drained foams and emulsions, self-organization, interfacial energy

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THE FILLING UP TETRAHEDRAL NODES IN THE MONODISPERSE FOAMS AND EMULSIONS WITH REULEAUX-LIKE TETRAHEDRA

The formation energy of cellular systems composed of two immiscible fluids, A and B, immersed in a continuous liquid medium C, has been calculated in order to test the possibility of decoration of tetrahedral nodes in the cellular B network, with smaller A cells. Interfacial tensions acting along A-C and B-C interfaces were assumed to be the only driving forces determining the polyhedral shape of network cells. The self-organization of mixed networks, occurring as a result of cell rearrangement during the draining process as well as due to topological transformation in drained systems, has been discussed.

The drained foams and emulsions (*i.e.* systems with a negligibly small volume fraction of the continuous phase, often termed as cellular fluids) are space filling structures composed of polyhedral cells. The 2D networks are highly-ordered patterns when composed of monodisperse or bidisperse cells [1, 2]. The 2D bidisperse patterns demonstrate a very interesting pseudo-phase behavior and anisotropic properties, which might be of interest in a number of practical applications [3].

The paper concerns the formation and stability of 3D patterns in three-phase, bidisperse cellular fluids. It deals with structures formed as a result of the introduction of smaller cells into a monodisperse cellular fluid composed of larger cells and represented by the Kelvin [4], Weaire-Phelan [5] or ideal [6] network.

1. MODEL

The initial two-phase system consists of monodisperse fluid cells B dispersed in a liquid C. The volume of the dispersion medium is so low that the B cells form the space-filling polyhedra organized into a network. The network fulfills the Plateau requirement. We consider the insertion of A cells ($V_A << V_B$, V is the volume of a

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single cell) into the B network (see Fig. 1). The shape of A cell depends on its target place in the network. The spherical, di-, tri- and tetrahedral shapes of A cells are taken into consideration (Fig. 2).

The relative interfacial energy excess, Ψ, resulting from the insertion of A cells into the network, further also named as the relative mixing energy, is defined by:

$$\Psi = \left(E_{\mathrm{mix}} - E_{\mathrm{ref}}\right) / E_{\mathrm{ref}} \tag{1}$$

where E_{mix} is the interfacial energy of a mixed network whereas E_{ref} is the sum of interfacial energies of two reference networks, *i.e.* composed of monodisperse A and B cells, respectively. Systems under consideration are assumed to be unbounded networks or networks large enough to neglect the influence of boundary conditions on their topology.

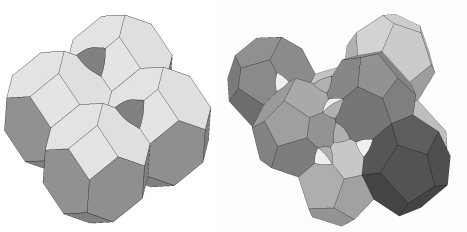

Fig. 1. The fragments of exemplary mixed networks: tetrahedral nodes decorated with A cells in the Kelvin network (left) and Weaire-Phelan network (right).

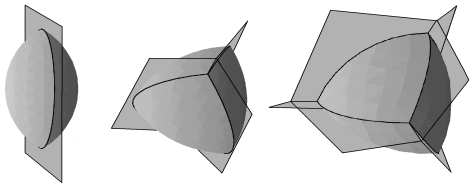

Fig. 2. The shapes of A cells (from the left: the lens ($1_2 1_{-1}$), the trihedron ($2_3 2_{-3}$), and the tetrahedron ($3_4 3_{-6}$)), corresponding to different cell locations in the network (wall, edge and tetrahedral node, respectively).

The value of E_{mix} is calculated from the equation:

$$E_{\mathrm{mix}} = W\, s_{\mathrm{R}}\, L^2\, \gamma_{22} + N_{\mathrm{Ins}}\, E_{\mathrm{A}} \tag{2}$$

where N_{Ins} is the number of A cells per one B cell in the mixed network, W is the coefficient identifying the recurrent part of the B polyhedron surface in the network, L is the length of the B polyhedron edge and E_{A} is the interfacial energy of the polyhedron A incorporated into the network:

$$E_{\mathrm{A}} = S_{\mathrm{n+}}\, \gamma_{12} - S_{\mathrm{n-}}\, \gamma_{22} \tag{3}$$

where S denotes the total surface area of A cell and γ stands for the film tensions. The indices "n+" and "n–" correspond to two opposite effects exerted by the A cell insertion on the network film surface area, that is, the simultaneous gain and reduction of the surface due to the introduction of a number f_{outer} and the elimination of a number f_{inter} of polygons, respectively. The values of f_{outer} and f_{inter}, corresponding to different A cell shapes, are collected in the Table 1, where the following notation describing the cell topology is used: $\mathrm{X_aY_{-b}}$ denotes a polyhedron formed by a number a of X-gons, which cuts out a number b of Y-gons from the initial network films.

The film tensions in Eq. (3) and the relative film tension, μ, are defined as:

$$\gamma_{22} = 2\gamma_2/\gamma_1\,, \qquad \gamma_{12} = (\gamma_1 + \gamma_2)/\gamma_1\,, \qquad \mu = \gamma_2/\gamma_1 \tag{4-6}$$

where γ_1 and γ_2 are interfacial tensions acting along A-C and B-C interfaces.

The s_R coefficient, whose value depends on the network type (Table 1), is defined as:

$$s_R = S_B/L^2 \tag{7}$$

where S_B denotes the surface area of B polyhedra.

The values of S_{n+} and S_{n-} together with A cell volumes, V_A, are calculated for different film curvatures and cell sizes. Below, there are shown, for the sake of illustration, the calculations performed in cases of very simple topologies, that is, if A cells are spherical:

$$V_A = \frac{4}{3}\pi R^3, \qquad S_{1+} = 4\pi R^2\,, \qquad S_{1-} = 0 \tag{8-10}$$

and, if A cells are dihedral:

$$V_A = \frac{2}{3}\pi h^2(3R - h), \qquad S_{2+} = 4\pi R\,h\,, \qquad S_{2-} = \pi r^2 \tag{11-13}$$

where R is the outer face curvature radius, r is the radius of sphere-sphere intersection area and $h = R - \sqrt{R^2 - r^2}$.

Table 1. The parameters characterizing polyhedra in the mixed and initial networks

	Topology	f_{outer}	f_{inter}	N_{Ins}	k_{Sp}	s_R	Q *
Sphere (A)	1_1	1	0	–	–	–	(1)
Lens (A)	$1_2 1_{-1}$	2	1	–	–	–	–
Trihedron (A)	$2_3 2_{-3}$	3	3	–	–	–	–
Tetrahedron (A)	$3_4 3_{-6}$	4	6	–	–	–	0.302
Kelvin net. (B)	$4_6 6_8$ (5.14_{14})	14	–	6	0.5	26.78	0.753 (0.757**)
Weire-Phelan n. (B)	$5.11_{13.5}$	13.5	–	5.75	0.522	26.65	0.764
Ideal network (B)	$5.10_{13.39}$	13.39	–	5.695	0.527	26.16	0.776

* Isoperimetric quotiens for flat faced polyhedra except values placed in parenthesis.

** The value corresponding to the deformed Kelvin tetrakaidecahedron variant of the network.

2. RESULTS AND DISCUSSION

The influence of the relative interfacial tension on the film curvature radius, for the different A cell shapes, is illustrated in Fig.3. The R values have been found by the minimization of the total interfacial energy of A cells. As follows, only for the

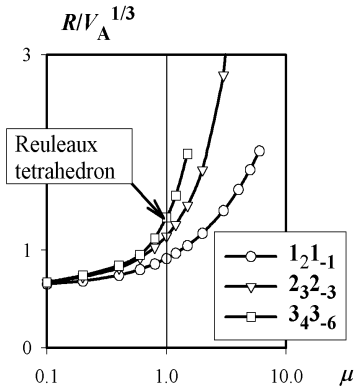

Fig. 3. The influence of the relative film tension (μ) on the film curvature radius (R).

extremely low μ values the curvature radius takes a minimum value corresponding to the spherical A cell. An increase in μ is accompanied by an increase in R, irrespective of the object shape. If $R \to \infty$ the $3_4 3_{-6}$ solid tends to the regular flat-walled tetrahedron, whereas the $1_2 1_{-1}$ and $2_3 2_{-3}$ solids collapse. For μ=1 the $3_4 3_{-6}$ solid gets the shape of a Reuleaux-like tetrahedron (the Reuleaux tetrahedron is the solid common to four spheres of equal radius placed so that the center of each sphere lies on the surface of the other three).

The dependencies of the mixing energy Ψ on the A cell volume fraction in the system, for different A shapes, are collected in Fig. 4. The results presented correspond to the introduction of A cells into the ideal network. However, the results obtained with the networks based on the Kelvin and Phelan-Weaire conjectures are very similar to those presented in Fig. 4, which is due to the fact, that the isoperimertic quotients[1], Q, of these networks take almost the same values as the quotient of the ideal polyhedron (Table 1). In Fig. 4 the effect of the relative film tension on the mixing energy is also shown. As seen, the values of μ, needed to get $\Psi<0$, depend on A cell shape and increase in the sequence: spheres, di-, tri- and tetrahedra; the limiting μ value found in the case of spheres is very small and unrealistic. It is noteworthy that for the $3_4 3_{-6}$ objects with faces of the optimized curvature, placed at tetrahedral nodes, $E_{mix} < E_{ref}$ in the whole range of the μ values studied.

The effect of A cell shape on E_{mix} at different values of μ and A cell volume fractions is illustrated in Fig. 5. As shown, if $\mu \geq 1$, the only stable form of A cell is the tetrahedron $3_4 3_{-6}$, which means that the mixed network is stable but it cannot be formed spontaneously because the energies of transient states, containing 1_1, $1_2 1_{-1}$ and $2_3 2_{-3}$ species, are positive. Formation of a mixed network requires an additional energy supply. For all mixed network studied there is a range of μ values at which $\Psi<0$, however, the networks containing $3_4 3_{-6}$ objects are always of the lowest energy. Thus, the A cells can migrate inside the B network taking different shapes (spheres in the B cell interior, dihedra at the walls and trihedra at the edges), corresponding to various local minima. The longest way that the A cell can pass in the process of mixing, is represented by the following sequence:

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[1] Isoperimeric quotient of the polyhedron is a dimensionless quantity characterizing the polyhedron surface to volume ratio obtained using the sphere as a reference: $Q=36\pi V^2/S^3$.

$$5.10_{13.39} \rightarrow 1_1 \rightarrow 1_2 1_{-1} \rightarrow 2_3 2_{-3} \rightarrow 3_4 3_{-6} \qquad (14)$$

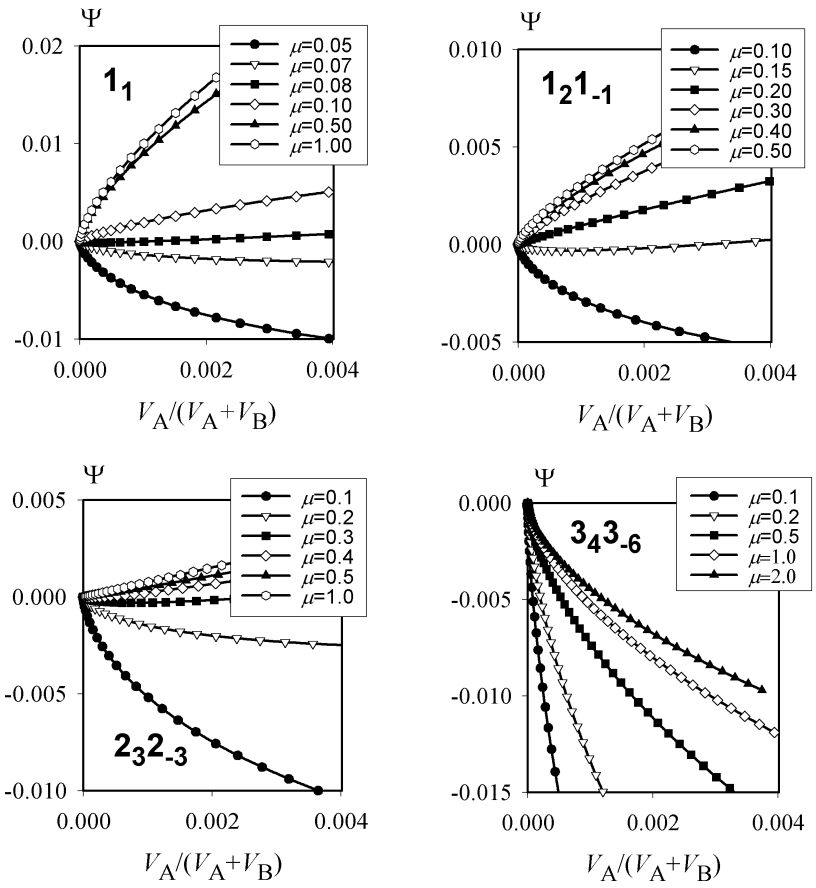

Fig. 4. The dependence of the interfacial energy excess, released by the transfer of A cell from the reference network to the mixed A-B network, on the relative cell volume fraction, calculated for different values of the relative interfacial tension and different cell topologies.

A mixed network can be also formed as a result of gradual withdrawal of the dispersion medium from a diluted mixture of A and B cells. During this process a transient state, characterized by the hexagonal or cubic dense packing of larger spheres (B cells), is attained. The transient state contains a number of tetrahedral and octahedral vacancies which can be filled up with small A cells. The number of vacancies per one B cell is equal to 3 irrespective of the packing symmetry. In the final mixed cellular network the N_{Ins} numbers (indicated in Table 1) can be calculated as follows:

$$N_{\mathrm{Ins}} = f_{\mathrm{outer}}/2 - 1 \tag{15}$$

Taking a number of A cells equal to the number of all vacancies in the transient stage one will find it insufficient to fill up all tetrahedral nodes in the resulting cellular system. As shown in Table 1, the fraction of network nodes that will be occupied with A cells, k_{Sp}, depends on the network type. In all cases, however, in the absence of long-range repulsion between A cells, the draining process is expected to produce disordered patterns.

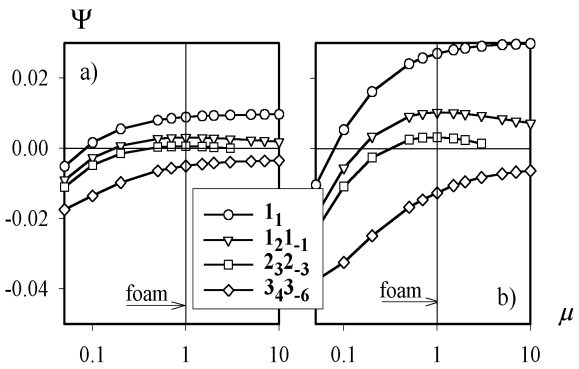

Fig 5. The dependence of relative interfacial energy of mixed network formation on the relative interfacial tension for different volume fractions (a) – 0.001 and b) – 0.005) and topologies of A cell.

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WYPEŁNIANIE WĘZŁÓW TETRAEDRYCZNYCH W MONODYSPERSYJNYCH PIANACH I EMULSJACH PRZEZ CZWOROŚCIANY ZBLIŻONE KSZTAŁTEM DO CZWOROŚCIANÓW REULEAUX

Obliczono energię powstawania cieczy komórkowych złożonych z dwu niemieszających się płynów A i B zanurzonych w ciekłym ośrodku C. Zbadano możliwość wypełnienia tetraedrycznych węzłów w monodyspersyjnej sieci złożonej z komórek B znacznie mniejszymi komórkami A, zakładając, że napięcia międyfazowe działające na granicach faz A-C i B-C są jedynymi czynnikami określającymi kształt wielościanów tworzących sieć. Przedyskutowano możliwość wystąpienia zjawiska samoorganizacji w takich układach zarówno wskutek stopniowego usuwania ośrodka dyspersyjnego (wyciekanie), jak również w wyniku transformacji topologicznej cieczy komórkowej o znikomej zawartości fazy ciągłej.