Emulsification

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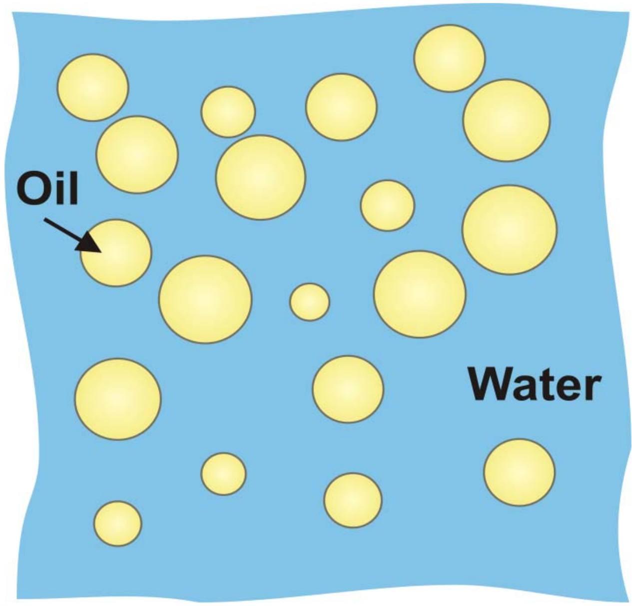
7. Microfluidics.

Types and applications of emulsion

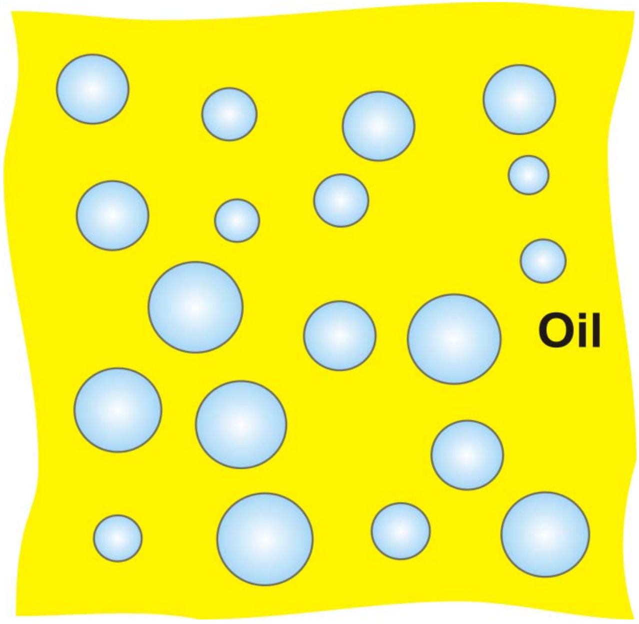
Emulsion types

Oil-in-Water (O/W)



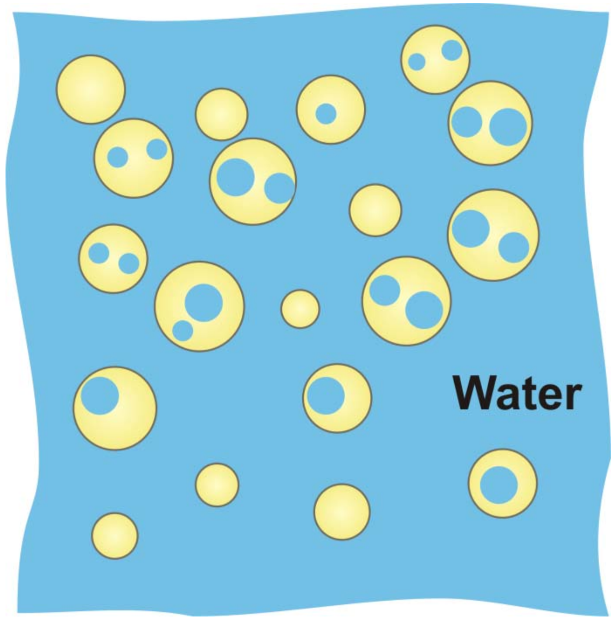
Direct emulsion

Water-in-oil (W/O)



Inverse emulsion

W/O/W



Double emulsion

Cosmetic and pharmaceutical products








Creams, Lotions, Conditioners, Body wash, …

Food and beverages

Milk

Mayonnaise

Margarine

Butter

Cheese

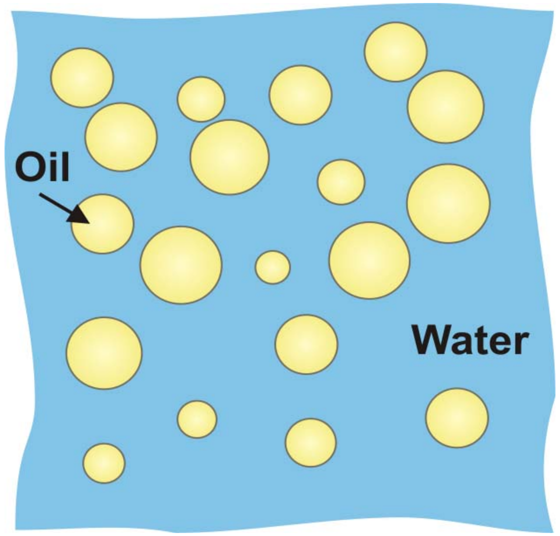
…

Oil recovery and processing

Both W/O and O/W emulsions are often encountered

Main characteristics of the emulsions

Oil-in-Water (O/W)



Oil volume fraction

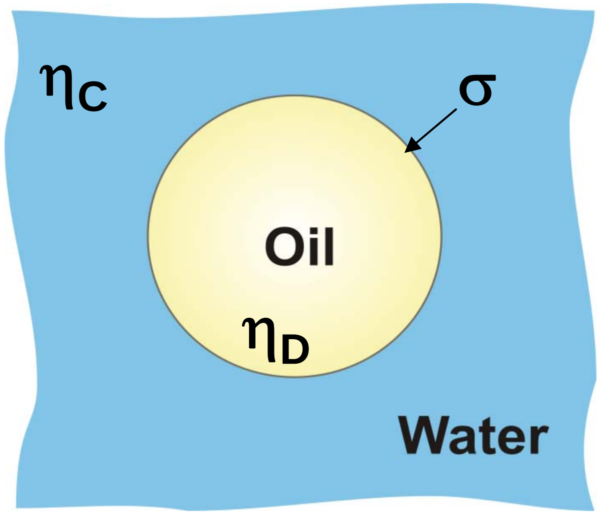
$$\Phi = \frac{V_{OIL}}{V_{EM}}$$

Mean volume-surface radius

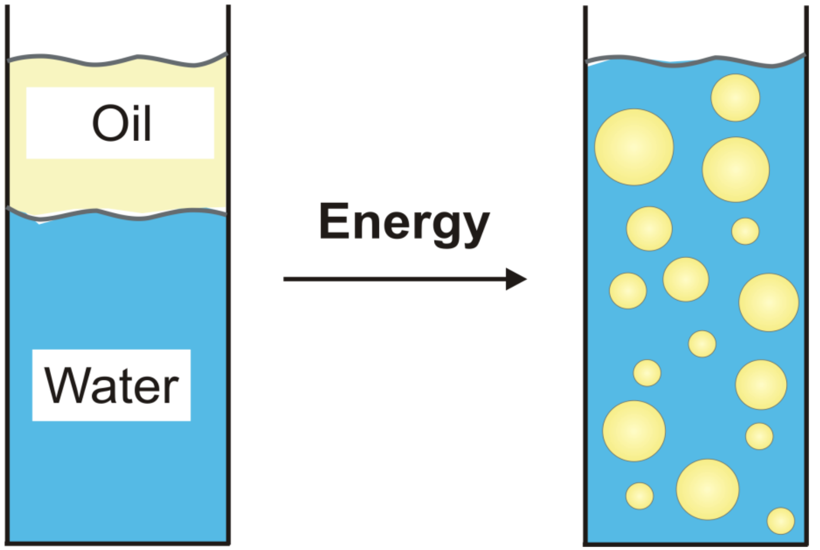
$$R_{32} = \sum N_i R_i^3 \Big/ \sum N_i R_i^2$$

Direct emulsion

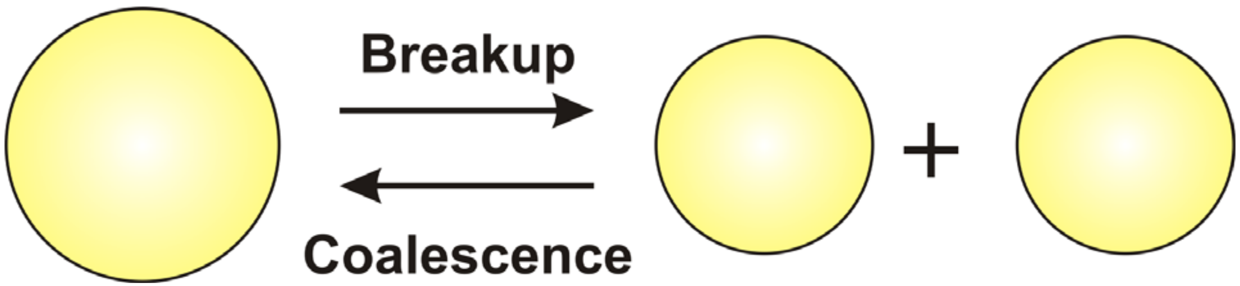
- Viscosity of dispersed phase, η_D
- Viscosity of continuous phase, η_C
- Interfacial tension, σ



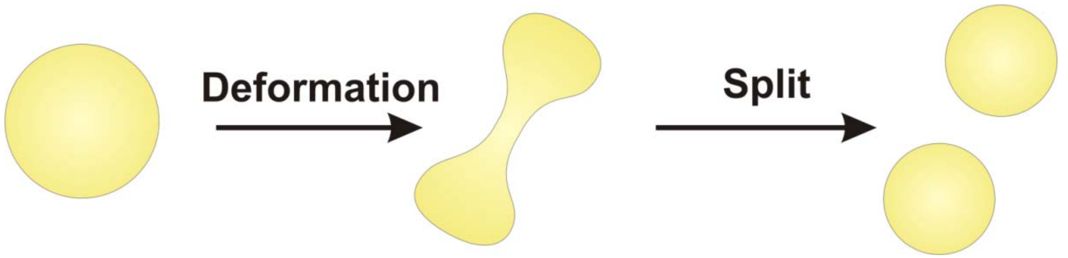
Emulsification



Processes during emulsification



Requirements for drop breakup



Pressure balance, Davies 1985

Applied stress = Capillary pressure + Viscous stress inside drop

$$\tau \sim \sigma/d + \eta_D\left[\delta\langle u_d\rangle/\delta x\right]$$

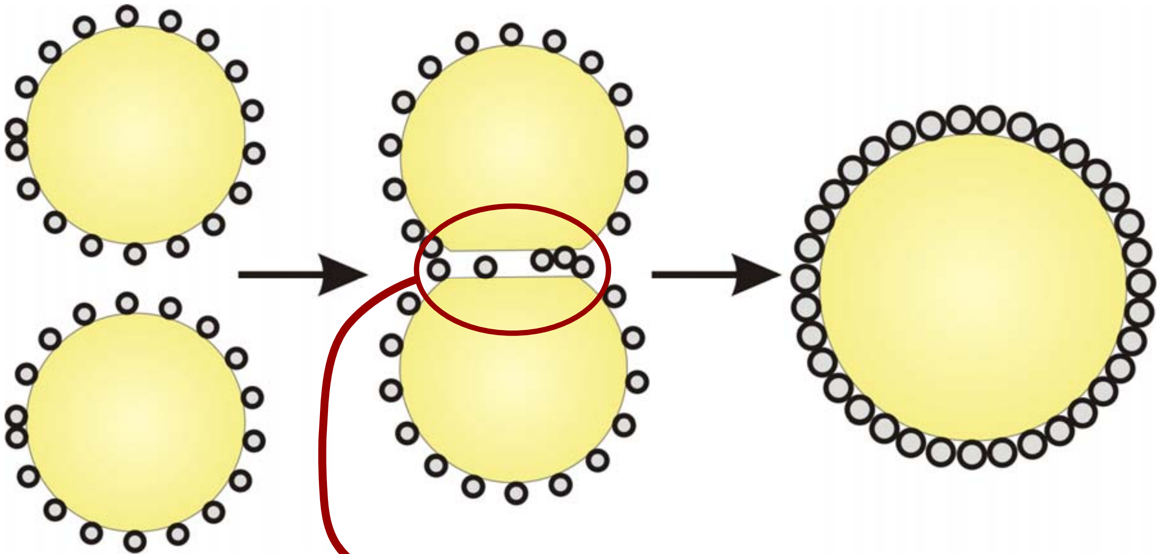
Time scales (Walstra, 1983)

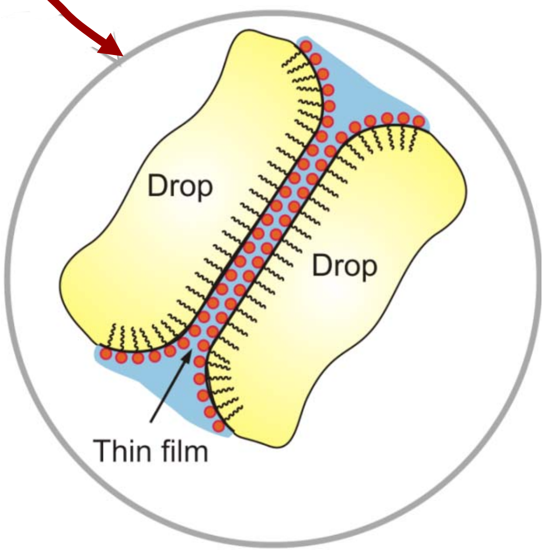
Deformation time, t_{DEF}

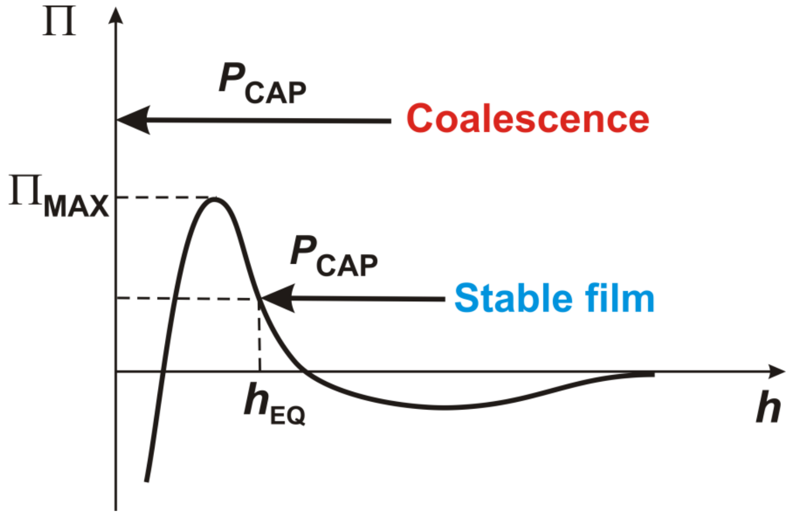
Characteristic time for applied stress

$t_{DEF} < t_C$

Drop-drop coalescence



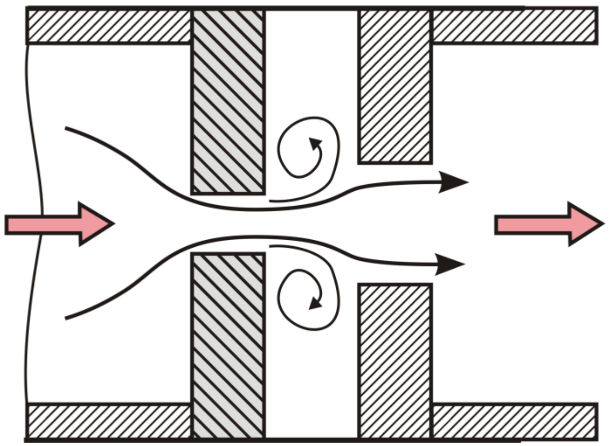




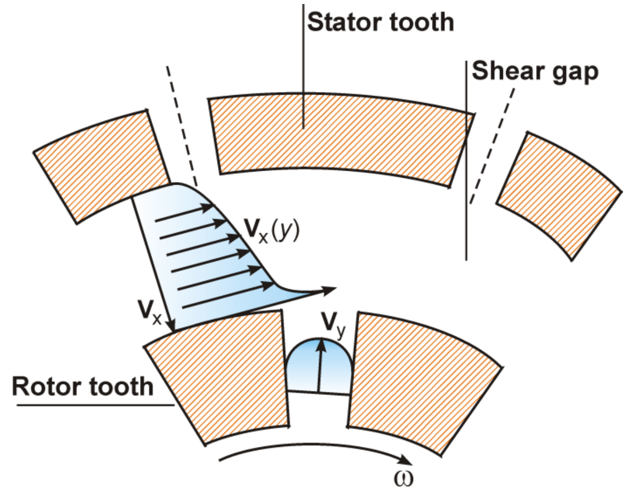
Stability of the emulsion film is determined by the surfactants adsorbed

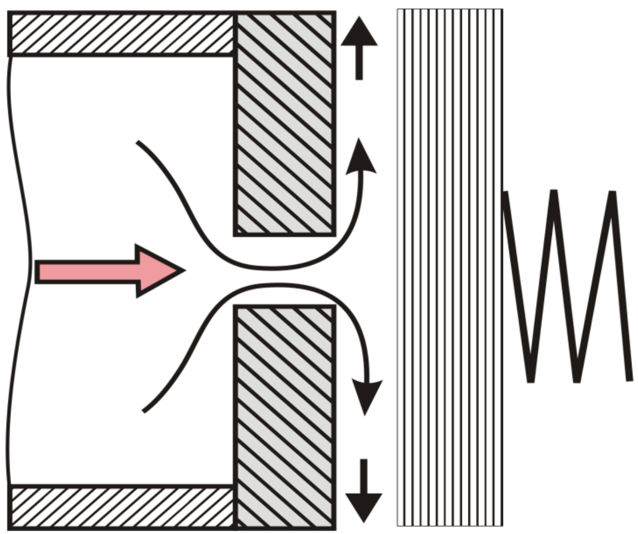
Types of apparatuses

Microfluidizer



Rotor-stator homogenizer

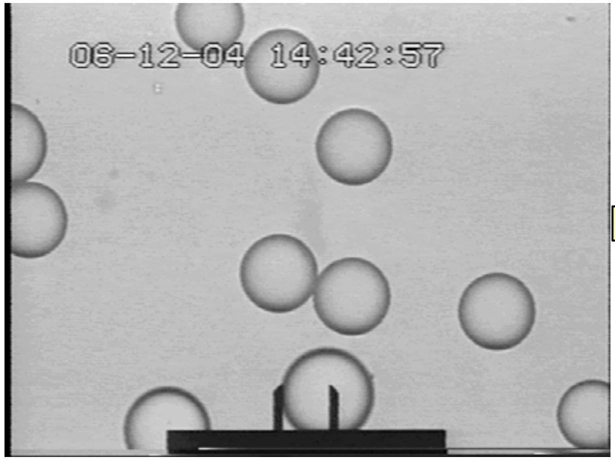




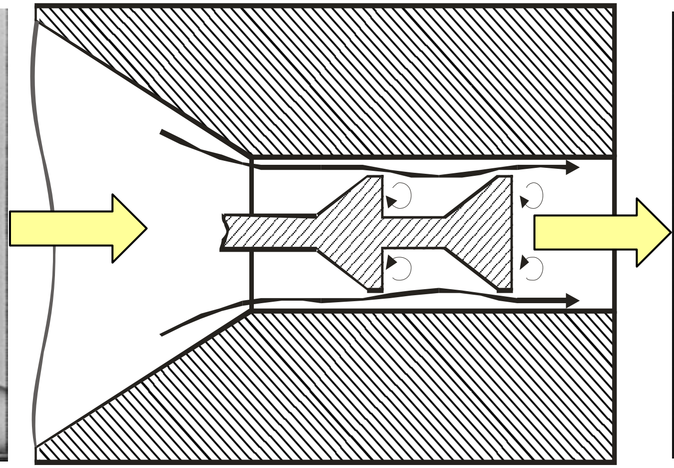
Valve homogenizer

Emulsification method:
narrow gap homogenizer

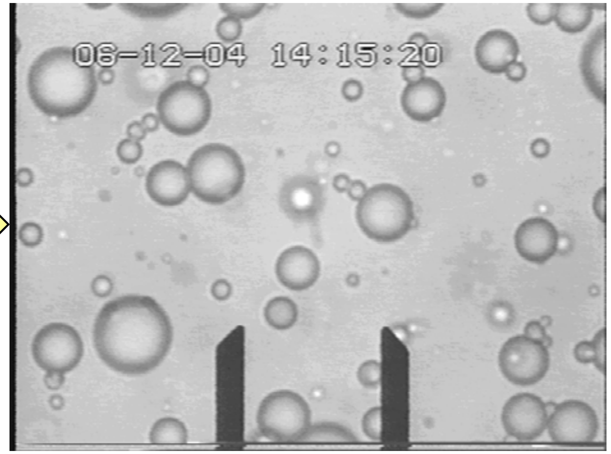
Initial premix



Narrow-gap homogenizer



Final emulsion

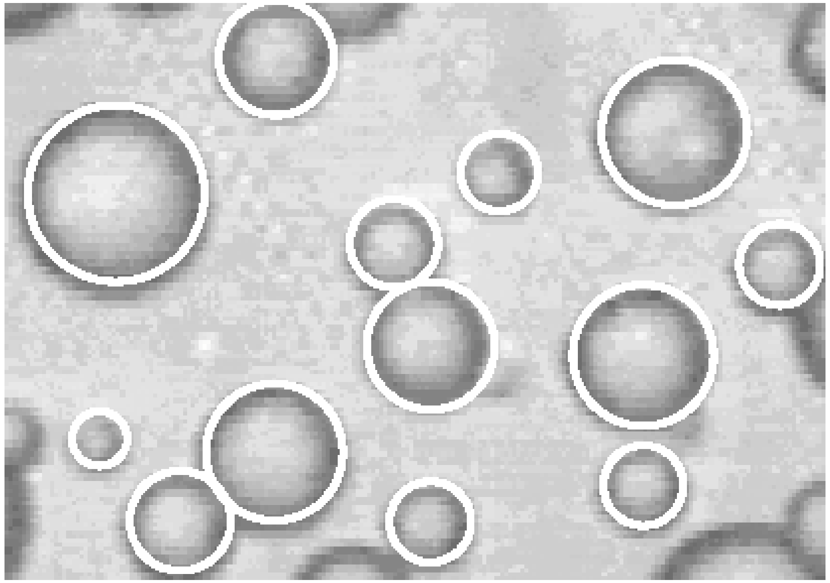


Main advantage - well defined hydrodynamic conditions

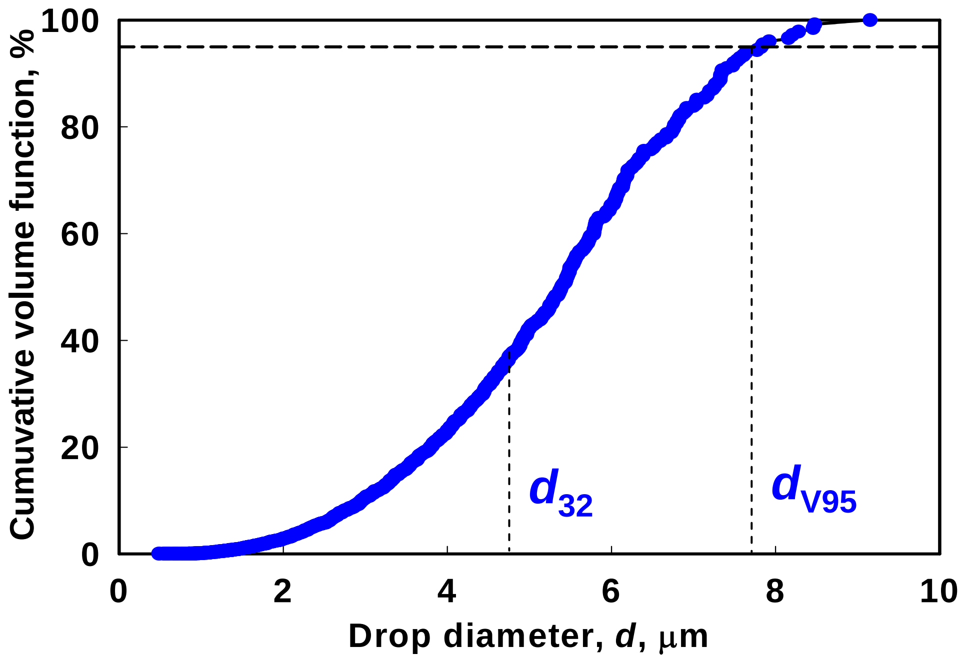
- **Rate of energy dissipation per unit mass, ε**
- **Residence time, θ**

Drop-size distribution

Optical microscopy



Maximum diameter, d_{V95}

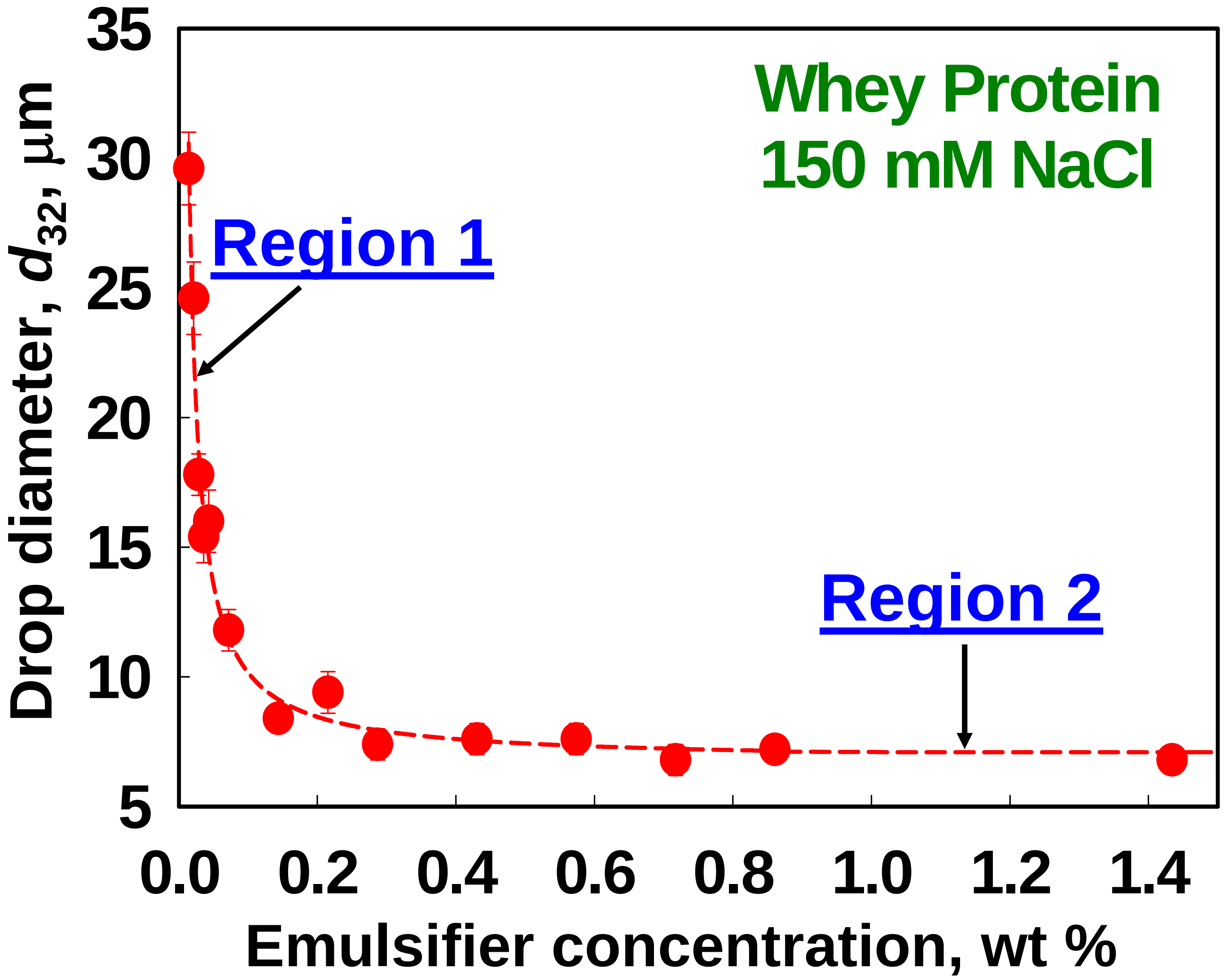


Mean volume-surface diameter, d_{32}

$$d_{32} = \frac{\sum N_i d_i^3}{\sum N_i d_i^2}$$

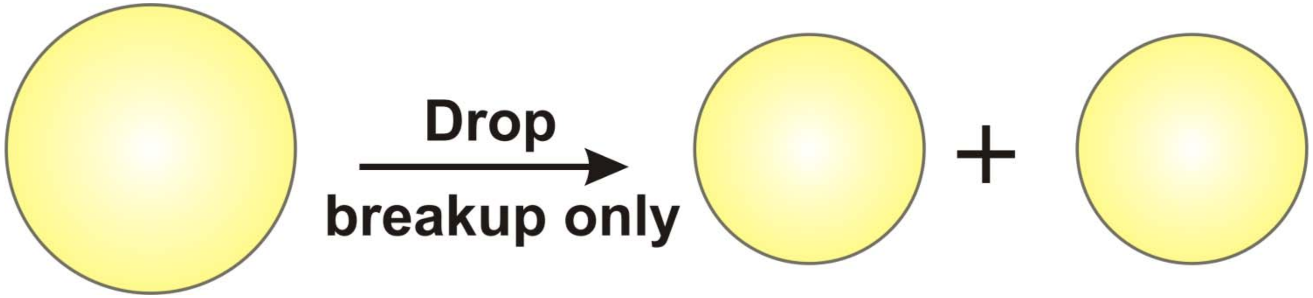
Main advantage – very precise characterization

Effect of emulsifier concentration



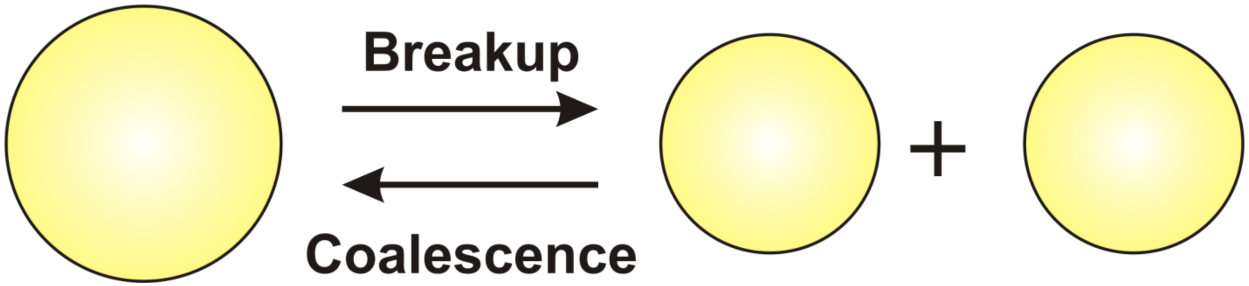
High emulsifier concentration

- Negligible coalescence
- d_{32} is determined by drop breakup only



Low emulsifier concentration

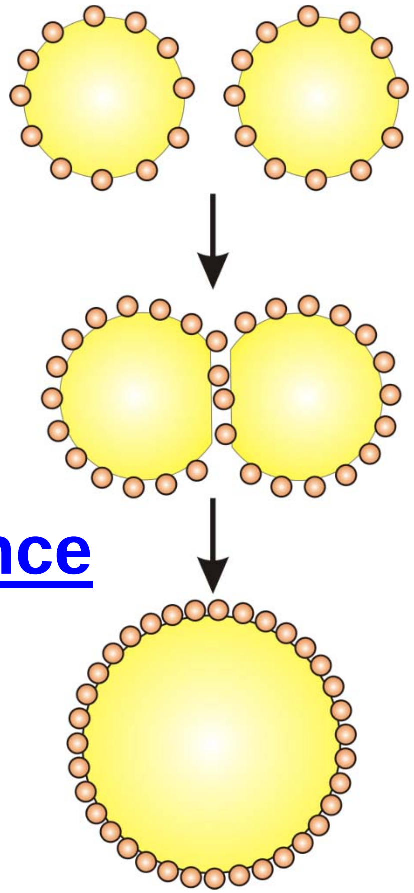
- Significant effect of drop coalescence on d_{32}



Emulsification with coalescence

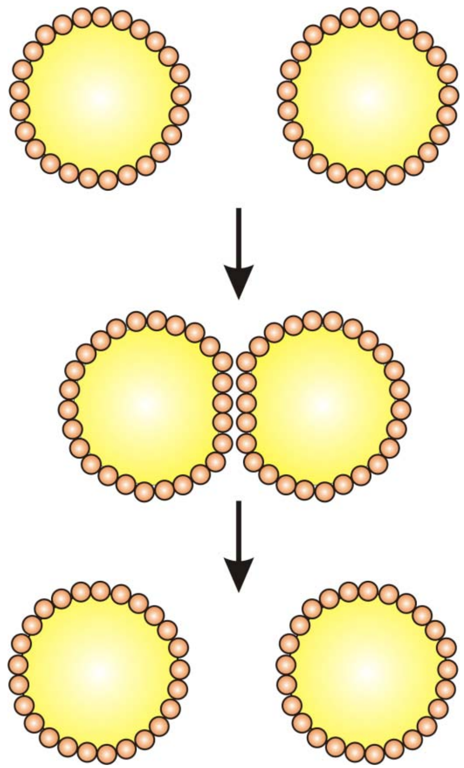
(A) No electrostatic repulsion

Monolayer adsorption Γ_M needed to stabilize the drops



Coalescence

$\Gamma < \Gamma_M$



No coalescence

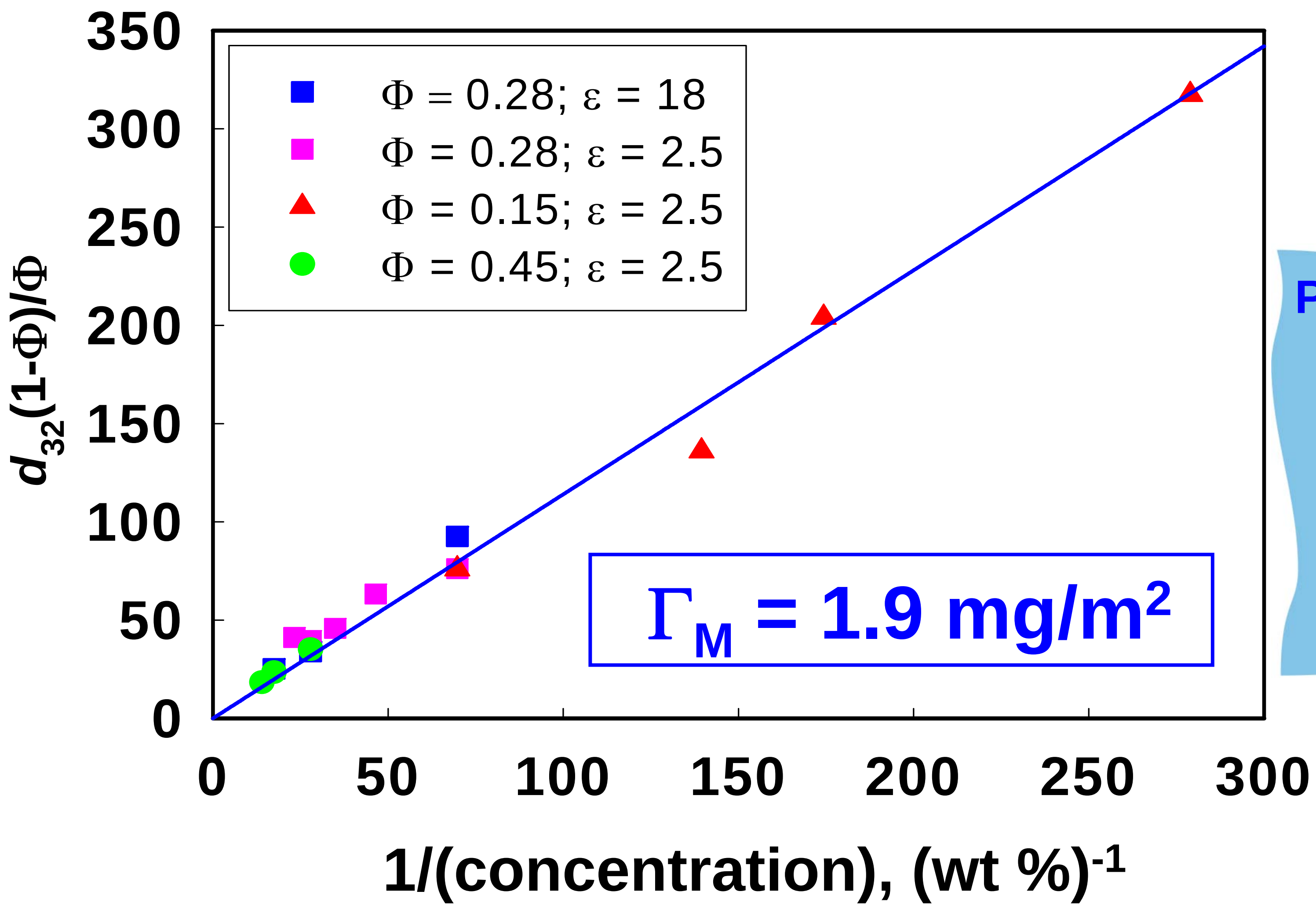
$\Gamma \geq \Gamma_M$

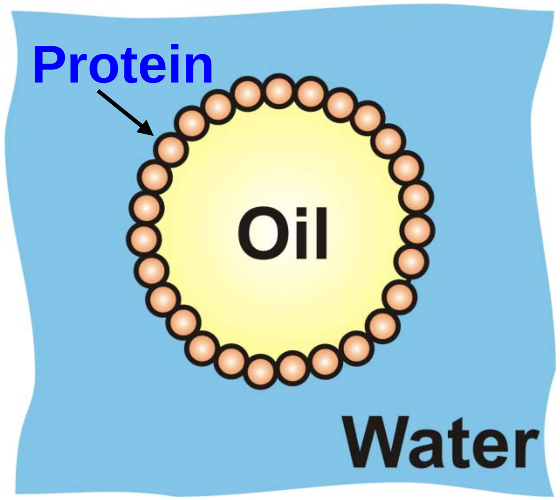
$\Rightarrow$ **Drop size:**

$$d_{32} \approx \frac{6\Phi}{10\left(1-\Phi\right)} \frac{\Gamma_M}{C_{INI}}$$

Comparison with experimental data

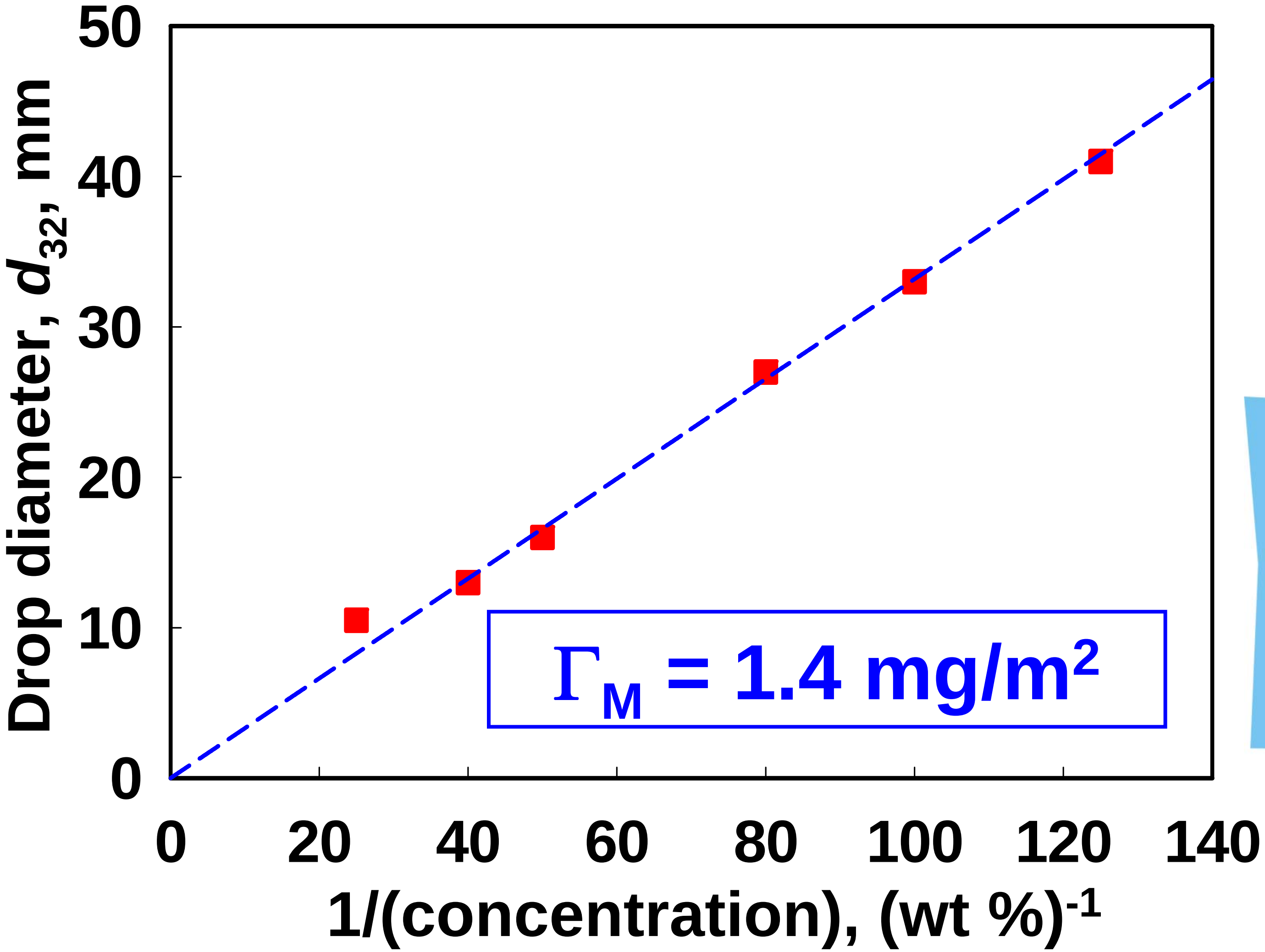
(whey protein + 150 mM NaCl)

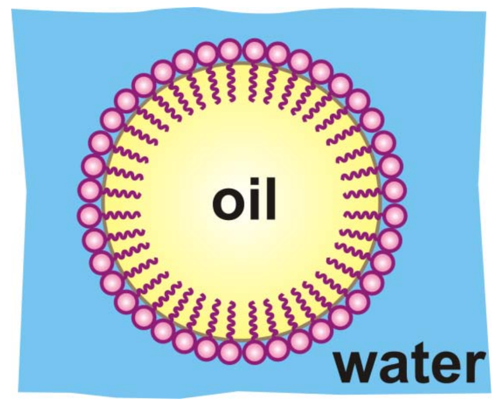




Tcholakova et al, *Langmuir*, 2003, *19*, 5640; *Langmuir*, 2004, *20*, 7444;

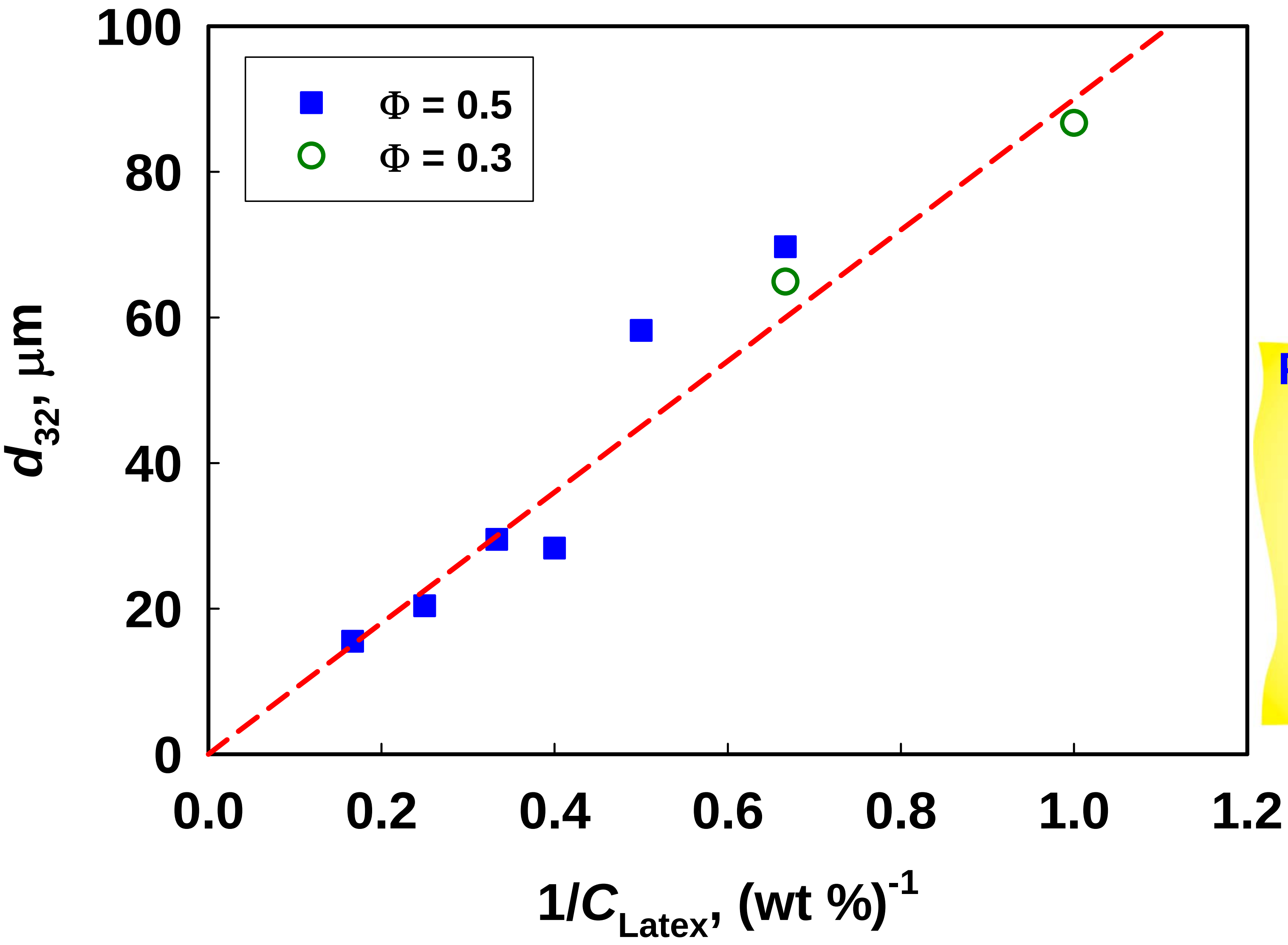
Nonionic surfactant Brij 58 + 150 mM NaCl

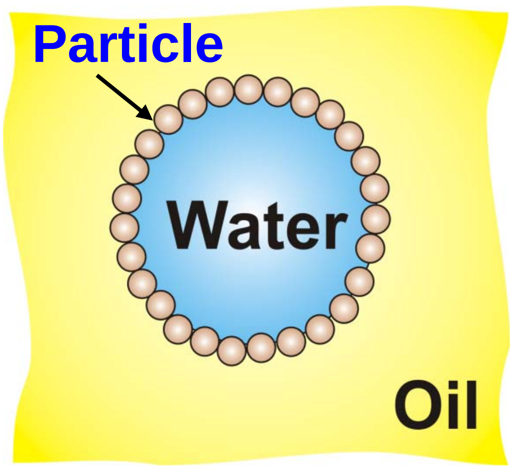




Tcholakova et al, *Langmuir*, 2004, *20*, 7444; Tcholakova et al, *PCCP*, 2008, *10*, 1608.

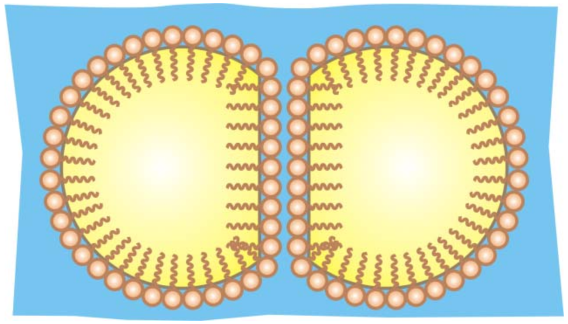
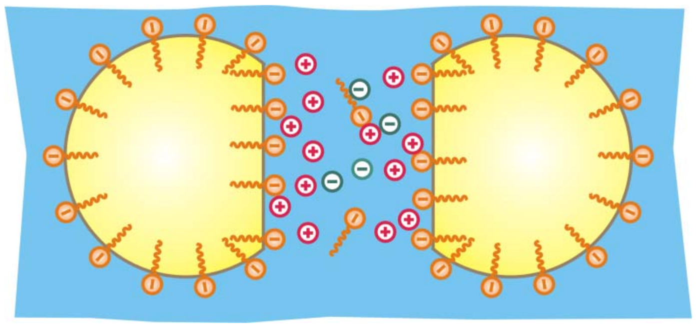
Solid latex particles + 500 mM NaCl





Golemanov et al, *Langmuir*, 2006, *22*, 4698; Tcholakova et al, *PCCP*, 2008, *10*, 1608.

Degree of coverage, $\theta = \Gamma / \Gamma_M$, preventing coalescence

System	Theory	Experimental	
WPC 150 mM NaCl	≥ 1	≥1	**Steric repulsion** 
Brij 58 150 mM NaCl	≈ 1	≈ 1	
SDS 10 mM NaCl	≈ 0	< 0.05	**Electrostatic repulsion** 
SDS 150 mM NaCl	≈ 0.23	≈ 0.3	

S. Tcholakova; N. Denkov and T. Danner, *Langmuir*, 2004, *20*, 7444.

Conclusions
– emulsification with coalescence

A. Suppressed electrostatic repulsion

The model with Γ_M describes very well the data !

$\Rightarrow$ Typical for nonionic surfactants, solid particles and proteins at high electrolyte concentration.

B. Significant electrostatic repulsion

DLVO theory describes well the data !

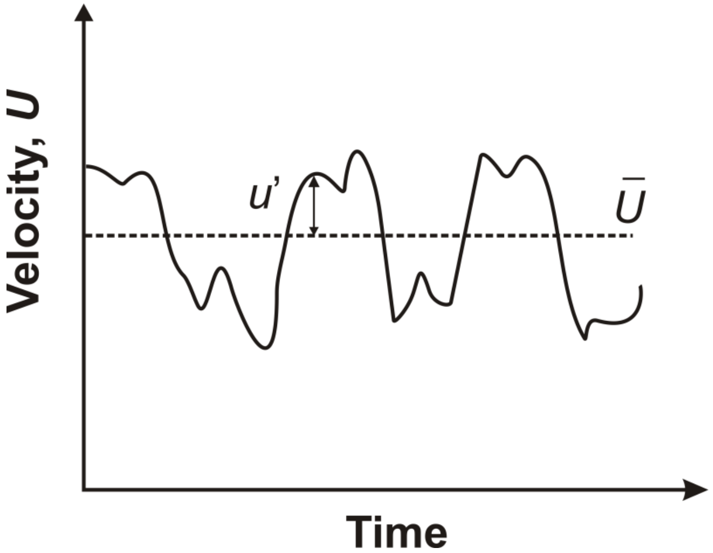
$\Rightarrow$ Typical for ionic surfactants and proteins.

Tcholakova et al, *Langmuir*, 2004, *20*, 7444; *PCCP*, 2008, *10*, 1608.

Emulsification in turbulent flow without coalescence

1. **Main characteristics of turbulent flow**
    - **Velocity fluctuation**
    - **Rate of energy dissipation**
2. **Emulsification in inertial regime**
3. **Emulsification in viscous regime**

Main characteristics of turbulent flow



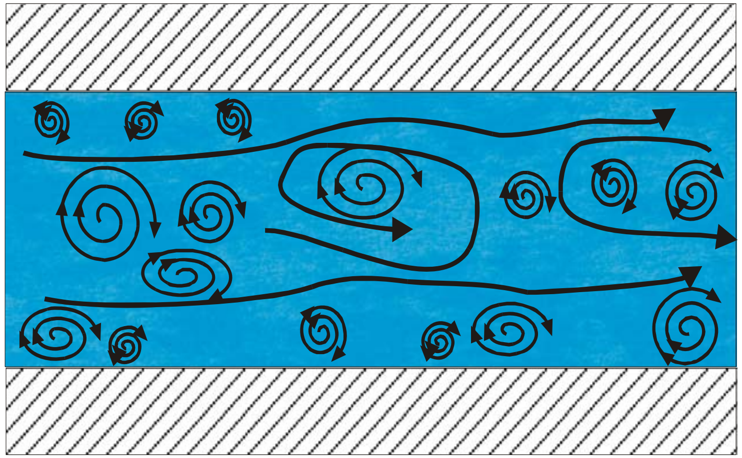
Velocity fluctuation

$$u = \left\langle \left(U - \overline{U} \right)^2 \right\rangle^{1/2}$$

Rate of energy dissipation

$$\varepsilon \sim \frac{\dot{E}_{KIN}}{m} \sim \frac{m u^2}{m\left(l/u \right)} \sim \frac{u^3}{l}$$

Size of the eddies in the turbulent flow



Largest eddies ≈ diameter of the pipe

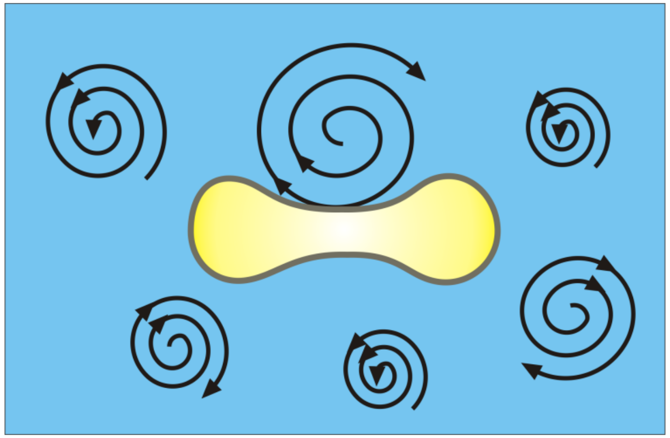
The smallest eddies

$$\mathrm{Re} \sim \frac{H u \rho_C}{\eta_C} \sim 1$$

$$\boxed{\lambda_0 = \varepsilon^{-1/4} \eta_C^{3/4} \rho^{-3/4}}$$

Drops in the turbulent flow

Inertial regime

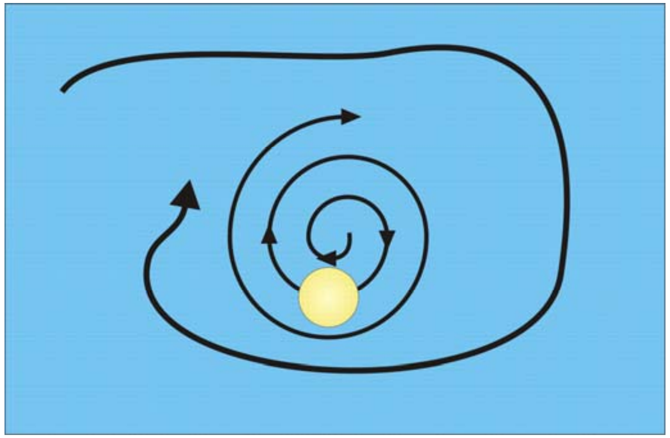


$$d > \lambda_0$$

Pressure fluctuations

$$\rho \langle u \rangle^2$$

Viscous regime



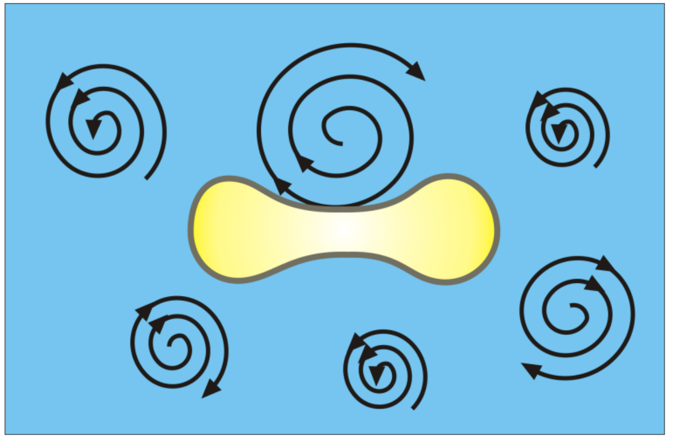
$$d < \lambda_0$$

Viscous stresses inside smallest eddies

$$\eta_C \left(dU/dx \right)$$

Drop breakup in inertial turbulent regime

(Kolmogorov, Hinze; Davies, Calabrese)



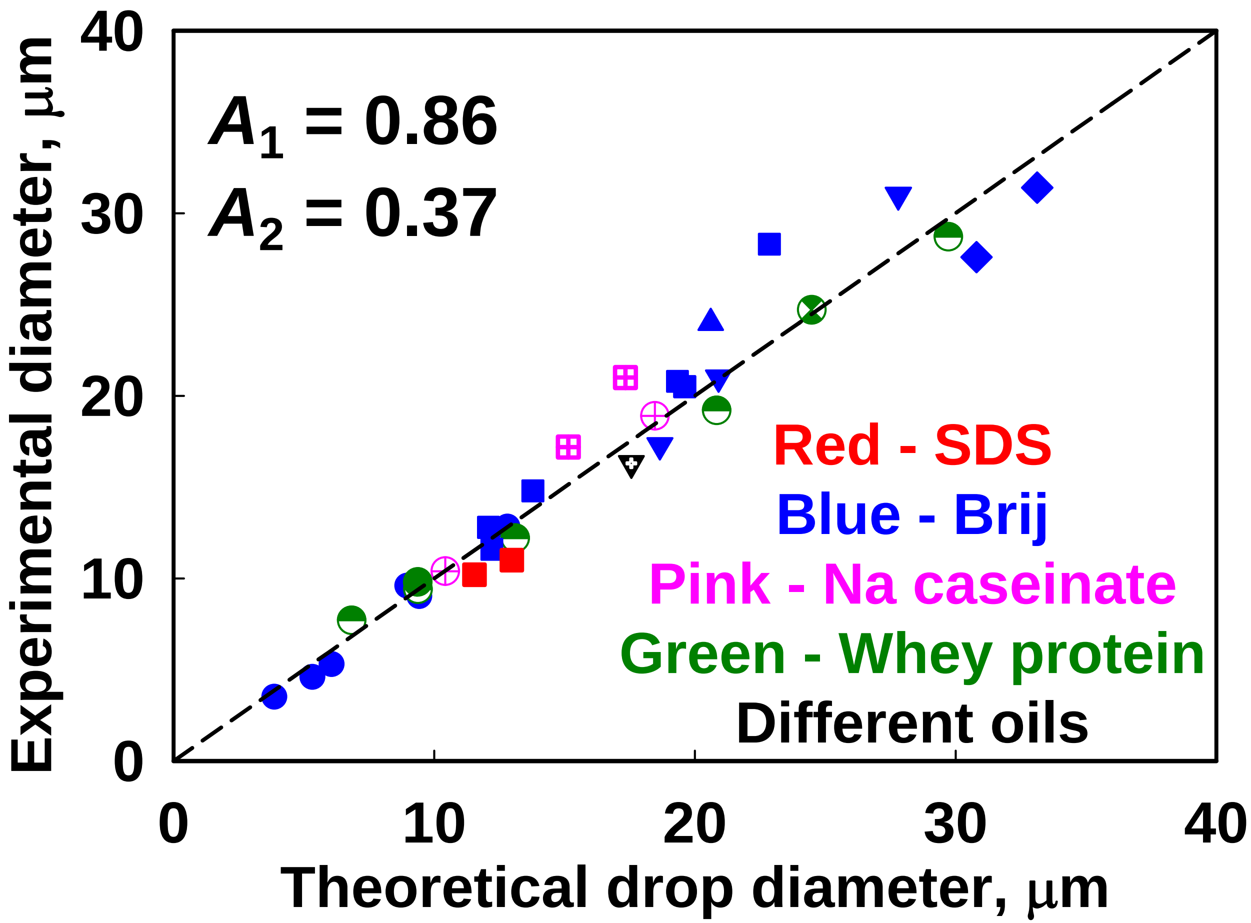
Pressure fluctuations	=	Capillary pressure	+	Viscous stress inside drop

$$\rho\langle u\rangle^2 \sim \sigma/d + \eta_D\left[\delta\langle u_d\rangle/\delta x\right]$$

$$\rho(\varepsilon d)^{2/3} = C_1\,\sigma/d + C_2\,\eta_D\varepsilon^{1/3}/d^{2/3}$$

Predicted vs. measured drop diameter (inertial regime)

$$d = A_1\left(\sigma + A_2 \eta_D \varepsilon^{1/3} d^{1/3}\right)^{3/5} \rho_C^{-3/5} \varepsilon^{-2/5}$$



Effect of oil viscosity on emulsification in inertial regime

Oil Viscosity, η_D, Pa.s	0.1	0.6	1.5	10	60	100
1 wt % PVA σ = 21 mN/m	19 ± 4 μm	24 ± 6 μm	Millimeter sized drops + Non emulsified oil			
10 wt % SDS σ = 7.0 mN/m	10 ± 2 μm	13 ± 3 μm				

Time scales (Walstra, 1983)

Deformation time

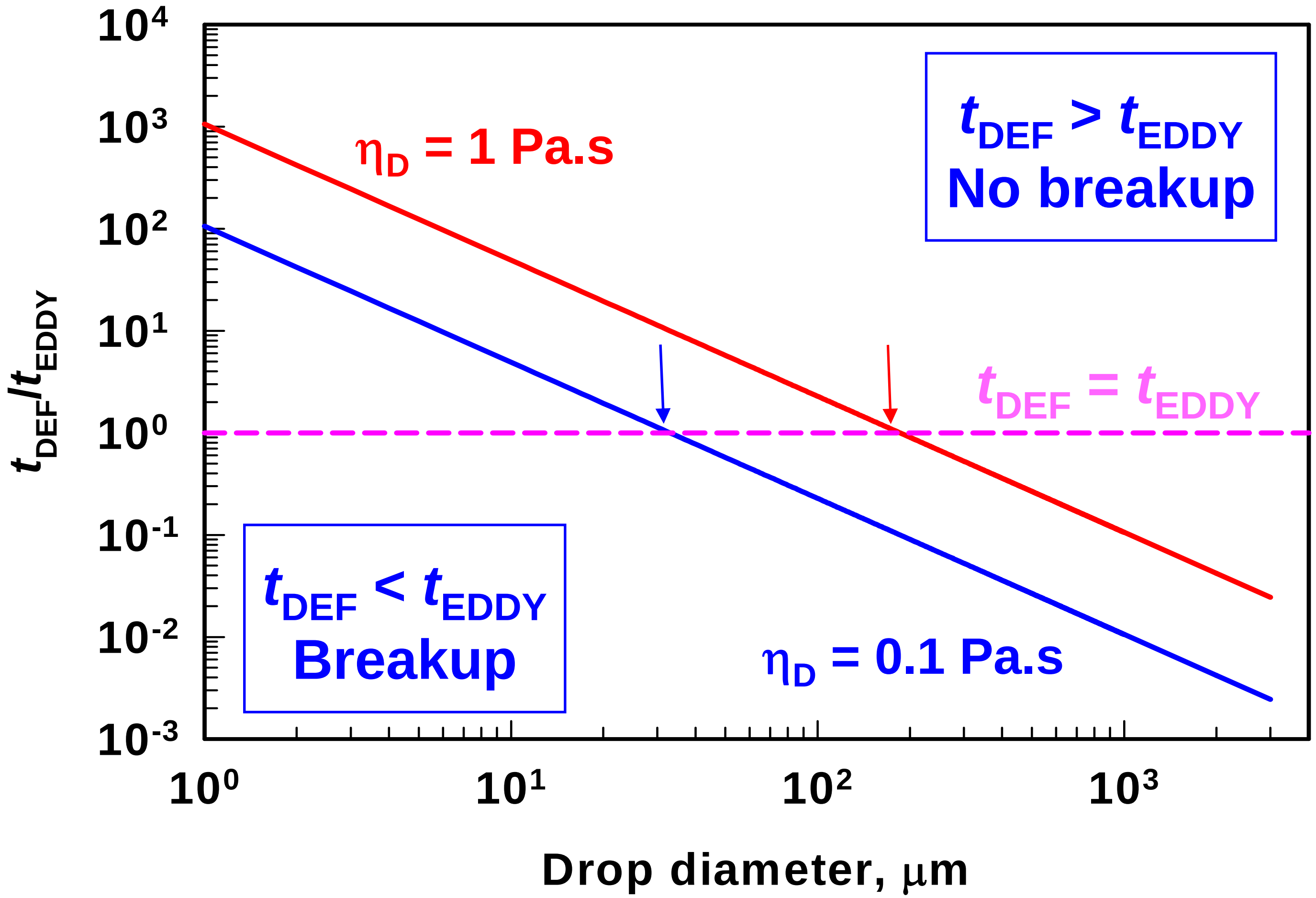
$$t_{DEF} = \frac{\eta_D}{5\varepsilon^{2/3} d^{2/3} \rho_C^{1/3}}$$

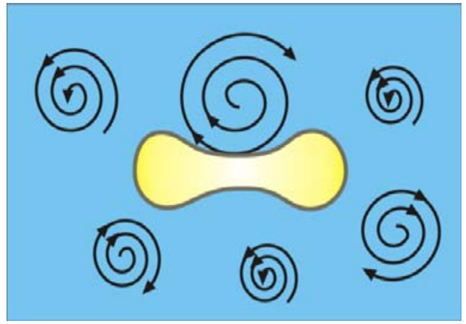
Eddies life time

$$t_{EDDY} = \frac{d^{2/3} \rho_C^{1/3}}{\varepsilon^{1/3}}$$

$t_{DEF} < t_{EDDY} \Rightarrow t_{DEF}/t_{EDDY} < 1$

Deformation vs life time of eddies





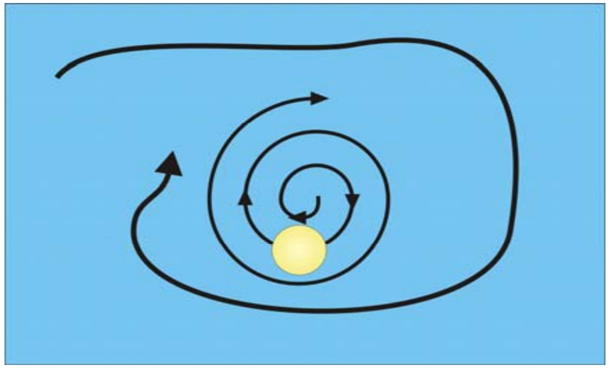
Requirement for drop breakup

η_D = 1 Pa.s d > 270 μm

η_D = 0.1 Pa.s d > 27 μm

Inertial regime of emulsification is unsuitable for oils with viscosity ≥ 1 Pa.s, because of too long deformation time!

Emulsification in viscous turbulent regime



Maximal stable drop diameter

Kolmogorov, 1949; Hinze, 1955

$$d_V = A_3\, \sigma \big/ \left(\varepsilon \eta_C \rho_C \right)^{1/2}$$

Deformation vs residence time

Walstra, 1983

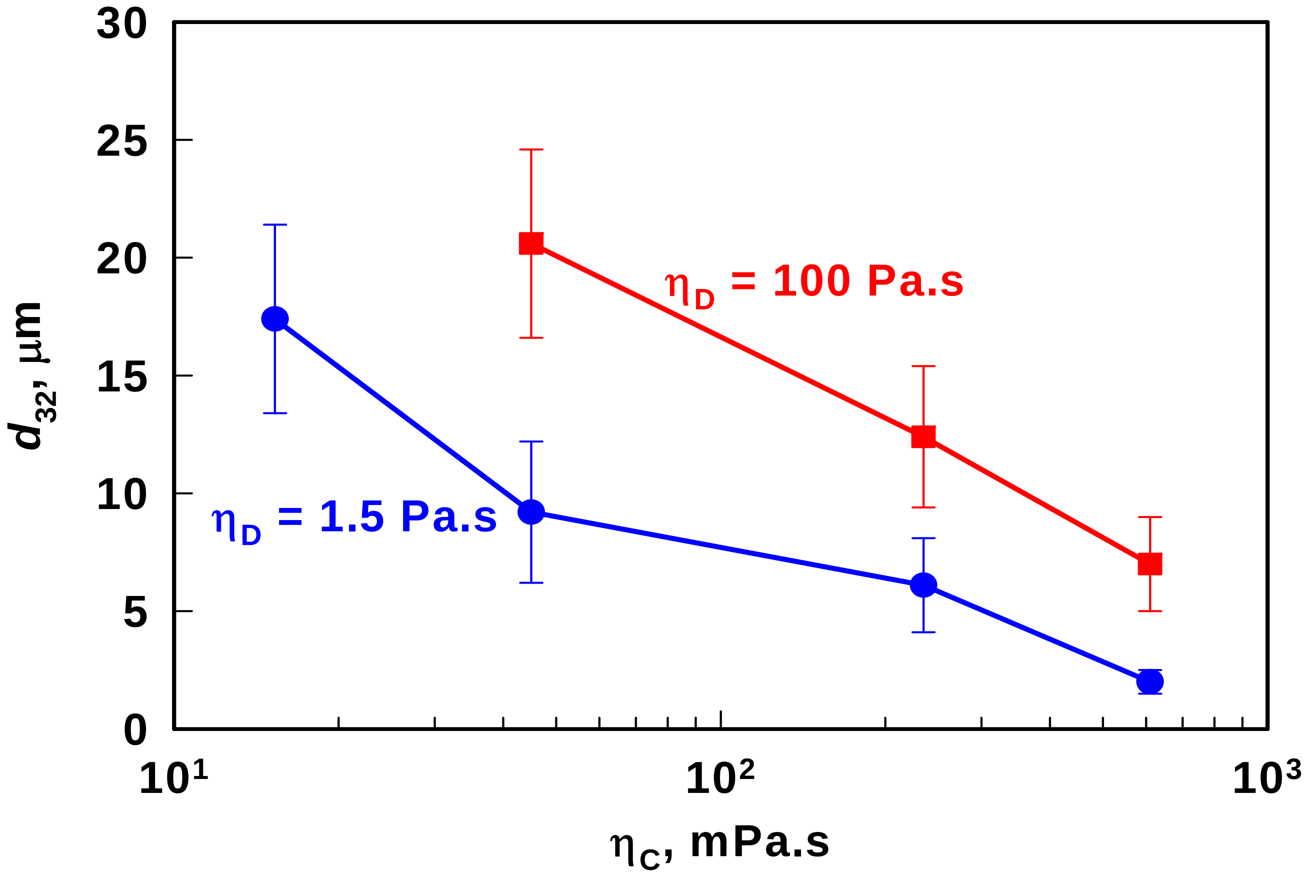
$$\tau_{DEF} = \frac{\eta_D}{\left(9\, \varepsilon\, \eta_C\right)^{1/2}}$$

$$t_{RES} \approx 4 \text{ ms}$$

η_D = 10 Pa.s; $\varepsilon = 2 \times 10^8$ J/m^3.s; $\rho_C = 10^3$ kg/m^3

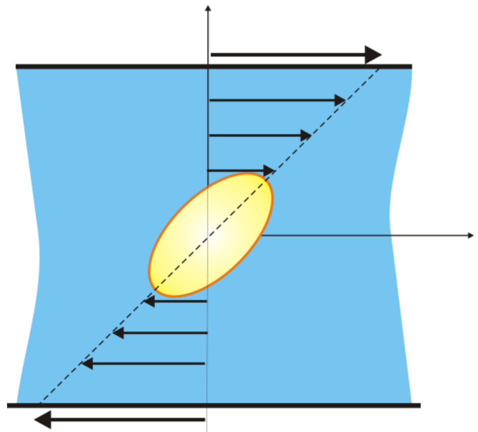
$\Rightarrow t_{RES} > t_{DEF}$, when η_C > 35 mPa.s

Effect of solution and oil viscosity on mean drop size in viscous regime

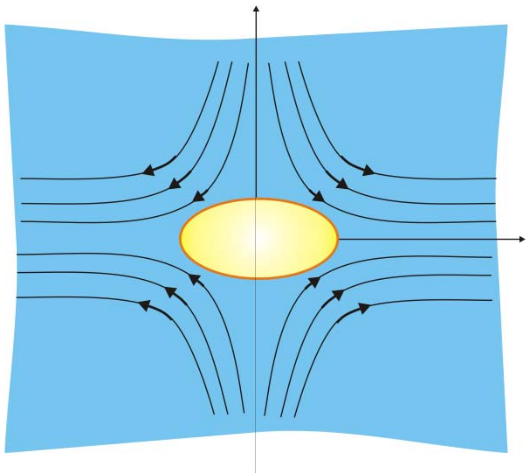


Successful emulsification even for oils with η_D ~ 100 Pa.s

Emulsification in Laminar flows



Simple shear, α = 0



Elongational, α = 1

S. Guido and co-authors, 2006

(1) Drop stretching

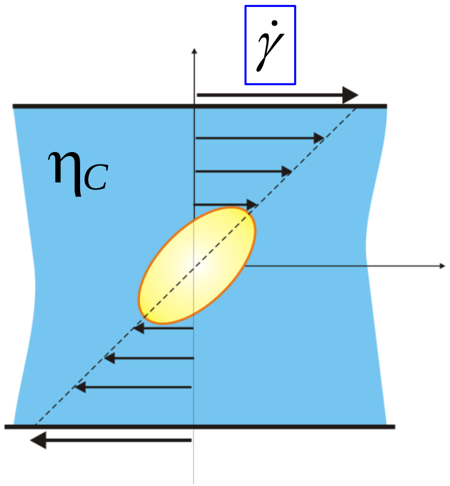
(2) Capillary instability

(3) Daughter drops of different sizes

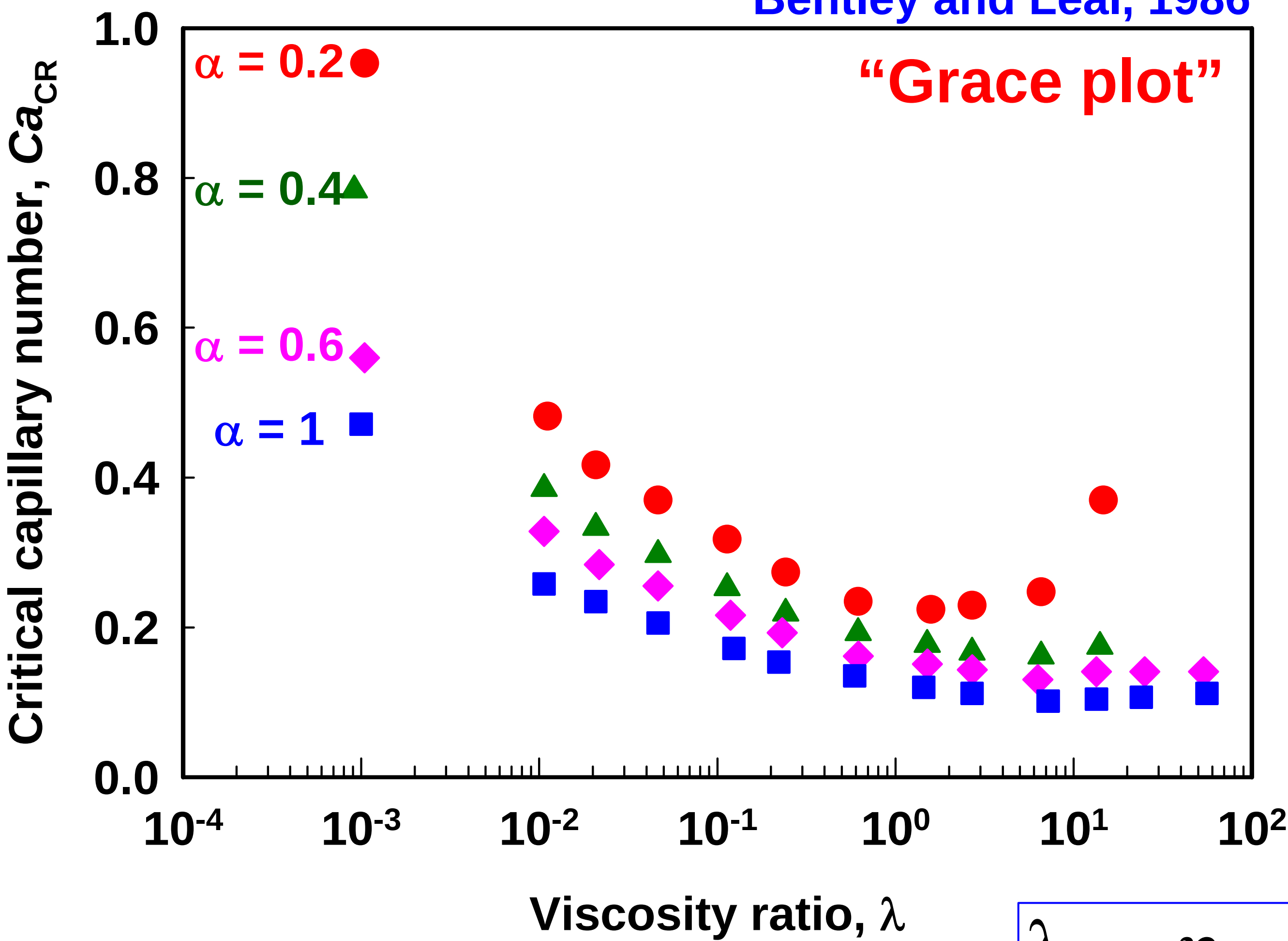
Main factors controlling drop breakup in laminar flows

Capillary number

$$Ca = \left(\frac{\eta_C \dot{\gamma}}{\sigma / R}\right)$$

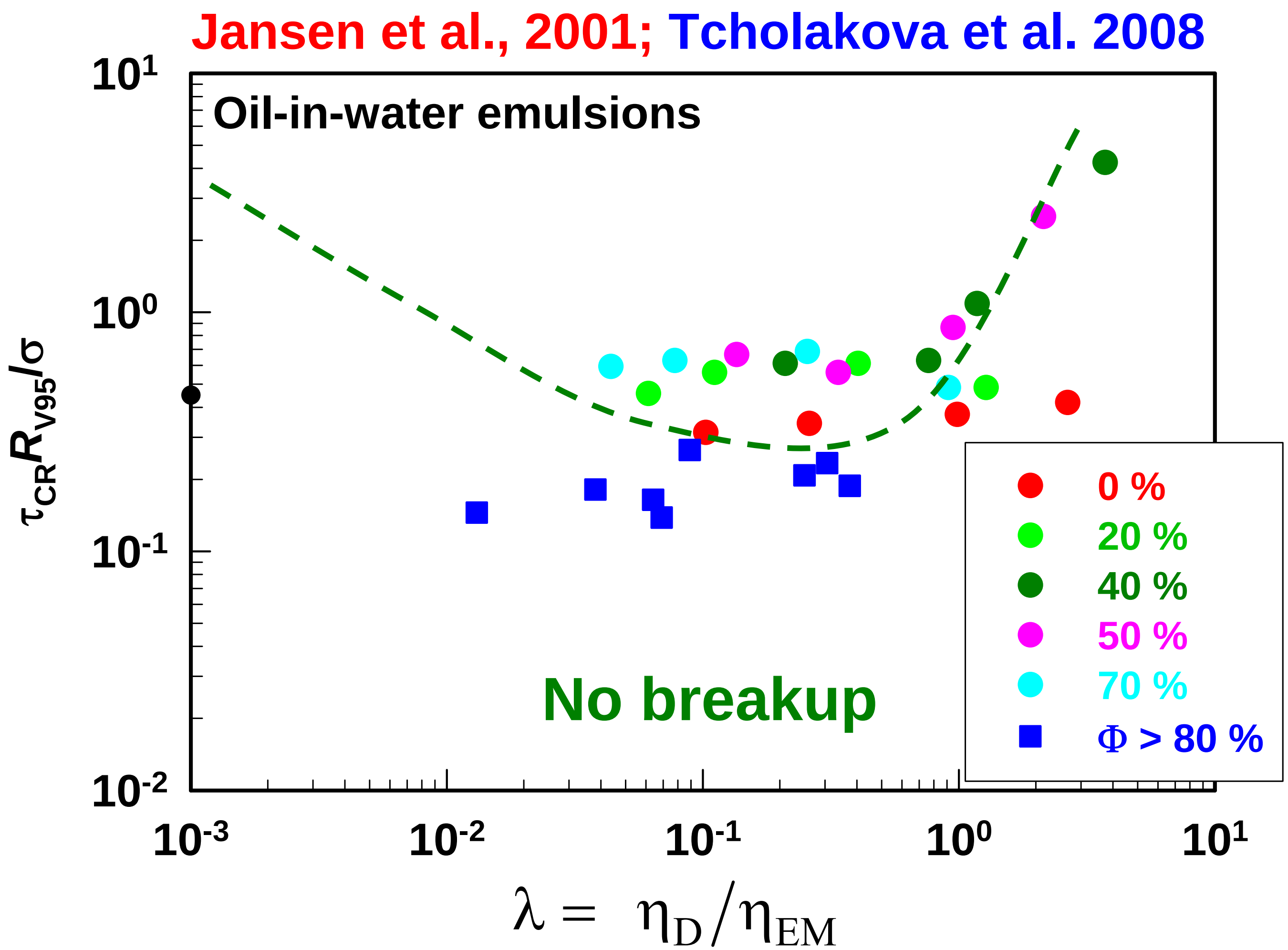


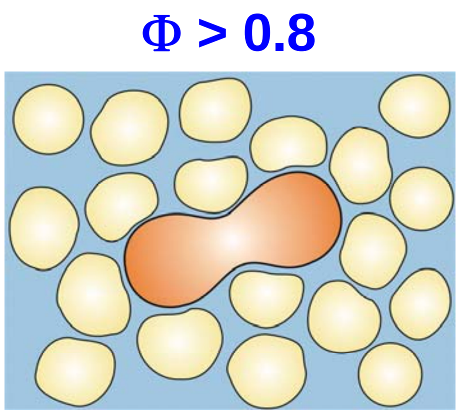
Bentley and Leal, 1986



$$\lambda = \eta_D / \eta_C$$

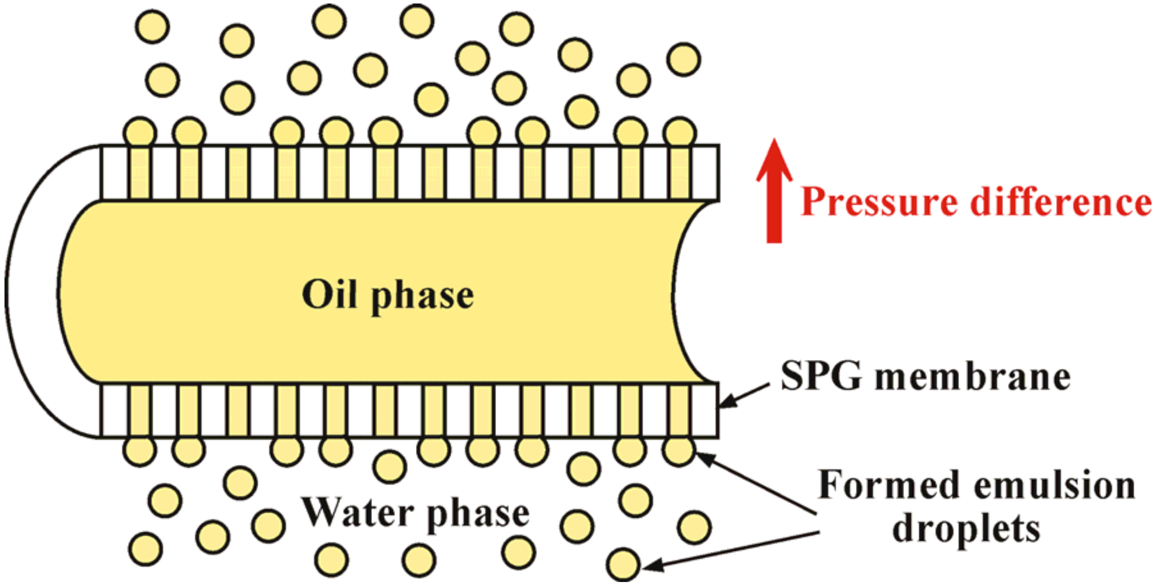
Drop breakup in concentrated emulsions

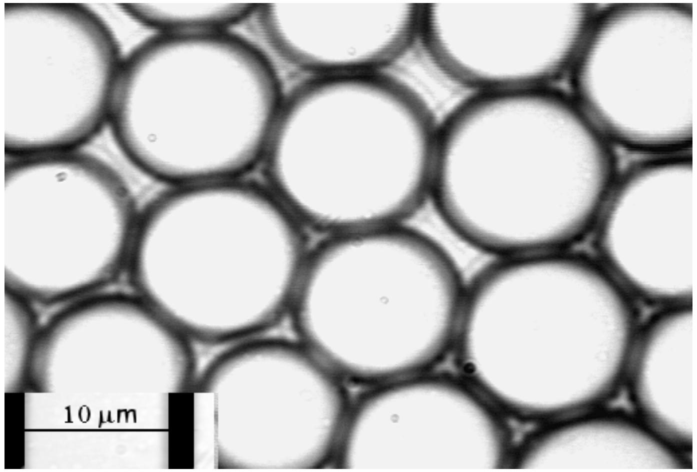




Agreement, if emulsion viscosity, η_{EM}, is used instead of η_C

Membrane emulsification





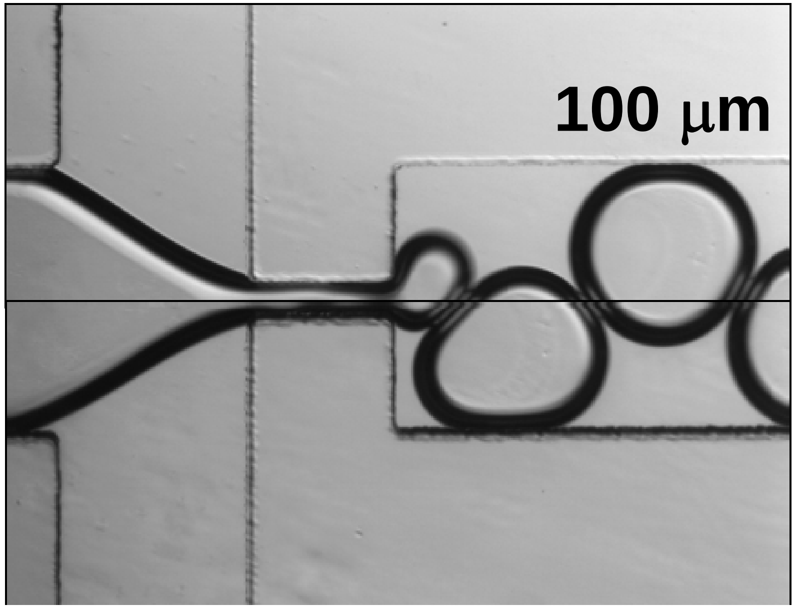
10 μm monodisperse drops

Main factors: Pore size, driving pressure, cross-flow, membrane surface

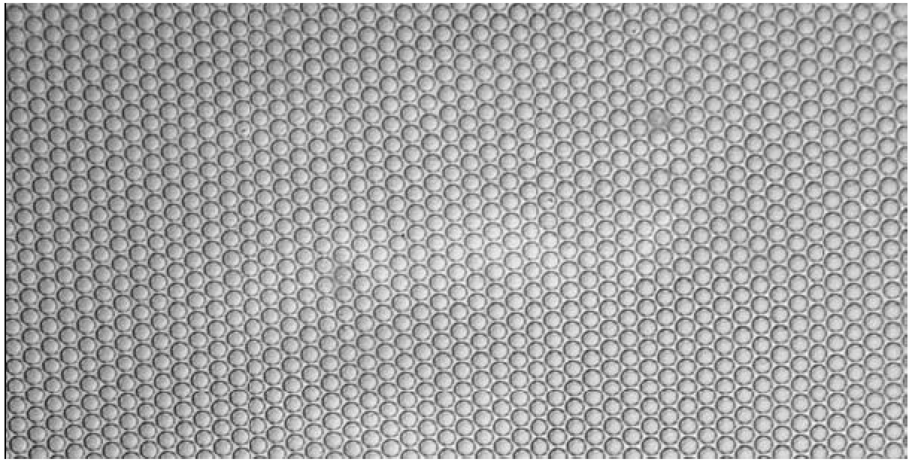
Main advantage: Monodisperse drops

Main disadvantage: Low production capacity

Microfluidics



Monodisperse drops



Applications: Microreactors, Nanotechnology, Gene engineering…

Main factors: Channel size, driving pressure, co-flow

Main advantages: Monodisperse drops; Micromanipulation

Main disadvantage: Very low production capacity