

Particles as surfactants and antifoams

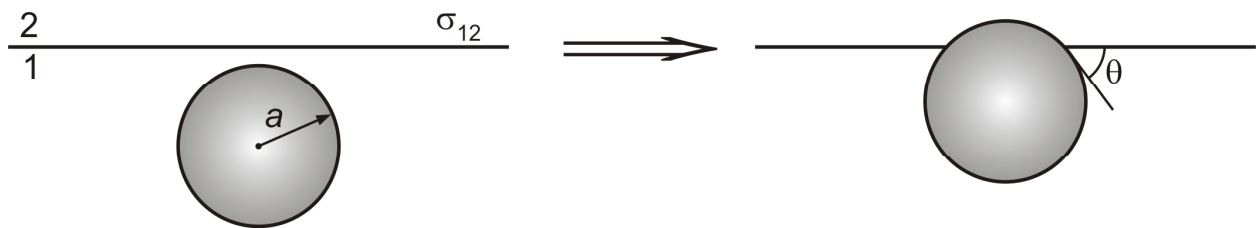
**Solutions of the problems for the Workshop 10:00-11:30
on 14th April, 2011 (Thursday)**

Problem 1 - Energy of particle adsorption.

The energy of particle adsorption on a fluid interface between phases 1 and 2 is given by the expression:

$$E_A = -\pi a^2 \sigma_{12} (1 - \cos \theta)^2 \quad (1)$$

where a is the particle radius and θ is the three-phase contact angle, measured through the phase from which the particle is adsorbed.



- (a) Calculate E_A for particles with radius 1 nm, 10 nm, and 100 nm. Assume a contact angle of 90° and $\sigma_{12} = 30$ mN/m. Compare the calculated adsorption energies to the thermal energy $kT = 4.1 \times 10^{-21}$ J.

Substituting $\cos(90^\circ) = 0$ and $\sigma_{12} = 0.03$ N/m into the equation for E_A , one obtains

$$E_A = -3.14 \times 10^{-18} \times 0.03 \approx -9.4 \times 10^{-20} \text{ J} \approx -23 \text{ } kT \text{ for particles with } a = 1 \text{ nm.}$$

$$E_A \approx -9.4 \times 10^{-18} \text{ J} \approx -2300 \text{ } kT \text{ for particles with } a = 10 \text{ nm.}$$

$$E_A \approx -9.4 \times 10^{-16} \text{ J} \approx -2.3 \times 10^5 \text{ } kT \text{ for particles with } a = 100 \text{ nm.}$$

It is seen that the adsorption energy is $|E_A| \gg kT$ even for nanometer sized particles. As a result, the adsorption of particles with size larger than several nanometers is practically irreversible (unless strong external detachment force is applied).

- (b) Calculate the energy of particle adsorption for particles with $a = 10$ nm, with contact angles of 10° , 90° , 150° .

As calculated above, $E_A \approx -9.4 \times 10^{-18}$ J ≈ -2300 kT for particles with $a = 10$ nm and $\theta = 90^\circ$.

For other contact angles, the result changes with the multiplier $(1 - \cos \theta)^2$, which leads to:

$$E_A \approx -2.2 \times 10^{-21} \text{ J} \approx -0.5 \text{ } kT \text{ for particles with } a = 10 \text{ nm and } \theta = 10^\circ.$$

$$E_A \approx -3.3 \times 10^{-17} \text{ J} \approx -8008 \text{ } kT \text{ for particles with } a = 10 \text{ nm and } \theta = 150^\circ.$$

These estimates show that the contact angle has strong effect on the energy of adsorption, especially when θ is very close to zero (or close to 180° , when the particle desorption into phase 2 is favored).

(c) For the particles described in (b), calculate the energy of particle desorption from the fluid interface – consider possible desorption into either of the neighboring fluid phases.

By definition, the desorption energy, E_D , is equal in magnitude and opposite in sign to the adsorption energy. Note that desorption is favored into the phase which wets better the particle – therefore, the desorption energy should be the smaller one (in magnitude) from the two energies:

$$E_D = \pi a^2 \sigma_{12} (1 \mp \cos \theta)^2 = \pi a^2 \sigma_{12} (1 - |\cos \theta|)^2 \quad (1.1)$$

where the “minus” sign corresponds to desorption into phase 1, whereas the “plus” sign corresponds to desorption into phase 2.

This means that $E_D = -E_A$ for particles with $\theta = 10^\circ$ and $\theta = 90^\circ$, whereas E_D for particles with $\theta = 150^\circ$ is

$$E_D = \pi a^2 \sigma_{12} (1 - |\cos 150^\circ|)^2 \approx 1.6 \times 10^{-19} \text{ J} \approx 41 kT \quad (1.2)$$

(d) Define the contact angle corresponding to the most stable particle attachment to the interface – explain your answer.

Equation (1.1) for E_D predicts maximum desorption energy at $\cos \theta = 0$, that is at $\theta = 90^\circ$.

Problem 2 – Interfacial tension of particle adsorption monolayers.

Calculate the surface tension, σ , of an interface with adsorbed particles (radius $a = 10 \text{ nm}$) or surfactant molecules (area per surfactant molecule 0.4 nm^2), assuming that the surface tension of the bare interface is $\sigma_0 = 72 \text{ mN/m}$, for the following cases:

(a) Surface coverage $\Theta = 30 \%$, equation of state of two-dimensional ideal gas:

$$\sigma = \sigma_0 - \Gamma kT \quad (2)$$

where Γ is the surface number concentration (number of particles or molecules per unit area) and $kT = 4.1 \times 10^{-21} \text{ J}$ is the thermal energy.

The area occupied per 1 particle in the monolayer is $A_0 = \pi a^2 \approx 3.14 \times 10^{-16} \text{ m}^2$. Therefore, the number concentration of particles in a 30 % occupied layer is $\Gamma = 0.3/A_0 \approx 9.6 \times 10^{14} \text{ particles/m}^2$. Thus we calculate $\sigma = 0.072 - 9.6 \times 10^{14} kT \approx 0.072 - 3.9 \times 10^{-6} \approx \sigma_0$.

For the surfactants $A_0 = 4 \times 10^{-19} \text{ m}^2$. The number concentration of surfactant molecules is $\Gamma = 0.3/A_0 \approx 0.75 \times 10^{18} \text{ molecules/m}^2$ and $\sigma = 0.072 - 0.75 \times 10^{18} kT \approx 0.072 - 0.003 \approx 69 \text{ mN/m}$.

(b) Surface coverage $\Theta = 80 \%$, equation of state of Volmer:

$$\sigma = \sigma_0 - \Gamma_\infty kT \frac{\Theta}{(1 - \Theta)} \quad (3)$$

By definition $\Gamma_\infty = 1/A_0$. Thus $\Gamma_\infty \approx 3.2 \times 10^{15} \text{ particles/m}^2$ and $\Gamma_\infty \approx 5 \times 10^{19} \text{ molecules/m}^2$. Substituting these values in the Volmer equation one obtains $\sigma \approx 0.072 - 0.53 \times 10^{-4} \approx \sigma_0$ for the particles, and $\sigma \approx 0.072 - 0.041 \approx 31 \text{ mN/m}$ for the surfactant.

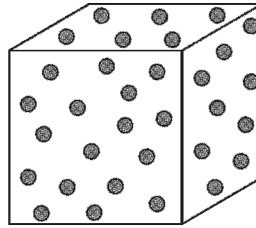
From these estimates one can conclude that the surfactant molecules start reducing the surface tension even at low surface coverage (30 %), whereas the particles are very inefficient at reducing surface tension even at very high surface coverage.

Problem 3 – Concentration of solid particles needed to form complete monolayers on the surface of dispersed drops in emulsions.

The specific surface area of the droplets in an emulsion (drop surface area per unit volume of the emulsion) is given by the expression:

$$S = 3\Phi/R \quad (4)$$

where Φ is the volume fraction of the dispersed drops and R is the mean drop radius.



(a) Derive eq. (4).

The specific surface area of all N droplets present in a given volume of the emulsion, V_{EM} , is

$$S = NA_d/V_{EM} = NA_d/(NV_d/\Phi) = 3\Phi/R \quad (5)$$

where we have used the fact that for spherical drops $A_d = 4\pi R^2$ and $V_d = (4/3)\pi R^3$ are the area and volume of a single drop.

(b) Derive an equation for the weight concentration of spherical solid particles with radius a and mass density ρ_p (initially dispersed in the continuous phase), needed to cover completely the surface of dispersed drops in an emulsion with drop radius R and volume fraction Φ .

Per unit volume of the emulsion we have surface area of the drops $S = 3\Phi/R$. To cover this area we need the following number of particles:

$$N_p \approx S/(\pi a^2) = 3\Phi/\pi R a^2 = 4\Phi a/RV_p \quad (6)$$

where $V_p = (4/3)\pi a^3$ is the particle volume. This number of particles are dispersed in the continuous phase, which has a volume $(1-\Phi)$ for unit volume of the emulsion. Therefore, the weight concentration of these particles in the continuous phase, used to prepare the emulsion is

$$C_p = N_p V_p \rho_p / (1 - \Phi) = 4 \rho_p \frac{\Phi}{(1 - \Phi)} \frac{a}{R} \quad (7)$$

More precisely, one can cover the surface by $C_p = 3.6 \rho_p \frac{\Phi}{(1 - \Phi)} \frac{a}{R}$, because the close packing of spherical particles on planar interface corresponds to ≈ 0.91 coverage of the surface.

- (c) Calculate the weight concentration of spherical solid particles with radius 30 nm, initially dispersed in the continuous phase, which are needed to cover completely the surface of the dispersed drops in 50 vol. % emulsion, with drop radius $R = 1 \mu\text{m}$. The mass density of the particles is 1 g/cm^3 .

Substituting these numbers in eq. (7) one obtains

$$C_p = 4 \times 10^3 \frac{0.5}{(1 - 0.5)} \frac{3 \times 10^{-8}}{10^{-6}} = 120 \text{ kg/m}^3 = 12 \text{ wt \%} \quad (8)$$

Note that around 25 times lower concentrations ($\approx 0.45 \text{ wt \%}$) are sufficient to cover the surface of the same drops by surfactant molecules, because the typical surfactant adsorption in complete adsorption monolayer is $\approx 1.5 \text{ mg/m}^2$.

- (d) Show that one can still use eq. 1 for emulsions containing polydisperse droplets, with R being the so-called “mean volume-surface radius” $R_{32} = \frac{\sum R_k^3}{\sum R_k^2}$, where the sums are taken over the third and the second moments of the radii of dispersed drops.

Following the derivation of eq. (4), but this time for polydisperse droplets, one obtains

$$S = A_t / V_{EM} = A_t \Phi / V_t = \Phi \frac{\sum (4\pi R_k^2)}{\sum \left(\frac{4}{3} \pi R_k^3 \right)} = 3\Phi / R_{32} \quad (9)$$

where A_t and V_t denote the total area and the total volume of all drops per unit volume of the emulsion.

Problem 4 – Maximal capillary pressure for rupturing of liquid film, stabilized by particle monolayer.

The capillary pressure of the fluid menisci, formed in the gaps between particles stabilizing liquid film (see the Figure below), is given by:

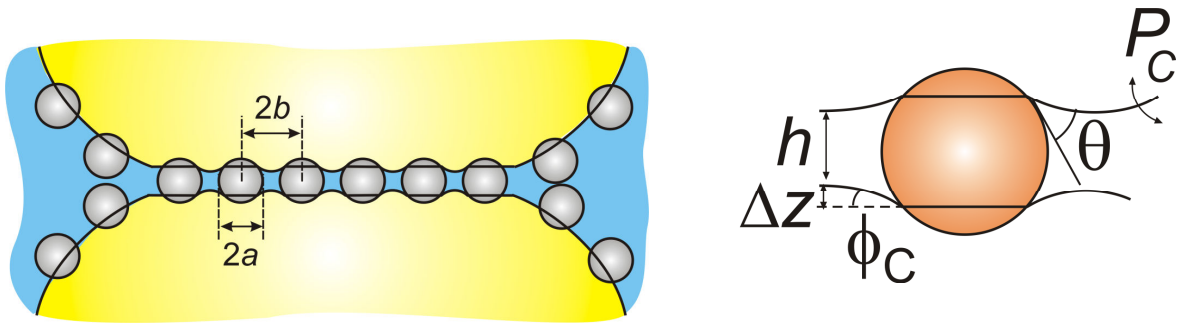
$$P_C = 2p(\sigma/a) = 2 \frac{\sin(\varphi_C + \theta) \sin \varphi_C}{\tilde{b}^2 - [\sin(\varphi_C + \theta)]^2} (\sigma/a) \quad (10)$$

where a is the particle radius, $\tilde{b} = b/a$ is the dimensionless distance between particles in the monolayer, θ is the three-phase contact angle, and φ_C is the slope angle at the contact line. For particles arranged in a uniform monolayer, the minimal distance between the two fluid film surfaces is given by the expression:

$$\tilde{h} = h/a = 2(\cos(\varphi_C + \theta) - \Delta\tilde{z}) \quad (11)$$

where $\Delta\tilde{z} = \Delta z/a$ is the dimensionless elevation of the meniscus above the level of the three-phase contact line:

$$\Delta\tilde{z} = \int_{\sin(\varphi_C + \theta)}^{\tilde{b}} \frac{\tilde{b}^2 - \tilde{r}^2}{\sqrt{(\tilde{r}/p)^2 - (\tilde{b}^2 - \tilde{r}^2)^2}} d\tilde{r} \quad (12)$$



- Calculate P_C as a function of h for particles with radius $a = 10$ nm. Assume contact angle $\theta = 0^\circ$, $\tilde{b} = b/a = 1.5$, and $\sigma_{12} = 30$ mN/m. For $\Delta\tilde{z}$ use the numerical data presented in Table 1. Find the maximum capillary pressure, P_C^{MAX} , at which the two fluid surfaces touch each other ($h = 0$) and the film ruptures.
- Calculate P_C as a function of h for particles with radius 10 nm and $\sigma_{12} = 30$ mN/m, at $\tilde{b} = b/a = 2$ and contact angles 0° , 45° and 85° . Calculate P_C^{MAX} for these conditions.
- Comment the dependence of P_C^{MAX} on the main physical variables – a , σ_{12} , θ , and b .

Solution

From the data presented in Table 1, for given slope angle, φ_C , one can calculate the thickness, h , using eq. (11) and the pressure using eq. (10). The results of such calculations are presented in Table 2 and plotted in the Figure below.

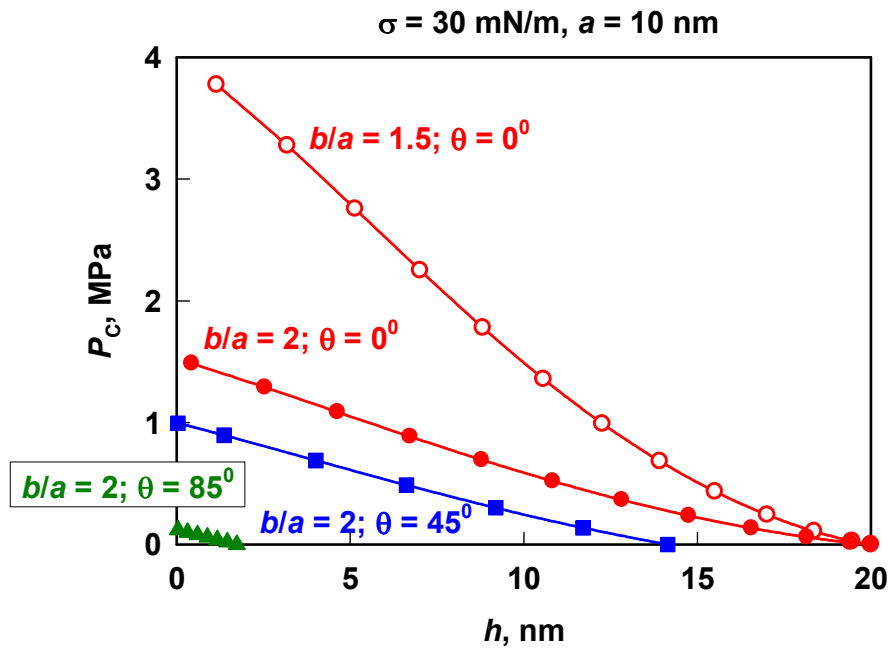
Table 2. $\Delta\tilde{z} = \Delta z/a$ for different values of the slope angle φ_C (expressed in radians), at different values of $\tilde{b} = b/a$ and θ . Calculated dimensionless thickness, h/a , and dimensionless pressure, p . The actual thickness in nanometers and the capillary pressure in MPa are also shown.

$\tilde{b} = b/a = 1.5; \theta = 0^\circ$					
φ_C	$\Delta\tilde{z} = \Delta z/a$	h/a	p	h, nm	P_C, MPa
0	0	2	0	20	0
0.1	0.022154	1.945699	0.004449	19.45699	0.026696
0.2	0.061638	1.836856	0.017855	18.36856	0.107131
0.3	0.104657	1.701359	0.040382	17.01359	0.24229
0.4	0.145518	1.551087	0.072269	15.51087	0.433616
0.5	0.181556	1.392052	0.113778	13.92052	0.682668
0.6	0.21177	1.227132	0.165091	12.27132	0.990549
0.7	0.236173	1.057338	0.226169	10.57338	1.357014
0.8	0.255436	0.882541	0.296531	8.825413	1.779185
0.9	0.27063	0.701959	0.37497	7.019592	2.249822
1	0.283039	0.514527	0.459213	5.145269	2.755281
1.1	0.293959	0.319275	0.545596	3.192749	3.273574
1.2	0.3044	0.115827	0.628897	1.158272	3.77338

$\tilde{b} = b/a = 2; \theta = 0^\circ$					
φ_C	$\Delta\tilde{z} = \Delta z/a$	h/a	p	h, nm	P_C, MPa
0	0	2	0	20	0
0.1	0.024972	1.940065	0.002498	19.40065	0.014987
0.2	0.07241	1.815312	0.009966	18.15312	0.059794
0.3	0.127483	1.655707	0.02232	16.55707	0.133922
0.4	0.183318	1.475487	0.039406	14.75487	0.236434
0.5	0.236094	1.282977	0.060965	12.82977	0.365793
0.6	0.283733	1.083205	0.086608	10.83205	0.519651
0.7	0.325274	0.879137	0.115765	8.791371	0.694591
0.8	0.360487	0.672439	0.147644	6.724385	0.885866
0.9	0.389616	0.463988	0.181196	4.639884	1.087174
1	0.413167	0.254271	0.215094	2.542709	1.290564
1.1	0.431759	0.043675	0.247758	0.436747	1.486549

$\tilde{b} = b/a = 2; \theta = 45^\circ$					
φ_C	$\Delta\tilde{z} = \Delta z/a$	h/a	p	h, nm	P_C, MPa
0	0	1.414214	0	14.14214	0
0.1	0.047671	1.17062	0.022727	11.7062	0.136363
0.2	0.092868	0.919326	0.050098	9.193258	0.30059
0.3	0.135318	0.662485	0.081234	6.624847	0.487403
0.4	0.175195	0.401467	0.114873	4.01467	0.68924
0.5	0.212946	0.137186	0.149397	1.371864	0.896381
0.55	0.231203	0.004055	0.166407	0.04	0.996

$\tilde{b} = b/a = 2; \theta = 85^\circ$					
ϕ_c	$\Delta\tilde{z} = \Delta z/a$	h/a	p	h, nm	P_c, MPa
0	0	0.174311	0	1.743115	0
0.01	0.004251	0.145878	0.003317	1.458779	0.0199
0.02	0.008497	0.117438	0.006641	1.174377	0.039847
0.03	0.012739	0.088992	0.009971	0.889916	0.059827
0.04	0.016979	0.06054	0.013305	0.605403	0.07983
0.05	0.021216	0.032084	0.01664	0.320844	0.099843
0.06	0.025451	0.003624	0.019976	0.036245	0.119854



These results show that the critical capillary pressure for film rupture, P_c^{MAX} , decreases with increasing the distance between the particles, b , and with the increase of the particle contact angle, θ . However, the highest critical pressures at $\theta \approx 0$ cannot be realized in practice, because the adsorption energy of the particles is low and the particles escape from the film during its formation and thinning. The experiments show that the optimal contact angle for emulsion and foam stabilization is in the range between 60° and 80° . Angles in this range ensure both sufficient particle adsorption on the interface and high film stability.

As seen from eq. (10), the smaller particles lead to higher pressure, because the curvature of the liquid meniscus around such particles is higher. In contrast, if the particles are separated from each other ($b/a \gg 1$), the capillary pressure decreases significantly even for small particles, because the curvature of the meniscus between such separated particles is smaller. Therefore, dense particle monolayers are required for high film stability.

It should be mentioned that, due to the action of lateral capillary forces, the particles can aggregate on the surface, thus forming empty regions in the film. Such regions lead to much lower film stability than that predicted for uniformly distributed particles. Therefore, in practice, the stability of the particle stabilized films is much lower than that predicted by these equations.