Self-Assembly of Polymer Brushes in the Presence of a Surfactant: A System of Strands

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Abstract—This theoretical study is focused on the formation of a cylindrical microstructure in a planar polymer brush in the presence of a surfactant. It is assumed that the brush may be nonuniform in the direction along the grafting plane and that there are regions with constant concentrations of monomer units and regions occupied only by the surfactant. The surfactant molecule is simulated by a dimer whose parts interact in a different manner with the monomer units of the polymer. At the interface between these regions, dimer molecules are oriented mainly perpendicularly to this interface and the surface tension is reduced. If the surface energy becomes negative, the formation of a structured brush is more favorable in terms of energy than that of a uniform brush. As a result, there may appear a cylindrical microstructure in which grafted macromolecules are united into strands perpendicular to the grafting plane. The stretching of macromolecules and their interaction with the solvent within the strands are described by the Alexander–de Gennes model, whereas the surface energy is calculated with allowance for the surface curvature of strands at a high degree of amphiphilicity of the surfactant molecules. It is shown that the arising strands have radii of the order of the surfactant-molecule length, while the number of macromolecules per strand is proportional to the surface density of their grafting. With an increase in the grafting density, the strand length increases initially, while the volume fraction of the polymer in a strand remains constant. Furthermore, strands start to shorten and their density grows. Structural characteristics are calculated as a function of the parameter characterizing the degree of amphiphilicity of the solvent molecules, their sizes, and their average energy of interaction with monomer units.

INTRODUCTION

Layers of macromolecules with one end anchored to a surface (polymer brushes) may be obtained via surface-initiated polymerization or formed during self-organization of block-copolymer systems [1, 2]. Structural studies of such layers are important for understanding the phenomena underlying their elastic properties, permeability, and interactions with each other and other surfaces.

Grafted macromolecular layers were investigated theoretically via scaling and mean-field methods, starting with papers by Alexander and de Gennes [3, 4], where a volume-uniform layer with fixed positions of ends of macromolecules was considered. The structuring of layers was studied via the mean-field method in a good solvent [5] and as a function of solvent quality [6, 7] under the assumption that the second chain end is free.

The model of a polymer brush interacting with such dissolved molecules or aggregates as surfactant micelles or proteins was investigated within the self-consistent-field theory with allowance for the "unfrozen" excluded volume of the monomer units [8]. It is predicted that either the brush density continuously decreases with the distance from the grafting plane or there is a jump in density, and the adsorbed particles are concentrated in the outer layer of the brush. In any of these cases, the number of adsorbed particles increases with the distance from the surface.

Meanwhile, the experimental neutron-scattering investigation of the interaction of a polymer brush (PEG) with a globular protein showed [9] that adsorbed globules are concentrated predominantly near the grafting surface of the macromolecules, rather than in the outer layer. Thus, the polymer brush is not an obstacle to the penetration of the surface by even large objects. Note that the surface of the globular protein is amphiphilic, and it is the interaction of macromolecules with such surfaces that could play a major role in the formation of the general layer structure.

Amphiphilic surfactant molecules promote structuring processes in various polymer and low-molecular-mass systems. Complex micelles, bubbles, inverted microemulsions, and layered structures may be formed in the solution volume [10–18]; in addition, cylindrical micelles are observed in mixtures of poly(4-vinylpyridine) and surfactants [18].
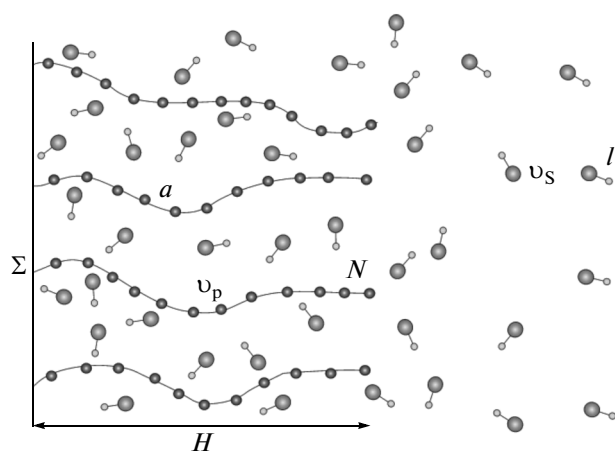
Fig. 1. Macromolecules of the grafted layer and amphiphilic solvent (surfactant) molecules.

As was shown by Monte Carlo computer simulations [19] for not very long macromolecules, the stiffness of bonds connecting mobile grafting points to certain points on the surface is one of the key factors affecting structuring in the grafted layer (the formation of the system of micelles). This model describes the behavior of the layer of outer blocks of graft diblock copolymers. In the present study, long macromolecules that form a polymer brush of stretched chains in the absence of structuring are considered.

Recently, reproduction of a structured (striped) modified surface in a polymer layer adsorbed on the surface was investigated via a computer simulation (the Monte Carlo method in the generalized ensemble) with respect to the energy of attraction of the monomer units to the surface and temperature [20]. No data are available on the self-organization of grafted layers in the direction along the grafting surface during their interaction with an amphiphilic substance.

Structuring in bulk may proceed in a two-component-polymer–surfactant system [14, 17] and in a three-component system in the presence of a solvent when the solvent is dried and the formed structure is investigated [13–16, 18]. In this case, the main role of the solvent in the structuring process is to ensure the mobility of macromolecules and surfactant molecules. For the sake of simplicity, we consider the most energetically favorable structure for a two-component system in which an amphiphilic oligomer (surfactant) is a solvent for macromolecules of the grafted layer.

The surfactant molecule is simulated by a dimer whose parts interact in a different manner with monomer units. Earlier, structuring in the presence of such a dimer surfactant was investigated in terms of the weak-segregation theory for polymer solutions [21] and polymer globules [22]. Phase diagrams were built, and the formation of various types of microstructures was predicted for the case when the second virial coefficients for interactions of monomer units, surfactant molecules, and monomer units with the surfactant were nearly identical. Structural changes in a polymer globule with an increase in the concentration of the dimer surfactant were studied via the molecular-dynamics method [23], and disintegration of the initial globule, accompanied by the formation of smaller and flatter clusters, was observed.

In this study, the structuring induced in the polymer brush in the direction along the grafting plane by interactions with the surfactant is studied theoretically. The model is based on the assumption that, under certain conditions, regions (systems of cylindrical globules or strands) whose surface-tension values are negative owing to the orientation of surfactant molecules on the surface may form.

MODEL

Let us consider a layer of M macromolecules grafted to a flat surface of area S. The grafting density of chains may be characterized by the surface area per molecule, $\Sigma = S/M$. Each macromolecule consists of N units of volume υ_p and size a (Fig. 1). The grafted layer is immersed into an amphiphilic solvent (surfactant), and its molecules of volume υ_s consist of two parts with distance l between their centers. These parts, conventionally denoted as P and H groups, interact differently with macromolecular units. The averaged interaction of polymer units with dimer solvent molecules in a uniform phase will be described by Flory–Huggins parameter χ. The density of grafting of the macromolecules to the surface is considered to be high enough for a brush of strongly stretched polymer chains to be formed: $\Sigma \ll Na^2$. The surrounding solution is considered to be uniform.

Let us assume that contacts of macromolecules with P groups are more favorable in terms of energy than their contacts with H groups. In the presence of the interface between the region containing both macromolecules and the solvent and the region containing only the solvent, dimer molecules of the solvent tend to orient perpendicularly to the surface, thereby creating a negative contribution to the surface energy. If, in this case, the surface energy becomes negative, the formation of the structured brush may prove to be energetically more favorable than the formation of the uniform brush. Let us accept that, then, regions (strands or cylinders with axes perpendicular to the surface) with constant concentrations of monomer units surrounded by the pure solvent arise in the brush. The thickness of the surface layer of the strands is assumed to be low (on the order of the monomer-unit size), a circumstance that corresponds to a high degree of amphiphilicity of the dimer molecules.
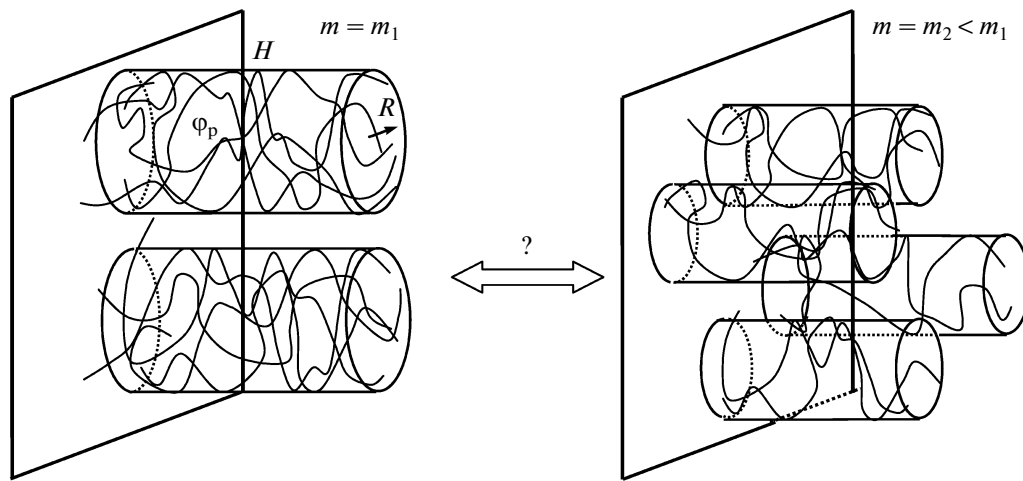
Fig. 2. Grafted layer of macromolecules structured with the formation of a system of strands. The number of macromolecules in a strand, m; the volume fraction of the polymer in the strand, φ_p; and strand radius R (or strand length H) characterize the structure of the system.

Let us consider a system of M_c such strands with radius R and length H. The volume fraction of polymer units in them is

$$\varphi_p = \frac{mN\upsilon_p}{\pi R^2 H}, \tag{1}$$

where $m = M/M_c$.

Let us express free energy F of the system of strands in terms of the Alexander–de Gennes uniform layer model [3, 4] and add the energy of the side surfaces of the strands to the elastic energy of macromolecules and the energy of volume interactions:

$$\frac{F}{kT} = Mf_{el} + N_2\ln(1 - \varphi_p) + \chi NM(1 - \varphi_p) + M_c\sigma S_c \tag{2}$$

Here, f_{el} is the elastic energy of the stretched macromolecule, $N_2 = MN\dfrac{(1 - \varphi_p)}{\varphi_p}\dfrac{\upsilon_p}{\upsilon_s}$ is the total number of solvent molecules within the strands, σ is the surface tension on the side surface of a strand, $S_c = 2\pi RH$ is the area of its side surface, k is the Boltzmann constant, and T is temperature. Within the Gaussian chain model, the elastic energy is

$$f_{el(G)} = \frac{3H^2}{2Na^2} = Nf_{ell(G)}(h) = N\frac{3}{2}h^2, \quad h = \frac{H}{Na} \tag{3}$$

In the case of high stretching, the expression of elastic energy for a freely jointed chain is used [24, 25]:

$$f_{el(L)} = Nf_{ell(L)}(h)$$
$$= N(hL^{-1}(h) + \ln(L^{-1}(h)/\sinh L^{-1}(h))), \tag{4}$$
$$L(x) = \coth x - \frac{1}{x}$$

Let us explain the relationship between Flory–Huggins parameter χ and the energy of interaction of individual units and groups with allowance made for the difference in their volumes. Let us suppose that

each ith element ($i = p$ is the monomer unit; $i = P$ and $i = H$ are P and H groups of the surfactant, respectively) interacts with all elements surrounding it within certain large enough volume V_0. (Value V_0 is analogous to the coordination number in the lattice model.) Let ε_{ip} and ε_{is} be the interaction energies of the ith element with its surrounding, consisting of either the polymer or the solvent only, respectively. The volume density of the interaction energy in the region of uniform mixing of the polymer and solvent with volume V is $E\upsilon_p/V = \varepsilon_{pp}\varphi_p^2/2 + \varepsilon_{ps}\varphi_p(1 - \varphi_p) + (\upsilon_p/\upsilon_s)\varepsilon_{ss}(1 - \varphi_p)^2/2$, where the number of solvent molecules in the considered region is $V(1 - \varphi_p)/\upsilon_s$ and $\varepsilon_{ss} = \varepsilon_{Ps} + \varepsilon_{Hs}$. Total interaction energy E_0 of the same number of molecules in pure phases is $E_0\upsilon_p/V = \varepsilon_{pp}\varphi_p/2 + (\upsilon_p/\upsilon_s)\varepsilon_{ss}(1 - \varphi_p)/2$. Their difference may be presented as $(E - E_0)\upsilon_p/V = \chi\varphi_p(1 - \varphi_p)$, where $\chi = \varepsilon_{ps} - (\varepsilon_{pp} + (\upsilon_p/\upsilon_s)\varepsilon_{ss})/2$.

With the use of relationship (1) and dimensionless parameters $\tilde{R} = R/a$ and $\tilde{\sigma} = \sigma\upsilon_p/a$, layer free energy (2) per monomer unit may be rewritten as

$$\frac{F}{MNkT} = f_{ell}(h) + \frac{\upsilon_p}{\upsilon_s}\frac{(1 - \varphi_p)}{\varphi_p}\ln(1 - \varphi_p)$$
$$+ \chi(1 - \varphi_p) + \frac{2\tilde{\sigma}}{\tilde{R}\varphi_p}, \tag{5}$$
$$h = \frac{\upsilon_p}{a^3}\frac{m}{\pi}\frac{1}{\varphi_p\tilde{R}^2}.$$

While analyzing free-energy equation (5), let us investigate the equilibrium state of the system of strands: the number of macromolecules they contain and their geometric parameters (Fig. 2). With allowance for condition (1), the equilibrium structure of the system of strands within the considered model is fully described by the volume fraction of the polymer in a

strand, φ_p; strand radius R (or strand length H), and number m of macromolecules in a strand.

Note that structuring in the close vicinity of the surface cannot be clearly pronounced, because some grafting points are outside the volume of the strands, and the initial "transient" parts of chains are not involved in their formation. The size of these parts is approximately $\sqrt{S_m} = \sqrt{m\Sigma}$, where S_m is the surface area per strand. Then, the number of polymer units in the "transient" part of a macromolecule during a fully random conformation of the polymer chain is $N_{tr} \approx m\Sigma/a^2$, while, in a fully stretched linear conformation, $N_{tr} \approx \sqrt{m\Sigma}/a$. The model of the polymer brush implies high stretching of chains. Therefore, the second estimation will be used. The contribution of "transient" regions of the free energy may be disregarded if $N_{tr} \ll N$. This condition corresponds to a restriction on number m of macromolecules in a strand:

$$m \ll \frac{N^2 a^2}{\Sigma} \qquad (6)$$

When a large number of macromolecules are united, their long parts do not participate in the formation of the strand. As a result, its surface area and surface-energy contribution decrease above all. Hence, the calculation of the surface energy via formula (5) at high values of m is somewhat underestimated.

The structuring of polymer brushes via their self-organization is possible only if surfaces with negative surface tension arise. Geometry and energy conditions under which strands with negative surface tension may form will be considered in the next section. If such surfaces cannot form ($\sigma = 0$), there are no thermodynamic causes of structuring and the grafted layer remains uniform.

Free energy F_0 of the uniform layer with a volume fraction of monomer units of φ_0 is given by the expression

$$\frac{F_0}{MNkT} = f_{el1}(h) + \frac{\upsilon_p}{\upsilon_s}\frac{1-\varphi_0}{\varphi_0}\ln(1-\varphi_0) + \chi(1-\varphi_0), \quad (7)$$

where the relationship between the volume fraction of monomer units and the layer thickness may be written as

$$\varphi_0 = \frac{N\upsilon_p}{H\Sigma} = \frac{1}{h\tilde{\Sigma}}, \quad \tilde{\Sigma} = \Sigma a/\upsilon_p.$$

The equilibrium volume fraction of the polymer in the uniform layer, φ_0, should satisfy the condition of a free-energy minimum: $\partial F_0/\partial \varphi_0 = 0$. Then

$$u_{el0}(h_0) + \frac{\upsilon_p}{\upsilon_s}(\ln(1-\varphi_0) + \varphi_0) + \chi\varphi_0^2 = 0$$

$$u_{el0(G)}(h_0) = \frac{3}{2\tilde{\Sigma}^2}, \qquad (8)$$

$$u_{el0(L)}(h_0) = \frac{1}{\tilde{\Sigma}}L^{-1}(h_0), \quad h_0 = \frac{1}{\varphi_0\tilde{\Sigma}}.$$

The corresponding values of free energy of the layer and its thickness were calculated for further comparison with parameters of the structured layer.

Note that the minimum free energy of a brush with respect to its geometric parameters corresponds to the equality of the chemical potentials of surfactant molecules in the regions outside and inside the brush because the surfactant molecules are redistributed between the indicated regions with a change in the brush volume.

SURFACE TENSION

In the considered model, the amphiphilicity of the solvent molecules is responsible for the separation into regions containing macromolecules in solution and regions containing pure solvent. In order to characterize this property of molecules, let us introduce single energy parameter ε, the energy difference (in kT units) between the interaction of an H group with polymer units and the interaction of an H group with solvent molecules: $\varepsilon = \varepsilon_{Hp} - \varepsilon_{Hs}$, where $\varepsilon > 0$.

The theoretical considerations of a polymer globule formed by a macromolecule with amphiphilic units [26] and a polymer globule in the presence of an amphiphilic dimer solvent demonstrated [27] that allowance for amphiphilicity results in narrowing of the surface layer. Let us assume that the fact that the surface layer of the considered strands is narrow (on the order of monomer-unit size a) is the limiting case corresponding to a strong amphiphilicity effect.
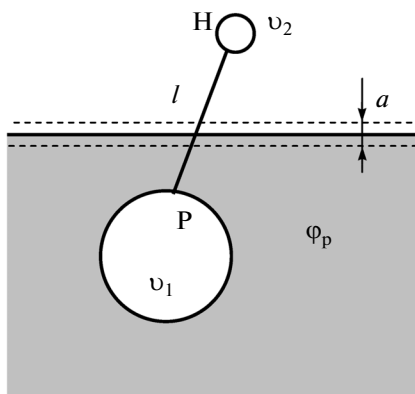
In addition to the energy of volume interactions (the second and third terms in free energy (2)), it is supposed that the energy of interaction between the H group of a dimer surfactant molecule occurring close to the strand surface and the surrounding is

$$\varepsilon_H = \begin{cases} -\varepsilon\varphi_p & \text{outside the strand,} \\ 0 & \text{inside the strand,} \end{cases}$$

if the P group is inside the strand. The dependence of the energy of steric interactions for surfactant molecules on their orientation is disregarded. This model description of interactions corresponds to the dimer surfactant molecule with volume υ_1 of the P part that is much higher than volume υ_2 of the H part: $\upsilon_1 \gg \upsilon_2$, $\upsilon_s \approx \upsilon_1$, and bond length $l \gg a$ (Fig. 3). A similar model was used to describe an amphiphilic-polymer unit in calculations of the surface tension of globules of amphiphilic macromolecules [28, 29].

It is assumed that H groups outside the strand are surrounded by solvent molecules, and only in this case do these groups possess energy $-\varepsilon\varphi_p$. Therefore, as the necessary condition for the existence of surfaces with negative surface tension, it is accepted that shortest distance s between the surfaces of strands is at least as long as bond length l of a solvent molecule (Fig. 4).

In the limit of a high degree of amphiphilicity (at $\varepsilon\varphi_p \gg 1$), it may be assumed that all dimer surfactant

Fig. 3. Model of a dimer amphiphilic surfactant molecule on the strand surface.

Fig. 4. Arrangement of strands of radius R with minimum distance s between the surfaces of strands for their most dense packing on the grafting surface (cross-sectional view parallel to this surface).
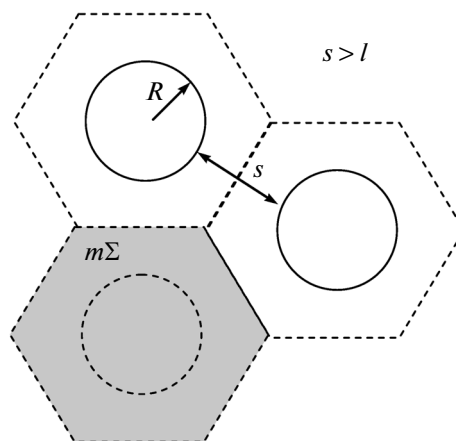
molecules near the surface with P parts inside the strand are oriented such that the H parts are outside the strand, thereby creating the negative contribution to energy $-N_{surf}\varepsilon\, kT\varphi_p$, where N_{surf} is the number of dimers in the subsurface layer of the strand [26]. For a flat surface of area S, the number of molecules is $N_{surf} = (1 - \varphi_p)lS/\upsilon_s$. Then, surface tension σ_0 of the flat surface may be written as

$$\tilde{\sigma}_0(\varphi_p) = \sigma_0(\varphi_p)\frac{\upsilon_p}{a} = \varphi_p s_0 - \varepsilon\frac{\upsilon_p}{\upsilon_s}\frac{l}{a}(1 - \varphi_p)\varphi_p \qquad (9)$$

where the first term describes the restrictions on the conformation of macromolecules and the surface energy of interactions at the side surfaces of strands with no allowance for the amphiphilicity of dimer molecules ($s_0 > 0$). It is assumed that the second contribution dominates and $\sigma_0 < 0$. In order to take into account the dependence of surface tension on the curvature of the side surfaces of strands, we will use the data on globules of macromolecules with amphiphilic units [28, 29]. In the limit of a high degree of amphiphilicity of dimer molecules ($\varepsilon\varphi_p \gg 1$), the surface tension may be represented as

$$\tilde{\sigma} = \tilde{\sigma}_0(\varphi_p) - \frac{\upsilon_p}{\upsilon_s}\frac{l}{a}(1 - \varphi_p)\frac{l}{R}(1.47 - \varepsilon\varphi_p/2)$$
$$+ \frac{1}{8}\frac{\upsilon_p}{\upsilon_s}\frac{l}{a}(1 - \varphi_p)\frac{l^2}{R^2}, \qquad \frac{l}{R} \ll 1. \qquad (10)$$

Note that corrections describing the dependence of surface tension on surface curvature correspond to the calculated corrections in [28, 29] if $\varepsilon\varphi_p$ is used instead of ε. This circumstance is due to the fact that, in our model, the difference of interaction energies of the H group with the surrounding inside and outside the strand depends on the concentration of monomer units in the strand. This value is equal to $\varepsilon\varphi_p$, rather than to ε, as was supposed for globules with a constant density.

EQUILIBRIUM STRUCTURE

Free energy (3)−(5), (9), (10) of a system of cylinders at fixed number m of macromolecules per strand is a function of two independent variables: radius R and volume fraction φ_p. The conditions of the free-energy minimum with respect to these variables may be conveniently written in the form of a system of equations for the parameters φ_p and $x = l/R$:

$$u_{el}(x, \varphi_p) - \frac{\tilde{\sigma}_0(\varphi_p)}{\tilde{l}}x$$
$$+ \frac{\upsilon_p}{\upsilon_s}(1 - \varphi_p)\left(2.94 - \varepsilon\varphi_p - \frac{3}{8}x\right)x^2 = 0, \qquad (11)$$

$$z_{el}(x, \varphi_p) + f_{vol}(\varphi_p) + 2\frac{\upsilon_p}{\upsilon_s}\varepsilon\varphi_p^2 x$$
$$+ \frac{\upsilon_p}{\upsilon_s}\left(2.94 - \varepsilon\varphi_p^2 - \frac{x}{4}\right)x^2 = 0, \qquad (12)$$

where

$$u_{el(G)}(x, \varphi_p) = z_{el(G)}(x, \varphi_p) = -3\left(\frac{\upsilon_p}{a^3}\frac{m}{\pi}\right)^2\frac{1}{\varphi_p\tilde{l}^4}x^4, \quad \tilde{l} = \frac{l}{a},$$

$$u_{el(L)}(x, \varphi_p) = -2\frac{\upsilon_p}{a^3}\frac{m}{\pi\tilde{l}^2}x^2 L^{-1}(h),$$

$$h = \frac{\upsilon_p}{a^3}\frac{m}{\pi}\frac{x^2}{\varphi_p\tilde{l}^2}, \quad z_{el(L)}(x, \varphi_p) = \frac{1}{2}u_{el(L)}(x, \varphi_p),$$

$$f_{vol}(\varphi_p) = -\frac{\upsilon_p}{\upsilon_s}(\varphi_p + \ln(1 - \varphi_p)) - \chi\varphi_p^2.$$

The maximum allowable value of the strand radius, $R_{max}(m, \Sigma)$, and, hence, the minimum value of dimensionless curvature, x_{min}, are determined by the surface grafting density of macromolecules (area Σ) and the number of macromolecules per strand. For hexagonally arranged strands with the minimum distance
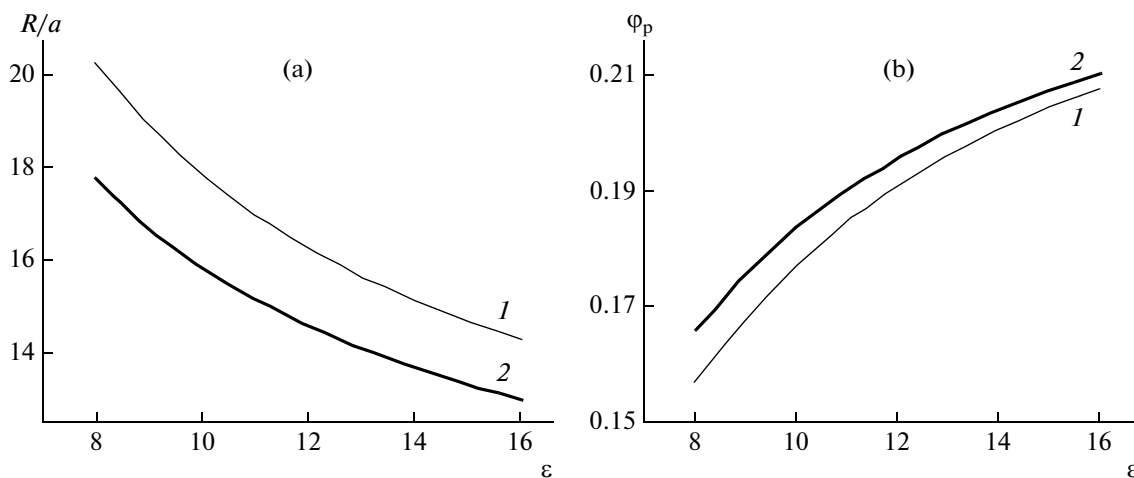
Fig. 5. Plots of (a) radius R of the strand formed by $m = 40$ macromolecules and (b) polymer volume fraction φ_p in the strand vs. ε, characterizing the degree of amphiphilicity of dimer solvent molecules (the Gaussian model of elasticity of macromolecules), at $\upsilon_p/\upsilon_s = $ (*1*) 0.1 and (*2*) 0.125; $\upsilon_p/a^3 = 1$, $\chi = 0.05$, $s_0 = 1$, and $l/a = 4$.
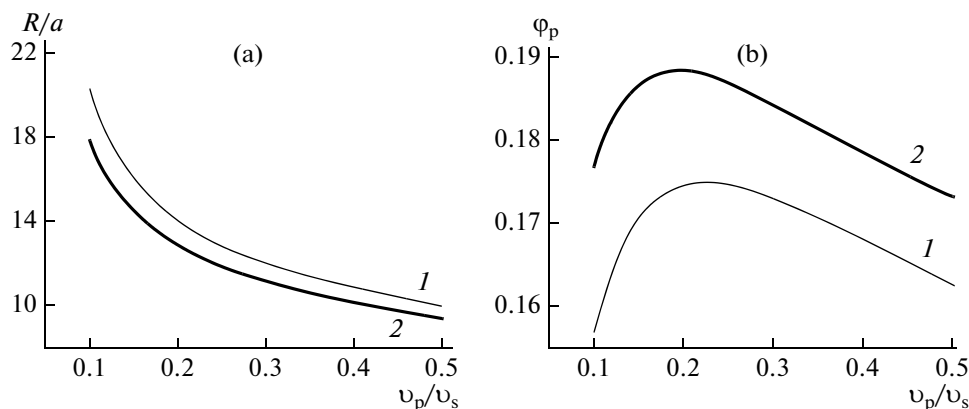
Fig. 6. Plots of (a) radius R of the strand formed by $m = 40$ macromolecules and (b) polymer volume fraction φ_p in the strand vs. the volume ratio υ_p/υ_s of a monomer unit and amphiphilic solvent molecule (the Gaussian model of elasticity of macromolecules) at $\varepsilon = $ (*1*) 8 and (*2*) 10; $\upsilon_p/a^3 = 1$, $\chi = 0.05$, $s_0 = 1$, and $l/a = 4$.

$s = l$ between their surfaces (Fig. 4), the indicated parameters are defined by the geometric relationship

$$6(R_{max} + l/2)^2 \tan 30° = m\Sigma, \quad x_{min} = l/R_{max}. \quad (13)$$

At high values of m and Σ, the condition $x > x_{min}$ is fulfilled for those parameters of the system of strands that are solutions to system of equations (11) and (12) and that correspond to the free-energy minimum at a fixed m value.

Figures 5 and 6 show dependences of strand radius R and polymer volume fraction φ_p on parameter ε, which characterizes the amphiphilicity of dimer solvent molecules, and on volume ratio υ_p/υ_s of the monomer unit and solvent molecule. As the value of ε in Eq. (5) is increased, the role of the last term, i.e., the free energy of the side-strand surface, becomes more pronounced than the elastic energy of macromolecules and the energy of volume interactions due to the negative contribution to the surface tension in formula (9) (in the flat-surface approximation). This circumstance causes a stronger stretching of macromolecules with an increase in ε, the radius of the strand decreases (Fig. 5a), and the density of the strand (volume fraction φ_p) increases (Fig. 5b). The gain in volume fraction φ_p is primarily related to the fact that, for a denser strand, energy contribution $-\varepsilon\varphi_p$, which is proportional to the volume fraction and which arises when H groups of dimer amphiphilic molecules in the strand subsurface layer are oriented outside, is greater.

In addition, with an increase in υ_p/υ_s (a decrease in surfactant molecular volume), macromolecules are stretched stronger and the strand radius decreases

(Fig. 6a). The dependence of volume fraction φ_p on υ_p/υ_s is nonmonotonic: The curve has a maximum. As υ_p/υ_s increases, all surface-energy contributions (the last term in free energy (5)) determined by the amphiphilicity of surfactant molecules increase proportionally, including both the contribution due to the flat surface in (9) and contributions due to curvature of the surface in (10). This circumstance is due to the fact that a higher number of surfactant molecules are embedded into the subsurface layer at the same polymer concentration in the strand. The dependence of free energy (5) on φ_p has a complicated character. At low υ_p/υ_s values, volume fraction φ_p increases with an increase in υ_p/υ_s mainly owing to an increase in the absolute value of energy contribution $-\varepsilon\varphi_p$ of a dimer molecule oriented on the surface. However, the number of these molecules depends on φ_p, and in the flat-surface approximation, this value is $N_c = (1 - \varphi_p)lS_c/\upsilon_s$, where $S_c = 2\pi RH \sim mN\upsilon_p/(\varphi_p R)$ is the side surface area of strand. With an increase in the surface curvature, the number of surfactant molecules embedded into the subsurface layer at a given surface area decreases. This leads to a situation when strand radius R changes weakly with an increase in υ_p/υ_s if the values of υ_p/υ_s are high enough (R is low). In this case, the side surface area $S_c \sim 1/\varphi_p$, and the surface-energy contribution from oriented surfactant molecules, $-\varepsilon\varphi_p N_c$, is proportional to coefficient $(1 - \varphi_p)$, which describes the fraction of the volume occupied by surfactant molecules. Therefore, a decrease in volume fraction φ_p becomes energetically favorable. Moreover, with an increase in υ_p/υ_s, the contribution of volume interactions in Eq. (5) for free energy increases, while promoting a decrease in φ_p.

Depending on Flory–Huggins parameter χ, the parameters of strands change weakly (in the range of χ values 0–0.2): The stretching of macromolecules and strand radius R decrease slightly, while volume fraction φ_p increases somewhat. This circumstance is due to the fact that surfactant molecules are replaced from strands with an increase in the effective energy of repulsion between the monomer units and surfactant molecules. It is noteworthy that the plots in Figs. 5 and 6 are built for long macromolecules under the assumption that the contribution from the initial parts, which have not yet formed strands, may be disregarded; that is, condition (6) is satisfied.

RESULTS AND DISCUSSION

Equilibrium number m of macromolecules per strand is an important parameter characterizing the structure of the grafted layer. Figure 7 plots dependence (5) of the free energy per macromolecule, F/M, for the structured layer on the number of macromolecules, m, at R and φ_p values satisfying minimum conditions (11) and (12) for the Gaussian elasticity model.
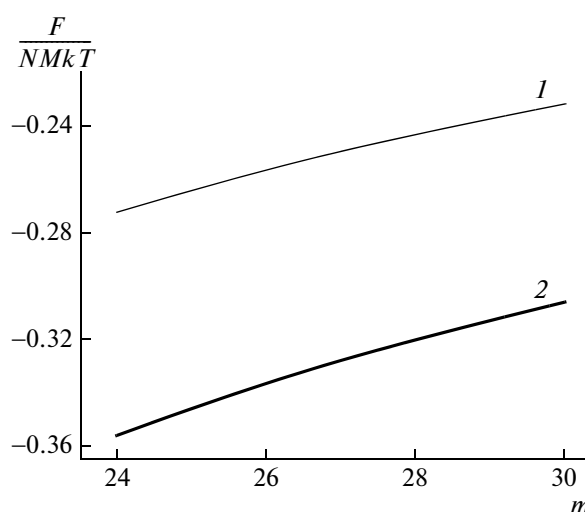

Fig. 7. Free energy per monomer unit for the system of strands with fixed number m of macromolecules in a strand as a function of m (the Gaussian elasticity model) at $\varepsilon = (1)$ 8 and (2) 10; $\upsilon_p/a^3 = 1$, $\chi = 0.05$, $s_0 = 1$, $\upsilon_p/\upsilon_s = 0.1$, and $l/a = 4$.

It is seen that structuring with a lower value of number m of macromolecules in a cylinder is more favorable (in the absence of additional restrictions on R and φ_p). This circumstance is due to the fact that the elastic energy per macromolecule for the strand with the same geometric parameters, that is, the first term in free energy (5), declines with a decrease in m. Note that allowance for the fact that initial parts of the macromolecules do not participate in the formation of strands (see the text after formula (6)) results in an even higher growth of F/M with an increase in m.

At low m values, the layer parameters cannot be calculated via Eqs. (11) and (12) in terms of the Gaussian chain elasticity model, because, first, the stretching of macromolecules is very high and the conformational energy of macromolecules cannot be described by the Gaussian model and, second, the value of R_{max} (13), which restricts the range of allowable values of the cylinder radius, decreases with a decrease in m. Values satisfying system of equations (11) and (12) may be outside the given region. Furthermore, the considered structuring model implies that the strand surface with a negative surface tension may form. This phenomenon requires a large strand size sufficient for free placement of surfactant molecules in the strand and a high amphiphilicity of surfactant molecules ($\varepsilon\varphi_p \gg 1$). Therefore, it was accepted that the strand radius cannot be lower than the surfactant molecule size; that is, $R \geq l$, while the values of the polymer volume fraction in the strand should exceed the threshold value, $\varphi_p > \varphi_{min} = C_\varepsilon/\varepsilon$, because otherwise, no energy-related causes of structuring would arise. Thus, the surface tension is defined by formulas (9) and (10) and additional restrictions:
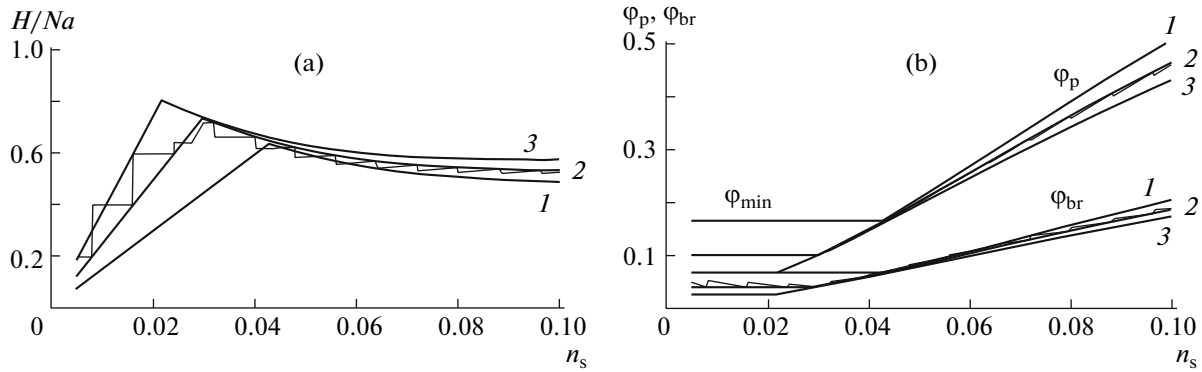
Fig. 8. Plots of (a) strand length H and (b) polymer volume fractions φ_p and φ_{br} in the strand and on average in the layer, respectively, vs. the surface grafting density of macromolecules, n_s, at $\varepsilon = (1)$ 6, (2) 10, and (3) 16; $\upsilon_p/a^3 = 1$, $\upsilon_p/\upsilon_s = 0.1$, $\chi = 0.05$, $s_0 = 1$, $C_\varepsilon = 1$, and $l/a = 4$.

$$\sigma = 0 \quad \text{at} \quad R < l, \quad s < l \quad u \quad \varphi_p < \varphi_{min} = C_\varepsilon/\varepsilon. \quad (14)$$

A negative value of surface tension of the strands being formed is a prerequisite for the structuring of the grafted layer. The range of parameters where the surface tension is negative at $\varphi_p > \varphi_{min}$, is estimated via Eq. (9) for the surface tension of the flat surface: $\sigma_0 < 0$. From this, it follows that

$$\varepsilon > C_\varepsilon + \frac{s_0 a \upsilon_s}{l \upsilon_p}. \quad (15)$$

At low m values, calculations were performed only for the elastic model of a freely jointed chain; that is, the elastic energy per monomer unit, f_{el1}, in free energy (5) was defined by formulas (4): $f_{el1}(h) = f_{el1(L)}(h)$.

Conditions (13) and (14) restrict the range of allowable values of the strand radius to the interval $l < R < R_{max}(m, \Sigma)$. In this case, at low m values, the minimum with respect to φ_p corresponds to $\varphi_{min} = C_\varepsilon/\varepsilon$. Calculations show that the minimum free energy per macromolecule with respect to R and φ_p increases with an increase in m for all values of the external parameters. This circumstance is explained by the fact that, at fixed values of the strand radius and density (R and φ_p), strand length H and elastic energy f_{el1} increase with an increase in m, while all the remaining contributions to free energy (5) are independent of m. Consequently, formation of a strand with the lowest possible number of macromolecules is energetically favorable. Because $R_{max}(m, \Sigma)$ declines with a decrease in m, m is limited from below by the value corresponding to the condition $R_{max} = l$:

$$m \geq \frac{9\sqrt{3}}{2} \frac{l^2}{\Sigma}. \quad (16)$$

In other words, the number of macromolecules in the strand is equal to the minimum integer number satisfying this condition and is independent of the length of macromolecules and the value of ε. Note that, if free energy (5), (9), and (10) is minimized without conditions (13) and (14) being imposed, the minimum

obtained value corresponds to $m = 1$ at a very low volume fraction of monomer units.
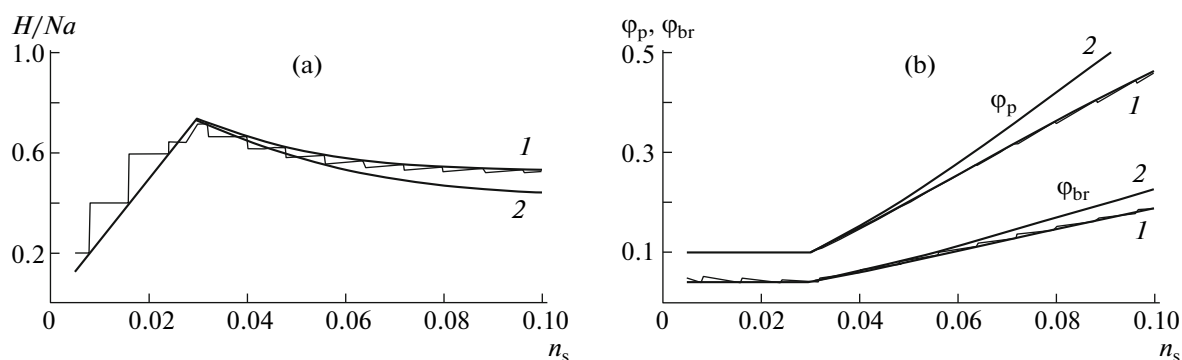
Dependences of strand length H, polymer volume fraction φ_p in a strand, and mean volume fraction φ_{br} of monomer units in a layer of same thickness H (as if the layer were uniform: $\varphi_{br} = \frac{\pi R^2}{m\Sigma}\varphi_p$) on the surface grafting density of macromolecules, $n_S = 1/\Sigma$, at various values of the parameters are presented in Figs. 8–10. Steplike curves are calculated for the case when the number of macromolecules per strand, m, takes natural-number values. All the remaining curves are obtained under the assumption that $R = l$, while m is defined by the equality in (16), that is, may be any real not necessarily integer number. Steplike curves on all plots are calculated for the parameters $\varepsilon = 10$, $\upsilon_p/\upsilon_s = 0.1$, and $\chi = 0.05$. All remaining parameters take the same values as those in Figs. 8–10, and the value of m increases from 1 to 13 with an increase in n_s. Solid curves calculated for the same parameters (curve 2 in Fig. 8 and curves 1 in Figs. 9, 10) are circumflex steplike curves and, at integer m values, have common points with them.

At a very low grafting density of macromolecules (a high value of Σ), strands with the minimum possible volume fraction of monomer units, φ_{min}, are formed by individual macromolecules ($m = 1$). With an increase in grafting density n_s, the number of macromolecules in a strand and, hence, their length H (at a constant value of φ_{min}) grow. In calculations with discretely changing number m, the strand radius takes the minimum possible value, $R = l$, thereby providing the maximum possible surface area for a strand with a fixed density. Upon a further increase in grafting density n_S, more and more macromolecules appear in a strand (m increases) and the relative contribution of the elastic energy to free energy (5) increases. This leads to a decrease in the degree of stretching of macromolecules in the equilibrium state and to the short-
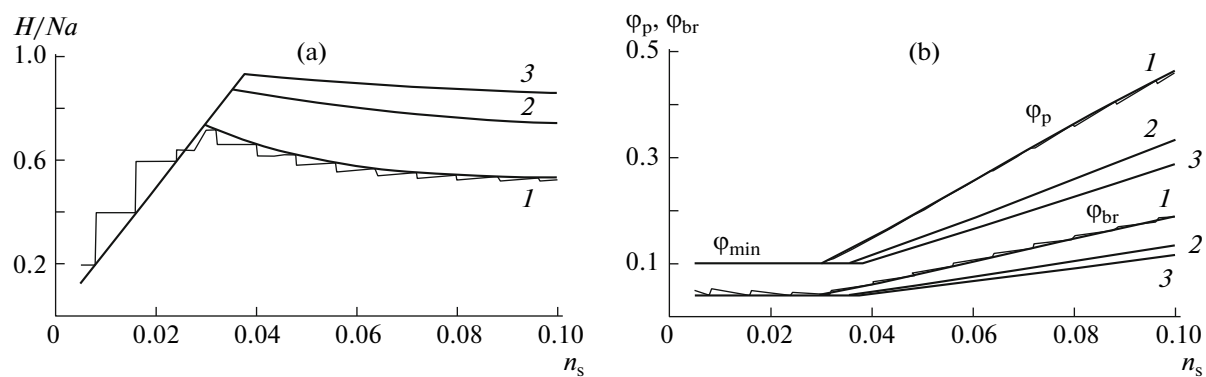
Fig. 9. Plots of (a) strand length H and (b) polymer volume fractions φ_p and φ_{br} in the strand and on average in the layer, respectively, vs. the surface grafting density of macromolecules, n_s, at $\upsilon_p/\upsilon_s = (1)\ 0.1$, $(2)\ 0.25$, and $(3)\ 0.5$; $\upsilon_p/a^3 = 1$, $\varepsilon = 10$, $\chi = 0.05$, $s_0 = 1$, $C_\varepsilon = 1$, and $l/a = 4$.

Fig. 10. Plots of (a) strand length H and (b) polymer volume fractions φ_p and φ_{br} in the strand and on average in the layer, respectively, vs. the surface grafting density of macromolecules, n_s, at $\chi = (1)\ 0.05$ and $(2)\ 0.5$; $\upsilon_p/a^3 = 1$, $\varepsilon = 10$, $\upsilon_p/\upsilon_s = 0.1$, $s_0 = 1$, $C_\varepsilon = 1$, and $l/a = 4$.

ening of strands due to their densification (H declines, while φ_p rises at $\varphi_p > \varphi_{min}$). In calculations with discretely changing number m, the strand radius takes the maximum possible value, $R = R_{max}$, determined via relationship (13) in order to increase the side surface area during restricted growth of H.

As the degree of amphiphilicity of dimer molecules (curves 1–3) is increased, the side surface area of the strand tends to increase owing to its lengthening and decrease in density (Fig. 8). Moreover, the higher the ε value, the lower the density of strands (φ_{min}) formed by a low number of macromolecules at a low density of their grafting to the surface.

With an increase in υ_p/υ_s, the volume of a surfactant molecule decreases (mainly the volume of its P group); therefore, at the given sizes of the strand, a higher number of surfactant molecules is involved in its volume and is embedded into the surface layer. The second virial coefficient of interactions between monomer units, $B/\upsilon_p = \upsilon_p/(2\upsilon_s) - \chi$ increases with

υ_p/υ_s ($1 \to 2 \to 3$ in Fig. 9). Therefore, the solvent quality improves, a phenomenon that promotes an increase in the strand volume. Furthermore, the surface-energy contribution increases with respect to the elastic energy. This circumstance results in the lengthening of strands and a decrease in their density (H grows, while φ_p decreases at $\varphi_p > \varphi_{min}$) with an increase in υ_p/υ_s. For smaller surfactant molecules, the maximum stretching of macromolecules is observed at a higher surface density of their grafting, n_s, and, consequently, at a larger number of macromolecules per strand, starting from which the densification and shortening of strands with an increase in n_s become favorable.

Figure 10 compares characteristics of the layer at different values of Flory–Huggins parameter χ, that is, with variations in the solvent quality, which, however, does not affect surface interactions. Small changes of the Flory–Huggins parameter near the value $\chi_\theta = \upsilon_p/(2\upsilon_s)$, corresponding to the θ tempera-

ture, have no effect on the layer structure. (The curve related to $\chi = 0.02$ would practically coincide with the curve for $\chi_\theta = 0.05$.) Only in a very poor solvent at a high grafting density of macromolecules, n_s, does densification and shortening of strands become noticeable. (Curves *2* correspond to $\chi_\theta = 0.5$.) The maximum stretching of macromolecules is practically independent of χ and is observed at the same value of surface density n_s. As expected, the main role in the considered model belongs to the amphiphilicity of surfactant molecules and surface properties of strands.

Changes in length l of the dimer surfactant molecules have almost no effect on the volume fraction of the polymer in the strand, φ_p, and on length H of strands calculated under the assumptions that number m of macromolecules per strand may take noninteger values and that $R = l$. In this case, $m \sim l^2$, and the only l-dependent contribution to free energy (5) is the term in the surface-energy (proportional to s_0 in formula (9)) not depending on the degree of amphiphilicity of surfactant molecules. At the same time, the form of the steplike curves calculated for discretely changing m changes with variation in l because the width of the "steps" on the plots is proportional to l^2.

Although our model suggests that the surface grafting density of macromolecules is high enough for the uniform layer to be represented by a brush of stretched chains, the finding that, for individual macromolecules, it may be favorable for them to undergo compaction and form a strand (cylindrical globule) is the more so valid for loosely grafted macromolecules.

CONCLUSIONS

In this study, self-assembly of polymer brushes on a flat surface through the interaction with an amphiphilic substance (surfactant) has been investigated. The model is based on the assumption that, under certain conditions, there may be formation of regions (strands) in which surface tension is negative owing to surfactant molecules oriented on the surface. Similarly to situations where the presence of a surfactant causes structuring in the bulk of polymer solutions, here, it is assumed that the grafted layer of macromolecules may be nonuniform in the direction along the grafting plane.

Necessary conditions for the formation of surfaces with negative surface tension include a large scale of microstructure exceeding the surfactant-molecule size and a large increase in energy due to the orientation of a surfactant molecule on the surface. This situation is possible when the difference between the energies of interaction between different parts of an amphiphilic molecule and monomer units is substantial and structuring is well-pronounced. It has been predicted that the formation of a microstructure (a system of strands) satisfying these conditions is energetically more favorable than that of the uniform grafted layer owing to

negative surface tension. In this case, the strand radius takes the minimum allowable value, on the order of the size of an amphiphilic molecule.

At a low surface grafting density of macromolecules, compaction of one or several macromolecules to form a strand (cylindrical globule) with a density that is minimally sufficient for the strand surface tension to become negative is more favorable. At a sufficiently high grafting density, the density of strands and the number of macromolecules in them grow with this value, while the strand length decreases.

In the long term, it would be interesting to theoretically investigate the possibility to form various types of grafting-layer microstructures, e.g., flat layers oriented perpendicularly to the grafting plane or a porous layer. If it would be possible to additionally fix (crosslink) the grafted layer structure via chemical methods and then to remove (to wash out) the surfactant, it seems that such a layer would possess some specific properties relative to those of the uniform layer; in particular, it would have large values of thickness and permeability.

Experimentally, the structuring of the grafted layers of macromolecules has been investigated via different methods [1, 9, 30]. However, the possible structuring along the grafting surface has not yet been studied, and it presents a complicated experimental problem.

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