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Structure of bidisperse foams and emulsions on flat surfaces

The model calculations have been performed of the energy of miscibility related to the formation of concentrated dispersion systems composed of two types of liquid or gas particles A and B, immersed in a liquid medium C, placed between two parallel plates. The most important characteristic of the systems is the determining effect of the surface tension acting along the A–C and B–C interfaces on the structure of the forming foams or emulsions. It has been found that the bidisperse mixtures of particles A and B at the ratio 1:2 are not stable if the surface tension of particles B is greater than that of particles A. The mixing of particles A and B of the same surface tension is not spontaneous, which excludes a spontaneous formation of ordered bidisperse foams. However, there are certain ranges of the size ratio of the particles A and B, in which spontaneous structures can be observed to form, provided that the surface tension of particles B is low as compared with that of particles A.

Fast development of nanotechnology in recent years has aroused an increasing interest in the self-organized structures, in which the range of the ordering forces and the ordering scale lie between the atomic and macroscopic scale, known as the mesoscale self-assembly MESA [1]. Porous materials showing high degree of ordering have become a subject of considerable interest because of their potential application in science and technology [2] as photonic bandgaps [3] and optical stop-bands [4] for electromagnetic radiation of the wavelength comparable to the pore diameters, as structural materials of low density [5], or thermal and acoustic insulators [6]. Of particular concern are the methods of obtaining such materials employing the process of self-organization.

The three-dimensional hexagonal MESA can be obtained (due to the capillary interactions) from the concentrated monodisperse emulsions through polymerisation (organic MESA) or gelation (inorganic MESA, e.g. titania, silica, zirconia) [7] and evaporation of the redundant phase. The use of drained monodisperse foams for production of highly-organized structures has not been worked out yet. The reason seems to be the much complex structure of the foams. The problem is not new [8] but still controversial [9].

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The aim of the study is to assess the energies of formation of the mixed emulsions or foams composed of two types of particles placed in a thin region between the parallel plates, assuming that the volume of the dispersion medium is small enough for the system to be classified as Polyedershaum [10].

1. A SIMPLIFIED MODEL

Let's consider a three-phase system made of a concentrated foam or emulsion composed of two types of particles (A and B) dispersed in the phase C. The amount of the dispersion medium is so low that it occurs in the system as a thin film amongst the particles A and B. The system is placed between two parallel plates. The distance between the plates is so small that the particles assume the shape of a prism, whose bases are at the surface of the plates. The change in the surface energy corresponding to the formation of boundary walls between the particles A and B in the mixture can be calculated for a given structure of the mixture, according to simple geometry laws, (see Fig. 1) from the equations:

$$E_{\mathrm{M}} = \frac{2}{3}\sqrt[4]{3^3}\sqrt{2V_0}\,d\left(\sqrt{3\Phi}\left(\gamma_{\mathrm{A}}-\gamma_{\mathrm{B}}\right)+3\gamma_{\mathrm{B}}\right) \qquad \text{for} \quad \Phi \le 3/4 \qquad (1)$$

$$E_{\mathrm{M}} = 2\sqrt[4]{3}\sqrt{2V_0}\,d\left(\gamma_{\mathrm{A}}+\sqrt{1-\Phi}\left(\sqrt{3}\left(\gamma_{\mathrm{A}}-\gamma_{\mathrm{B}}\right)-2\gamma_{\mathrm{A}}\right)\right) \qquad \text{for} \quad \Phi \ge 3/4 \qquad (2)$$

where Φ is the volume fraction of particles A in the mixture (because of a very low volume of phase C, $\Phi = V_{\mathrm{A}}/(V_{\mathrm{A}}+2V_{\mathrm{B}})$, E_{M} – is the surface energy of the mixture of particles A and B, V_{A} and V_{B} – are the volumes of the particles A and B, V_0 – the total volume of the elementary cell in the emulsion (A+2B), γ_{A} and γ_{B} – are the values of surface tension acting along the A–C and B–C interfaces, and the values of γ_{A} and γ_{B} do not characterize pure components but saturated solutions.

The change in the surface energy corresponding to the formation of two separated regions containing particles A or B can be found from the formula:

$$E_{\mathrm{D}} = 2\sqrt[4]{3}\,d\left(\sqrt{2V_0\Phi}\,\gamma_{\mathrm{A}}+2\sqrt{V_0\left(1-\Phi\right)}\gamma_{\mathrm{B}}\right) \qquad (3)$$

Fig. 1 presents the dependence of the relative energy of mixing $E=E_{\mathrm{M}}/E_{\mathrm{D}}$ on the volume fraction of particles A for different values of γ_{A} and γ_{B}. As follows from this dependence, apart from the case when particles A and B form regular hexagons (the structure 5 in Fig. 1, $\Phi = 1/3$), relative mixing energy is higher than one, which means that particles A and B will separate spontaneously, if $2\gamma_{\mathrm{B}} > \gamma_{\mathrm{A}}$. This also means that a foam or emulsion composed of one type of particles and forming one of the structures shown in Fig. 1 cannot be stable (except the structure 5). If $2\gamma_{\mathrm{B}} < \gamma_{\mathrm{A}}$, the relative energy of mixing for $\Phi > 3/4$ takes values lower than one, which indicates a tendency to a spontaneous formation of a mixture.

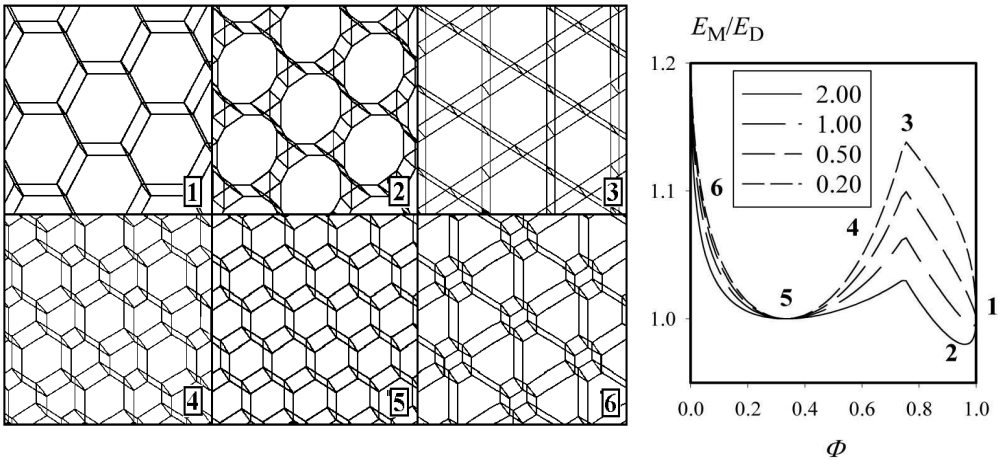

Fig. 1. Hypothetical structures of emulsions obtained by mixing A and B particles (the number ratio of A and B particles is equal to 1:2) at a different volume ratio Φ and the corresponding dependencies of the relative energy of mixing $E=E_M/E_D$ on Φ (values of γ_B/γ_A are included in the figure).

2. THE MODEL TAKING INTO ACCOUNT THE WALL CURVATURE

If the particles A and B differ in the surface tension, the walls between them must be curved. The volumes of particles A and B (curved triangular and hexagonal prisms) are then expressed as:

$$V_A = 6R^2\left(\sqrt{3}\sin\left(\frac{L_A}{2R}\right)^2 - \frac{1}{2}\sin\left(\frac{L_A}{R}\right) + \frac{1}{2}\frac{L_A}{R}\right)d \tag{4}$$

$$V_B = \frac{3}{2}R^2\left(\frac{2}{\sqrt{3}}\sin\left(\frac{L_B}{2R}\right)^2 + \sin\left(\frac{L_B}{R}\right) - \frac{L_B}{R}\right)d \tag{5}$$

where L_A and L_B stand for the lengths of the curved edges of particles A and B, R – is the radius of the wall curvature.

Minimising the energy of mixing calculated on the basis of the lengths of the curved A–B walls in the mixture, (eq. (4) and (5)), the radii of the wall curvature and the values of the relative energy of mixing E, were obtained. The results are presented in Fig. 2.

The convexity of A–B walls decreases with the volume fraction of particles A. The $R=f(\Phi)$ dependencies are strongly influenced by the surface tension ratio γ_B/γ_A. Analysis of the values of the energy of mixing shows that at low values of γ_B/γ_A there is a wide range of the volume fraction for which a spontaneous formation of highly organized bidisperse foams and emulsions can be expected in the system analyzed. This result encourages the search for other self-organizing structures in more complex systems.

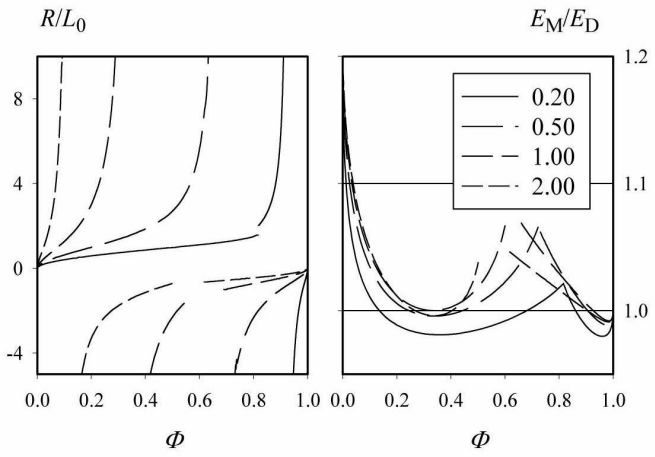

Fig. 2. The relative radius of the A–B walls curvature and the relative energy of mixing versus the volume fraction of particles A, for different ratios of the surface tensions (γ_B/γ_A values are included in the figure)

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STRUKTURA BIDYSPERSYJNYCH PIAN I EMULSJI NA PŁASKICH POWIERZCHNIACH

Przeprowadzono obliczenia modelowe energii mieszania związanej z powstawaniem stężonych układów dyspersyjnych złożonych z dwóch rodzajów ciekłych lub gazowych cząstek A i B rozproszonych w ciekłym ośrodku C znajdującym się pomiędzy zbliżonymi do siebie równoległymi płytami. Zasadniczą cechą rozważanych układów jest decydujący wpływ napięcia powierzchniowego działającego wzdłuż powierzchni A-C i B-C na powstające struktury pian lub emulsji. Stwierdzono, że bidyspersyjne mieszaniny cząstek A i B w stosunku 1:2 nie są stabilne, jeżeli napięcie powierzchniowe cząstek B jest większe niż cząstek A. Mieszanie cząstek A i B o takim samym napięciu powierzchniowym nie zachodzi samorzutnie, co między innymi wyklucza spontaniczne tworzenie uporządkowanych bidyspersyjnych pian. Stwierdzono natomiast, że istnieją określone przedziały stosunku wielkości cząstek A i B, w których można obserwować powstawanie samoporządkujących się struktur, jeżeli napięcie powierzchniowe cząstek B jest małe w porównaniu z napięciem powierzchniowym cząstek A.