

Particles as surfactants and antifoams

**Problems for solving during the Workshop
10:00-11:30 on 14th April, 2011 (Thursday)**

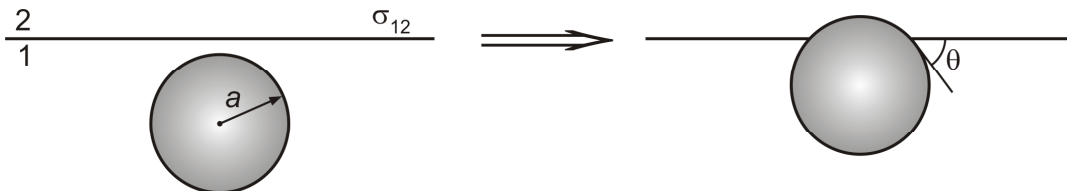
Problem 1 - Energy of particle adsorption.

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.
- (b) Calculate the energy of particle adsorption for particles with $a = 10$ nm, with contact angles of 10° , 90° , 150° .
- (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.
- (d) Define the contact angle corresponding to the most stable particle attachment to the interface – explain your answer.



Problem 2 – Interfacial tension of particle adsorption monolayers.

Calculate the surface tension, σ , of an interface with adsorbed particles (radius $a = 10$ nm) or surfactant molecules (area per surfactant molecule 0.4 nm²), assuming that the surface tension of the bare interface is $\sigma_0 = 72$ mN/m, for the following cases:

- (a) Surface coverage $\Theta = \Gamma/\Gamma_\infty = 30$ %, 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 $kT = 4.1 \times 10^{-21}$ J is the thermal energy.

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

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

Compare the efficiency of particles and surfactants to reduce the surface tension of liquids.

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).
- (b) Derive an equation for the weight concentration of spherical solid particles with radius a and mass density ρ (initially dispersed in the continuous phase), needed to cover completely the surface of dispersed drops in an emulsion.
- (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 .
- (d) Show that one can still use eq. 1 for emulsions containing polydisperse droplets, with R being the so-called “mean volume-surface radius” $R_{32} = \sum R_k^3 / \sum R_k^2$, where the sums are taken over the third and the second moments of the radii of dispersed drops.

Problem 4 – Maximal capillary pressure for rupturing of liquid film, stabilized by particle monolayer (only if you have time and software for numerical calculations).

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

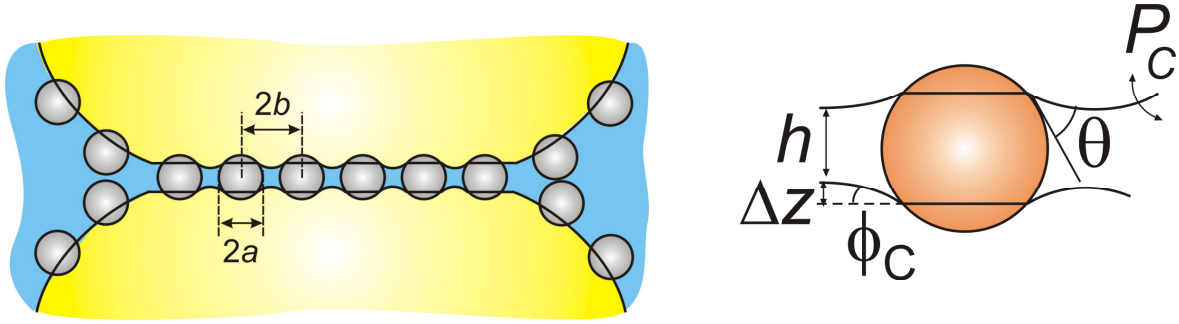
$$P_C = 2p(\sigma/a) = 2 \frac{\sin(\varphi_C + \theta) \sin \varphi_C}{\tilde{b}^2 - [\sin(\varphi_C + \theta)]^2} (\sigma/a) \quad (5)$$

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:

$$\tilde{h} = h/a = 2(\cos(\varphi_C + \theta) - \Delta\tilde{z}) \quad (6)$$

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

$$\Delta\tilde{z} = \int_{\sin(\varphi_C + \theta)}^{\tilde{b}} \frac{\tilde{b}^2 - \tilde{r}^2}{\sqrt{(\tilde{r}/p)^2 - (\tilde{b}^2 - \tilde{r}^2)^2}} d\tilde{r} \quad (7)$$



- (a) 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.
- (b) 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.
- (c) Comment the dependence of P_C^{MAX} on the main physical variables – a , σ_{12} , θ , and b .

Table 1. $\Delta\tilde{z} = \Delta z/a$ for different values of the slope angle φ_c (expressed in radians), at different values of $\tilde{b} = b/a$ and θ .

$\tilde{b} = b/a = 1.5; \theta = 0^\circ$		$\tilde{b} = b/a = 2; \theta = 0^\circ$		$\tilde{b} = b/a = 2; \theta = 45^\circ$		$\tilde{b} = b/a = 2; \theta = 85^\circ$	
φ_c	$\Delta\tilde{z} = \Delta z/a$	φ_c	$\Delta\tilde{z} = \Delta z/a$	φ_c	$\Delta\tilde{z} = \Delta z/a$	φ_c	$\Delta\tilde{z} = \Delta z/a$
0	0	0	0	0	0	0	0
0.1	0.022154	0.1	0.024972	0.1	0.047671	0.01	0.004251
0.2	0.061638	0.2	0.07241	0.2	0.092868	0.02	0.008497
0.3	0.104657	0.3	0.127483	0.3	0.135318	0.03	0.012739
0.4	0.145518	0.4	0.183318	0.4	0.175195	0.04	0.016979
0.5	0.181556	0.5	0.236094	0.5	0.212946	0.05	0.021216
0.6	0.21177	0.6	0.283733	0.55	0.231203	0.06	0.025451
0.7	0.236173	0.7	0.325274				
0.8	0.255436	0.8	0.360487				
0.9	0.27063	0.9	0.389616				
1	0.283039	1	0.413167				
1.1	0.293959	1.1	0.431759				
1.2	0.30444						