Coil–Globule Type Transitions in Polymers. 1. Collapse of Layers of Grafted Polymer Chains

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ABSTRACT: The mean-field analytical theory describing the conformational transition related to the collapse of the layers of polymer chains grafted onto the impermeable surfaces of different morphologies (a planar surface, a sphere, and a cylinder) has been developed. The dependence of the character of this transition on the type of the surface morphology is analyzed. It is shown that in the case of a planar surface this transition is not a true thermodynamic phase transition. The structural rearrangement of the layers accompanying their collapse is investigated. The most precise analysis was carried out for the case of a planar layer. It is shown that in contrast to the blob picture the planar layer is inhomogeneous as a whole at any solvent strength. Analytical expressions describing the distribution of monomer units density and chain ends along the layer height at arbitrary solvent strength are obtained.

Introduction

The layers of polymer chains grafted at one end onto impermeable surfaces (matrices) with different morphologies and immersed (or not) in a solvent are the basic models for theoretical investigation of a number of complex polymer systems. On the basis of these models, the theories of steric stabilization of colloids,[1] conformations of regularly branched polymers in solutions,[2-6] and supermolecular structures formed by linear and branched block copolymers in solutions and melts[8-10] were developed.

An analysis of conformations of macromolecules in layers of polymer chains grafted onto an impermeable planar surface and immersed in a good solvent was first carried out by Alexander[11] and de Gennes[12] on the basis of the scaling approach.[13] It is known that the scaling method makes it possible to obtain only asymptotic scaling dependences of thermodynamic and structural characteristics of the system (numerical coefficients and nonpower dependences are not calculated). The main conclusion of these investigations was that in a good solvent the overlapping of the chains in the planar layer results in their stretching normally to the grafting surface so that the layer height $H_0 \sim N$.

Further development of this scaling approach permitted us to take into account the chain stiffness[3] and to generalize the method for the case of the Θ-solvent[14] and for the layers of different morphologies (spherical and cylindrical).[3,15-17] As shown in refs 15–17 the chain overlapping results in their stretching in layers of arbitrary morphology. This stretching decreases in the following order: a planar, a cylindrical, and a spherical matrix. The results obtained for spherical and cylindrical layers made it possible to develop the scaling theories of the solutions of star- branched[2-4] and comblike[5,6] polymers, respectively.

The scaling analysis showed that the principal difference between the structures of grafted polymer layers of different morphologies exists. In the cylindrical and spherical layers monomer concentration decreases with the distance from the surface according to the power law. In the planar layer the power dependence of the concentration on the distance from the surface is absent so that a primitive interpretation of the blob picture proposed by de Gennes for the planar layer led to the conclusion that the monomer concentration is constant along the layer height (with the exception of the end effects near the matrix and at the periphery of the layer).

However, the numerical calculations made by Birshtein and Karaev[18] and Skvortsov et al.[19,20] showed that this picture is not adequate. A rigorous conclusion about the inhomogeneity of the planar layer as a whole and the parabolic character of the density profile in the layer under the conditions of a good solvent has been made independently and practically simultaneously by two research groups: in Leningrad (USSR) by Zhulina, Borisov, Pryamitsyn, and Birshtein[21] and at Exxon Research and Engineering (U.S.A.) by Milner, Witten, and Cates[22] (see also refs 23–27). These results have been obtained on the basis of slightly different mean-field analytical theories by using the so-called Newtonian approximation suggested by Semenov for block copolymer systems[28] (see also ref 29).

The purpose of the present paper was the investigation of the structural changes in grafted polymer layers of different morphologies immersed in a solvent over a wide range of temperature (or solvent strength) from the conditions of a good solvent ($T > \Theta$) up to the poor solvent ($T < \Theta$). The conformational transition related to the collapse of grafted polymer layers caused by a decrease in temperature (solvent strength) will be analyzed in a more consistent manner than in our previous short communications.[30,31] After the publication of our preliminary results concerning the collapse of grafted polymer layers[30,31] a very similar approach was applied to the consideration of the collapse of a planar layer by Halperin.[32] However, some conclusions of his paper seem to us to be paradoxical and unreliable, and we shall discuss them below.

For the analysis of the collapse of layers of arbitrary morphologies the Flory-type approach will be used. This method makes it possible to analyze the dependence of the character of the collapse transition on the morphology of the matrix.

The collapse of the layer is always accompanied by the changes in its structure. In order to develop the complete theory of the collapse, one should take into account the distribution of monomer concentration in a layer. This complete theory will be constructed on the basis of formalism previously developed[21,23,33] for the analysis of the structure of a planar layer.

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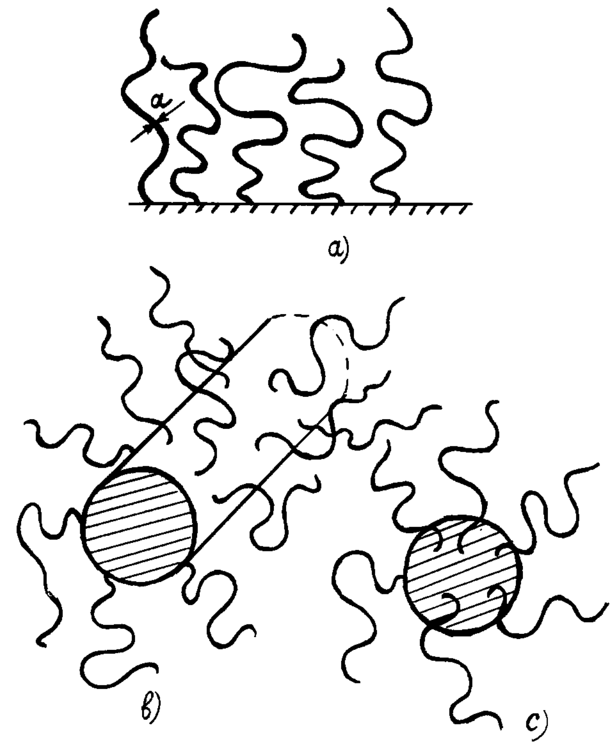

Figure 1. Layer of polymer chains grafted onto a planar (a), a cylindrical, (b) and a spherical (c) surface.

The Appendix deals with the application of this method to the structural analysis of densely grafted layers (see also ref 23).

Results

Layers of polymer chains consisting of $N \gg 1$ units will be considered. These chains are grafted at one end onto an impermeable surface with a density ensuring overlapping of polymer coils and immersed in a solvent the quality of which is characterized by a relative deviation from the Θ-temperature, $\tau \equiv (T - \Theta)/T \geqslant 0$ (or the second virial coefficient of unit interaction $v \sim \tau$), Figure 1. A chain part of length equal to chain thickness a with a volume $v_0 \sim a^3$ is chosen as the unit. The asymmetry parameter is $p = l/a \geqslant 1$ where l is the length of the Kuhn chain segment ($p = 1$ for a flexible chain and $p > 1$ for a semirigid chain, $N/p \gg 1$). The radii of the curvature of spherical and cylindrical surfaces will be assumed to be much smaller than the average equilibrium layer thickness.

General Theory of the Collapse of Grafted Polymer Layers. We will start from the description of dependences of integral characteristics of grafted layers on the layer morphology and the solvent quality. This description is based on the well-known mean-field Flory theory reduced to the presentation of the chain free energy in a layer in the form of a sum of free energies of elastic stretching, ΔF_{el}, and of chain units' interaction with the environment ΔF_{conc}:

$$\Delta F = \Delta F_{\mathrm{el}} + \Delta F_{\mathrm{conc}} \tag{1}$$

In the first approximation, the internal structure of the layer (concentration distribution of monomer units in the layer, the distribution of the degree of extention along the chains, chain-end distribution in the layer, etc.) is not taken into account. A layer with the given morphology is characterized only by its mean height (mean distance of the free ends of the chain from the grafting surface), H, and mean unit concentration in the layer, $\bar{\varphi}$. In this approximation, it is possible to obtain a unified description of the characteristics of grafted layers for different morphologies if the dimensionality, d_{M}, of the matrix ($d_{\mathrm{M}} = 2, 1$, or 0 for the cases of grafting onto a plane, a cylinder, or a sphere, respectively) or the effective "dimensionality" of grafted chains in the layer d ($d = 3 - d_{\mathrm{M}}$) is introduced. The corresponding characteristic of the grafting density, f_{d}, is the surface, linear, or angular density

$$\begin{aligned} f_{\mathrm{d}} &= a^2/\sigma, \quad d = 1 \\ &= a/h, \quad d = 2 \\ &= f, \quad d = 3 \end{aligned} \tag{2}$$

where σ is the surface area per chain, $1/h$ is the chain number per unit cylinder length, and f is the complete number of chains on the sphere. The radii of the spherical and cylindrical matrices are assumed to be small as compared to the total layer height.

The equilibrium structural characteristics of the layer will be determined from the condition of the minimum of free energy (eq 1).

In the approximation used, it may be assumed that ΔF_{el} is equal to the free energy of homogeneous deformation of a Gaussian chain to the size H_{d}. In this case above the Θ-point (at $\tau > 0$) it is sufficient to consider only chain stretching in the layer with respect to Gaussian dimensions. By introduction of the swelling coefficient of the layer with respect to Gaussian dimensions

$$\alpha \equiv H_{\mathrm{d}}/(N^{1/2}p^{1/2}a) \tag{3}$$

it is possible to represent the free energy of chain stretching in the form

$$\Delta F_{\mathrm{el}} \simeq \alpha^2 - \ln \alpha^2, \quad \alpha > 1 \tag{4}$$

Here and below all energetic values are expressed in kT units.

In the range of $\tau < 0$ the stretching of the chains in the layer with respect to their Gaussian dimensions may be retained (at a relatively dense grafting). However, when grafting is not very dense, chain dimensions in this range may become smaller than the Gaussian dimensions, although the chains in the layer will still overlap. In this case (at $\alpha < 1$), as has been shown in detail in refs 34 and 35, eq 4 is not valid and should be replaced by eq 5.

$$\Delta F_{\mathrm{el}} \simeq 1/\alpha^2 + \ln \alpha^2, \quad \alpha < 1 \tag{5}$$

In the approximation used, the free energy of volume interactions (per chain), ΔF_{conc}, is equal to the free energy of volume interactions in the layer with the constant concentration equal to

$$\bar{\varphi}_{\mathrm{d}} \simeq N f_{\mathrm{d}} a^d H_{\mathrm{d}}^{-d}$$

$$\Delta F_{\mathrm{conc}} \simeq N v (N f_{\mathrm{d}} a^d / H_{\mathrm{d}}^{\,d}) + N w (N f_{\mathrm{d}} a^d / H_{\mathrm{d}}^{\,d})^2 \tag{6}$$

where $v \simeq v_0 \tau$ and w are the dimensionless second and third virial coefficients of unit interactions, respectively.

Minimizing the free energy (eq 1) for H_{d} (or for $\bar{\varphi}_{\mathrm{d}}$) and applying eqs 3–6, we obtain the equations for the equilibrium coefficient of layer swelling

$$\alpha^{d+2}(1 - 1/\alpha^2) \simeq B\tau + C/\alpha^d, \quad \alpha > 1 \tag{7}$$

$$-\alpha^{d-2}(1 - \alpha^2) \simeq B\tau + C/\alpha^d, \quad \alpha < 1 \tag{8}$$

where

$$\begin{aligned} B &\simeq v_0 f_{\mathrm{d}} N^{(4-d)/2} p^{-d/2} \\ C &\simeq w f_{\mathrm{d}}^{\,2} N^{3-d} p^{-d} \end{aligned} \tag{9}$$

are the renormalized parameters characterizing the binary and ternary interactions in the layer, respectively.

Equations 7 and 8 describe the decrease in layer height with decreasing temperature (decrease in τ), and the layer as a whole is transformed from the swollen into the collapsed (globular) state. Note that a nonscaling term included in eqs 4, 5, 7, and 8 (term $\pm\ln \alpha^2$ in eqs 4 and 5, causing the appearance of the second term in parentheses in eqs 7 and 8) is significant only at the values of α close to unity. It ensures the crossover between the two expressions for elastic free energy, eqs 4 and 5, at the point $\alpha = 1$, $\Delta F_{\mathrm{el}}(\alpha{=}1) = 0$ (see for details refs 34 and 35). Of course this term does not effect all the results at $\alpha \gg 1$ (see for example eq 14), particularly the scaling dependences.

The transition from eq 7 to eq 8 occurs at $\alpha = 1$, i.e., at

$$\tau' = -C/B \equiv -(w/v_{\mathrm{o}})f_{\mathrm{d}}N^{(2-d)/2}p^{-d/2} \tag{10}$$

Equation 7 will be considered first. This equation makes it possible to obtain power asymptotes for layer size in solvents of different qualities under the condition $\tau > \tau'$, i.e., $\alpha > 1$.

$$\begin{aligned} H_{\mathrm{d}} &\simeq a(v_{\mathrm{o}}p\tau f_{\mathrm{d}}N^3)^{1/(d+2)}, \quad \tau > 0 \\ &\simeq a(wpf_{\mathrm{d}}N^2)^{1/(d+1)}, \quad \tau = 0 \\ &\simeq a(wv_{\mathrm{o}}^{-1}|\tau|^{-1}f_{\mathrm{d}}N)^{1/d}, \quad \tau < 0 \end{aligned} \tag{11}$$

(In order to obtain these asymptotes, only two terms dominating in the corresponding range are retained in eq 7 for each asymptote, viz., elastic (only the scaling term) + binary interaction terms; elastic (scaling term) + ternary interactions terms; binary interactions + ternary interactions terms, respectively).

It can be seen from eq 11 that the exponent ν_{d} in asymptotes $H_{\mathrm{d}} \sim N^{\nu_{\mathrm{d}}}$ depends on the dimensionality d and the solvent quality just as for an isolated chain of dimensionality d in the mean-field Flory theory

$$\begin{aligned} \nu_{\mathrm{d}} &= 3/(d+2), \quad \tau > 0 \\ &= 2/(d+1), \quad \tau = 0 \\ &= 1/d, \quad \tau < 0 \end{aligned} \tag{12}$$

The determination of the asymptote for N at $\tau < 0$ according to eq 7 assumes that the crossover point τ^* between the Θ-state and the collapsed state is above τ' ($\tau^* > \tau'$), so that $\alpha(\tau^*) > 1$. The determination of τ^* from the condition of the crossover of the dependence $H_{\mathrm{d}}(\tau)$ at $\tau = 0$ and $\tau < 0$ gives

$$\tau^* = -C^{(d+2)/[2(d+1)]}B^{-1} \equiv -v_{\mathrm{o}}^{-1}(w^{(d+2)/2}f_{\mathrm{d}}N^{1-d}p^{-d/2})^{1/(d+1)} \tag{13}$$

A comparison with eq 10 shows that the condition $\tau' < \tau^*$ is obeyed at $C > 1$. In this case at the point τ^* the layer remains stretched as compared to the Gaussian dimensions. At $C < 1$ the value of $\tau^* < \tau'$ and the collapse of the layer proceeds under the condition $\alpha < 1$ when the dependence $\alpha(\tau)$ is described by eq 8. Note that the parameter of ternary interactions $C \sim N^{3-d}$ increases infinitely with N at $d = 1$ and $d = 2$. Hence, for planar ($d = 1$) and cylinder ($d = 2$) layers, all three asymptotes (eq 11) are determined from eq 7. For spherical ($d = 3$) layers, $C \sim N^{0}$, and depending on the values of other parameters both $C > 1$ and $C < 1$ are possible. Moreover, eqs 7 and 8 give the same asymptote at $\tau < 0$.

It was already mentioned above that the exponents ν_{d} of asymptotic power dependences of the size of the d-dimensional layer on N coincide with those for mean-field dimensions of an isolated chain in a d-dimensional space. Analogously, the main relationship of the collapse of the d-dimensional layer coincides with those of the collapse of an isolated d-dimensional chain. For $d = 3$ and $d = 2$ (spherical and cylindrical layers), the transition range $\Delta\tau \simeq |\tau^*|$ becomes more narrow with increasing N (see eq 13); the transition is displaced toward the point $\tau = 0$ and, in the limit $N \to \infty$, is a second-order phase transition (free energy per unit $\Delta F/N \to 0$ at $\tau > 0$ and $\Delta F/N \to -\tau^2$ at $\tau < 0$). In the case when $d = 1$ (planar layer), the position of the transition τ^* and its range are independent of N. It means that the transition is not truly a thermodynamic phase transition but only a cooperative conformational transition.

The absence of phase transition in the collapse of the planar layer (or an isolated 1-dimensional chain) is also clearly seen in eq 12 from which it follows that at $d = 1$ we have $\nu_{\mathrm{d}} = 1$; i.e., $H_{\mathrm{d}} \sim N$ at any τ. Hence, our results show that strong repulsion of chains in the layer due to ternary interactions leads to a shift of the transition into the collapsed state toward the range of lower temperatures and makes it more smooth than in the case of a free 3-dimensional chain (for which this transition occurs in the range of $\Delta\tau \sim N^{-1/2}$ about the Θ-point). This effect increases with decreasing dimensionality, d, of chains in the layer and is at a maximum at $d = 1$ when the transition becomes a nonphase transition. At a fixed morphology of the matrix, the transition range increases with grafting density (see eq 13).

Note that recently Halperin[32] considering the collapse of a planar ($d = 1$) layer on the basis of the mean-field theory has come to a paradoxical result that first-order phase transition is possible in this effectively 1-dimensional system. The form of the dependence $\alpha(\tau)$ at $\tau < 0$ has been considered in ref 32. It has been shown that this dependence may have an unstable region (a loop) at $\alpha < 1$ and $C \lesssim 10^{-1}$, and a conclusion has been drawn about the phase transition with a jumpwise change in layer size. However, the analysis shows that this looplike dependence of α on τ is an artifact because it has been obtained by Halperin from the equation equivalent to eq 7 that is not valid at $\alpha < 1$ and $C < 1$. Under these conditions, it is necessary to use eq 8, which does not give a loop at $d = 1$ (and also at $d = 2$), so that in these cases the dependence $\alpha(\tau)$ is described by a smooth curve at any values of the parameters B and C. In contrast, the existence of loops on the dependence $\alpha(\tau)$ at $\tau < 0$ and $C \ll 1$ in the case $d = 3$ corresponding to a jump in size occurring when an isolated 3-dimensional chain collapses is a well-known fact (see, for example, ref 36 and discussion in refs 34 and 35).

It is of interest that the correct expression (eq 5) of the entropy term in the theory of the random coil–globule phase transition[34,35] makes it possible to eliminate the unrealistic result (first-order phase transition in a 1-dimensional system).

Note, that this effective unidimensionality of the chains in a planar layer has a very simple interpretation: in a mean-field approximation the behavior of a chain in a layer is equivalent to that of a chain located in a "tube" with a section σ randomly bent in the direction parallel to the grafting surface.

It should also be noted that eq 8 assumes the retention of a continuous layer at $\alpha < 1$. In the case when grafted chain ends can move freely on the matrix surface, i.e., when only the mean grafting density is fixed and $\bar{C} < 1$, the collapse of planar ($d = 1$) and cylindrical ($d = 2$) layers should be accompanied by the separation into two phases with different grafting densities: $f_{\mathrm{d}}^{(1)}(\tau) > \bar{f}_{\mathrm{d}}$ and $f_{\mathrm{d}}^{(2)}(\tau) \ll \bar{f}_{\mathrm{d}}$ (nonoverlapping globules) and $\alpha^{(1)} = 1$.

In further discussion, only that case will be considered in which grafting density ensures chain stretching in the layer with respect to Gaussian dimensions ($\alpha > 1$) over the entire temperature range considered here, $\tau > 0$, $\tau = 0$, $\tau < 0$; $\tau > \tau'$. Under these conditions, eq 7 is valid and at $\alpha \gg 1$ may be represented in the form

$$\tilde{\alpha}^{2d+2} - \beta_{\mathrm{d}}\tilde{\alpha}^{d} - 1 = 0 \tag{14}$$

where a nonscaling term is omitted and a new relative characteristic of the layer size is introduced: the swelling coefficient with respect to equilibrium dimensions at the Θ-point

$$\tilde{\alpha}(\tau) \equiv H_{\mathrm{d}}(\tau)/H_{\mathrm{d}}(\tau{=}0) \equiv \alpha(\tau)/\alpha(\tau{=}0) \tag{15}$$

and the new universal parameter β_{d} is determined by the relation

$$\beta_{\mathrm{d}} \simeq \tau/|\tau^*| \equiv \upsilon(w^{(d+2)/2}f_{\mathrm{d}}N^{1-d}p^{-d/2})^{-1/(d+1)} \tag{16}$$

It follows from eq 14, at least near the transition point into the collapsed state $\beta_{\mathrm{d}} = 0$ (at $\tau > \tau'$), that the swelling coefficient of the layer α is the function of the parameter β_{d} alone and monotonically decreases with β_{d} (decreasing temperature). The range of $\beta_{\mathrm{d}} \gg 1$ corresponds to the high-temperature asymptote (conditions of a good solvent), and the range $\beta_{\mathrm{d}} < 0$, $|\beta_{\mathrm{d}}| \gg 1$ corresponds to the low-temperature asymptote (conditions of the precipitant) of the dependence $\tilde{\alpha}(\beta)$ or to asymptotic power expressions in eq 11 for the layer height H_{d}.

In the general case, the layer collapse should be accompanied by its structural rearrangement and, in particular, by a change in distribution of unit density (it should be noted that the simple form of eqs 7, 8, and 14 for swelling coefficients $\alpha(\tau)$ and $\tilde{\alpha}(\tau)$ is caused by neglecting this effect). In general terms it is possible to analyze the change in unit density distribution, neglecting as before the distribution of chain ends in the layer (forcing all ends to H_{d}) and representing the free energy of the "d-dimensional" layer as a functional of density profile

$$\Delta F \simeq \int_0^{H_{\mathrm{d}}} \left\{ \frac{f_{\mathrm{d}}a^{d-2}}{pr^{d-1}\varphi(r)} + [\upsilon\varphi^2(r) + w\varphi^3(r)]\frac{r^{d-1}}{a^d f_{\mathrm{d}}} \right\} \mathrm{d}r \tag{17}$$

where r is the coordinate in the direction normal to the matrix and the first term is the elastic free energy.

The minimization of the functional in eq 17 with respect to $\varphi(r)$ and H_{d} with the application of the normalization condition

$$Nf_{\mathrm{d}}a^d \simeq \int_0^{H_{\mathrm{d}}} \varphi(r)\, r^{d-1}\, \mathrm{d}r$$

makes it possible to obtain the equilibrium density profile in the "d-dimensional" layer, which may be approximated by the piecewise smooth power function[31]

$$\begin{aligned} \varphi(r) &\simeq \left(\frac{f_{\mathrm{d}}a^{d-1}}{r^{d-1}}\right)^{1/2} (wp)^{-1/4}, \quad r \ll \kappa_{\mathrm{d}} \\ &\simeq \left(\frac{f_{\mathrm{d}}a^{d-1}}{r^{d-1}}\right)^{2/3} (\upsilon p)^{-1/3}, \quad r \gg \kappa_{\mathrm{d}}, \upsilon > 0 \\ &\simeq |\upsilon|/w, \quad r \gg \kappa_{\mathrm{d}}, \upsilon < 0 \end{aligned} \tag{18}$$

where

$$\kappa_{\mathrm{d}} \simeq (f_{\mathrm{d}}a^{d-1}|\upsilon|^{-2}w^{3/2}p^{-1/2})^{1/(d-1)} \tag{19}$$

is the size of the inner part of the layer in which the density distribution does not depend on solvent strength.

Hence, it follows from eq 18 that the layer structure is profoundly affected by its morphology.

At $d = 1$, the layer is homogeneous in the sense that the power dependence of density on the coordinate in the direction normal to the plane is absent.

At $d < 1$, the layer is inhomogeneous and is characterized by the power density profile. At $\upsilon > 0$, the unit density decreases monotonically with the distance from the matrix according to the power law, and at $\upsilon < 0$ a region of constant density coinciding with that of the globule in volume approximation is formed at the periphery of the layer as a result of a decrease in chain-end stretching. Hence, the layer collapse always starts from its outer, looser part.

Structure and Collapse of a Planar Layer. The development of a complete theory of structure of a planar layer in a wide range of solvent strength is based as before on the minimization of the free energy, eq 1, where

$$\Delta F_{\mathrm{conc}} = (\sigma/a^3)\int_0^H f[\varphi(x)]\, \mathrm{d}x \tag{20}$$

and $f[\varphi(x)]/a^3$ is the density of free energy of volume interactions between units in a layer, and $\varphi(x)$ is the dimensionless concentration (volume fraction) of units at a height x from the grafting plane. In order to calculate the stretching entropy $-\Delta F_{\mathrm{el}}$, the Gaussian approximation for the free energy δF_{el} of local stretching of a chain part consisting of δn units by a distance of δx will be used.

$$\delta F_{\mathrm{el}} = \frac{3}{2pa^2}\frac{\delta x^2}{\delta n}$$

Passing to the continual limit, one may write the free energy of stretching of the entire chain in the form

$$\Delta F_{\mathrm{el}}(x') = \frac{3}{2pa^2}\int_0^{x'} E(x,x')\, \mathrm{d}x$$

where x' is the height of the free chain end above the plane, and the function $E(x,x') = \mathrm{d}x/\mathrm{d}n$ characterizes the local chain stretching at a height x. The physical sense of the function $E(x,x')$ is relatively simple: it determines the value of the elastic force $\mathcal{F} = (3/pa^2)E(x,x')$ acting in an extended chain at a height $x \le x'$.

In order to take into account the possibility of different chain stretchings in a layer, the distribution function of free chain ends, $g(x')$, along the layer height is introduced. Then $g(x')\, \mathrm{d}x'$ is the fraction of chains, the ends of which are located in a layer when a thickness $\mathrm{d}x'$ lying at a height x' from the surface (normalization: $\int_0^H g(x')\, \mathrm{d}x' = 1$). Then the entropy contribution to the free energy of the layer per chain is given by

$$\Delta F_{\mathrm{el}} = \int_0^H \Delta F_{\mathrm{el}}(x')\, g(x')\, \mathrm{d}x' = \frac{3}{2pa^2}\int_0^H g(x')\, \mathrm{d}x' \int_0^{x'} E(x,x')\, \mathrm{d}x \tag{21}$$

Approximation 21 for the stretching entropy of a grafted layer has first been used by Semenov[28] in the analysis of the structure of densely packed domains in block copolymer systems and assumes strong chain stretching normal to the surface.

The concentration (volume fraction) of units $\varphi(x)$ at a height x may be expressed by the functions $E(x,x')$ and $g(x')$ with the aid of the equation

$$\varphi(x) = \frac{a^3}{\sigma}\int_x^H \frac{g(x')\, \mathrm{d}x'}{E(x,x')} \tag{22}$$

The equilibrium characteristics of the layer may be obtained from the condition of the minimum of free energy ΔF determined by eqs 1 and 20–22 as a function of two unknown functions $E(x,x')$ and $g(x')$ taking into account additional normalization conditions

$$\int_0^{x'} \frac{\mathrm{d}x}{E(x,x')} = N \qquad (23)$$

$$\frac{\sigma}{a^3}\int_0^H \varphi(x)\,\mathrm{d}x = N \qquad (24)$$

The solution of this variational problem makes it possible to obtain the expression for the function of local chain stretching in a layer

$$E(x,x') = (\pi/2N)(x'^2 - x^2)^{1/2} \qquad (25)$$

and to write the equations for the profile of layer density

$$\frac{2pa^2}{3}\{\tilde{\lambda} + \mu[\varphi(x)]\} = -\frac{\pi^2}{4N^2}x^2 \qquad (26)$$

where $\mu[\varphi(x)] = \delta f[\varphi]/\delta\varphi(x)$ is the chemical potential and $\tilde{\lambda} = \tilde{\lambda}(H)$ is the indefinite Lagrangian multiplier, the value of which is determined from the normalization condition (eq 24).

It should be noted that the distribution of local chain stretching along the height, described by the function $E(x,x')$ given by eq 7, is of universal character. It is independent of both the type of density of free energy of volume interactions $f[\varphi]$ and the slit width H. The explicit form of $E(x,x')$ is determined only by the Gaussian character of local chain stretching. Any chain in the layer is stretched to the greatest extent near the surface ($x = 0$). With increasing distance from the surface, local chain stretching decreases, becoming equal to zero at the free end.

One of the consequences of this universal character of function $E(x,x')$ is the universal relationship between the moments $\langle x^n\rangle_g$ of the distribution function of free chain ends $g(x)$ and the moments $\langle x^n\rangle_\varphi$ of the distribution function of unit density $\varphi(x)$.

It follows from eqs 22 and 25 that

$$\langle x^n\rangle_\varphi = B_n\langle x^n\rangle_g, \quad n = 0, 1, 2, \ldots \qquad (27)$$

where

$$\begin{aligned} B_n &= \frac{2}{\pi}\int_0^1 \frac{t^n\,\mathrm{d}t}{(1-t^2)^{1/2}} = \frac{(2k-1)!!}{(2k)!!}, \quad n = 2k \\ &= \frac{2}{\pi}\frac{(2k)!!}{(2k+1)!!}, \quad n = 2k+1 \qquad (28) \end{aligned}$$

In order to determine the explicit form of the density profile of units in the layer $\varphi(x)$ and the distribution function of chain ends along the height $g(x)$, it is necessary to know the explicit form of the dependence of chemical potential $\mu = \mu[\varphi]$ on concentration φ. Under the conditions of moderate grafting density ($a^2/\sigma \ll 1$), it is possible to use virial expansion for the density of the free energy of volume interactions

$$f[\varphi(x)] \simeq \upsilon\varphi^2(x) + w\varphi^3(x) \qquad (29)$$

where $\upsilon \sim \tau$ and w are the second and third dimensionless virial coefficients of interaction between units. Then, applying eqs 26 and 29, we obtain the expression for the density profile of units in the layer

$$\varphi(x) = \frac{\upsilon}{3w}\{\mathrm{sign}\,(\upsilon)(1 + \kappa^2(\lambda - x^2))^{1/2} - 1\} \qquad (30)$$

where the following designations are introduced: $\lambda = -\tilde{\lambda}(8a^2N^2p/3\pi^2)$ and $\kappa^2 = 9\pi^2 w/8\upsilon^2 a^2N^2p$.

In order to calculate the function $g(x)$, eq 24 will be used as an integral equation with respect to the unknown function $g(x)$. Its solution with the application of eqs 25 and 30 is given by

$$g(x) = \frac{x\sigma}{Na^3}\frac{\upsilon}{3w}\left\{\frac{\mathrm{sign}\,(\upsilon)(1 + \kappa^2(\lambda - H^2))^{1/2} - 1}{(H^2 - x^2)^{1/2}} + \frac{\kappa}{2}\left[\frac{\pi}{2} + \arcsin\frac{2H^2 - x^2 - \kappa^{-2} - \lambda}{\lambda - x^2 + \kappa^{-2}}\right]\right\} \qquad (31)$$

Equations 30 and 31 were obtained from the condition of the minimum free energy of the layer at a fixed H (i.e., the layer located in a slit of width H) and make it possible to obtain the equilibrium value of the conformational free energy of the layer $\Delta F(H)$ in a slit of a fixed width H.

The condition

$$\left(\frac{\partial\Delta F(H)}{\partial H}\right)_{H_0} = 0 \qquad (32)$$

equivalent to that of the disappearance of pressure on the upper plane in combination with eqs 24 and 30 determines the equilibrium value of the height of the free layer H_0 and the corresponding value of the indefinite multiplier $\lambda = \lambda_0$.

Now the equilibrium structure of the free layer will be considered in detail (the analysis of properties of the layer located in a slit of a given width is presented in the authors' paper[1]). Particular attention will be paid to the structural changes caused by the change in solvent strength. Here we will restrict ourselves to the case of moderately dense grafting ($\sigma/a^2 \gg 1$). The case of the most dense grafting will be considered in the Appendix.

Layer Height, H_0. The equation for the height of the free layer, H_0, assumes a simple closed-form solution only at the Θ-point ($\upsilon = \tau = 0$).

$$H_0^{\Theta} \equiv H_0(\upsilon{=}0) = (4/\pi)(wp/2)^{1/4}(\sigma/a^2)^{-1/2}Na \qquad (33)$$

However, the analysis of the temperature dependence of the layer height shows that the swelling coefficient of the layer with respect to its Θ-dimensions $\alpha \equiv H_0(\upsilon)/H_0(\upsilon{=}0)$ is the function of only one parameter (compare eqs 14–16)

$$\beta = (1/3)(p/2)^{1/4}\upsilon w^{-3/4}(\sigma/a^2)^{1/2} \qquad (34)$$

The range $\beta \gg 1$ corresponds to the conditions of a strong solvent, $|\beta| \lesssim 1$ corresponds to Θ-conditions, and $\beta \ll -1$ corresponds to the precipitant conditions. The closed equation for the swelling coefficient $\tilde{\alpha}$ may be obtained and is given by

$$\begin{aligned} \frac{\pi}{2\beta^2} &= -\tilde{\alpha}/\beta + (1 + \tilde{\alpha}^2/\beta^2)\arctan\,(\tilde{\alpha}/\beta), \quad \beta \geqslant 0 \\ &= -(5/2)(\tilde{\alpha}/\beta) + (1/4 + \tilde{\alpha}^2/\beta^2)\arctan\,(2\tilde{\alpha}/\beta), \quad \beta \leqslant 0 \qquad (35) \end{aligned}$$

Figure 2 shows the universal dependence $\alpha(\beta)$ plotted according to eq 35. It is clear that the decrease in temperature (inferior solvent strength) leading to a decrease in β results in a monotonic decrease in the layer height, H_0. The high- ($\beta \gg 1$) and low-temperature ($\beta \ll -1$) asymptotes of the function $\tilde{\alpha}(\beta)$ obtained from eq 35 are shown by dotted and dashed lines, respectively.

$$\begin{aligned} \tilde{\alpha}(\beta) &\simeq ((3\pi/4)\beta)^{1/3}, \quad \beta \gg 1 \\ &\simeq (\pi/6)|\beta|^{-1}, \quad \beta \ll -1 \qquad (36) \end{aligned}$$

These asymptotes make it possible to obtain the layer size, H_0, under the conditions of a strong solvent ($\beta \gg 1$)

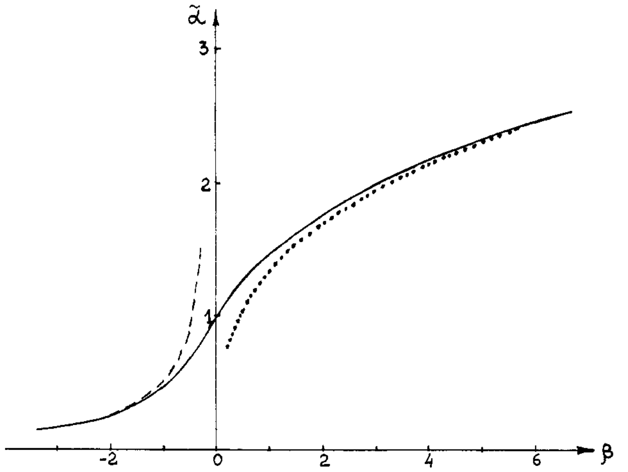

Figure 2. Dependence of the swelling coefficient of the layer with respect to the Θ-size, $\tilde{\alpha}$, on the parameter β. Dotted and dashed lines show the corresponding high- and low-temperature asymptotes of the dependence $\tilde{\alpha}(\beta)$.

and a precipitant ($\beta \ll -1$).

$$H_0 \simeq (8/\pi^2)^{1/3}(vp)^{1/3}(\sigma/a^2)^{-1/3}Na, \quad \beta \gg 1$$
$$\simeq (2w/|v|)(\sigma/a^2)^{-1}Na, \quad \beta \ll -1 \qquad (37)$$

It is noteworthy that, in the range $\beta < 0$, the applicability of eqs 36 and 37 is limited by the condition $\bar{\varphi} \ll 1$ ensuring the possibility of virial expansion for the density of free energy (eq 29) and by the condition of chain stretching with respect to Gaussian dimensions (see above).

Density Profile of Units in a Layer. The density profile of units in a free layer is described by eq 30 at $\lambda = \lambda_0$. Taking into account the definition of swelling coefficient $\tilde{\alpha}$, the density profile is given by

$$\varphi_0(z)/\bar{\varphi}_0 = (4/\pi)\beta\tilde{\alpha}[(1 + (\tilde{\alpha}^2/\beta^2)(1 - z^2))^{1/2} - 1], \quad \beta \geq 0$$
$$= (4/\pi)|\beta|\tilde{\alpha}[((1/4) + (\tilde{\alpha}^2/\beta^2)(1 - z^2))^{1/2} + 1], \quad \beta \leq 0 \qquad (38)$$

where the relative coordinate $z = x/H_0$ and the mean unit density in a layer $\bar{\varphi}_0 = Na^3/(\sigma H_0)$ are introduced. When asymptotes (eq 36) are used for the swelling coefficient of the layer $\tilde{\alpha}(\beta)$, it is easy to obtain the asymptotic forms of the density profile in the high- (see also refs 22 and 23) and low-temperature ranges and at the Θ-point

$$\varphi_0(z) \simeq (3/2)\bar{\varphi}_0^{+}(1 - z^2), \quad \beta \gg 1 \qquad (39.1)$$
$$\simeq (4/\pi)\bar{\varphi}_0^{\Theta}(1 - z^2)^{1/2}, \quad \beta = 0 \qquad (39.2)$$
$$\simeq \bar{\varphi}_0^{-}, \quad \beta \ll -1 \qquad (39.3)$$

where

$$\bar{\varphi}_0^{+} = (1/2)\pi^{2/3}(vp)^{-1/3}(\sigma/a^2)^{-2/3} \qquad (40.1)$$
$$\bar{\varphi}_0^{\Theta} = (2/wp)^{1/4}(\sigma/a^2)^{-1/2} \qquad (40.2)$$
$$\bar{\varphi}_0^{-} = |v|/(2w) \qquad (40.3)$$

are the asymptotic values of the mean density in a layer.

Hence, the free planar layer of grafted chains at any $N \gg 1$ is inhomogeneous as a whole: in reduced variables $(\varphi_0/\bar{\varphi}_0, z)$ the density profile is described by a unified monotonically decreasing function of the coordinate z, depending only on one parameter β. In this case the degree of polymerization, N, plays only the role of the scale factor. Figure 3 shows the dependence of $\varphi_0(z)/\bar{\varphi}_0^{\Theta}$ on z plotted according to eq 38, taking into account eq 35 for the case of a strong solvent ($\tilde{\alpha} = 1.3$, curve 1), a Θ-solvent ($\tilde{\alpha} = 1$, curve 2), and a poor solvent ($\tilde{\alpha} = 0.68$, curve 3).

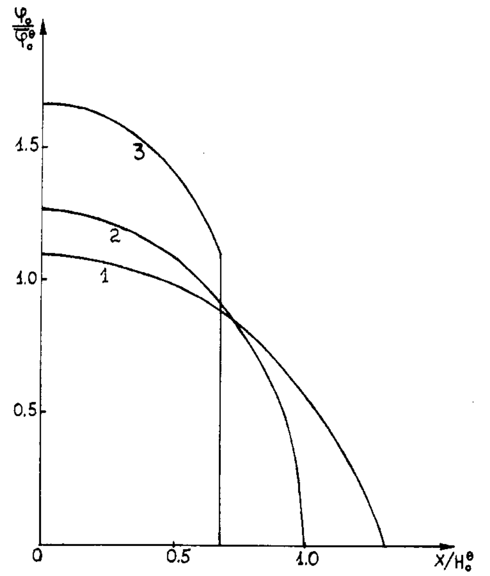

Figure 3. Density profile in the layer in reduced coordinates $(\varphi_0/\varphi_0^{\Theta}, x/\underline{H}_0^{\Theta})$ for the cases of a strong solvent, $\tilde{\alpha} = 1.3$ (1), a Θ-solvent, $\tilde{\alpha} = 1$ (2), and a poor solvent, $\tilde{\alpha} = 0.68$ (3).

It can be seen from Figure 3 that the decrease in temperature (inferior solvent strength), leading to the collapse of the layer as a whole, is also accompanied by the redistribution of unit density in the layer. In the high-temperature range ($\beta \gg 1$), the density profile is of a parabolic shape (eq 39.1). With decreasing temperature (decreasing solvent strength), the layer contracts as a whole and the average unit density increases. In this case the density of the outer, looser part of the layer increases preferentially, and the decrease in density on its periphery becomes more abrupt. Below the Θ-point (at $\beta < 0$), the unit density at the layer boundary, $x = H$, becomes equal to zero not smoothly but with a jump, and the value of this jump $\Delta\varphi = |v|/2w$ coincides with the density of an isolated globule in volume approximation (equilibrium density of the precipitated polymer). In the low-temperature range $\beta \ll -1$, the density profile tends to the stepwise shape (eq 39.3).

Distribution of Free Chain Ends. The distribution function of free chain ends in a free layer may be obtained by the substitution of $\lambda = \lambda_0$ into eq 31 and in reduced variables is given by

$$g_0(z) = \tilde{\alpha}^2 z\left[1 + (2/\pi)\arcsin\left(\frac{1 - z^2 - \beta^2/\tilde{\alpha}^2}{1 - z^2 + \beta^2/\tilde{\alpha}^2}\right)\right], \quad \beta > 0$$
$$= 2z, \quad \beta = 0$$
$$= \tilde{\alpha}^2 z\left[1 + (2/\pi)\arcsin\left(\frac{1 - z^2 - \beta^2/(4\tilde{\alpha}^2)}{1 - z^2 + \beta^2/(4\tilde{\alpha}^2)}\right) - \frac{6\beta}{\pi\tilde{\alpha}(1 - z^2)^{1/2}}\right], \quad \beta < 0 \qquad (40)$$

Figure 4 shows the dependences $g_0(z)$ calculated from eq 40 for the value of $\tilde{\alpha} = 1.3$ (strong solvent, curve 1), $\tilde{\alpha} = 1$ (Θ-solvent, curve 2), and $\tilde{\alpha} = 0.68$ (precipitant, curve 3). The asymptotic functions of free end distribution $g_0^{\pm}(z)$ corresponding to the high- and low-temperature limits in

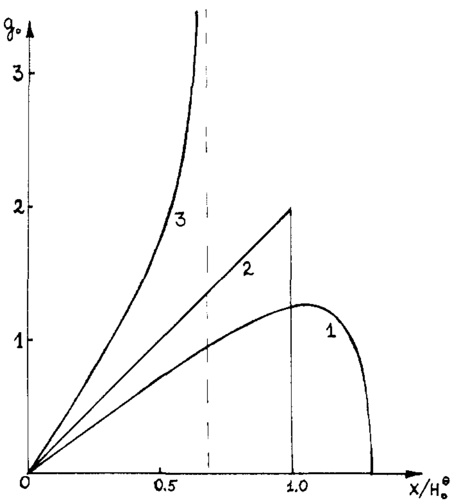

Figure 4. Distribution function of chain ends in the layer, $g(z)$ (in a system of reduced coordinates). Curve 1: the case of a good solvent ($\tilde{\alpha}$ = 1,3). Curve 2: the case of the Θ-solvent ($\tilde{\alpha}$ = 1). Curve 3: the case of a poor solvent ($\tilde{\alpha}$ = 0.68).

eq 40 are given by

$$g_o(z) \simeq 3z(1-z^2)^{1/2}, \quad \beta \gg 1$$
$$\simeq z(1-z^2)^{-1/2}, \quad \beta \ll -1 \qquad (41)$$

(See also refs 22, 23, and 28.) Hence, the free chain ends are distributed throughout the layer thickness, and the character of their distribution is determined by solvent strength (temperature): the decrease in temperature is accompanied by a decrease in stretching, mainly by that of the most extended chains in the layer.

Bond Orientational Order. Chain stretching in the direction normal to the grafting surface results in the orientational ordering of chain units in a layer. In this case the direction of predominant orientation coincides with that normal to the surface. It follows from the results of ref 14 that the degree of orientational order, i.e., the order parameter $\eta \equiv \langle P_2(\cos\theta)\rangle$ in a part of a freely jointed chain consisting of δn units and stretched at the ends by the distance of δx is given by

$$\eta = (3/2a^2)(\delta x/\delta n)^2 \qquad (42)$$

Taking into account the definition of the function $E(x,x')$, the expression for the local value of the order parameter in a nonuniformly stretched chain may be written as

$$\eta(x,x') = (3/2a^2)E^2(x,x') \qquad (43)$$

The mean value of the order parameter in a nonuniformly stretched chain, the end of which is located at a height x' above the surface, is given by

$$\bar{\eta}_{x'} = (3/2a^2N)\int_0^{x'} E(x,x')\,\mathrm{d}x = (3\pi^2/16)(x'/Na)^2 \qquad (44)$$

where the last expression is obtained by the substitution of eq 25 for the equilibrium function of local stretching, $E(x,x')$, of chains in a layer. Averaging eq 44 over the positions of chain ends, we obtain the expression for the mean order parameter in a layer

$$\bar{\eta} = (3\pi^2/16)(\langle x^2\rangle_g/N^2a^2) \equiv (3\pi^2/8)(\langle x^2\rangle_\varphi/N^2a^2) \qquad (45)$$

Applying eq 43, it is also easy to obtain the expression for the profile of the orientational order in a layer, i.e., the dependence of the mean order parameter at a distance x from the surface on x

$$\eta(x) = (3/2)(H/Na^2)(\bar{\varphi}/\varphi(x))\int_x^H g(x')\,E(x,x')\,\mathrm{d}x' \qquad (46)$$

Taking into account eqs 22 and 25, it can easily be seen that the order parameter $\eta(x)$ in a layer is at a maximum near the grafting surface and decreases monotonically with the distance from it becoming equal to zero at the layer boundary $x = H$.

When the above expressions obtained for the distribution function of free chain ends (eq 40) and the density profile (eq 38) are used, it is easy to calculate the profile of the order parameter in a free layer with the aid of eq 46

$$\eta_o(z)/\bar{\eta}_o = \frac{4}{3}\frac{(1-z^2+\beta^2/\tilde{\alpha}^2)^{3/2}-(\beta/\tilde{\alpha})\left(\frac{3}{2}(1-z^2)+\beta^2/\tilde{\alpha}^2\right)}{[(1-z^2+\beta^2/\tilde{\alpha}^2)^{1/2}-\beta/\tilde{\alpha}][1+\beta^2/\tilde{\alpha}^2-4\tilde{\alpha}\beta/3\pi]}, \quad \beta \geqslant 0$$
$$= \frac{4}{3}\frac{\left[(1-z^2+\beta^2/(4\tilde{\alpha}^2))^{3/2}-(\beta/\tilde{\alpha})\left(\frac{3}{2}(1-z^2)-\beta^2/8\tilde{\alpha}^2\right)\right]}{[(1-z^2+\beta^2/(4\tilde{\alpha}^2))^{1/2}-\beta/\tilde{\alpha}][1+\beta^2/(4\tilde{\alpha}^2)-4\tilde{\alpha}\beta/3\pi+3\beta^3/(2\pi\tilde{\alpha})]}, \quad \beta \leqslant 0 \qquad (47)$$

where

$$\bar{\eta}_o = \frac{3\pi^2}{32}\left(\frac{H_o}{Na}\right)^2(1+\beta^2/\tilde{\alpha}^2-4\tilde{\alpha}\beta/3\pi), \quad \beta \geqslant 0$$
$$= \frac{3\pi^2}{32}\left(\frac{H_o}{Na}\right)^2(1+\beta^2/(4\tilde{\alpha}^2)-4\tilde{\alpha}\beta/3\pi+3\beta^3/(2\pi\tilde{\alpha})), \quad \beta \leqslant 0 \qquad (48)$$

is the mean value of the order parameter in the layer, which may also be calculated with the aid of eq 45. The asymptotic expressions for the mean order parameter are given by

$$\bar{\eta}_o \simeq (3\pi^{4/3}/10)(vp)^{2/3}(\sigma/a^2)^{-2/3}, \quad \beta \gg 1$$
$$\simeq (3/2^{3/2})(wp)^{1/2}(\sigma/a^2)^{-1}, \quad \beta = 0$$
$$\simeq (\pi^2/2)(w/v)^2(\sigma/a^2)^{-2}, \quad \beta \ll -1 \qquad (49)$$

It is clear from eqs 48 and 49 that the mean value of the order parameter in a free layer does not depend on the degree of polymerization, N, and increases monotonically with grafting density and solvent strength (increasing temperature). It is interesting to note that all three asymptotic forms of the profile of the order parameter are of the same parabolic shape in reduced coordinates differing only in the numerical coefficient. The profiles of the order parameter in the system of coordinates ($\eta_o/\eta_o^\Theta, x/H_o^\Theta$) plotted from eq 47 at different values are shown in Figure 5.

Discussion

The distinguishing features of the conformational transitions related to the collapse of the grafted polymer layers are governed by the layer morphology via the effective dimensionality of the system.

For a spherical layer (3-dimensional system) just as for an isolated chain it is the second-order phase transition with the possibility of a jump in layer dimensions below the Θ-point under certain conditions (for example, for very stiff chains). For a cylindrical layer (quasi-2-dimensional system) it is also the second-order phase transition but without the possibility of a jump.

In contrast to these results the collapse of a planar layer is not a true thermodynamic phase transition. The latter result is caused by the effective "unidimensionality" of the chains in a planar layer (quasi-1-dimensional system).

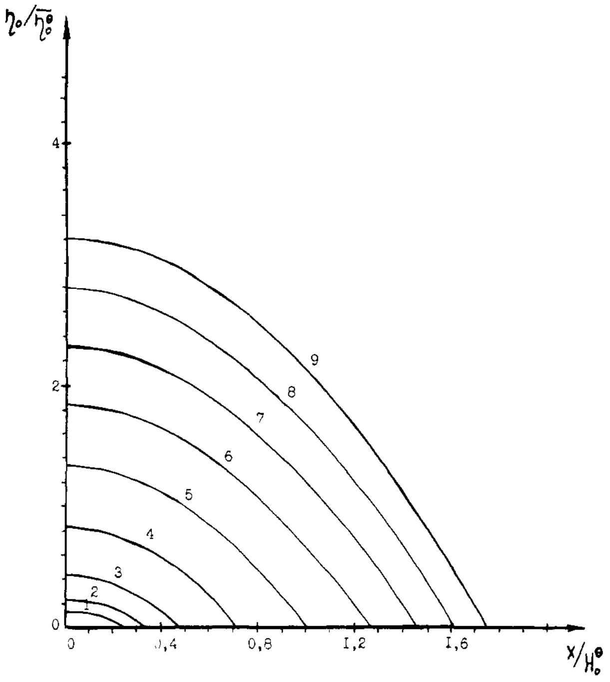

Figure 5. Profiles of the order parameter in the layer in reduced coordinates ($\eta_0/\bar{\eta}_0^\Theta$, x/H_0^Θ) for different values of the parameter β = −2.0 (1), −1.5 (2), −1.0 (3), −0.5 (4), 0 (5), 0.5 (6), 1.0 (7), 1.5 (8), 2.0 (9).

The reason for this is a strong interchain interaction under the condition of dense grafting onto a plane.

In each case the interchain interactions in a layer make the collapse transition weaker than in an isolated 3-dimensional chain: the shift of the transition point to temperatures below the Θ-temperature increases and the temperature range of the transition becomes broader. These effects become more pronounced with the decrease in effective dimensionality, *d*, of the chains in the layer and with the increase in grafting density. (For a 3-dimensional system the increase in grafting density results in a decrease in the range of the values of the parameters corresponding to the jump.)

If the grafting density is enough to provide the fulfillment of the condition $C > 1$, the chains in a layer are stretched with respect to their Gaussian dimensions not only above but also below the Θ-point. Under these conditions the swelling coefficient of the layer with respect to its Θ-dimensions, $\bar{\alpha}$, is a function of only one universal combination of all the parameters of the system $\beta_d \sim \tau \sim v$. The exponents of power dependences of β_d on all other parameters (N, f_d, w, p) and the numerical coefficient in β_d depend on the effective dimensionality, *d*, of the system.

The analysis of the structural changes accompanying the collapse of the layer showed that at $T > \Theta$ the unit density in the layer decreases with the distance from the matrix. In spherical and cylindrical layers the main dependence of the concentrational gradient is of the power type whereas in a planar layer it is weaker (of the nonpower type). The collapse of the layer always begins from the most loose periphery region. At $T < \Theta$ the region of the nonpower concentration decrease is also formed on the periphery of spherical and cylindrical layers.

The most precise investigation of the structural characteristics was made for a planar layer on the basis of an analytical mean-field theory, which makes it possible to take into account the distributions of chain ends, the local chain stretching, and the concentrational gradient in a layer.

It is shown that at any solvent strength the planar layer of grafted polymer chains is inhomogeneous as a whole. The profile of unit density in the layer is described by a monotonically decreasing function, and the characteristic scale of density decrease coincides with the entire layer height. The stretching is inhomogeneous within each chain and different for different chains, and their ends are distributed throughout the layer. However, all these dependences of structural characteristics of a planar layer on the distance from the matrix are of the nonpower type. Hence, in the scaling approach the planar layer may be considered to be homogeneous.

The collapse of a planar layer is accompanied by a change in distribution of unity density, which tends to the step function, and by the rearrangement of the chain ends to the periphery of the layer.

Appendix

Structure of Densely Grafted Layers. The above expressions obtained for the density profile of units in the layer (eqs 30 and 38) and the distribution function of free chain ends (eqs 31 and 40) are valid only provided the mean unit density in the layer is $\bar{\varphi} \ll 1$ since their derivation was based on using the virial expansion for the density of free energy of volume interactions (eq 29). However, the condition $\bar{\varphi} \ll 1$ is known to be invalid at strong layer compressions or at a very high density of chain grafting ($a^2/\sigma \lesssim 1$).

In this Appendix, the layer structure will be analyzed at very high grafting densities including those close to the limiting values, and the expressions for the functions $\varphi(x)$ and $g(x)$ valid throughout the entire concentration range $\varphi \lesssim 1$ will be obtained. Moreover, for simplicity only the case of the limiting strong (athermic) solvent and flexible chains will be considered. It should be borne in mind that eq 25 for the function $E(x,x')$ obtained above remains valid at any grafting densities when chain stretching is still of the Gaussian type.

In order to solve this problem, the densities of free energy of volume interactions in the layer will be written as the density of entropy of chain mixing in a semidilute solution.

$$f[\varphi(x)] = (1-\varphi(x))\ln(1-\varphi(x)) \qquad \text{(A.1)}$$

This equation is valid at $\varphi \leqslant 1$; the contribution related to translational entropy for grafted chains is absent.

Substituting this expression into eq 26 for the density profile and taking into account that in the case of a strong solvent $\varphi(x)$ continuously tends to zero and becomes equal to zero at $x = H_0$, we obtain the equation for the density profile of units in the layer

$$\varphi_0(x) = 1 - \exp\{-k^2(H_0/Na)^2(1-(x^2/H_0^2))\},$$
$$k = \pi(3/8)^{1/2} \qquad \text{(A.2)}$$

Using the normalization condition (eq 24), we obtain the transcedental equation relating the reduced layer height, H_0/Na, to grafting density $1/\sigma$

$$H_0/Na - (1/k)\mathcal{D}(k(H_0/Na)) = a^2/\sigma \qquad \text{(A.3)}$$

where

$$\mathcal{D}(\zeta) \equiv \exp(-\zeta^2)\int_0^{\zeta}\exp(\zeta'^2)\,d\zeta' \qquad \text{(A.4)}$$

is Dawson's integral.

Finally, the substitution of eq A.2 for $\varphi_0(x)$ and eq 25 and $E(x,x')$ into eq 22 yields the integral equation for the

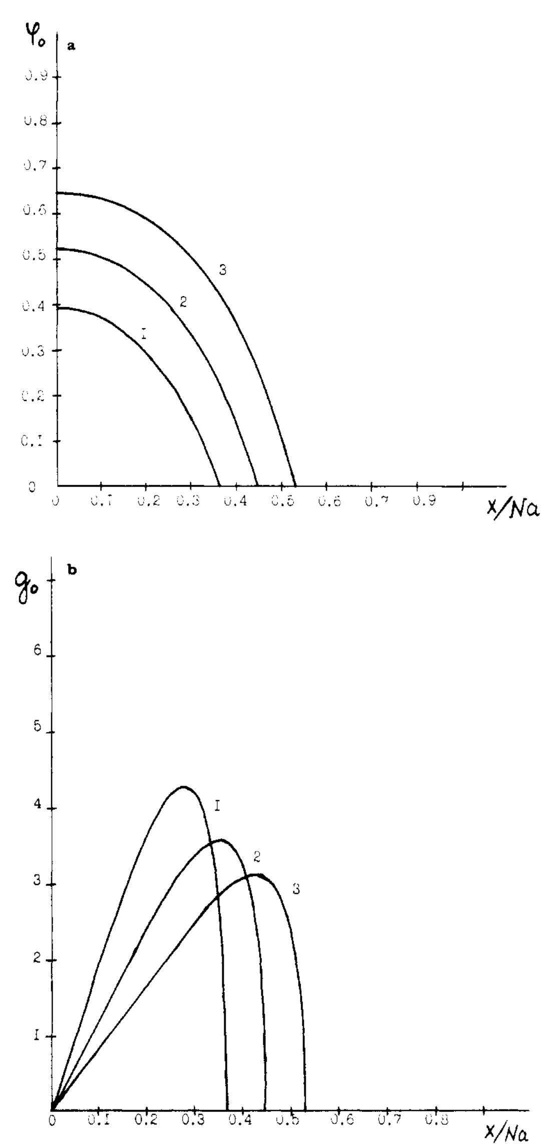

Figure 6. (a) Density profile $\varphi(x/Na)$ and (b) chain end distribution $g(x/Na)$ in the range of universality ($\sigma/a^2 = 10$, curve 1) and in the range of dense grafting ($\sigma/a^2 = 6$, curve 2, and $\sigma/a^2 = 4$, curve 3).

function $g_0(x)$, the solution of which gives

$$g_0(x) = [2kx/(Na)^2](\sigma/a^2)\mathcal{D}(k[(H_0^{\ 2} - x^2)^{1/2}]/Na) \tag{A.5}$$

Equations A.2–A.5 describe the structure of the layer of grafted chains in an athermic solvent over a wide range of changes in $0 < \varphi \lesssim 1$. If the grafting density is not too high ($a^2/\sigma \ll 1$), then it follows from eq A.3 that the layer height, H_0, remains much smaller than the contour length of the chain, Na ($H_0 \ll Na$). Then using the expansion of Dawson's integral

$$\mathcal{D}(\zeta) \simeq \zeta - (2/3)\zeta^3 + ...$$

valid at $\zeta \ll 1$ and restricting ourselves to the first terms of this expansion (which is equivalent to the retention of only the quadratic term in the expansion of eq A.1 in the powers of φ), it can be easily seen that, at $a^2/\sigma \ll 1$, eqs A.2 and A.5 are transformed into eqs 39.1 and 41.1, respectively, and the solution of eq A.3 for the layer height coincides with eq 37.1 (in this case it is necessary to assume in eqs 40.1 and 37.1 that $v = 1/2$).

As mentioned above, the range of values of grafting density $R^{-2} \ll \sigma^{-1} \ll a^{-2}$ is that of "universality": in the reduced variables $z = x/H_0$, the density profile, $\varphi_0(z)/\bar{\varphi}_0$, and the free end distribution, $g_0(z)$, are described by unified (independent of N and σ) functions. It is clear from eqs A.2–A.5 that, upon passing to denser graftings, this universality disappears. Figure 6 shows the density profiles and distribution functions of free chain ends both for the region of "universality" (moderately dense grafting) and for the case of more dense grafting (for two different σ values). The figure shows that, at high grafting density, the density profile of units becomes more shallow near the surface and steeper at the layer end as compared to the "universal" density profile (eq 39.1). With increasing density the distribution maximum of free chain ends is displaced toward the layer end and becomes sharper. It should be noted that the applicability of all the expressions obtained in the Appendix is restricted from the side of the most dense graftings ($a^2/\sigma \rightarrow 1$) because in this range chain stretching is non-Gaussian.

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