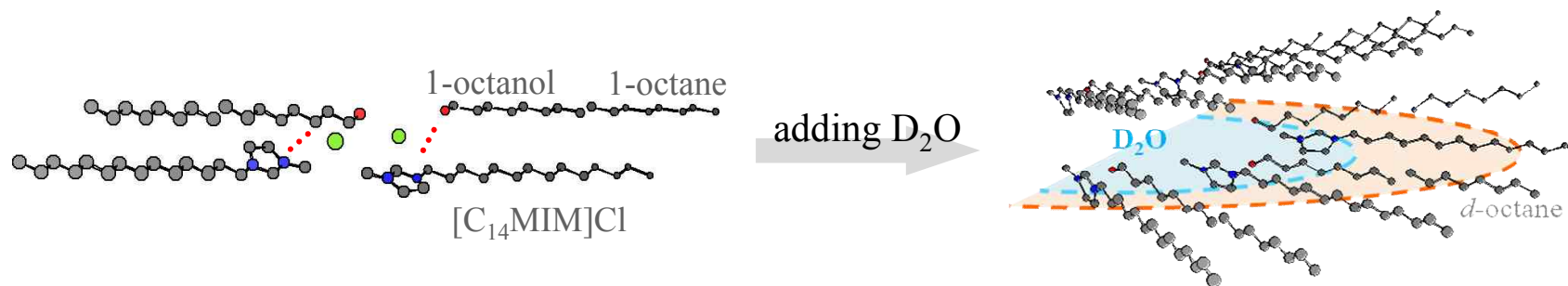


# Microemulsions and the Flexibility of Oil/Water Interfaces

P. G. de Gennes and C. Taupin, *J. Phys. Chem.* 1982, 86, 2294-2304

Yoonnam Jeon (2015. 01. 24)

# Introduction



## Question

1. Is it possible ellipsoidal microemulsion?
2. What is the origin of non-spherical structure?
  - Curvature free energy ( $F$ ) =  $F_\gamma + F_{\text{bending}} + F_{\text{entropy}}$



France, 1932 – 2007



1991 Nobel Prize (Physics)

“for discovering that methods developed for studying order phenomena in simple systems can be generalized to more complex forms of matter, in particular to liquids crystals and polymers”



2294

*J. Phys. Chem.* **1982**, *86*, 2294–2304

## FEATURE ARTICLE

---

### Microemulsions and the Flexibility of Oil/Water Interfaces

**P. G. De Gennes\* and C. Taupin**

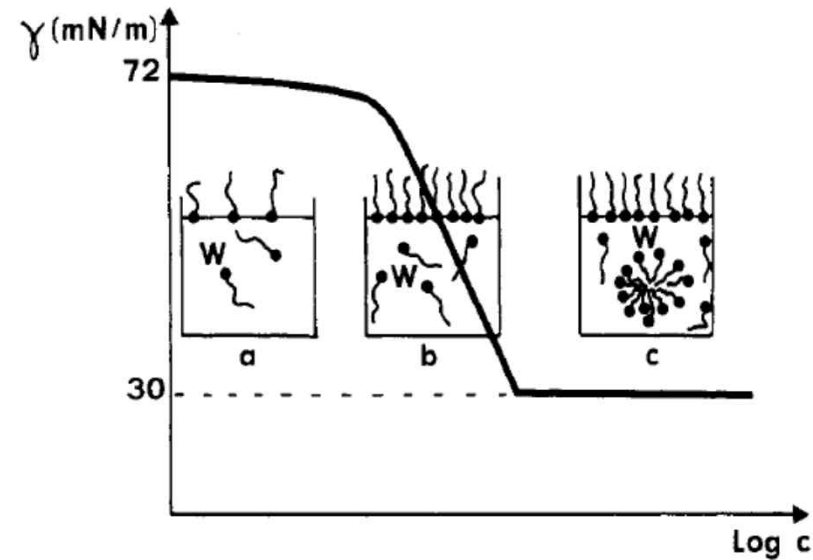
*Collège de France, 75231 Paris Cedex 05, France (Received: November 30, 1981; In Final Form: February 1, 1982)*

The phase diagram of a system of oil + water + surfactant is usually dominated by a variety of regularly organized phases (lamellar, hexagonal, etc.) which are highly viscous. However, in some favorable cases, these organized phases are less stable than a certain “microemulsion” where no periodicity occurs. These microemulsions are much more fluid than the regularly organized phases. They often exist over a broad domain of concentrations. In some limiting cases a microemulsion is simply made of swollen micelles (of oil in water or water in oil). However, various experiments indicate that “bicontinuous” structures also occur. Our aim is to understand why a random structure of this type does not collapse into an ordered phase. The interface saturated by surfactant has a nearly vanishing surface tension; one essential parameter is then the elastic constant  $K$  describing the curvature elasticity of the interface. The “persistence length”  $\xi_K$  of the interface increases exponentially with  $K$ . This should have some important effects. (1) When  $K$  is above a certain critical value  $K_c$  the interfaces tend to stack or, more generally, to build up a periodic, stable, phase. (2) When  $K$  is below  $K_c$  the interface can become extremely wrinkled and the resulting gain in entropy is larger than the loss of energy due to the departure from a periodic array. This case  $K < K_c$  would correspond to microemulsions. In this picture one major effect of cosurfactants (additives which favor the microemulsion phase) is to increase the flexibility of the layers.



Sogang University

# I. Distinct Features of Microemulsions



by adding oil

**Emulsion** with finite but small interfacial tension



# I. Distinct Features of Microemulsions



- mixture of two or more immiscible liquids
- **unstable & cloudy appearance**
- examples
  - Mayonnaise, crema (in espresso)
  - lotion, soybean oil
  - in fire fighting : encapsulating the fuel

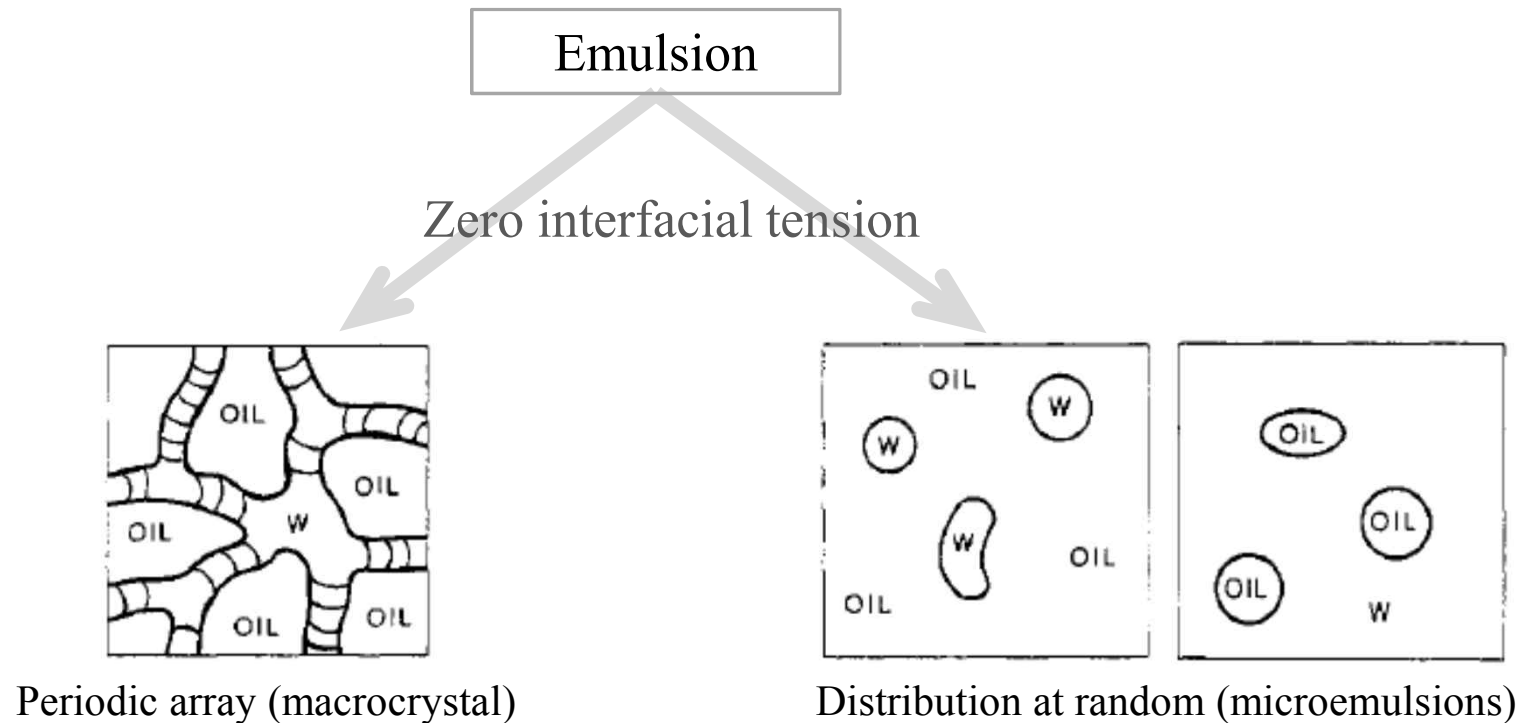


## microemulsion

- don't require the high shear conditions generally used in the formation of ordinary emulsions
- **stable & clear (size below 100nm)**

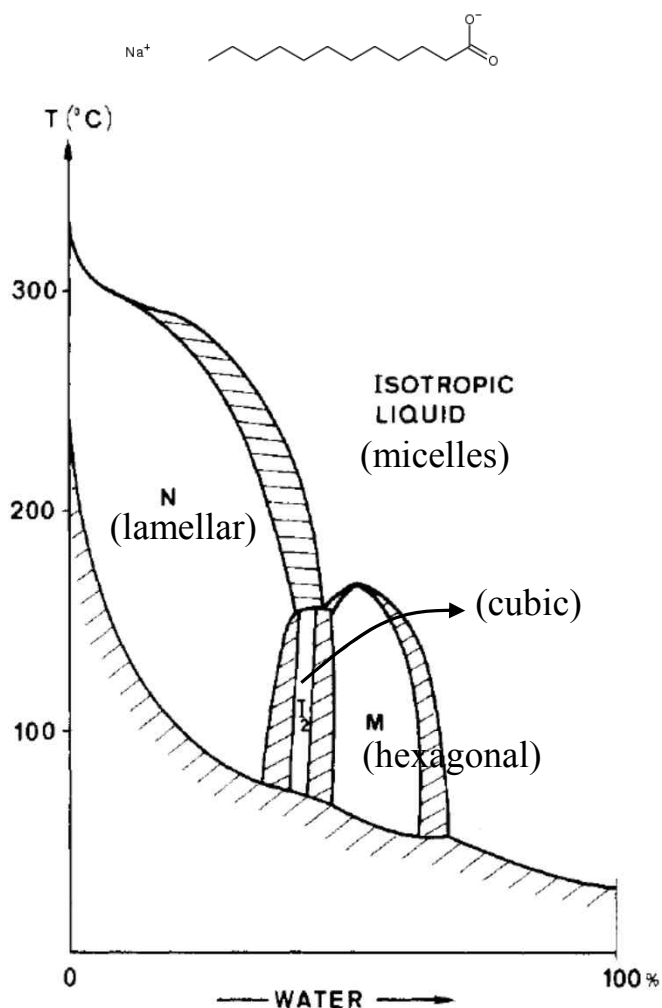


# I. Distinct Features of Microemulsions



## II. A Selection of Experimental Facts

(ex.) sodium laurate + water



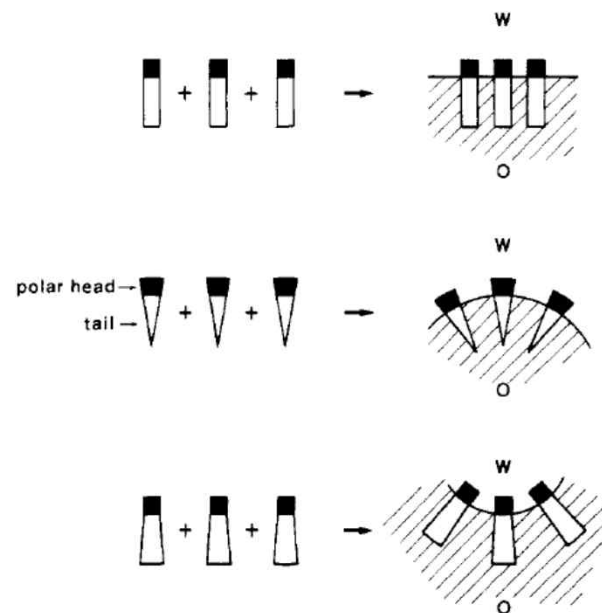
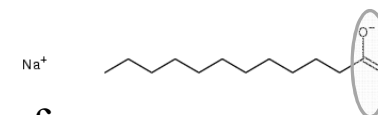
### Stabilizing forces for micelles

1.  $\Sigma$  (area per surfactant)

2. Curvature  $1/R$  of the interface

$> 0$  for direct micelle

$< 0$  for inverse micelle



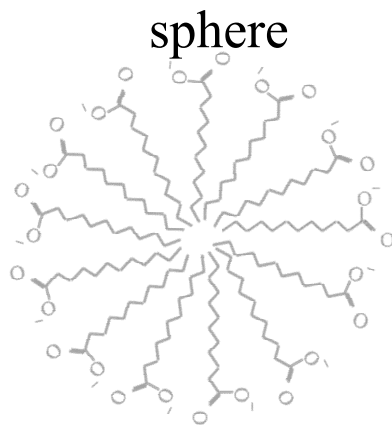
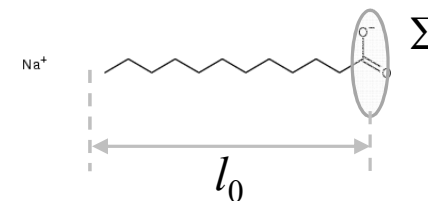
## II. A Selection of Experimental Facts

$V$  : volume of a surfactant molecule

$R_0$  : natural radius curvature

$n_s$  : number of surfactant molecule

$l_0$  : length of extended surfactant molecule ( $\sim R_0$ )



$$\left. \begin{aligned} 4\pi R_0^2 &= n_s \Sigma \\ 4\pi R_0^3/3 &= n_s V \end{aligned} \right\} l_0 = 3V/\Sigma$$

cylinder  $l_0 \sim 2V/\Sigma$

lamellar  $l_0 \sim V/\Sigma$



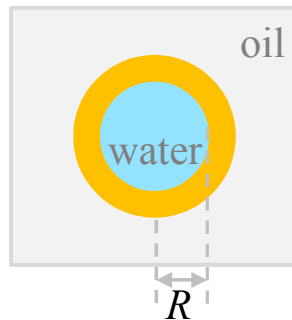


## II. A Selection of Experimental Facts

**Main features** for microemulsions :

1. Area & curvature
2. Structure of the Interface

$p$  : number of droplet  
 $R$  : spherical radius  
 $\phi_w$  : volume of water



$$\left. \begin{aligned} n_s \Sigma &= 4\pi R^2 p \\ \phi_w &= 4\pi R^3 p / 3 \end{aligned} \right\} \Sigma R = 3\phi_w / n_s$$

- ✓ Valid for systems with a single surfactant as well as for the more frequent cases with surfactant + cosurfactant
- ✓ A number of microemulsions transform without any apparent discontinuity from water/oil to oil/water  
➡ average curvature is not a leading feature of their stability

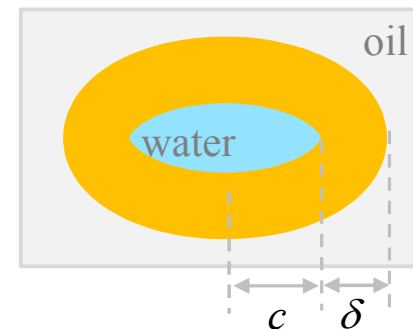


# II. A Selection of Experimental Facts

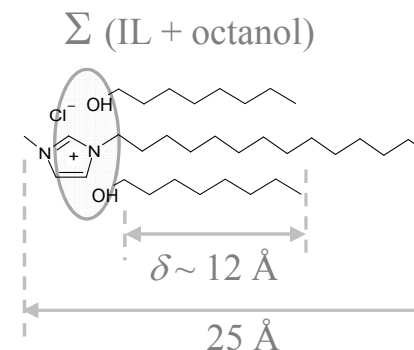
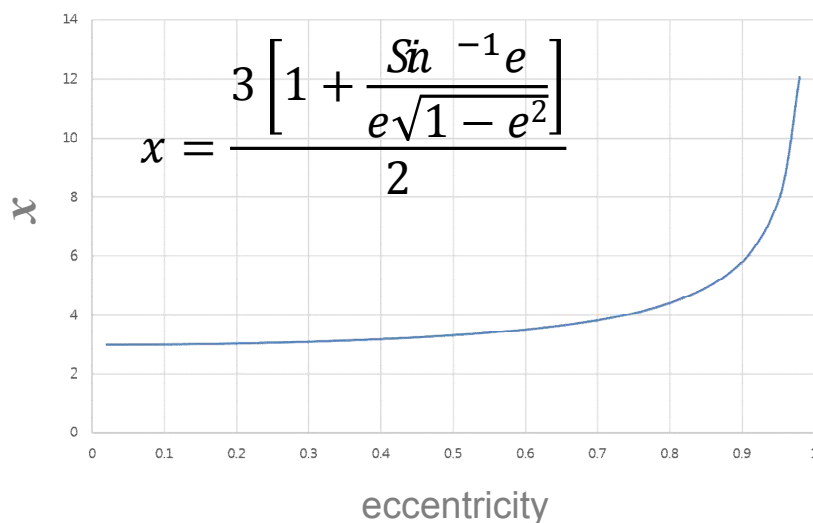
## Exercise - prolate

### Exercise

$$\left. \begin{aligned} n_s \Sigma &= 2\pi c^2 p (1 - e^2) \left(1 + \frac{\sin^{-1} e}{e\sqrt{1 - e^2}}\right) \\ \phi_w &= 4\pi (1 - e^2) c^3 p / 3 \end{aligned} \right\} \Sigma c = x \frac{\phi_w}{n_s}$$



$$\text{Eccentricity } e = (1 - a_2/c_2)^{1/2}$$



**$\phi_m = 2.1$  w.t.% microemulsion**

$c = R_g - \delta = 26 \text{ \AA}$  (by Guinier plot) -  $12 \text{ \AA}$

$\phi_w = 1.14 \mu\text{l}$

$n_s = 2.9 \times 10^{-5} \text{ mol (IL)} = 1.7 \times 10^{19} \text{ molecules}$

$\Sigma \sim 15 \text{ \AA}^2$  (IL : octanol = 1:2)

or  $24 \text{ \AA}^2$  (IL : octanol = 1:4)

$$\left. \begin{aligned} x &= 3.1 \sim 5.0 \\ (e &= 0.3 \sim 0.85) \end{aligned} \right\}$$

**$\phi_m = 4.2$  w.t.%**

$R_g = 20 \text{ \AA}$

$x = 1.8 \sim 2.8$



Sogang University

## II. A Selection of Experimental Facts

**Main features** for microemulsions :

1. Area & curvature
2. Structure of the Interface

✓ Studies of interfacial film

- Neutron scattering & hydrodynamic measurement : composition & thickness
- EPR & NMR relaxation & fluorescence depolarization  
: local state of the surfactant

\*EPR (Electron paramagnetic resonance)



The cosurfactant adsorbs strongly on the interface

- Typical ratio of surfactant : cosurfactant = 1 : 2
- Near a limit of stability : cosurfactant/surfactant is often much reduced



# III. Existing Models - The Saturated Interface (Schulman)

1. The Saturated Interface (Schulman)
2. Limitation of the Schulman Argument
3. Entropy Effects for Flexible Interfaces
4. Curvature Effects
5. Long-Range Interactions

Single interface of arbitrary shape separating the oil from the water

$$f(\text{free energy}) = f_{\text{bulk}} + \gamma_{\text{ow}} A + n_s G(\Sigma)$$

Bare interface (without surfactant)  
 $A$  (total area of interface) =  $n_s \Sigma$

$G(\Sigma)$  : a surfactant  
free energy

Langmuir surface pressure of the film :  $\Pi(\Sigma) = - \partial G / \partial \Sigma$

Actual interfacial tension :  $\gamma = \gamma_{\text{ow}} - \Pi$

Minimum free energy at fixed  $n_s$ ,

$$\begin{aligned} df / d\Sigma &= d(\gamma_{\text{ow}} (n_s \Sigma)) / d\Sigma + n_s dG(\Sigma) / d\Sigma \\ &= \gamma_{\text{ow}} n_s - n_s \Pi = n_s \gamma = 0 \end{aligned}$$

$\Sigma^*$  satisfying  $\gamma_{\text{ow}} = \Pi(\Sigma^*)$  : **Saturated state**



# III. Existing Models - Limitation of the Schulman Argument

1. The Saturated Interface (Schulman)
2. Limitation of the Schulman Argument
3. Entropy Effects for Flexible Interfaces
4. Curvature Effects
5. Long-Range Interactions

## a. Entropy effects

- Associated entropy is very small
- But all other contributions to the free energy are also small

## b. Curvature energies

- Weak and do not affect the local properties (ex.  $\Sigma$ ) very much
- But they influence the large-scale properties and the phase equilibria

## c. Electrostatic energies

- Play a role in the stability of swollen micelles of ionic surfactants

## d. Interactions between droplets

- tend to favor ordered structures or even to promote droplet coalescence



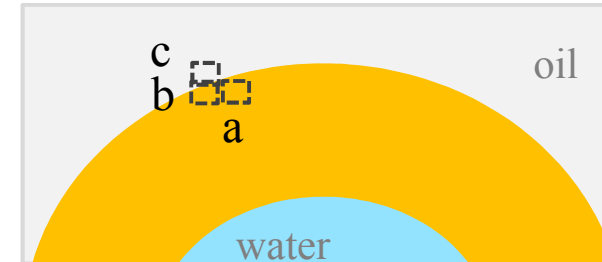
# III. Existing Models - Entropy Effects for Flexible Interfaces

1. The Saturated Interface (Schulman)
2. Limitation of the Schulman Argument
3. Entropy Effects for Flexible Interfaces
4. Curvature Effects
5. Long-Range Interactions

Persistence length in the interface :  $\xi_k$

( $\xi_k \sim 100 \text{ \AA}$  for common interface)

area :  $\xi_k^2$



a-b : no interface & no energy

b-c : free energy contribution  $\gamma \xi_k^2$

$$f(\text{free energy}) = f_{\text{bulk}} + \gamma_{\text{ow}} A + n_s G(\Sigma)$$



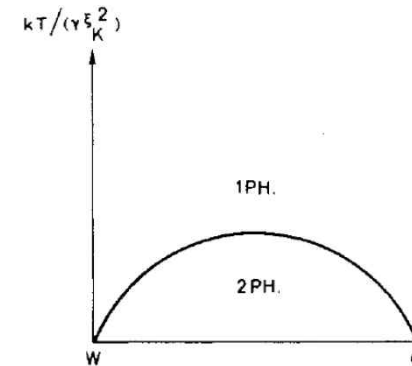
$$\begin{aligned} \mu_s (\text{chemical potential of surfactant}) &= df/dn_s \\ &= \gamma_{\text{ow}} dA/dn_s + G(\Sigma) = (\gamma + \Pi(\Sigma))\Sigma + G(\Sigma) \\ &= \Pi(\Sigma)\Sigma + G(\Sigma) \end{aligned}$$

$\gamma(\Sigma)$  : depends ultimately on  $\mu_s$



# III. Existing Models - Entropy Effects for Flexible Interfaces

1. The Saturated Interface (Schulman)
2. Limitation of the Schulman Argument
3. Entropy Effects for Flexible Interfaces
4. Curvature Effects
5. Long-Range Interactions



## Lattice Gas Model

oil (or water) regions : do not look like an assembly of cubes

lattice gas model : keeps some essential feature of a random surface

$$\gamma \xi_k^2 < \gamma_c \xi_k^2 = \alpha k_b T : \text{single phase} \\ (\alpha = 0.44 \text{ for a simple cubic lattice})$$

$$\gamma \xi_k^2 > \gamma_c \xi_k^2 = \alpha k_b T : \text{multi phase}$$

## General validity

- a. The values of  $\gamma$  involved are weak
- b. Phase separation : because of a balance between **interfacial entropy** and **interfacial energy**
- c. The region of phase separation :  $\gamma > \gamma_c$  (**low surfactant content**)



# III. Existing Models - Curvature Effects

1. The Saturated Interface (Schulman)
2. Limitation of the Schulman Argument
3. Entropy Effects for Flexible Interfaces
4. Curvature Effects
5. Long-Range Interactions

- ✓ Schulman description ignores all energies associated with the curvature of the interface.
- ✓ For many problems involving fluid/fluid interfaces :  $F_\gamma$  dominates
- ✓ When  $\gamma \rightarrow 0$  : curvature effects become relevant
- ✓ For a curvature  $1/R$ , curvature energy per unit area

$$F = \gamma - \frac{K}{R_0 R} + \frac{K}{2R^2}$$

$1/R_0$  : spontaneous curvature  
 $K$  : rigidity of interface (dimension of energy)

(holds only if  $R$  and  $R_0$  are much larger than the interfacial film thickness  $L$ )





# III. Existing Models - Curvature Effects

1. The Saturated Interface (Schulman)
2. Limitation of the Schulman Argument
3. Entropy Effects for Flexible Interfaces
4. Curvature Effects
5. Long-Range Interactions

$$F = \gamma - \frac{K}{R_0 R} + \frac{K}{2R^2}$$

- ✓ For ionic surfactants the steric considerations of Ninham and Mitchell may give an estimate of the spontaneous curvature.
- ✓ Addition of cosurfactant may act strongly on  $1/R_0$  and also on  $K$ .  
Theoretical two effects : **simple wedge effect & concentration effect**

## (1) Simple wedge effect

- Mitchell and Ninham : main role of cosurfactant is to change  $R_0$   
(different size of amphiphile molecules change its natural curvature)
  - Mitchell and Ninham, *J. Chem. Soc., Faraday Trans. 2* **77**, 601 (1981)
- de Gennes and Taupin : can adsorb and modify  $R_0$ ,  
but only a few are efficient to induce microemulsions

## (2) Concentration effect

- cosurfactant may migrate toward the regions of strong curvature : decreasing rigidity



### III. Existing Models - Curvature Effects

1. The Saturated Interface (Schulman)
2. Limitation of the Schulman Argument
3. Entropy Effects for Flexible Interfaces
4. Curvature Effects
5. Long-Range Interactions

$$F = \gamma - \frac{K}{R_0 R} + \frac{K}{2R^2}$$

Robbins writes the free energy  $F_d$  of one droplet in the form

$$F_d = \gamma(4\pi R^2) - \frac{K}{R_0}(4\pi R) + 2\pi K + \lambda \frac{4\pi R^3}{3}$$

Related to the chemical potential of the inner constituent.  
 $\lambda = 0$  for w/o in equilibrium with water

Optimal radius  $R$  by minimization of  $F_d$  and reaches the condition

$$dF_d/dR = \gamma(8\pi R) - 4\pi K/R_0 = 0 \quad \longrightarrow \quad \gamma = K/(2RR_0)$$

This procedure works remarkably well; both the estimates of  $R$  and  $\gamma$  are quite good for a number of nonionic surfactants.

All the discussion assumes droplets which are not far from spherical and rather monodisperse. But we should keep in mind that, whenever  $R > \xi_{k^2}$ , the shapes must be strongly nonspherical.



## IV. The Role of Flexibility - Comparison with Red Blood Cells

1. Comparison with Red Blood Cells
2. Statistics of a Random Interface

$$F = \gamma - \frac{K}{R_0 R} + \frac{K}{2R^2}$$

Two fundamental constants are associated with a saturated interface; the spontaneous curvature  $1/R_0$  and the curvature elastic constant  $K$ .

Models for red blood cells

The general idea is that, with  $\gamma = 0$ , we have giant fluctuations of the cell shape, which become observable (under phase contrast) with an optical microscope



# IV. The Role of Flexibility - Statistics of a Random Interface

1. Comparison with Red Blood Cells
2. Statistics of a Random Interface

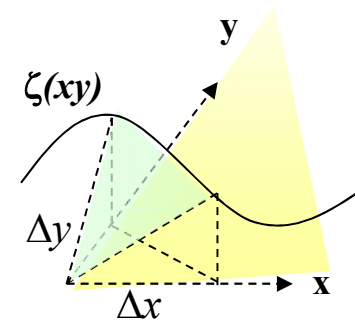
$$F = \gamma - \frac{K}{R_0 R} + \frac{K}{2R^2}$$

Assume that our interface has a negligible spontaneous curvature ( $1/R_0 \rightarrow 0$ ) and is close to a certain reference plane ( $xy$ ).

The distances between the plane and the interface will be called  $\zeta(xy)$ .  
The curvature is then

$$\frac{1}{R} = \frac{\partial^2 \zeta}{\partial x^2} + \frac{\partial^2 \zeta}{\partial y^2} \equiv \Delta_{\perp} \zeta$$

$$F_K = \int \frac{K(\Delta_{\perp} \zeta)^2}{2} = \sum_q \frac{K q^4 |\zeta_q|^2}{2}$$



Where we have gone to two-dimensional Fourier transforms

$$\zeta_q = \int dx dy \quad (xy) \exp [i(qxx + qyy)]$$

