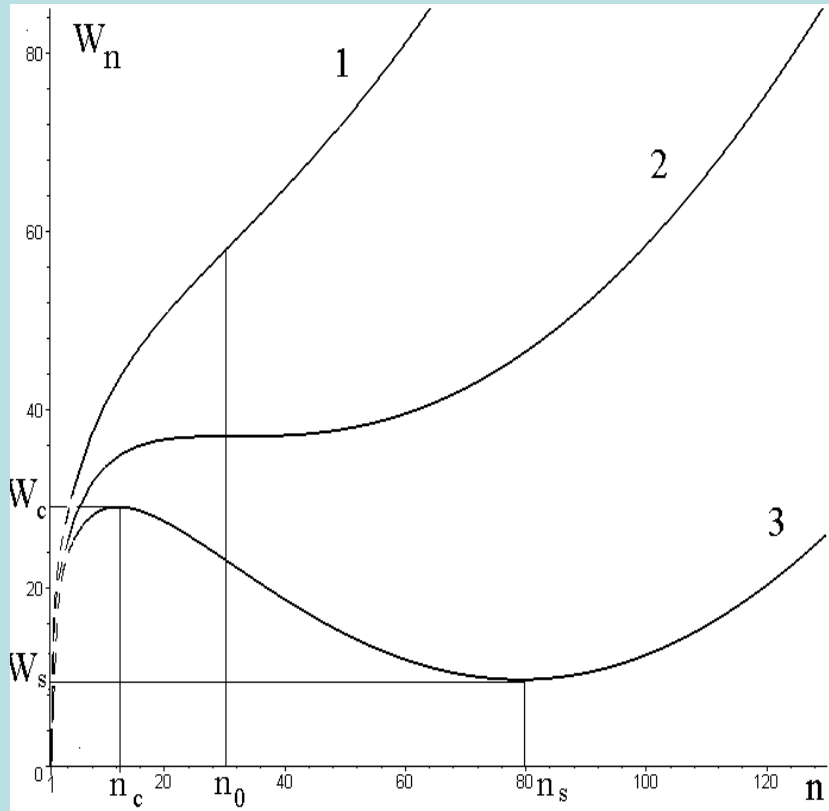


**Methods of the Nucleation  
Theory in Kinetics and  
Thermodynamics of  
Micellization**

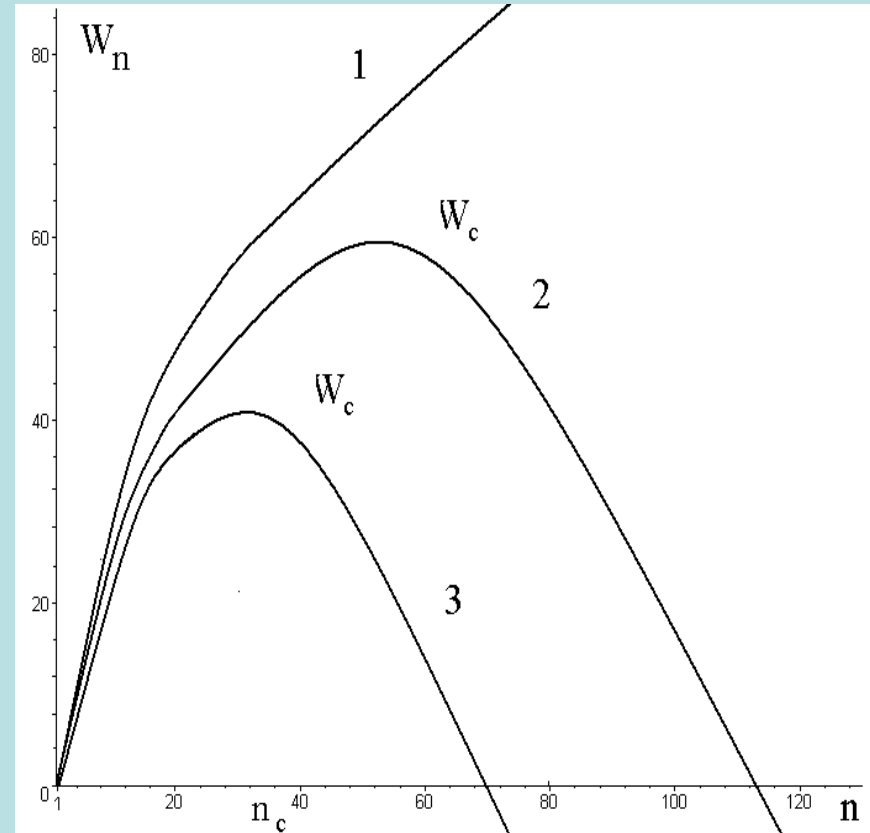
## Outline

- The work of aggregate formation in nucleation theory and micellization
- The droplet and quasi-droplet models
- Equilibrium and quasi-equilibrium Boltzmann distributions of aggregates
- Becker-Döring and fusion-fission kinetic equations of aggregation
- Fast and slow relaxation
- Ionic micellar solutions

# The work of aggregate formation in nucleation theory and micellization

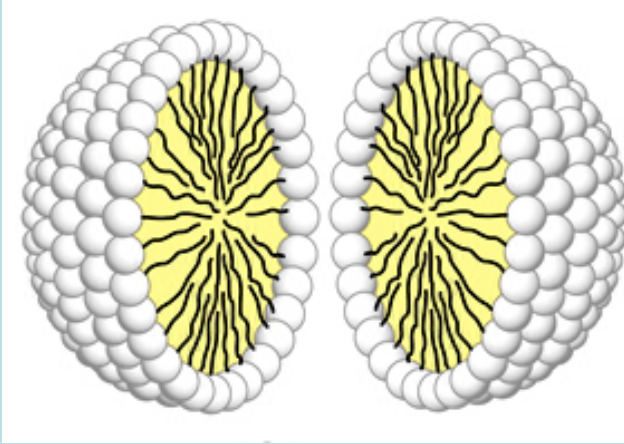


Work of aggregate formation as a function of aggregation number and concentration of surfactant monomers



Work of droplet formation as a function of aggregation number and vapor concentration

# The droplet model



$$W_n = b_1 n^{4/3} - \left[ \ln(c_1/c_{10}) + \frac{4}{3} (2b_1 b_3)^{1/2} \right] n + b_3 n^{2/3}$$

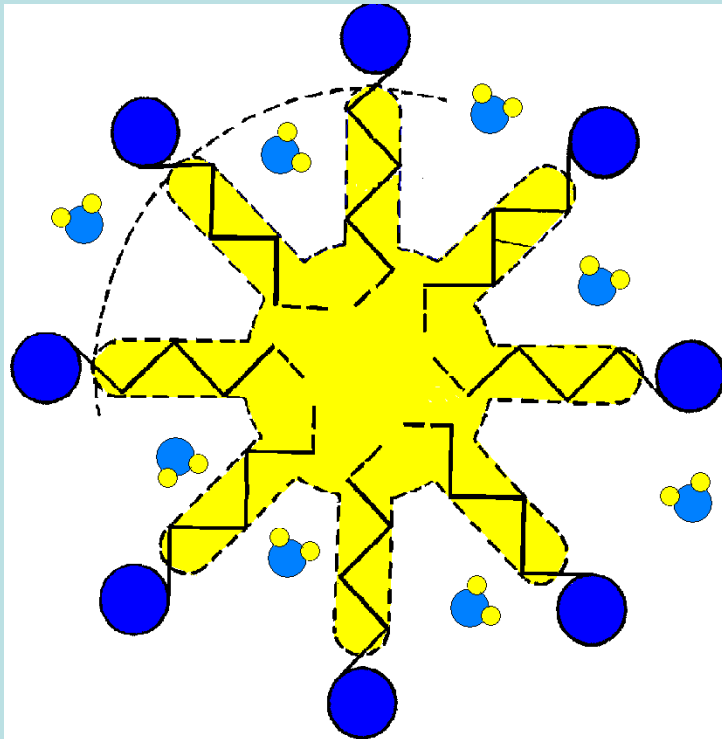
$$n_0 = (b_3 / 2b_1)^{3/2} \quad \text{the inflection point}$$

$b_1$  is proportional to the square of the monomer charge or to dipole moment (associated with the electric repulsion at the aggregate surface);

$b_3$  is proportional to the surface tension of the hydrophobic nucleus of the aggregate

The droplet model excludes a penetration of solvent molecules into the micelle core

# The quasi-droplet model



$$W_n = a_1 n^2 - a_3 n^{3/2} - \left[ \ln(c_1/c_{10}) - \frac{9a_3^2}{32a_1} \right] n$$

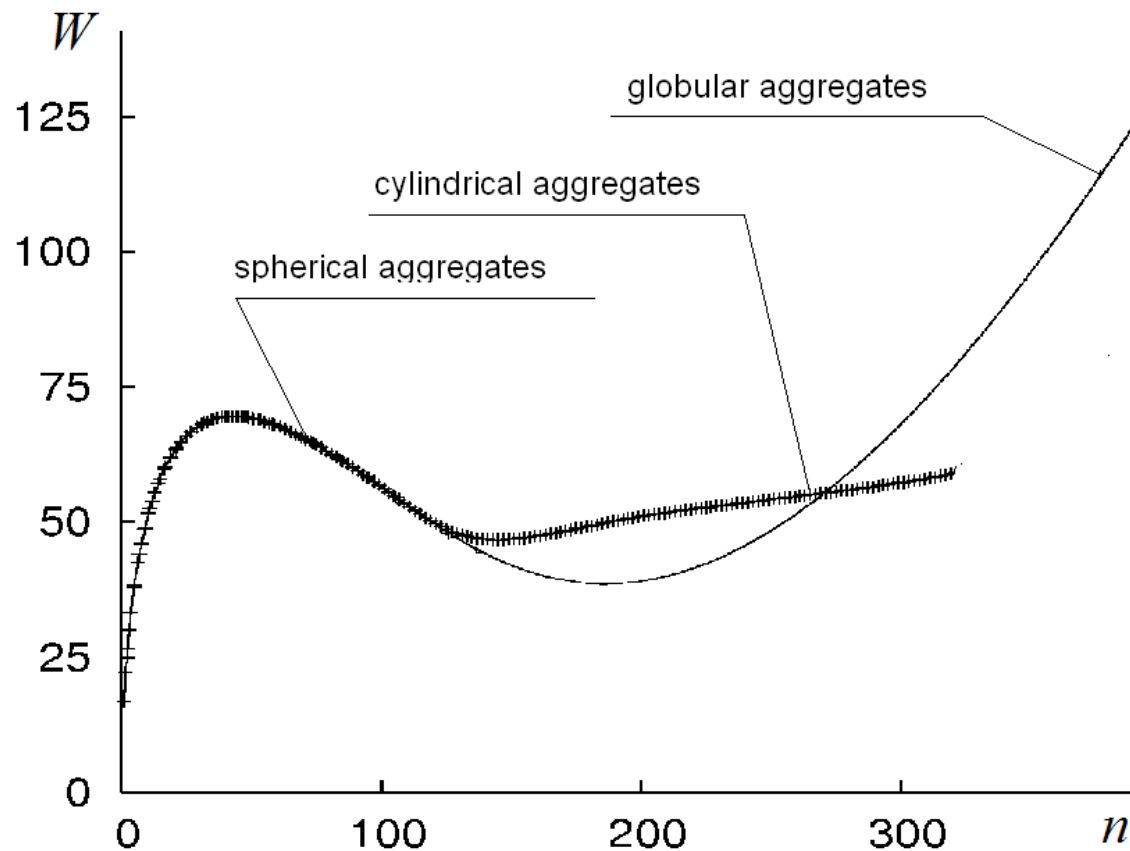
$$n_0 = 9a_3^2 / 64a_1 \quad \text{the inflection point}$$

$a_1$  is proportional to the square of the monomer charge or dipole (associated with the electric repulsion at the aggregate surface)

$a_3$  is proportional to the hydrophobic contribution per monomer

The quasi-droplet of molecular aggregate permits partial drowning of solvent molecules

# Polymorphic transformations of micelles

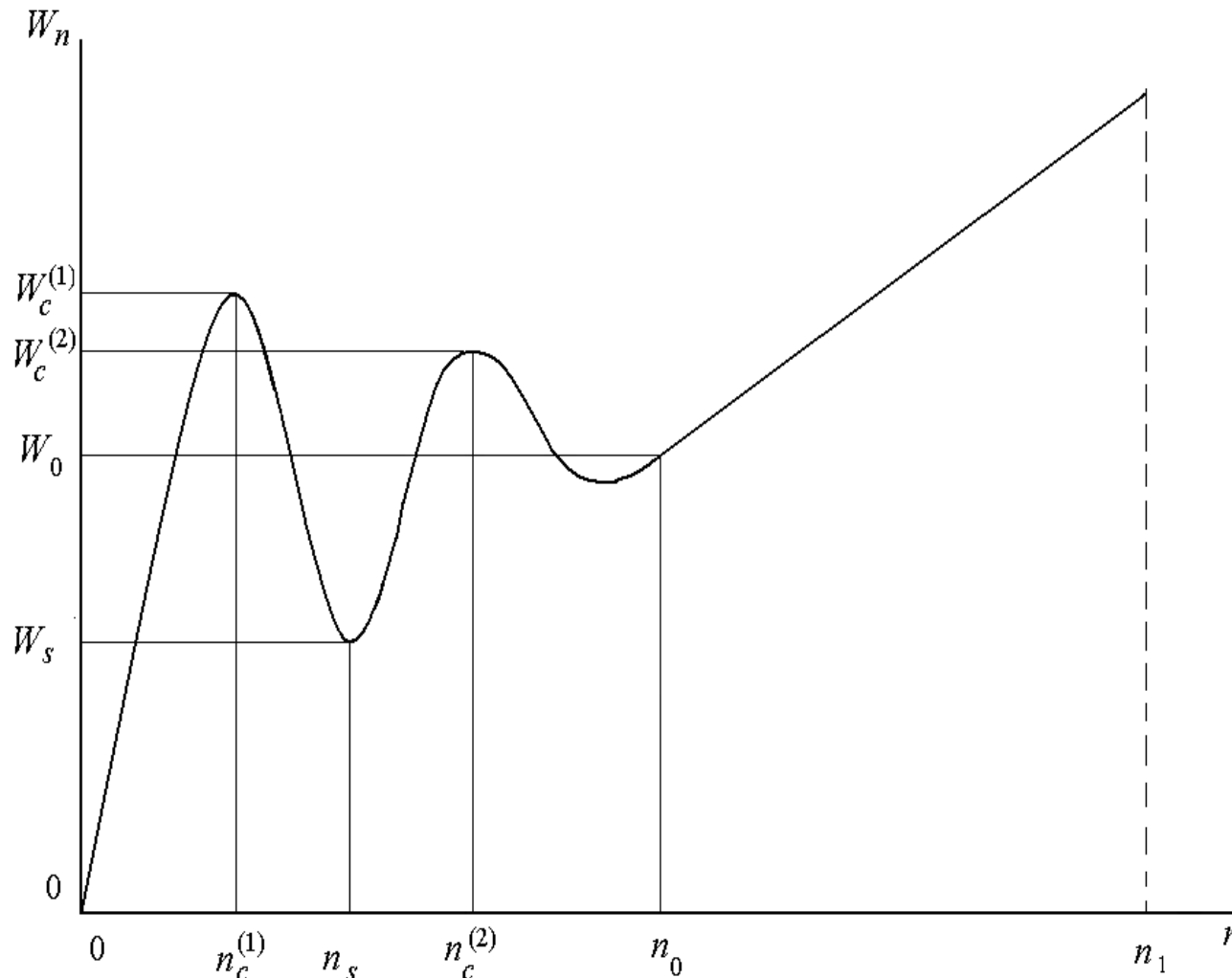


The work of aggregation was computed for a droplet model and the profiles for globular, spherical and cylindrical micelles as functions of the aggregation number. The results are shown for the total surfactant concentrations in solutions above the cmc<sub>2</sub>.

M.S.Kshevetskiy, A.K.Shchekin. The aggregation work and shape of molecular aggregates upon the transition from spherical to globular and cylindrical micelles. *Colloid Journal*. 2005. V.67.n.3.p.324-336.

M.S. Kshevetskiy, A.K. Shchekin, F. M.Kuni, Kinetics of Slow Relaxation upon the Competition between Globular and Small Spherocylindrical Micelles. *Colloid Journal*, 2008, Vol. 70, No. 4, pp. 455–461.

# Coexistence of spherical and cylindrical micelles



Work of aggregation as a function of aggregation number at the total surfactant concentration above cmc2

$$\frac{\partial W_n}{\partial c_1} = -(n-1)/c_1$$

$$W_n = W_s + \frac{(n - n_s)^2}{\Delta n_s^2}$$

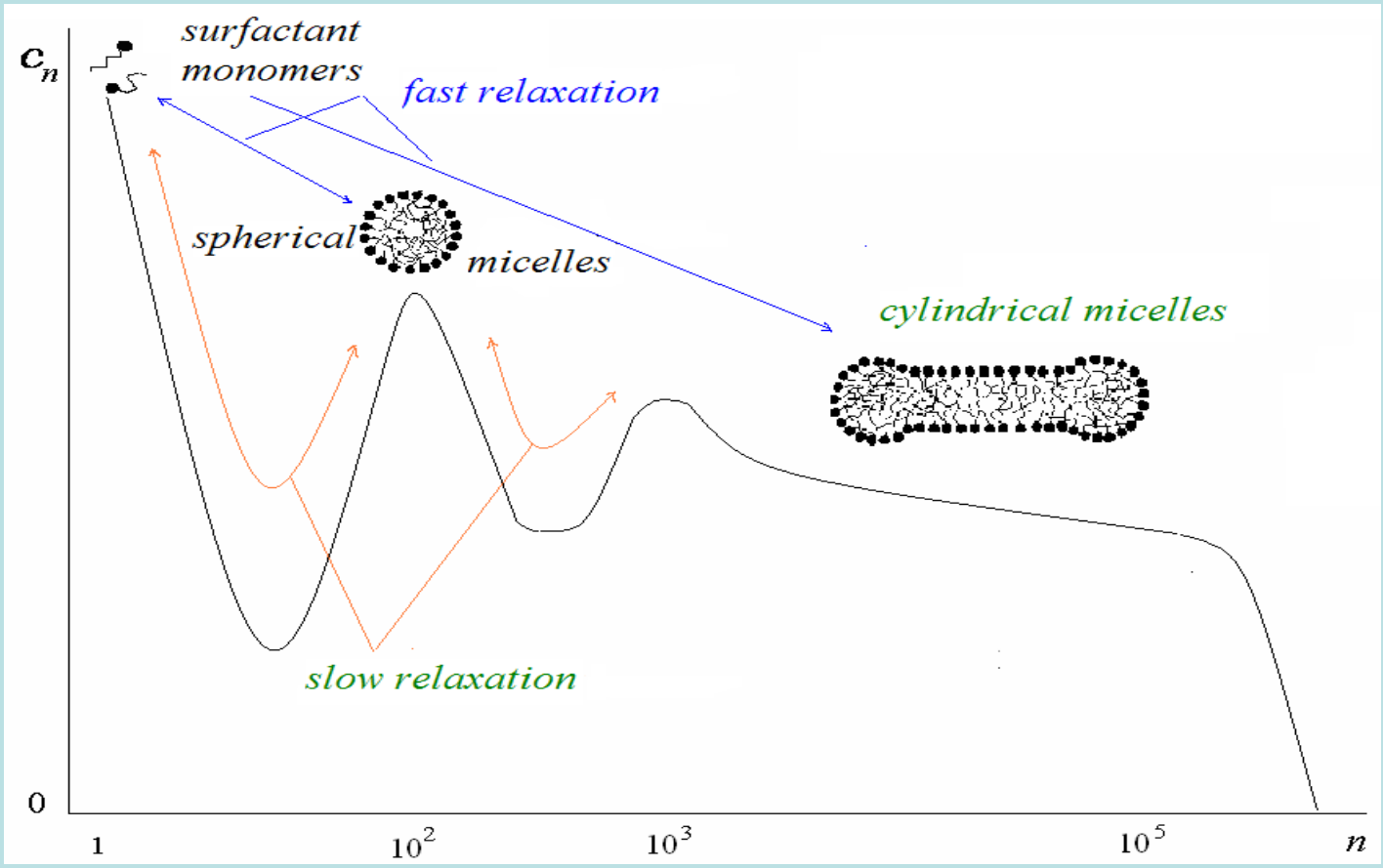
approximation for the aggregation work of stable spherical micelles

$$\Delta n_s = \left[ 2 / \left( \frac{\partial^2 W_n}{\partial n^2} \right)_{n=n_s} \right]^{1/2}$$

$$W_n = W_0 + \frac{n - n_0}{n_* - n_0}$$

approximation for the aggregation work of stable cylindrical micelles

# Equilibrium and quasi-equilibrium Boltzmann distributions of aggregates



quasi-equilibrium distribution of spherical aggregates

$$c_n = c_s e^{-(W_n - W_s)}$$

$$c_n = c_0 e^{-(W_n - W_0)}$$

quasi-equilibrium distribution of cylindrical aggregates

$$c_s = c_1 e^{-W_s}$$

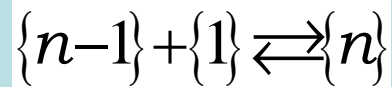
$$c_0 = c_1 e^{-W_0}$$

Condition of complete equilibrium



# Molecular mechanism of aggregation in surfactant solutions.

## Becker-Doring kinetic equation of aggregation



$$\frac{\partial c_n(t)}{\partial t} = J_{n-1} - J_n$$

$$J_n = j_n^+ c_n(t) - j_{n+1}^- c_{n+1}(t)$$

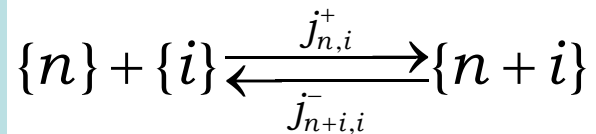
$$j_n^+ = \hat{j}_{\hat{n}_s}^+ \frac{c_1}{\hat{c}_1} \frac{n^{2/3}}{\hat{n}_s^{2/3}}$$

$$j_n^+ = \hat{j}_{\hat{n}_*}^+ \frac{c_1}{\hat{c}_1} \frac{n}{\hat{n}_*}$$

$$j_{n+1}^- = j_n^+ \frac{\hat{c}_n}{\hat{c}_{n+1}}$$

- stepwise attaching and detaching
- Becker-Döring kinetic equation of aggregation
- aggregation rate (nucleation rate)
- the attaching rate of surfactant molecules by a spherical aggregate
- the attaching rate of surfactant molecules by a cylindrical aggregate
- the detaching rate of surfactant molecules by an aggregate

# Fusion-fission kinetic equation of aggregation



aggregate attaching and detaching

$$\frac{\partial c_n}{\partial t} = \frac{1}{2} \sum_{i=1}^{n-1} J_{n-i,i} - \sum_{i=1}^{\infty} J_{n,i}$$

fusion-fission kinetic equation of aggregation

$$J_{n,i} \equiv j_{n,i}^+ c_n - j_{n+i,i}^- c_{n+i}$$

fusion-fission aggregation rate

$$j_{n,i}^+ = K_{n,i} c_i$$

the rate of of attaching aggregate  $\{i\}$   
by aggregate  $\{n\}$

# Kinetic description of fast relaxation

$$\xi_n \equiv (c_n - \hat{c}_n) / \hat{c}_n$$

deviation from the quasi-equilibrium distribution at the end of fast relaxation

As follows from the Becker-Döring equation

kinetic equation for spherical micelles and monomers at  $n_s - \Delta n_s < n < n_s + \Delta n_s$

$$\hat{c}_n \frac{\partial \xi_n(t)}{\partial t} = \hat{j}_s^+ \frac{\partial}{\partial n} \left( \hat{c}_n \frac{\partial \xi_n(t)}{\partial n} \right) - \xi_1(t) \hat{j}_s^+ \frac{\partial \hat{c}_n}{\partial n} - \xi_1(t) \hat{j}_s^+ \frac{\partial \hat{c}_n \xi_n(t)}{\partial n}$$

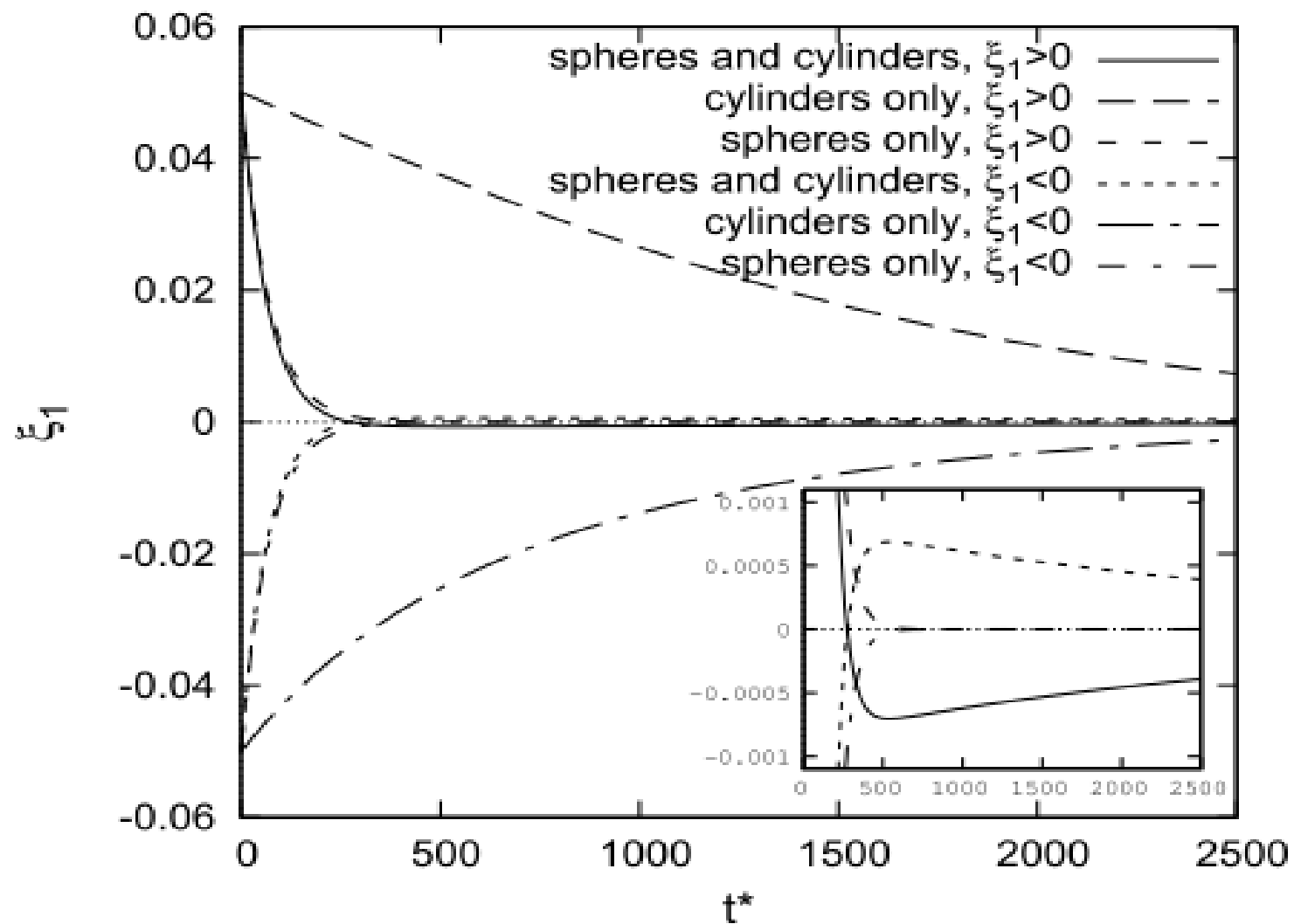
$$\hat{c}_n \frac{\partial \xi_n(t)}{\partial t} = \frac{\hat{j}_{\hat{n}_*}^+}{\hat{n}_*} \frac{\partial}{\partial n} \left( n \hat{c}_n \frac{\partial \xi_n(t)}{\partial n} \right) - \xi_1(t) \frac{\hat{j}_{\hat{n}_*}^+}{\hat{n}_*} \frac{\partial}{\partial n} (n \hat{c}_n) - \xi_1(t) \frac{\hat{j}_{\hat{n}_*}^+}{\hat{n}_*} \frac{\partial}{\partial n} (n \hat{c}_n \xi_n(t))$$

$$\hat{c}_1 \xi_1(t) = - \int_2^{\infty} n \hat{c}_n \xi_n(t) dn$$

Closed set of kinetic equations of fast relaxation

The balance of total amount of surfactant

kinetic equation for cylindrical micelles and monomers at  $n > n_0$



Relative deviation  $\xi_1$  of monomer concentration  $c_1$  from its quasi-equilibrium value

# Kinetic description of slow relaxation

$$c = c_1(t) + n_s c_{SM}(t) + n_* c_{CM}(t)$$

The balance of overall surfactant

$$dc_{SM}/dt = J^{(1)} - J''^{(1)} - (J^{(2)} - J''^{(2)}),$$

$$dc_{CM}/dt = J^{(2)} - J''^{(2)}$$

The last two equations follow from the Becker-Doering equation as the balance equations for variation of total concentrations of spherical and cylindrical micelles due to direct and reversal transitions in the quasi-steady regime over potential barriers between pre-micellar aggregates and spherical micelles and between spherical and cylindrical micelles.

$$J'_1 = \frac{c_1 j_c^{+(1)}}{\pi^{1/2} \Delta n_c^{(1)}} \exp(-W_c^{(1)}),$$

$$J''_1 = \frac{c_{SM} j_c^{+(1)}}{\pi \Delta n_c^{(1)} \Delta n_s} \exp[-(W_c^{(1)} - W_s)]$$

The direct and reversal steady fluxes over the first potential peak of the aggregation work

$$J'_2 = \frac{c_{SM} j_c^{+(2)}}{\pi \Delta n_c^{(2)} \Delta n_s} \exp[-(W_c^{(2)} - W_s)],$$

$$J''_2 = \frac{c_{CM} j_c^{+(2)}}{\pi^{1/2} (n_* - n_0) \Delta n_c^{(2)}} \exp[-(W_c^{(2)} - W_0)]$$

The direct and reversal steady fluxes over the second potential peak of the aggregation work

$\Delta n_c^{(1)}$  - the half-width of the first potential peak of the aggregation work

$\Delta n_c^{(2)}$  - the half-width of the second potential peak of the aggregation work

# Solution of kinetic equations of slow relaxation for coexisting spherical and cylindrical micelles

$$\delta c_1(t) \equiv c_1(t) - \tilde{c}_1$$

$$\delta c_{SM}(t) \equiv c_{SM}(t) - \tilde{c}_{SM}$$

$$\delta c_{CM}(t) \equiv c_{CM}(t) - \tilde{c}_{CM}$$

Closed set of equations of slow relaxation

$$d(\delta c_{SM})/dt = -\alpha_{11}\delta c_{SM} - \alpha_{12}\delta c_{CM}$$

$$d(\delta c_{CM})/dt = -\alpha_{21}\delta c_{SM} - \alpha_{22}\delta c_{CM}$$

if  $c \approx n_* c_{CM}$

$$\alpha_{11} \approx \frac{1}{\tilde{c}_{SM}} (\tilde{J}'_1 + \tilde{J}'_2),$$

$$\alpha_{12} \approx \frac{\tilde{n}_s}{c} \tilde{J}'_1 - \frac{2\tilde{n}_*}{c} \tilde{J}'_2,$$

$$\alpha_{21} \approx -\frac{1}{\tilde{c}_{SM}} \tilde{J}'_2,$$

$$\alpha_{22} \approx \frac{2\tilde{n}_*}{c} \tilde{J}'_2$$

$$\delta c_{SM} = A_1 e^{-t/t_{r1}} + A_2 e^{-t/t_{r2}}$$

$$\delta c_{CM} = B_1 e^{-t/t_{r1}} + B_2 e^{-t/t_{r2}}$$

$$t_{r2} \approx (2\tilde{c}_{SM} + \tilde{c}_{CM}) / 2\tilde{J}'_1$$

$$t_{r1} \approx \frac{1}{(1/\tilde{c}_{SM} + 2/\tilde{c}_{CM})} \frac{1}{\tilde{J}'_2}$$

These are the characteristic times of slow relaxation

$$t_{r2}/t_{r1} \gg 1$$

# Power and exponential laws of slow relaxation

In addition to the final stage of relaxation with the exponential law of decay of concentration disturbances in time, the preceding stage with the power law variation of concentrations in time has significance in the whole relaxation. It is just the power law stage when the main nonlinear changes in relaxing parameters of micellar solution occur that can be clearly fixed in experiment.

Between the first and second CMC

$$t_r \approx \frac{\tilde{c}_1}{\tilde{n}_s \tilde{J}'_1} \frac{1 + \frac{\tilde{\alpha}}{2} \frac{\Delta \tilde{n}_s^2}{\tilde{n}_s}}{\tilde{n}_s + \tilde{\alpha}^{-1}},$$

- the time of exponential relaxation

$$t_r^{(u)} \approx \frac{\tilde{c}_1}{\tilde{n}_s \tilde{n}_c \tilde{J}'_1} \left( 1 + \frac{\tilde{\alpha}}{2} \frac{\Delta \tilde{n}_s^2}{\tilde{n}_s} \right),$$

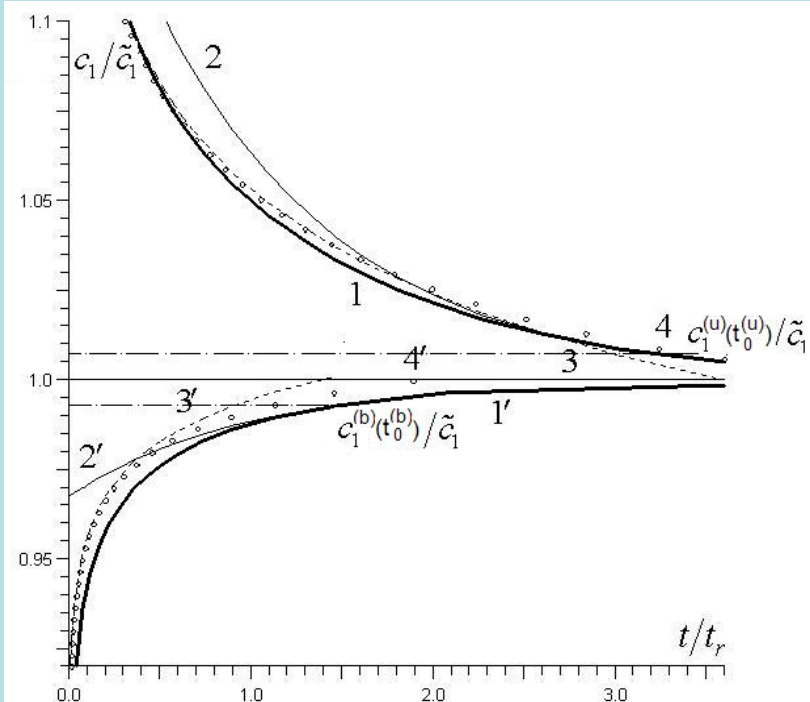
- the time of power relaxation from above

$$t_r^{(b)} \approx \frac{\tilde{c}_1}{\tilde{n}_s \tilde{J}'_1} \frac{\left( 1 + \frac{\tilde{\alpha}}{2} \frac{\Delta \tilde{n}_s^2}{\tilde{n}_s} \right)}{\left( \tilde{n}_s - \tilde{n}_c + \tilde{\alpha}^{-1} \right)}$$

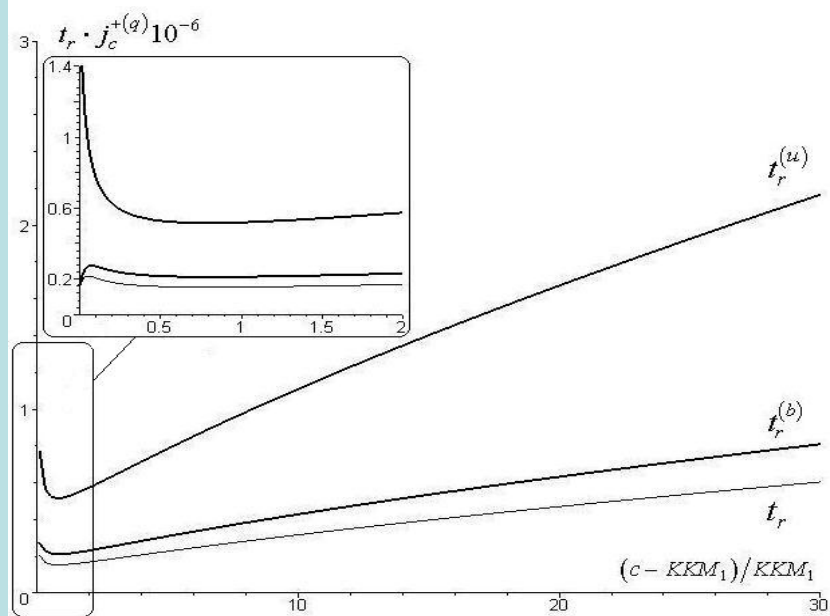
- the time of power relaxation from below

$$\tilde{\alpha} \equiv \frac{\tilde{n}_s \tilde{c}_M}{\tilde{c}_1}$$

micellization degree



The dependence of monomer concentration on time at slow relaxation between first and second cmc



The dependence of specific times of slow relaxation on the micellization degree



# Ionic micellar solutions

$$W_{\{n\}} \equiv \frac{\mu_{\{n\}}^s - \sum_i n_i \mu_i}{kT}$$

the minimal work required to form an ionic aggregate  $\{n\}$  around arbitrary surface-active ion

$$z_{\{n\}} = \sum_i n_i z_i$$

the aggregate charge number

$$\mu_{\{n\}}^s = G_{\{n\}}^0 + kT \ln \Lambda_{\{n\}}^3 + kT \ln a_1$$

the Gibbs energy of an ionic aggregate  $\{n\}$  around arbitrary surface-active ion

$$\mu_i = g_i^0 + kT \ln \Lambda_i^3 + kT \ln a_i$$

the chemical potential of the monomer of sort  $i$  in solution

$$\frac{\partial W_{\{n\}}}{\partial \ln a_i} = \delta_{i1} - n_i$$

$$W_{\{n\}} = W_{\{n\}}^h + W_{\{n\}}^{surf} + W_{\{n\}}^{conc} + W_q^{el}$$

$$W_q^{el} = \int_0^q \varphi_s(q') dq'$$

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