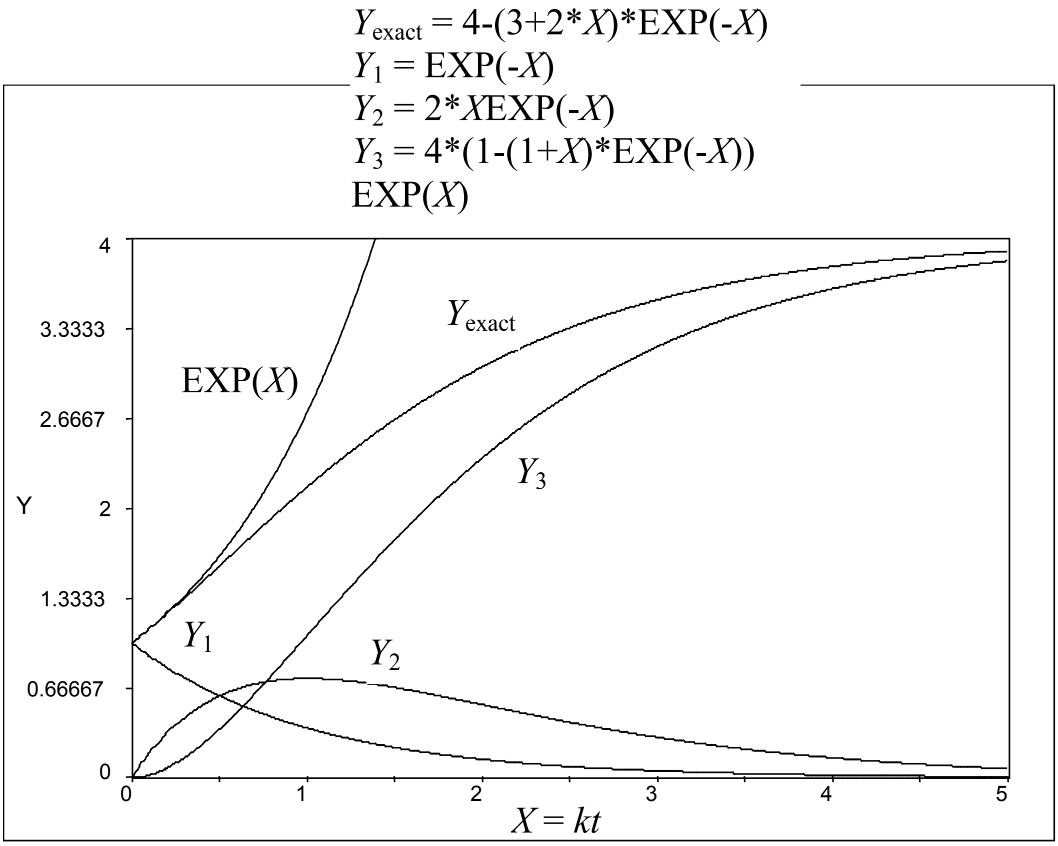
$$Y_{\text{exact}} = Y_1 + Y_2 + Y_k = 4-(3+2\,X)e^{-X}$$

- **If N_k can be neglected**

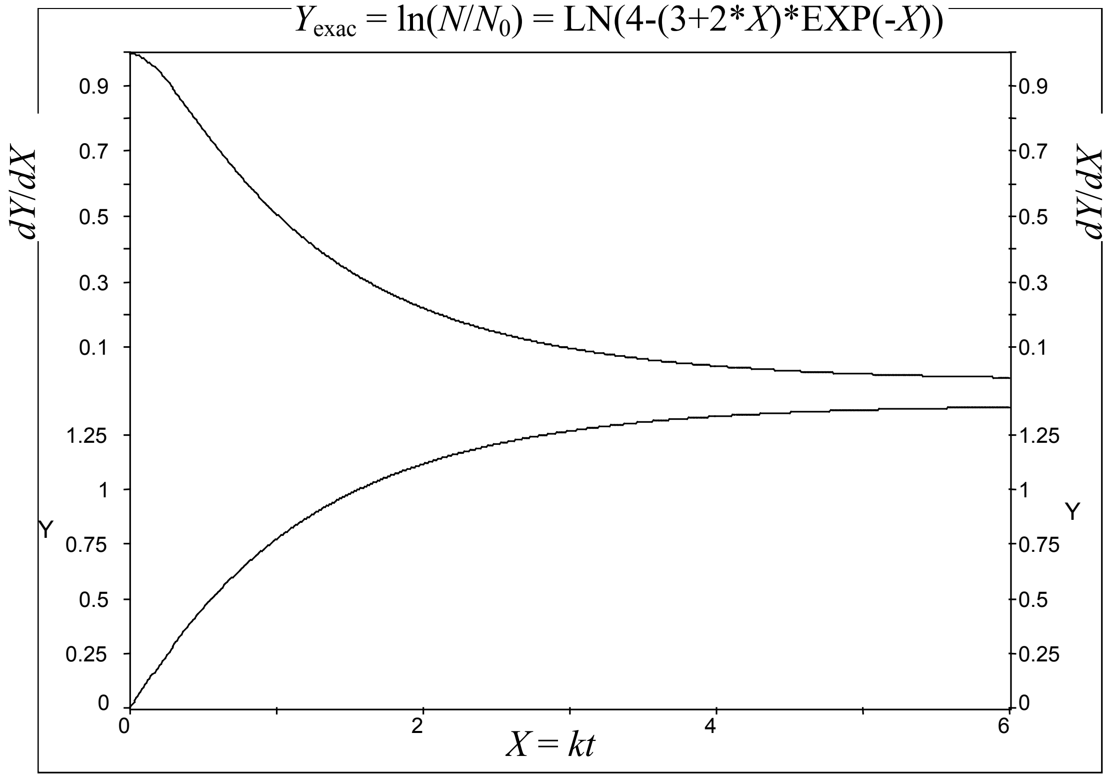
$$\frac{d\ln Y}{dt} = k^B \quad \text{or} \quad \frac{d\ln Y}{dX} = 1$$

- **If the exact function (i.e. experimental data) is approximated by ln$Y$, the apparent rate "constant" $k^B_{\text{app}}(t)$ is much smaller than k^B (see the second figure below):**

$$\frac{d\ln Y_{\text{exact}}}{dX} = k^B_{\text{app}}(X) << k^B$$



Yexact = 4-(3+2*X)*EXP(-X)
Y1 = EXP(-X)
Y2 = 2*XEXP(-X)
Y3 = 4*(1-(1+X)*EXP(-X))
EXP(X)
4
3.3333
2.6667
Y
2
1.3333
0.66667
0
EXP(X)
Yexact
Y3
Y1
Y2
0
1
2
3
4
5
X = kt



Yexac = ln(N/N0) = LN(4-(3+2*X)*EXP(-X))
dY/dX
0.9
0.7
0.5
0.3
0.1
dY/dX
Y
1.25
1
0.75
0.5
0.25
0
Y
0
2
4
6
X = kt

3. CONTINUOUS PROCESS WITHOUT COALESCENCE

For the *i*-size in moment *t*:

$$\frac{dN_i}{dt}=\frac{N_{if}}{\theta}-\frac{N_i(t)}{\theta}+2\,k_{i-1}^B\,N_{i-1}-k_i^B\,N_i(t)\quad (i=1,\ldots,K)$$

- **Sum up over all *i*.**
- **Summation stops at Kolmogorov size with $N_i = N_k$.**
- **Assume $k_i^B = k^B = 1/\tau^B$.**
- **For the *n*-th pass:**

$$\sum_{i=1}^{K} N_i^n(t)=N^n(t)$$

$$\boxed{\frac{dN^n}{dt}=\frac{N_f^n}{\theta}+\left(\frac{1}{\tau^B}-\frac{1}{\theta}\right)\left[N^n(t)-N_k^n(t)\right]}$$

<u>(a) Slow Breakage</u> ($\tau^B > \theta$)

$$\frac{1}{\tau^B}-\frac{1}{\theta}=-k^{sl}\qquad \left(k^{sl}>0\right)$$

- **Neglect** N_k^n

$$\boxed{N^n(t)=\frac{N_f^n}{1-\theta/\tau^B}\left(1-\frac{\theta}{\tau^B}\,e^{-k^{sl}t}\right)}$$

$$\boxed{N^n(t\to 0)=N_f^n\left(1+\frac{t}{\tau^B}\right)}$$

- **Steady state $k_{sl}t \to \infty$ (follows also from $dN^n/dt=0$):**

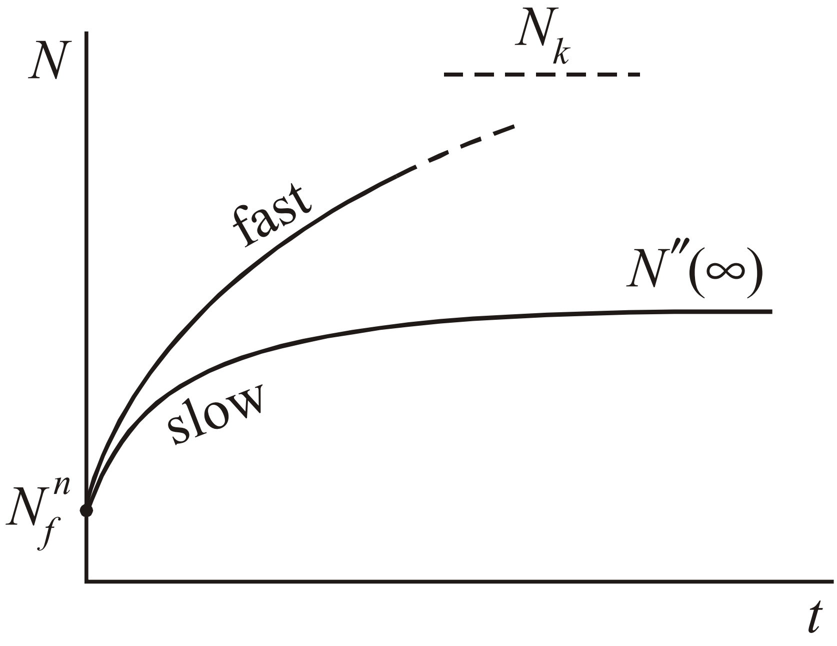
$$N^n(t\to\infty)=\frac{N_f^n}{1-\theta/\tau^B}$$

(b) Fast Breakage ($\tau^B < \theta$)

$$\frac{1}{\tau^B} - \frac{1}{\theta} = k^f > 0$$

$$\boxed{N^n(t) = \frac{N_f^n}{\theta/\tau^B - 1}\left(\frac{\theta}{\tau_B} e^{k^f t} - 1\right)}$$

$$\boxed{N^n(t \to 0) = N_f^n\left(1 + \frac{t}{\tau^B}\right)}$$



- **In the fast regime there can be also a plateau if the Kolmogorov size is reached.**

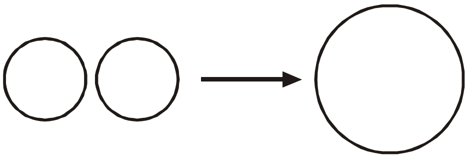
H. COALESCENCE RATE

$$\frac{dN_i}{dt} = \frac{N_{if}}{\theta} - \frac{N_i}{\theta} + 2k^B N_{i-1} - k_B N_i + \frac{\partial Z_{i+1}}{\partial t} - 2\frac{\partial Z_i}{\partial t}$$

$\frac{\partial Z_i}{\partial t}$ = number of coalescence events between drop of volume v_i in unit time.

1. COALESCENCE OF SPHERICAL DROPS (BIMOLECULAR REACTION)

$$2A_i \xrightarrow{k_1^C} A_2$$



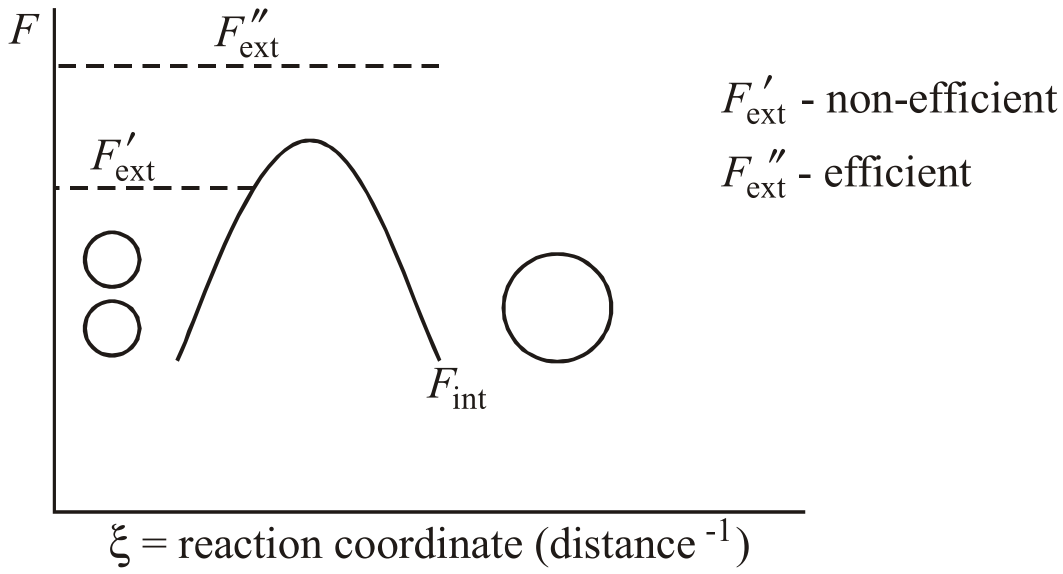
$\frac{\partial Z}{\partial t}$ = number of successful collisions

$$\frac{\partial Z}{\partial t} = \pi \varepsilon^{1/3} d^{7/3} N^2 E$$

E = efficiency factor, analog of activation energy
F = driving force for coalescence
F_{ext} = external (turbulent) force
F_{int} = interaction (repulsive) force between the drops

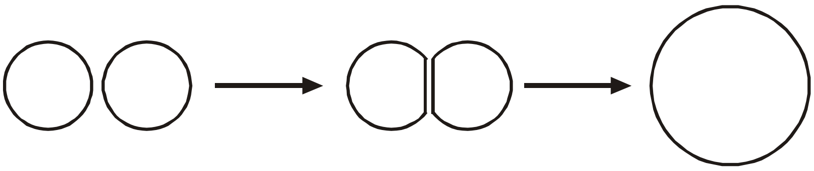
$$F = F_{\text{ext}} - F_{\text{int}}$$

- **Since both F_{ext} and F_{int} depend on R, some collisions (for which $F < 0$) will NOT be efficient.**

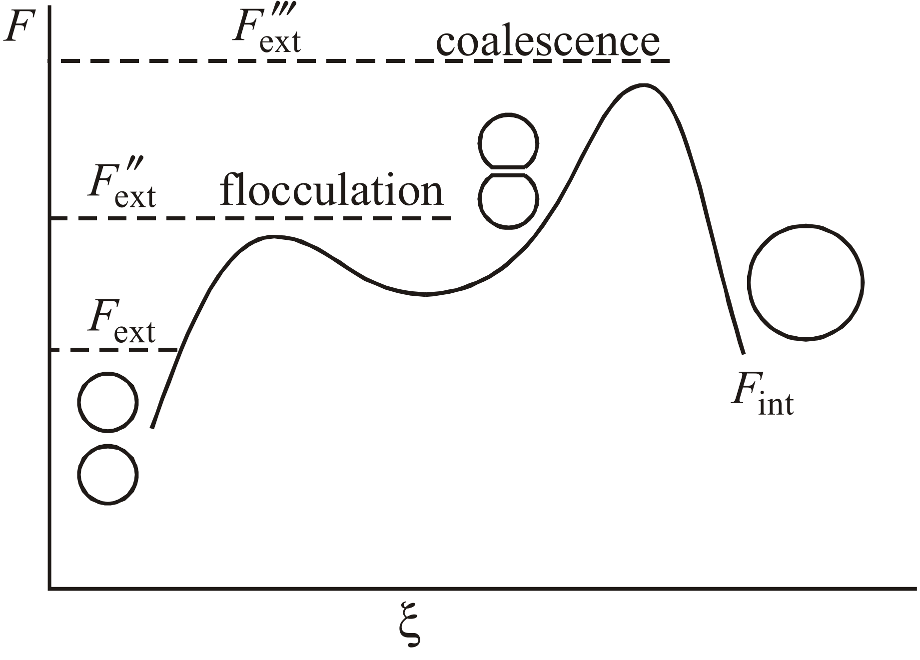


2. CONSECUTIVE IRREVERSIBLE REACTIONS FOR DROPS FORMING A FILM

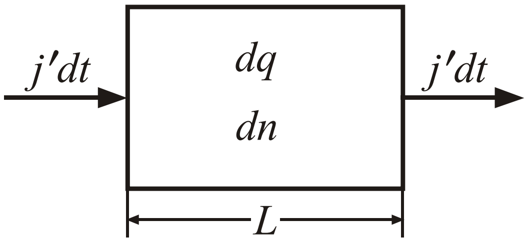
$$2\,A_1 \xrightarrow[\tau^c]{k^c} Z \xrightarrow[\tau^D]{k^D} A_2$$



Z = intermediate complex

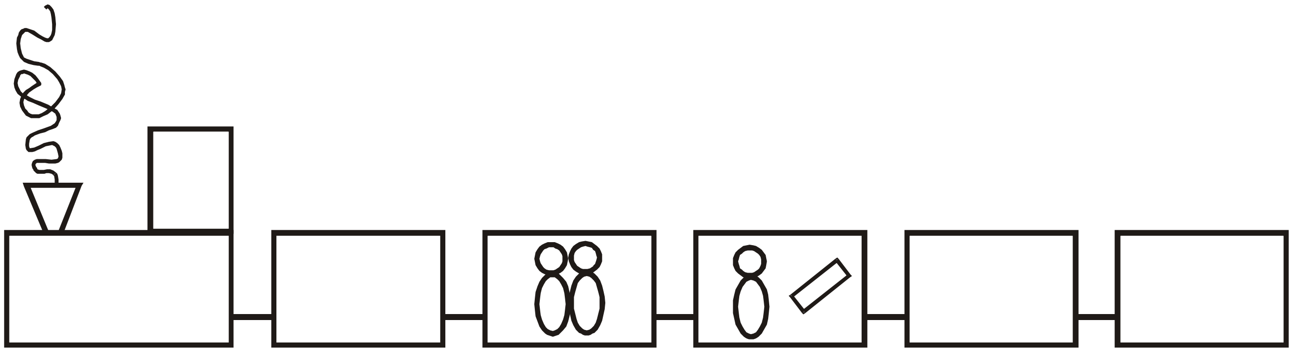


SINGULAR PERTURBATION



$$\frac{\tau}{\theta}\frac{dN_i}{dt} = \frac{\tau}{\theta}\Delta N_i + \frac{dq_i}{dt}$$

- **Macroscale**



- **Microscale**

- **Back to macroscale – coupling of macro and micro events:**
  - The rocket slows down the train
  - The speed of the train affects the taking aim

- **The barrier depends also on the size, since the driving pressure is $\Delta P = 2\sigma/R - \Pi$.**
- **Successful coalescence corresponds to**

$$\Delta P = \frac{2\sigma}{R} - \Pi_{\max} > 0$$

Kinetic Scheme

$$\frac{dN_i}{dt_0} = \frac{\Delta N_i}{\theta} + \frac{dq_i}{dt_0}\,; \qquad dq_i = dq_i^B + dq_I^C$$

t_0 and θ = macroscopic time and time scale
τ = microscopic time scale
scaled times: $t = t_0/\theta$ and $t = t_0/\tau$

$$\frac{\tau}{\theta}\frac{dN_i}{dt} = \frac{\tau}{\theta}\Delta N_i + \frac{dq_i}{dt}$$

If $\tau/\theta \to 0$, then $\frac{dq_i}{dt} = 0 \to$ blow up of the micro-events.

- **Micro-kinetic scheme in microtime t (scaling time is the collision time – scale, τ_c).**

$$\frac{1}{\tau}\frac{dN_1}{dt} = -2\,k_1^c\,N_1^2$$

$$\frac{1}{\tau}\frac{dZ}{dt} = k_1^c\,N_1^2 + \frac{\partial Z}{\partial t_0}$$

$$\frac{1}{\tau}\frac{dN_2}{dt} = -\frac{\partial Z}{\partial t_0}$$

Z = number of complexes (2 drops with film which can rupture). They must rupture at time $t_0 + \tau^D$, where τ^D is the drainage time:

$$Z\left(t_0 + \tau^D\right) = Z(t) + \frac{\partial Z}{\partial t_0}\,\tau^D = 0$$

$$\frac{\partial Z}{\partial t_0} = -\frac{1}{\tau^D}\,Z = -k_2^c\,Z$$

Estimate of τ_c

Scale N_1 by N_{10}, the number of drops 1 at $t = 0$ ($N_1 = N_{10}N_1'$)

$$\frac{N_{10}}{\tau}\,\frac{dN_1'}{dt} = -2\,k_1^c\,N_{10}^2\left(N_1'\right)^2 \rightarrow \boxed{\tau_c = 1/k_1^c\,N_{10}}$$

$$\frac{dN_1}{dt} = -\frac{2}{N_{10}}\,N_1^2 \tag{a}$$

$$\frac{dZ}{dt} = \frac{1}{N_{10}}\,N_1^2 - \frac{\tau_c}{\tau_D}\,Z \tag{b}$$

with $N_1(0) = N_{10}$ from (a) and (b):

$$N_1 = \frac{N_{10}}{1+2t}$$

$$\frac{dZ}{dN_1} = -\frac{1}{2} - \frac{K}{N_1^2}\,Z \qquad K = \frac{\tau_c\,N_{10}}{2\,\tau_D}$$

Introduce $x = K/N_1 << 1$

The solution of the linear equation is

$$Z = -\frac{1}{x} + 2\left(\ln x + x + \frac{x^2}{2\times 2!} + \ldots + \text{const}\right)e^{-x}$$

Keep only $1/x$. With $Z = 0$ at $x = x_0 = K/N_{10}$ (i.e. at $t = 0$) one obtains

For $x \to 0$ it becomes

$$Z = -\frac{1}{x} + \frac{1}{x_0} = \frac{N_{10}}{K}\,\frac{2t}{1+2t}$$

Going back to macro-time t_0 by substituting $t = t_0/\tau_c$, one obtains for any i (Note that N_{i0} is $N_i(t_0)$)

$$\boxed{\begin{aligned} \frac{dN_i}{dt_0} &= -2k_i^c\,N_i^2 = -2k_i^c\,\frac{N_{i0}^2}{\left(1+2N_{i0}\,k_i^c\,t_0\right)^2} \\ \frac{dN_{i+1}}{dt_0} &= -\frac{1}{\tau_D}Z_i = k_i^c\,N_{i0}^2\,\frac{4t_0}{1+2N_{i0}\,k_i^c\,t_0} \end{aligned}} \qquad \text{(c)}$$

- **For simplicity we have implicitly assumed (by taking $x \ll 1$) that the first process, collision, is the slow one – this is the inner solution. That is why the results depend only on τ_c (i.e. k_i^c).**
- **The realistic case, $\tau_D \gg \tau_c$, corresponds to the outer solution and to scaling $t = t_0/\tau_D$. The determination of the integration constants for this solution requires matching of the inner and outer solution (A.H. Nayfeh, Perturbation methods, John Wiley, 1973, p.114).**
- **The coalescence contribution to the balance of N_i is:**

$$\frac{dq_i^{\text{coal}}}{dt} = \begin{pmatrix}\text{rate of coalescence} \\ \text{of two } i+1\end{pmatrix} - 2\times\begin{pmatrix}\text{rate of death} \\ \text{of complexes } Z_i\end{pmatrix}$$

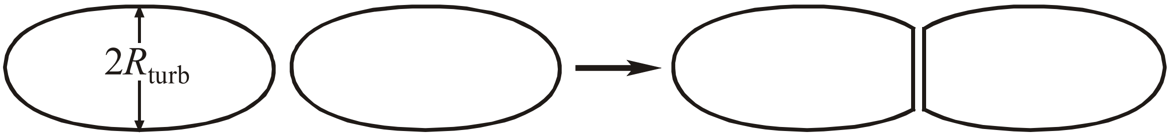
$$\boxed{\frac{dq_i^{\text{coal}}}{dt} = \frac{dN_{i+1}(t)}{dt} - 2x\,\frac{dN_i(t)}{dt}}$$

Here t is macro-time and the two derivatives are given by (c).

3. TURBULENT FORCE F_{ext} AND FILM RADIUS R_F

(a) Collision probability

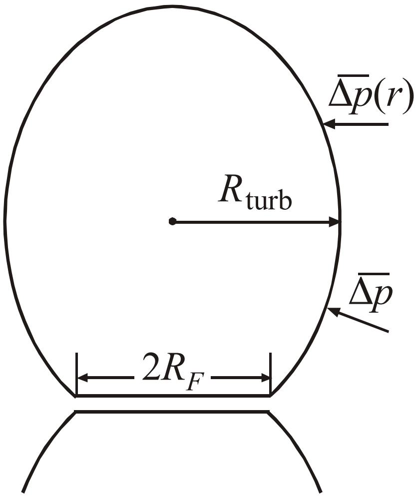
- **The coalescence process in the emulsion is an ensemble of parallel events, occurring between different pairs of drops. Hence, the overall speed will be determined by the fastest ones.**
- **Since $\tau^D \sim 1/R$, the most favorable collisions between the deformed drops are head on (corresponding to smaller R_F):**



- **If Z_{sph} are the collisions between spherical drops, the number of favorable collisions, Z, will be roughly**

$$Z = Z_{sph}\left(\frac{R_{turb}}{R}\right)^2$$

(b) Force Balance on Film



$$F_{\text{ext}} = \int \Delta p(r)\, 2\pi r\, dr$$

(area outside film)

$$F_{\text{ext}} \approx \frac{2\sigma}{R}\,\pi R_F^2$$