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interfacial tension, cellular fluids

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SPONTANEOUS TOPOLOGICAL TRANSITIONS IN BIDISPERSE CELLULAR FLUIDS

Concentrated foams and emulsions composed of two types of fluid cells, A and B, immersed in a liquid medium C, have been studied. Interfacial tensions acting along A-C and B-C interfaces have been assumed to be the only driving forces determining the topology of the network. The spontaneous processes induced by the insertion of A multiplets into the three 3D B/C network have been examined.

1. INTRUDUCTION

A cellular fluid is a material that consists of a collection of cells surrounded by a continuous phase of films tending to minimize its surface energy. This definition covers a class of systems which include soap foams, emulsions, magnetic garnets etc. with many potential practical applications. The cellular fluid structure is similar to that of biological tissues thus the studies of cellular materials can help understand the biological cells. If a volume fraction of dispersed liquid is much greater than the critical volume fraction necessary for the close packing of an equivalent suspension of hard spheres (systems called drained foams or emulsions), the cells form a network of space filling polyhedra. The geometry of monodisperse network is the experimental answer to the so-called Kelvin problem [1] – the question of space division into equal volume cells with minimum partition area. The films, edges and vertices of the polyhedral network are governed by celebrated set of Plateau's laws. For two phase systems the laws can be formulated as follows: i) films meet at the edges at the angle Θ=arcos(–1/2) and ii) mean curvature of each film (κ) is determined by film tension (γ) and the pressure difference (Δp) between neighbouring cells [2]:

$$\kappa=\Delta p/2\gamma \tag{1}$$

A more general situation should be considered when the surface tension has different values on different sides of the film (thus the film tension is $\gamma=\gamma_1+\gamma_2$, where γ_1 and γ_2 are the interfacial tensions at both sides of the film; the three phase system) [3]. The topological equilibrium of such systems can be described by generalized Plateau law obtained from the mechanical equilibrium condition [4] of the network node:

$$\Theta_1 = ar\cos\left(\left(1-2\mu-\mu^2\right)/\left(1+\mu\right)^2\right) \text{ and } \Theta_2=\left(2\pi-\Theta_1\right)/2 \tag{2,3}$$

where Θ_1 is the angle between two films of the tension $\gamma_1+\gamma_2$. The tension of the third film is $2\gamma_2$ and $\mu=\gamma_1/\gamma_2$.

The paper concerns the processes of equilibration of the 3D two-phase cellular fluid after the incorporation some droplets/bubbles of another immiscible fluid. The final

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structure of the network is discussed in terms of the possibility of formation of highly-ordered patterns in the mixture.

2. MODEL

We focus our attention on the bidisperse drained cellular fluid in which monodisperse cells A and cells B filled with different fluids are immersed in liquid C. Cells A are small as compared with cells B. All fluids are immiscible and incompressible, so the only driving effect determining the system equilibration is the minimizing the interfacial energy. We restrict our studies to the processes occurring in the timescale between that of drainage of liquid C and that of cell coarsening and/or film breakage.

We have assumed that cells A (located at different positions in the B/C network) can form multiplets *i.e.,* objects composed of a certain number of cells separated by the liquid C film. The multiplets are ascribed by the topological symbol X_Y, where X denotes the object's multiplicity (the multiplicity from 1 to 5 was considered) and Y is a dimensionality of the B/C network element, at which the multiplet was placed. The index Y takes values of 0, 1, 2 and 3 for the object located at a node, an edge, a wall or inside cell B.

For each object studied we calculated the normalized total energy per one cell. The energy is a sum of energy contributions of all films introduced and eliminated by the insertion of the multiplet into B/C network:

$$E_T = E_{ACA} + E_{ACB} + E_{BCB} = \frac{2}{f}\sum_i A^i_{ACA}\frac{\gamma_{AC}}{\gamma_{BC}} + \frac{1}{f}\sum_i A^i_{ACB}\frac{(\gamma_{AC}+\gamma_{BC})}{\gamma_{BC}} - \frac{2}{f}\sum_i A^i_{BCB} \qquad (4)$$

where A^i is area of the i-th face and γ is the interfacial tension. The indices ACA, ACB and BCB denote films of liquid C immersed between fluids A-A, A-B and B-B, whereas the indices AC and BC refer to the A-C and B-C interfaces, respectively. The denominators guarantee that the film energies are dimensionless. *T*he normalization constant f and the relative film tension μ are defined by the equations

$$f = NV^{2/3} \qquad \mu = \gamma_{AC}/\gamma_{BC} \qquad (5, 6)$$

where N is a number of cells A in the multiplet and V is the average volume of a cell A.

In the calculations of energies of multiplets and their internal pressure the Surface Evolver program [5] was applied. Average curvature of the film was calculated by means of Eq. (1).

3. RESULTS

The multiplets inserted into B/C network adopt their face shapes and topology to the position in the network and to the μ value. For example, singlets placed at nodes, edges, films or in the interior parts of cell B take shapes of tetrahedra (1_0), trihedra (1_1), lenses (1_2) or spheres (1_3), respectively. The space configuration and the number of faces also depends on μ. For instance, doublets placed at the node (2_0) form two pentahedra at low μ value, whereas at $\mu \geq 0{,}3$ a trihedron and a trigonal prism is formed. The influence of μ on the film curvature radius R for 1_0 object is shown in Fig.1. As seen, at extremely high μ values the 1_0 object is a sphere with $R/V^{1/3} = 0.620$. A decrease in μ reduces the face convexity. Below $\mu \approx 0.2$, the tetrahedral faces become concave. The curvature radius of other singlets studied (except 1_3) depends on μ in a similar way – for high μ it takes a minimum value (corresponding to the spherical shape). An increase in μ is accompanied by the solid collapse

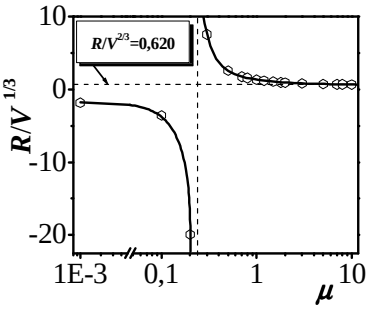

Fig. 1. The radius of curvature vs. μ dependencies calculated for the singlet located at a node

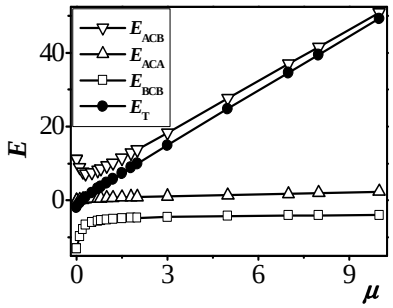

Fig. 2. Relationships of different interfacial energy components on μ for doublet located at a node.

The components of the normalized total energy per one cell, E_T, change with μ as illustrated in Fig.2 presenting some exemplary results obtained for the object 2_0. The interfacial energy of the eliminated fragment of B/C network (E_{BCB}) and the common A-A face (E_{ACA}) increase with increasing μ value, whereas the E_{ACB}=f(μ) dependence goes through a minimum which corresponds to the transition of the outer faces from the concave to convex shape. The superposition of these components gives a nearly linear dependence of E_T on μ.

E_T=f(μ) dependencies are monotonic functions of μ, however the shape of relevant curves depends on the object multiplicity and location in the B/C network (exemplary data for doublets are demonstrated in Fig. 3).

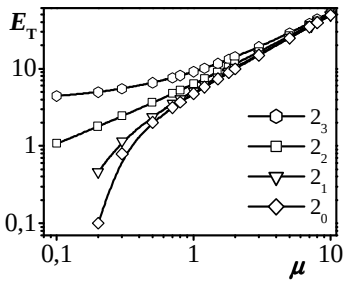

Fig. 3. Dependencies of the E_T on μ for doublets located at different positions in the network

Fig.4 presents the E_T values obtained for three different μ values and five object multiplicities. As seen the E_T values systematically diminish with decreasing Y, except for objects 5_Y located at the nodes. The increase in the number of cells causes a decrease in E_T of cells A incorporated in objects X_3 and X_2. The E_T=f(N) relationship for X_1 depends on μ: at low μ, E_T increases with N but at high μ, E_T E_T=f(N) is a decreasing function except for the decreases. For the object located at the nodes, local minima observed for 4_0; the tetraplets fit better the nodes having a tetrahedral symmetry and, hence, can have lower energy.

The data collected in Fig. 4 together with the topological restrictions of the object movements in the network (the object cannot jump from one node to another, the Y index should change at most by ±1) allow a formulation of some predictions concerning the spontaneous evolution of objects A after their insertion into the B/C network.

Possible processes of association/dissociation of multiplets and their translocation from edges to nodes are collected in Table I. As seen, the way of spontaneous evolution of the system depends on μ. At low μ, all processes initialized by the insertion of a multiplet into B/C network should finally produce singlets placed at nodes. When there are no empty nodes, also the X_1 objects can be formed. At higher μ value, no strictly defined final product is observed. Multiplets located at nodes can increase their multiplicities by

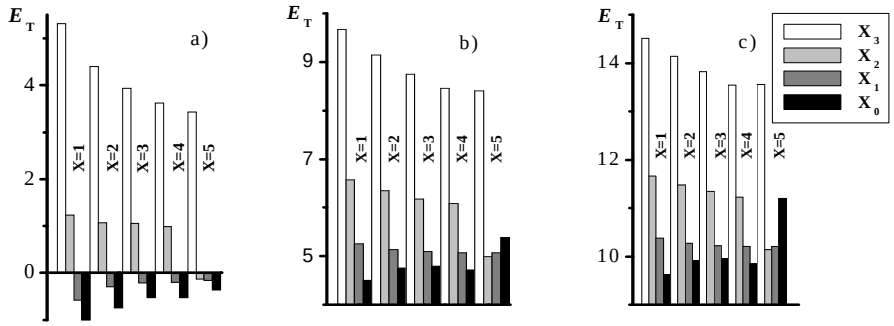

Fig. 4. Illustration of the values of E_T calculated for the different multiplets located at different positions in the network for μ=0,1 (a), μ=1,0 (b) and μ=2,0 (c).

Table I. Spontaneous processes induced by the insertion of A multiplets into B/C network and the energies of these processes calculated for different μ. The processes occurring in the second stage involve the dissociation of unstable multiplets located at the nodes at μ=0,1.

μ=0,1		μ=1,0		μ=2,0	
process	energy	process	energy	process	energy
stage 1		$1_1 \rightarrow 1_0$	–0,746	$1_1 \rightarrow 1_0$	–0,758
$1_1 \rightarrow 1_0$	–0,478	$2_1 \rightarrow 2_0$	–0,768	$2_1 \rightarrow 2_0$	–0,717
$2_1 \rightarrow 1_1+1_0$	–1,051	$1_1+1_0 \rightarrow 2_0$	–0,259	$1_1+1_0 \rightarrow 2_0$	–0,194
$3_1 \rightarrow 1_1+2_0$	–1,443	$3_1 \rightarrow 3_0$	–0,878	$3_1 \rightarrow 3_0$	–0,781
$4_1 \rightarrow 1_1+3_0$	–1,402	$2_1+1_0 \rightarrow 3_0$	–0,389	$2_1+1_0 \rightarrow 3_0$	–0,283
$3_1+1_0 \rightarrow 4_0$	–0,394	$1_1+2_0 \rightarrow 3_0$	–0,367	$1_1+2_0 \rightarrow 3_0$	–0,325
$5_1 \rightarrow 1_1+4_0$	–1,904	$4_1 \rightarrow 4_0$	–1,420	$4_1 \rightarrow 4_0$	–1,386
stage 2		$3_1+1_0 \rightarrow 4_0$	–0,924	$3_1+1_0 \rightarrow 4_0$	–0,874
$2_0 \rightarrow 1_1+1_0$	–0,163	$2_1+2_0 \rightarrow 4_0$	–0,923	$2_1+2_0 \rightarrow 4_0$	–0,940
$3_0 \rightarrow 1_1+2_0$	–0,479	$1_1+3_0 \rightarrow 4_0$	–0,792	$1_1+3_0 \rightarrow 4_0$	–0,851
$4_0 \rightarrow 1_1+3_0$	–0,092	$5_1 \rightarrow 1_1+4_0$	–1,207	$5_1 \rightarrow 1_1+4_0$	–1,199

the association of X_1 objects. Nevertheless some structures of geometry are not fully adaptable to the node symmetry (*e.g.* 5_0 are energetically forbidden).

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SPONTANICZNE PRZEMIANY TOPOLOGICZNE W BIDYSPERSYJNYCH CIECZACH KOMÓRKOWYCH

Praca dotyczy stężonych pian oraz emulsji zawierających dwa typy komórek (A i B) zanurzonych w cieczy C. Przyjęto założenie, że jedynym efektem decydującym o topologii sieci jest napięcie międzyfazowe działające wzdłuż powierzchni międzyfazowych A-C oraz B-C. Zbadano spontaniczne procesy zachodzące w wyniku wprowadzenia multipletów A do trójwymiarowej sieci B/C.