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Theory of a Planar Grafted Chain Layer Immersed in a Solution of Mobile Polymer

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ABSTRACT: The self-consistent field (SCF) theory of a planar grafted chain layer immersed in a solution of mobile polymer is developed. The equilibrium characteristics of the layer (its height, free energy, profiles of polymer units of grafted and mobile chains, and the distribution function of chain free ends) are obtained depending on the degrees of polymerization of grafted and mobile chains, the grafting density, and the content of mobile polymer chains in solution. The polydispersity of mobile chains in their lengths is also taken into account. It is shown that there are three different regimes of behavior of a grafted chain layer contacting a solution of mobile polymer. The increase in concentration of mobile chains in solution always leads to the densening of the grafted layer and it is a smooth process. The SCF results are compared with results of scaling analysis.

I. Introduction

Layers of long polymer chains grafted at one end onto impermeable surfaces of various morphologies are used as the basic model for the theoretical investigation of numerous polymer systems: melts and solutions of block copolymers under the conditions of microphase segregation, sterically stabilized colloidal dispersions, solutions of macromolecular micelles and branched polymers, etc. Initial theoretical investigations of equilibrium characteristics of grafted chain layers were carried out with the use of a scaling approach. The pioneering publication of Alexander[1] made it possible to obtain the power asymptotic dependences of the height and conformational free energy of a planar grafted chain layer immersed in athermal low molecular weight solvent. A later scaling approach was used by de Gennes[2] in the analysis of a planar grafted layer immersed in a melt (or solution) of mobile polymer chains. The account of the thermodynamic quality of the solvent and the stiffness of grafted chains[3,4] made it possible to extend the results of refs 1 and 2 to the cases of a Θ-solvent and a precipitant. The use of the scaling approach and the blob model permitted the analysis of the structures not only of a planar grafted chain layer but also of cylindrical and spherical morphologies.[5,6] The results obtained were applied to the investigation of various polymer systems: micellar and supermolecular structures forming in melts and solutions of block copolymers,[6–9] solutions of star- and comb-like polymers,[10–14] etc. Thus, a scaling analysis of grafted polymer layers made it possible to establish the main features of equilibrium behavior of numerous complex polymer systems: to derive the main power asymptotic dependences of their characteristics. At the same time, as is known,[15] a scaling scheme of analysis does not permit us to obtain weaker, nonpower dependences and numerical coefficients. Hence, one needs to use other theoretical methods to get additional information.

Further progress in the theory of grafted chain layers was attained due to the self-consistent field (SCF) approach proposed by Semenov in his pioneering publication.[16] This approach was further developed independently by two groups (refs 17 and 18 and 19–21, see also ref 22 for details) and permitted to obtain the detailed information about the structure and properties of a planar grafted layer: to calculate the profiles of density of polymer units, free chain ends, and local chain stretching in a layer immersed in solvents of various strengths. The orientational ordering of grafted chains was considered in ref 22; the effect of polydispersity of grafted chains was taken into account in refs 23 and 24. Recently, the SCF approach has been used to consider the properties of planar grafted layers immersed in a melt of mobile polymer chains[25] and the problem of adsorption of end-functionalized polymers.[26]

The present paper is devoted to further development of the equilibrium theory of grafted chain layers. Its aim is the SCF analysis of the structure and properties of a planar grafted chain immersed in a solution of mobile shorter polymer chains. It should be noted that the systems investigated in refs 17–21 were the two-component systems (grafted chain layer immersed in a solvent or a melt of mobile chains). The system considered here is now a three-component system containing grafted and mobile polymer chains and a low molecular weight solvent. Hence, one can expect its much more varied behavior in comparison with the two-component systems investigated in refs 17–21.

In this paper we shall pay the most attention to the equilibrium properties of a free, undeformed grafted chain layer. The properties of deformed layers will be considered in our subsequent paper. In section II of this paper we present the mathematical scheme of refs 17 and 18 generalized for the case when a grafted chain layer is immersed in a two-component medium–solution of mobile polymer. The situation when the mobile chains are chemically identical with the grafted chains is considered in detail. For this case the equation for the height H_0 of the layer is obtained determining the dependence of

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H_0 on the lengths of grafted and mobile chains and the grafting density.

The structural characteristics of the layer—the density profiles of units of grafted and mobile chains and the distribution function of free grafted chain ends—are obtained in the form of analytical expressions.

Section III contains the results of calculations of layer characteristics according to the relationships of section II. Section IV is devoted to the generalization of the data of sections II and III for the case of a polydisperse mobile polymer with arbitrary molecular weight distribution function. Finally, section V summaries the main results of the paper.

II. General Formalism

Consider a planar layer of polymer chains consisting of $N \gg 1$ units grafted at one end onto the impermeable surface with the grafting density $1/\sigma$ and immersed in a solution of mobile polymer. Let the mobile chains consist of $P \ll N$ units and Φ be the volume fraction of mobile polymer units in the bulk of solution. A chain part with a length equal to the chain thickness, a, is chosen, as before,[17,18] as the chain unit. Let the grafted and mobile chains be flexible, so that the asymmetry parameter of their Kuhn segment $p = A/a \simeq 1$.

Under the conditions of relatively dense grafting ensuring considerable overlapping of neighboring coils, grafted chains stretch normally to the surface and their free ends are distributed throughout the thickness of the layer.

Let us consider the free energy ΔF of the grafted chain layer restricted from above by the second impermeable plane surface located at a distance H from the grafting surface. For a fixed amount of mobile polymer in the layer

$$\Delta F = \Delta F_{\text{el}}(H) + \Delta F_{\text{conc}}(H) \tag{1}$$

where $\Delta F_{\text{el}}(H)$ is the free energy of elastic chain stretching and $\Delta F_{\text{conc}}(H)$ is the free energy of volume interactions in the layer. Under the conditions of considerable stretching of grafted chains with respect to their Gaussian dimensions, the free energy of chain stretching ΔF_{el} may be represented in the following form[16]

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

Here $E(x,x') \equiv \mathrm{d}x/\mathrm{d}n$ is the function of local chain stretching at point x under the conditions that its free end is located at point $x' > x$ and $g(x')$ is the distribution function of free chain ends in the layer. (Here and below all energetic values are expressed in kT units.) The above definition of $E(x,x')$ leads to the normalization condition

$$\int_0^{x'} \frac{\mathrm{d}x}{E(x,x')} = N \tag{3}$$

The second addend in (1)

$$\Delta F_{\text{conc}} = \frac{\sigma}{a^3}\int_0^H f[\varphi_N(x),\varphi_P(x)]\,\mathrm{d}x \tag{4}$$

is determined by the density of the free energy of volume interactions $f[\varphi_N(x),\varphi_P(x)]a^{-3}$ where $\varphi_N(x)$ and $\varphi_P(x)$ are the density profiles of polymer units of grafted and mobile chains, respectively. The expression for $f[\varphi_N(x),\varphi_P(x)]a^{-3}$ may be obtained within the framework of the Flory theory of polymer solutions[27] with due account of the fact that grafted chains do not contribute to the translational entropy of the system

$$f[\varphi_N(x),\varphi_P(x)] = (1 - \varphi_P(x) - \varphi_N(x)) \ln [1 - \varphi_P(x) - \varphi_N(x)] + \frac{\varphi_P(x)}{P} \ln \varphi_P(x) + \frac{1}{2}\sum_{k,k'} \varphi_k(x)\varphi_{k'}(x)\chi_{kk'} \tag{5}$$

where $k = N$, P, or S and $\chi_{kk'}$ are the Flory interaction parameters.

The relationship between the density profile of grafted chains, $\varphi_N(x)$, with the function of local chain stretching, $E(x,x')$, and the distribution function of free chain ends, $g(x,x')$, is given by (see, for details refs 16 and 22)

$$\varphi_N(x) = \frac{a^3}{\sigma}\int_x^H \frac{g(x')\,\mathrm{d}x'}{E(x,x')} \tag{6}$$

The equilibrium characteristics of the layer may be obtained by the minimization of the free energy functional (1)–(6) with account of additional normalizing conditions

$$\frac{\sigma}{a^3}\int_0^H \varphi_N(x)\,\mathrm{d}x = N \tag{7}$$

$$\frac{\sigma}{a^3}\int_0^H \varphi_P(x)\,\mathrm{d}x = L \tag{8}$$

where L is the given amount of mobile polymer in the layer per one grafted chain.

The detailed solution of this problem for the case of the grafted chain layer immersed in a low molecular weight solvent ($\Phi = 0$) is presented in refs 18 and 22. That is why we shall not perform the full minimization of ΔF here but use partly the results of refs 18 and 22 and also take into account the appearance of a new unknown function, $\varphi_P(x)$.

As was shown in refs 17 and 18, the function of local chain stretching, $E(x,x')$, does not depend on the character of volume interactions in the layer and is uniquely determined by the Gaussian type of local chain stretching

$$E(x,x') = \frac{\pi}{2N}(x'^2 - x^2)^{1/2} \tag{9}$$

The equation for the density profile of grafted chain units has the following form[18,22]

$$\frac{\delta f[\varphi_N(x)]}{\delta \varphi_N(x)} = \tilde{\Lambda}_N - k^2x^2 \tag{10}$$

where $\tilde{\Lambda}_N$ is the indefinite Lagrangian factor determined by the normalization condition (7) and $k^2 = 3\pi^2/8a^2N^2$.

As is seen from the structure of the free energy functional (1)–(6), the appearance of a new unknown function, $\varphi_P(x)$, leads to the change in the concentrational part of the free energy, ΔF_{conc}, and does not affect the stretching term, ΔF_{el}. This results in the retention of the relationship (9) determining the function of local chain stretching, $E(x,x')$, while eq 10 is now rewritten in the form

$$\frac{\delta f[\varphi_N(x),\varphi_P(x)]}{\delta \varphi_N(x)} = \tilde{\Lambda}_N - k^2x^2 \tag{11}$$

The additional equation for the unknown function $\varphi_P(x)$ is obtained by the variation of the concentrational part of the free energy functional (1), ΔF_{conc}, with respect to $\varphi_P(x)$ with account taken of normalizing condition (8) to give

$$\frac{\delta f[\varphi_N(x),\varphi_P(x)]}{\delta \varphi_P(x)} = \tilde{\Lambda}_P \tag{12}$$

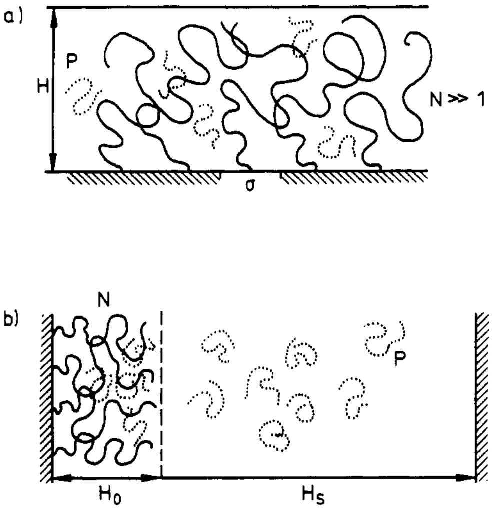

Figure 1. Grafted chain layer immersed in solution of mobile polymer.

Here $\tilde{\Lambda}_N$ and $\tilde{\Lambda}_P$ are the indefinite Lagrangian multipliers, the values of which are determined by normalizing conditions (7) and (8).

Equations 11 and 12 determine the density profiles of grafted and mobile chains in the layer at arbitrary values of Flory interaction parameters $\chi_{kk'}$. Let us consider in detail the case when the mobile chains are chemically identical with the grafted chains and the solvent is an athermal one. In this case all energetic contributions to the free energy of volume interactions diminish ($\chi_{kk'} = 0$ in eq 5) and one obtains the following system of equations for the density profiles $\varphi_N(x)$ and $\varphi_P(x)$

$$-[\ln (1 - \varphi_N(x) - \varphi_P(x)) + 1] = \tilde{\Lambda}_N - k^2x^2$$

$$\frac{1}{P}[\ln \varphi_P(x) + 1] - [\ln (1 - \varphi_N(x) - \varphi_P(x)) + 1] = \tilde{\Lambda}_P \qquad (13)$$

The solution of this system, with account taken of relationships (7) and (8), gives

$$\varphi_P(x) = \Lambda_P e^{k^2x^2P} \qquad (14)$$

$$\varphi_N(x) = 1 - \Lambda_P e^{k^2x^2P} - \Lambda_N e^{k^2x^2} \qquad (15)$$

where

$$\Lambda_P = \frac{La^3}{\sigma}\left(\int_0^H e^{k^2Px^2}\,\mathrm{d}x\right)^{-1} \qquad (16)$$

$$\Lambda_N = \left(H - \frac{Na^3}{\sigma} - \frac{La^3}{\sigma}\right)\left(\int_0^H e^{k^2x^2}\,\mathrm{d}x\right)^{-1} \qquad (17)$$

The distribution function of free ends, $g(x')$, is obtained as before,[18] by inverting the integral relationship (6) with account taken of relationships 9 and 15. Substituting $g(x')$ into the expression for ΔF_{el} and relationships 14–17 into the expression for ΔF_{conc} and omitting all intermediate algebraic transformations, one obtains the final expression for the free energy of the grafted chain layer

$$\Delta F(L,H) = \frac{\sigma H}{a^3}\left\{\frac{1}{3}H^2k^2 + \frac{La^3}{\sigma PH}\ln\left[\frac{La^3}{\sigma}\left(\int_0^H e^{k^2Px^2}\,\mathrm{d}x\right)^{-1}\right] + \left(1 - \frac{Na^3}{\sigma H} - \frac{La^3}{\sigma H}\right) \times \ln\left[\left(H - \frac{Na^3}{\sigma} - \frac{La^3}{\sigma}\right)\left(\int_0^H e^{k^2x^2}\,\mathrm{d}x\right)^{-1}\right]\right\} \qquad (18)$$

Relationship 18 determines the free energy of the grafted chain layer with a given height H and with a fixed amount of the mobile polymer L per grafted chain. In order to obtain the values of H and L corresponding to the conditions of the equilibrium between grafted chain layer and solution of mobile polymer consider a grafted chain layer contacting with solution of mobile polymer, Figure 1. The total free energy of this system (per unit area of grafted layer) is given by

$$\Delta F = \frac{\Delta F(L,H)}{\sigma} + f[\Phi]a^{-3}(H_S - H) \qquad (19)$$

where $f[\Phi] = (\Phi/P)\ln\Phi + (1 - \Phi)\ln(1 - \Phi)$ is the free energy density of volume interactions in the bulk of solution and $H_S \gg H$ is the linear dimension of the reservoir with a solution of mobile chains, Figure 1b. Minimization of ΔF with respect to parameters L and H under the conditions of retention of the overall amount of mobile polymer

$$\frac{L}{\sigma} + \frac{\Phi}{a^3}(H_S - H) = \text{constant} \qquad (20)$$

gives the following system of equations for L and H

$$\frac{\partial\Delta F(L,H)}{\partial L} = \frac{\partial f[\Phi]}{\partial\Phi} \qquad (21)$$

$$\frac{a^3}{\sigma}\frac{\partial\Delta F(L,H)}{\partial H} = f[\Phi] - \Phi\frac{\partial f[\Phi]}{\partial\Phi} \qquad (22)$$

Equation 21 determines the equilibrium amount of mobile polymer $L(H)$ in the grafted chain layer with a given height H, while eq 22 permits the calculation of the value of $H = H_0$ under the conditions of equilibrium between the layer and solution. (This equation is equivalent to the condition of equality of the pressure $-(a^3/\sigma)(\partial\Delta F(L,H)/\partial H)$ to the osmotic pressure π in the bulk of solution.) Substituting (18) into (21) and (22), one obtains two equations determining the equilibrium values H_0 and L_0

$$\frac{1}{P}\ln\left[\frac{L_0a^3}{\sigma\Phi}\left(\int_0^{H_0} e^{k^2Px^2}\,\mathrm{d}x\right)^{-1}\right] = \ln\left[\left(H_0 - \frac{Na^3}{\sigma} - \frac{La^3}{\sigma}\right)\frac{1}{1-\Phi}\left(\int_0^{H_0} e^{k^2x^2}\,\mathrm{d}x\right)^{-1}\right] \qquad (23)$$

$$1 - \frac{L_0a^3}{\sigma P}\frac{e^{k^2H_0^2P}}{\int_0^{H_0} e^{k^2x^2P}\,\mathrm{d}x} - \frac{\left(H_0 - \frac{Na^3}{\sigma} - \frac{L_0a^3}{\sigma}\right)e^{k^2H_0^2}}{\int_0^{H_0} e^{k^2x^2}\,\mathrm{d}x} + \ln\left[\frac{\left(H_0 - \frac{Na^3}{\sigma} - \frac{L_0a^3}{\sigma}\right)e^{k^2H_0^2}}{\int_0^{H_0} e^{k^2x^2}\,\mathrm{d}x}\right] = \ln(1 - \Phi) + \Phi\left(1 - \frac{1}{P}\right) \qquad (24)$$

It can be shown after some algebraic transformations that eqs 23 and 24 give

$$L_0 = \frac{\sigma}{a^3}\Phi e^{-k^2H_0^2P}\int_0^{H_0} e^{k^2x^2P}\,\mathrm{d}x = \frac{\sigma}{a^3}\Phi\frac{D(kH_0\sqrt{P})}{k\sqrt{P}} \qquad (25)$$

where H_0 is the root of the integral equation

$$H_0 = \frac{Na^3}{\sigma} + (1 - \Phi)\frac{D(kH_0)}{k} + \Phi\frac{D(k\sqrt{P}H_0)}{k\sqrt{P}} \qquad (26)$$

and $D(t) = e^{-t^2}\int_0^t e^{x^2}\,\mathrm{d}x$ is the Dawson integral. Then the Lagrangian multipliers (16) and (17) become

$$\Lambda_P{}^0 = \Phi e^{-k^2 H_0{}^2 P} \tag{27}$$

$$\Lambda_N{}^0 = (1 - \Phi) e^{-k^2 H_0{}^2} \tag{28}$$

and the equilibrium profiles of polymer units in the grafted chain layer and the distribution function of free ends of grafted chains are given by

$$\varphi_P(x) = \Phi e^{-k^2 P (H_0{}^2 - x^2)} \tag{29}$$

$$\varphi_N(x) = (1 - \Phi)[1 - e^{-k^2 (H_0{}^2 - x^2)}] + \Phi[1 - e^{-k^2 P (H_0{}^2 - x^2)}] \tag{30}$$

$$g(x') = \frac{2x'\sigma}{a^3 N}[(1 - \Phi) k D(k(H_0{}^2 - x'^{\,2})^{1/2}) + k\sqrt{P}\Phi D(k\sqrt{P}(H_0{}^2 - x'^{\,2})^{1/2})] \tag{31}$$

III. Results

Relationships 9, 26, and 29–31 determine the characteristics of the grafted layer under the conditions of the equilibrium with solution of mobile polymer at arbitrary values of parameters P, N, and $1/\sigma$ ($P \ll N$).

1. Layer Height and Average Concentration of Units. We begin the analysis of eq 26 with the consideration of two limiting cases of small ($\Phi \ll 1$) and high ($1 - \Phi \ll 1$) concentrations of mobile polymer in the bulk solution. If there is no mobile polymer in solution ($\Phi = 0$) relationships 26, 30, and 31 pass into the corresponding relationships of ref 17, determining the characteristics of a grafted chain layer immersed in a low molecular weight solvent in the wide range of grafting densities $1/\sigma$. Under the conditions of relatively loose grafting the expansion of the right-hand part of eq 26 to the powers of (kH_0) with the retention of the terms $(kH_0)^3$ gives

$$H_0 = aN\left(\frac{4}{\pi^2}\right)^{1/3}\left(\frac{\sigma}{a^2}\right)^{-1/3} \tag{32}$$

$$\bar{\varphi}_N = \frac{Na^3}{\sigma H_0} = \left(\frac{\pi^2}{4}\right)^{1/3}\left(\frac{\sigma}{a^2}\right)^{-2/3} \tag{33}$$

It should be noted that the above power dependences of H_0 and $\bar{\varphi}_N$ on N and σ/a^2 were obtained first by Alexander[1] by means of a scaling approach. They were determined from the condition of the balance of elastic stretching of the chains and volume interactions–pair contacts with the virial coefficient of unit interaction $v/a^3 \simeq 1$. The condition of validity of relationship 32 ($(kH_0)^2 \sim \bar{\varphi}_N \ll 1$) is fulfilled in the wide range of grafting densities $1/\sigma$

$$\frac{a^2}{\sigma} \ll \frac{4\sqrt{2}}{3\sqrt{3}\pi} \approx 0.35 \tag{34}$$

The increase in grafting density leads to an increase in average concentration of units, φ_N, in the layer and the contributions of unit interactions of higher orders become significant. This leads to an additional increase in H_0 with respect to relationship 32 and the rigorous eq 26 should be used, taking into account the unit interactions of all orders.[17] Finally, under the conditions of very dense grafting, $a^2/\sigma \approx 2$, finite expansibility of grafted chains should be taken into account.[21] In this paper we shall not consider this range of grafting densities a^2/σ.

Let us consider now the behavior of the solution of eq 26 at low Φ values, $1 - \Phi \ll 1$. Expanding the right-hand part of eq 26 to the powers of $\delta H_0 = H_0 - H_0(\Phi{=}0)$ one obtains

$$H_0(\Phi) - H_0(\Phi{=}0) \approx -\frac{\Phi}{2k^2 H_0(\Phi{=}0)}\left[1 - \frac{D(k\sqrt{P}H_0(\Phi{=}0))}{\sqrt{P}D(kH_0(\Phi{=}0))}\right] \tag{35}$$

Hence, an increase in the concentration Φ of mobile polymer in solution in the range $1 - \Phi \ll 1$ leads to the linear decrease of the layer height H_0. The effect increases with increasing P and is at a maximum in the limit $P \gg 1$.

In the second limiting case of high concentration of mobile polymer in solution, $\Phi = 1$, the relationships 26 and 29–31 pass into the corresponding relationships of ref 25, determining the characteristics of a grafted chain layer immersed in a melt of mobile polymer (see also ref 2). As was shown in refs 2 and 25, screening of volume interactions in the layer by mobile polymer chains leads to the diminishing of all virial coefficients of grafted chain unit interactions and corresponding densening of the layer with P increasing. Under the conditions of low N unit concentrations providing the domination of pair contacts between N units, the expansion of eq 26 to the powers of $kH_0\sqrt{P}$ with the retention of terms $\sim(kH_0\sqrt{P})^3$ gives

$$H_0 = \left(\frac{4}{\pi^2}\right)^{1/3} Na\left(\frac{a^2}{\sigma}\right)^{1/3} P^{-1/3} \tag{36}$$

$$\bar{\varphi}_N = \left(\frac{\pi^2}{4}\right)^{1/3} P^{1/3}\left(\frac{a^2}{\sigma}\right)^{2/3} \tag{37}$$

The range of validity of relationships 36 and 37 ($(kH_0)^2 P \sim \bar{\varphi}_N \ll 1$) is determined now by a stronger inequality

$$\frac{a^2}{\sigma}P^{1/2} \ll 0.35 \tag{38}$$

An increase in P leads to violation of the above inequality (38) and to an increase of the contributions of the higher order unit interactions. This leads to an increase in H_0 and the decrease in $\bar{\varphi}_N$ with respect to relationships 36 and 37. (A detailed analysis of the structure of a grafted chain layer immersed in a melt of mobile polymer is presented in ref 25.)

In the general case, $0 < \Phi < 1$, the expansion of eq 26 to the powers of (kH_0) and $(kH_0\sqrt{P})$ gives

$$H_0 = a(4/\pi^2)^{1/3} N (\sigma/a^2)^{-1/3} (1 - \Phi + P\Phi)^{-1/3} \tag{39}$$

$$\bar{\varphi}_N = (\pi^2/4)^{1/3} (\sigma/a^2)^{-2/3} (1 - \Phi + P\Phi)^{1/3} \tag{40}$$

It can be seen, however, that the range of validity of relationships 39 and 40 ($k^2 H_0{}^2 P \sim \bar{\varphi}_N[P/(1 - \Phi + P\Phi)] \ll 1$) is considerably diminished with respect to the condition (38) and is determined now by the inequality

$$\frac{a^2}{\sigma}P^{1/2}\frac{P}{1 - \Phi + P\Phi} \ll 0.35 \tag{41}$$

Hence, the domination of pair interactions with the virial coefficient $v/a^3 \sim 1/(1 - \Phi + P\Phi)$ occurs only under the conditions $\bar{\varphi}_N \ll (1 - \Phi + P\Phi)/P \leq 1$. With the increase of $kH_0\sqrt{P} \gg 1$ and violation of the inequality (41) the approximate dependence $H_0 = H_0(\Phi)$ may be obtained by

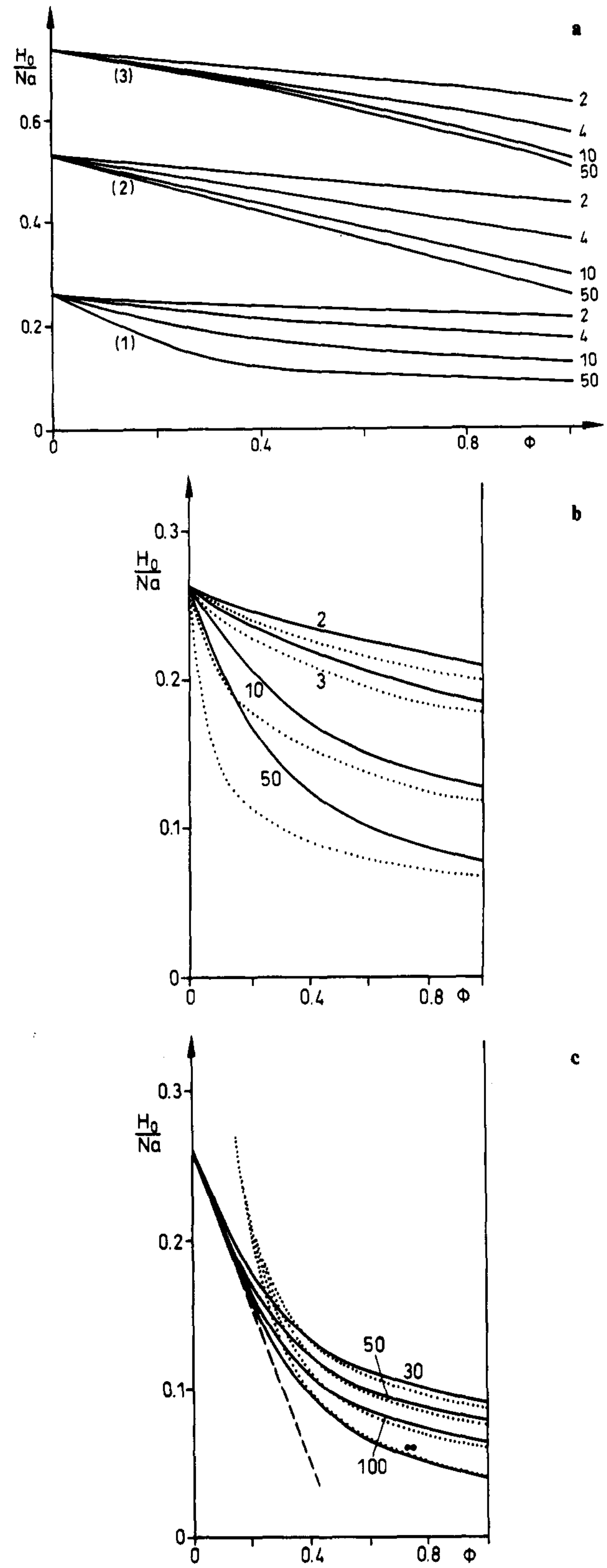

Figure 2. Dependences of the relative height of the layer on the concentration Φ of the mobile polymer in solution for the values of grafting densities a^2/σ = 0.04 (1), 0.25 (2), and 0.50 (3) and various mobile chain lengths P (numbers at the curves). The comparison of rigorous calculations (solid lines) with the approximate expressions (39) (dotted lines in part b) and (42) and (35) (dotted and dashed lines in part c) is presented in parts b and c for the value of grafting density a^2/σ = 0.04.

expansion of the first addend in the right-hand part of eq 26 to the powers of (kH_0) and the second addend to the powers of $(kH_0\sqrt{P})^{-1}$ with the retention of only first terms

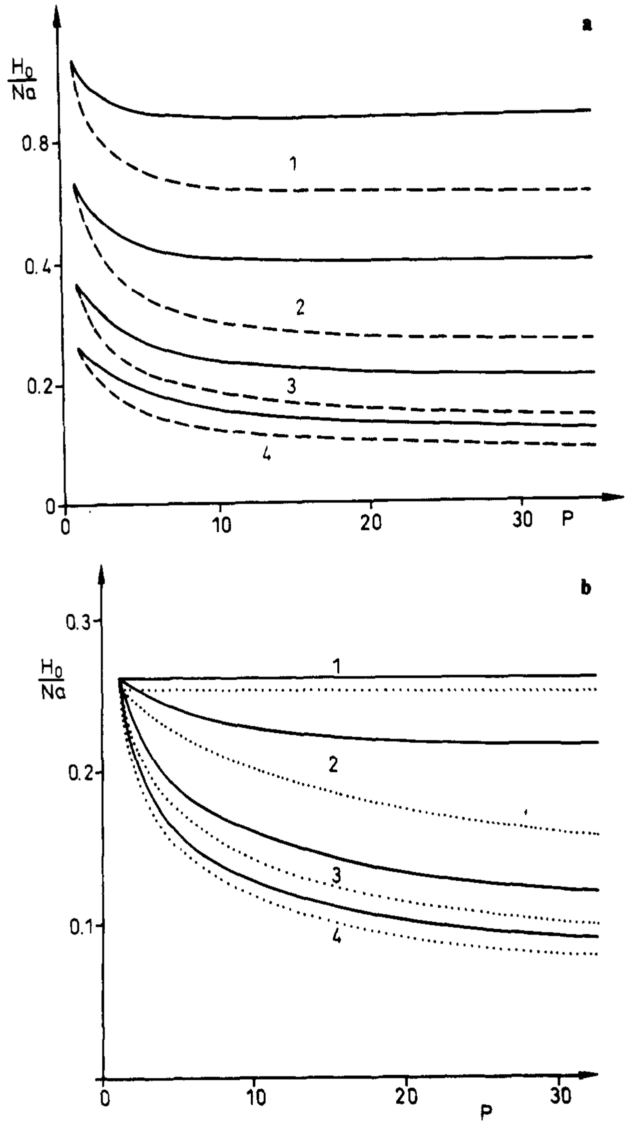

Figure 3. Dependences of the relative height H_0/Na of the layer on the length of the mobile chains P for various values of grafting densities a^2/σ = 0.50 (1), 0.25 (2), 0.10 (3), and 0.04 (4) (a) and various values of Φ = 0.0 (1), 0.1 (2), 0.5 (3), and 1.0 (4) (b). Dashed and solid lines in part a correspond to the values Φ = 1.0 and 0.5, respectively. Solid and dotted lines in part b are obtained from rigorous solution of eq 26 and the approximate formula (39), respectively.

of expansion to give

$$H_0 \approx \frac{Na^3}{\sigma\Phi}\left[\frac{1}{2}+\frac{1}{2}\left(1+\frac{16}{3\pi^2 P}\frac{\sigma^2\Phi^2}{a^4}\right)^{1/2}\right] \qquad (42)$$

The dependence (42) is the approximation of the rigorous solution of eq 26 in the range of Φ values $\Phi \ll (a^2/\sigma)P^{1/2}(\pi/2)(3/2)^{1/2}$. It is clear that the transition from the dependence (42) to the dependence (35) must occur in the range of small Φ values, $1 - \Phi \ll 1$. The crossover of relationships 42 and 35 with respect to their main power terms gives a rough estimation of the left boundary of the validity range of dependence (42).

Let us consider now the behavior of rigorous solution of eq 26. Figure 2 shows the dependences of the relative height of the grafted chain layer H_0/Na calculated from eq 26 on the concentration Φ of mobile polymer in solution for several values of a^2/σ and P (numbers at the curves). As is seen from Figure 2a, with the increase of grafting density a^2/σ the dependences $H_0 = H_0(\Phi)$ are shifted toward larger values of H_0 and change their shape (they are slightly convex under the conditions of loose grafting, curves 1 in Figure 2a, and are slightly concave under the conditions of dense grafting, curves 3 in Figure 2a). Figure 2b,c shows the rigorous dependences of H_0/Na on Φ at a fixed grafting density $a^2/\sigma = 0.04$ and various P values and the approximate dependences (35) (dashed lines) and (39) and (42) (dotted lines). According to inequality (41) the satisfactory agreement between the rigorous solution of eq 26 and the approximate dependence (39) in the whole range of Φ values $0 \leq \Phi \leq 1$ may be achieved at $a^2/\sigma = 0.04$ only for small P values, $P \leq 4$ (Figure 2b). As is seen from Figure 2b, an increase in P leads to an increase in the discrepancy between the rigorous solution (solid lines) and the approximate dependence (39) (dotted lines). This discrepancy is particularly noticeable in the range of small Φ values in accordance with the inequality (41). Further increase in P values leads to an approach to the second approximate dependence (42), Figure 2c.

Figure 3a shows the dependences of H_0/Na on the length of mobile polymer chains P calculated from eq 26 for various grafting densities a^2/σ and $\Phi = 0.5$ (solid lines) and $\Phi = 1$ (dashed lines). In Figure 3b the rigorous curves (solid lines) are compared with the approximate dependences (39) (dotted lines) for the given value of $a^2/\sigma = 0.04$ and various Φ values (numbers at the curves). As was already noted above, the validity range of relationship 39 is determined by the inequality (41). Under the conditions of low content of mobile chains in solution the validity range of the dependence (39) is small. For $\Phi = 0.1$ and $a^2/\sigma = 0.04$, the inequality (41) gives $P \leq 3$–4 and for $P \gg 3$ the discrepancy between the rigorous and approximate dependences is very noticeable, Figure 3b. With increasing Φ the validity range of relationship 39 increases and at $\Phi = 1$ and $a^2/\sigma = 0.04$ the approximate dependence (39) describes satisfactory the height of the layer H_0 in the wide range of P values, $P \leq 50$, Figure 3b.

Let us now consider the average unit concentration $\bar\varphi_N = Na^3/\sigma H_0$ and $\bar\varphi_P = L_0a^3/\sigma H_0$ of grafted and mobile polymer chains. According to relationship 25

$$\bar\varphi_P = \Phi\frac{D(kH_0\sqrt{P})}{k\sqrt{P}H_0} \tag{43}$$

Using the expansion of Dawson's integral ($D(x) \approx x$ at $x \ll 1$ and $D(x) \approx 1/2x$ at $x \gg 1$) and taking into account relationship 42, one obtains

$$\bar\varphi_P \approx \Phi \qquad kH_0\sqrt{P} \ll 1$$

$$\bar\varphi_P \approx \frac{4}{3\pi^2}\frac{\Phi^3\sigma^2}{a^4P} \qquad kH_0\sqrt{P} \gg 1 \tag{44}$$

Figure 4a shows the dependences of average concentration of grafted chain units in the layer, $\bar\varphi_N$, on Φ calculated from eq 26 for various grafting densities a^2/σ and $P = 4$ (solid lines) and $P = 20$ (dashed lines). Figure 4b,c shows the similar dependences of the average concentration of mobile chain units, $\bar\varphi_P$, and that of the solvent, $\bar\varphi_S = 1 - \bar\varphi_P - \bar\varphi_N$, in the layer. As is seen from Figure 4, under the conditions of relatively loose grafting and short mobile chains ($P = 4$), an increase in Φ leads to some densening of grafted chain layer (at $a^2/\sigma = 0.04$ the change in $\bar\varphi_N$ due to the variation of Φ from 0 to 1 is about 0.08). Simultaneously, according to the first part of relationship 44, the average concentration of P units, $\bar\varphi_P$, increases proportionally to Φ and the concentration of solvent decreases. Under the conditions of dense grafting the increase in $\bar\varphi_P$ caused by an increase in Φ becomes slower and the value of $\bar\varphi_P$ itself decreases according to the second part of relationship 44. The average concentration of the solvent $\bar\varphi_S$ also decreases. In the limit $a^2/\sigma \rightarrow 1$, $\bar\varphi_N \rightarrow 1$, $\bar\varphi_P \rightarrow 0$, and $\bar\varphi_S \rightarrow 0$ for any values of $\Phi \neq 1$.

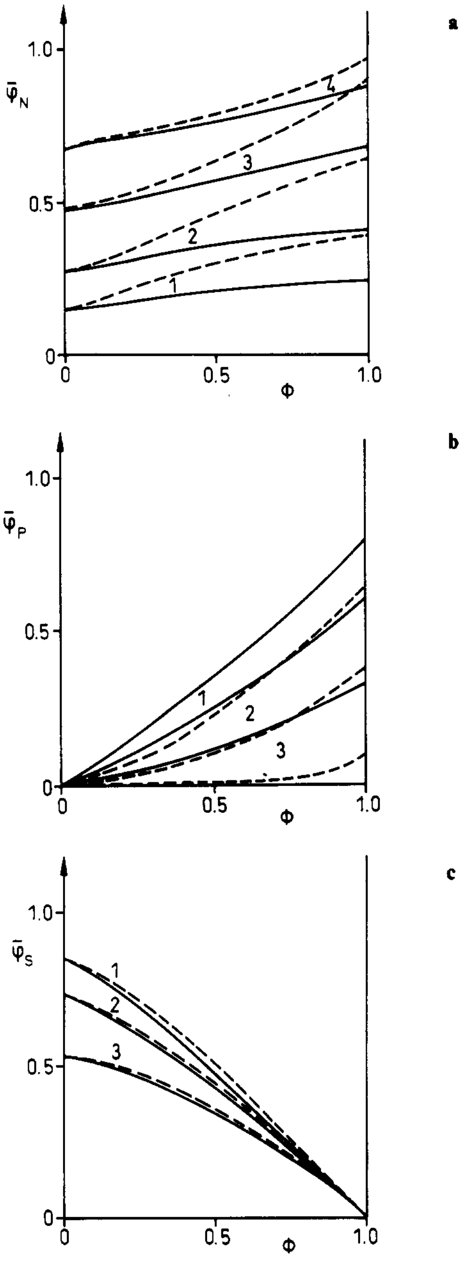

Figure 4. Average concentrations of units of grafted chains (a), mobile chains (b), and solvent (c) via the concentration Φ for the values of grafting densities $a^2/\sigma = 0.04$ (1), 0.10 (2), and 0.25 (3) and $P = 4$ (solid lines) and $P = 20$ (dashed lines).

An increase in mobile chain length P leads to a more pronounced variation of $\bar\varphi_N$ (layer densening) with increasing Φ. At a fixed value of Φ an increase in P leads to an increase in $\bar\varphi_N$, mainly due to the decrease in $\bar\varphi_P$ at practically constant average content of the solvent, $\bar\varphi_S$ (see Figure 4c).

2. Density Profiles and the Distribution Function of Free Chain Ends. Relationships 23–31 determine the equilibrium profiles of polymer units and the distribution of free ends of grafted chains in the layer at arbitrary values of N, P, and $1/\sigma$.

If there is no mobile polymer in solution ($\Phi = 0$ and $\bar\varphi_P(x) = 0$), the profile of unit density and the free ends distribution function are given by[17]

$$\varphi_N(x) = 1 - e^{-k^2(H_0^2 - x^2)} \tag{45}$$

$$g(x') = \frac{2x'\sigma}{a^3 N} k D(k(H_0^2 - x'^2)^{1/2}) \tag{46}$$

Expansion of relationships 45 and 46 to the powers of (kH_0) gives the parabolic profile[17,19]

$$\varphi_N = \frac{3}{2}\bar{\varphi}_N\left(1 - \frac{x^2}{H_0^2}\right) \tag{47}$$

and the corresponding distribution function

$$g(x') = \frac{3x'}{H_0^3}(H_0^2 - x'^2)^{1/2} \tag{48}$$

where $\bar{\varphi}_N$ and H_0 are determined by eqs 32 and 33.

In the opposite limiting case, $\Phi = 1$, and under the conditions $\bar{\varphi}_N \ll 1$ the density profiles of grafted chain units and the distribution of their free ends are still determined by eqs 47 and 48 where $\bar{\varphi}_N$ and H_0 are now given by eqs 36 and 37.

In the general case, $0 < \Phi < 1$, the density profile $\varphi_N(x)$ and the distribution function $g(x')$ are determined by eqs 47 and 48 in the range of parameters a^2/σ, P, and Φ, ensuring the validity of the inequality (41). With the violation of inequality (41) the deviations from relationships 47 and 48 become significant and rigorous expressions 30 and 31 are to be used.

Figure 5 shows the variation of the shape of density profiles of N and P units, $\varphi_N(x)/\bar{\varphi}_N$ (Figure 5a) and $\varphi_P(x)/\Phi$ (Figure 5b) caused by the change in grafting density $1/\sigma$ and in the mobile chain length P at the fixed content $\Phi = 0.5$ of the mobile polymer in solution. The dotted line corresponds to the approximate parabolic dependence (47).

Figure 6 shows the profiles $\varphi_N(x)$ (Figure 6a), $\varphi_P(x)$ (Figure 6b), and $\varphi_S(x) = 1 - \varphi_N(x) - \varphi_P(x)$ (Figure 6c) for various concentrations Φ of mobile polymer in solution (numbers at the curves). The abscissa in Figure 6 gives the relative coordinate $x/H_0(\Phi{=}0)$ that makes it possible to follow simultaneously the decrease in the layer height H_0 and the change in the profile shape with increasing Φ.

The distribution functions $g(x')$ are presented in Figures 7 and 8. Figure 7 shows the variation of the distribution of free chain ends caused by an increase in the length of mobile chains P for the cases of loose (1) and dense (2) grafting. Figure 8 illustrates the variation of free chain end distribution caused by an increase in Φ for the same values of parameters as in Figure 6.

IV. Effect of Polydispersity of Mobile Chains

The above results refer to the case when all chains of a mobile polymer consist of the same number P of units. Let us consider now the situation where the mobile chains are polydisperse and their lengths are distributed around some average value $P = \bar{P}$. We begin with the analysis of a discrete case when there are j fractions of mobile chains of length P_i and each fraction creates the concentration Φ_i of units in the bulk of solution. Then the total concentration of P units in solution $\Phi = \sum_{i=1}^{j}\Phi_i$ and the average length of P chains $\bar{P} = \Phi/(\sum_{i=1}^{j}\Phi_i/P_i)$. As is seen from the structure of the free energy functional (1)–(6), the appearance of the polydispersity in the lengths of mobile chains leads to the appropriate change only in the free energy of volume interactions, ΔF_{conc}. Now the density of the free energy of volume interactions is given by[26]

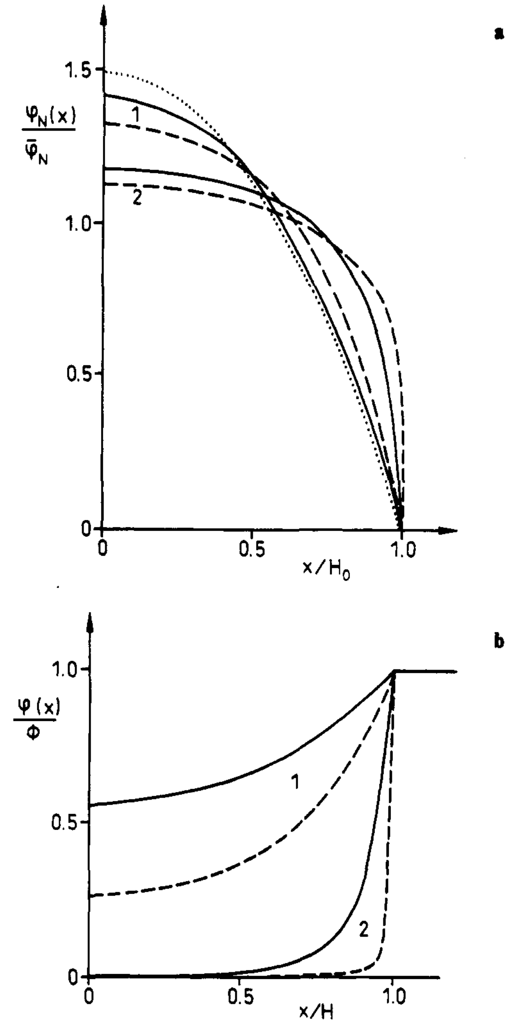

Figure 5. Density profiles of polymer units of grafted (a) and mobile (b) chains for the following values of parameters: $\Phi = 0.5$, $a^2/\sigma = 0.04$ (1) and 0.50 (2), $P = 4$ (solid lines) and $P = 20$ (dashed lines). Dotted line in part a corresponds to the parabolic dependence (47).

$$f[\varphi_N(x),\{\varphi_i(x)\}] = [1 - \varphi_N(x) - \sum_{i=1}^{j}\varphi_i(x)] \ln [1 - \varphi_N(x) - \sum_{i=1}^{j}\varphi_i(x)] + \sum_{i=1}^{j}\frac{\varphi_i(x)}{P_i} \ln \varphi_i(x) \tag{49}$$

where $\varphi_i(x)$ is the density profile of P units in the layer created by the ith fraction. Then the system of equations (13) may be generalized to the following form

$$\frac{\delta f[\varphi_N(x),\{\varphi_i(x)\}]}{\delta\varphi_N(x)} = \tilde{\Lambda}_N - k^2x^2$$

$$\frac{\delta f[\varphi_N(x),\{\varphi_i(x)\}]}{\delta\varphi_i(x)} = \tilde{\Lambda}_i \qquad i = 1, 2, \ldots, j \tag{50}$$

Solving this system and following the mathematical scheme of section II, one can obtain the characteristics of a grafted chain layer under the conditions of equilibrium with the solution of polydisperse mobile chains. We, however, will obtain these results directly taking into account the linear character of dependences 30 and 31. As can be seen from the relationship 30, in the case of a monodisperse mobile polymer the density profile of N units

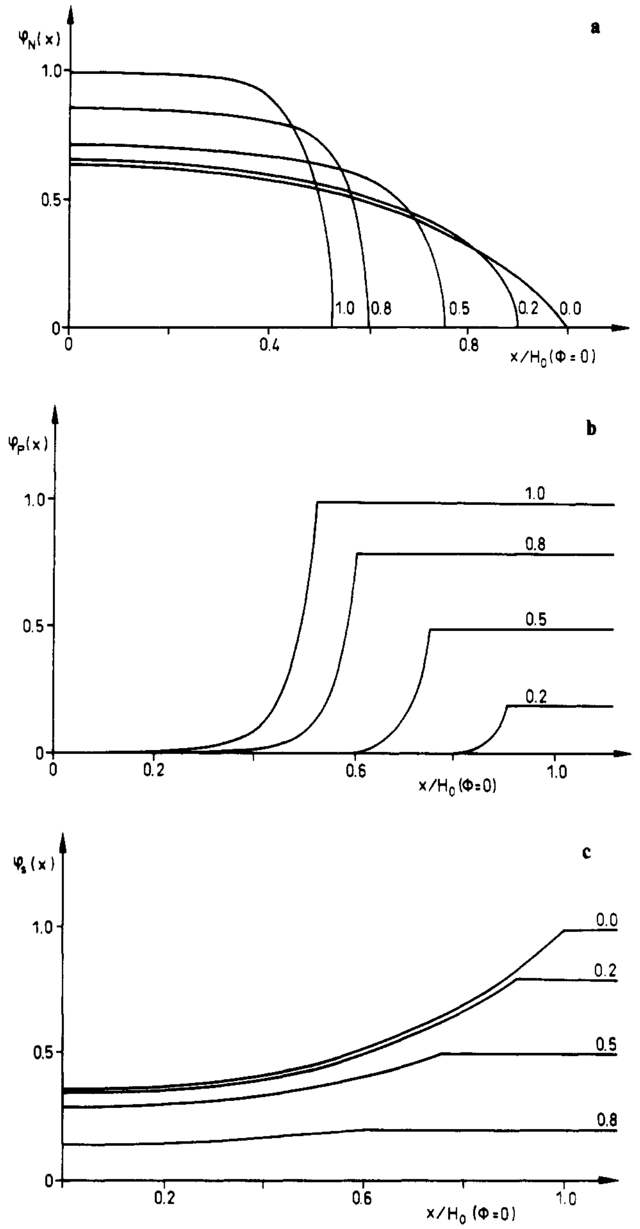

Figure 6. Density profiles of polymer units of grafted (a) and mobile (b) chains and the solvent (c) for various values of Φ (numbers at the curves) and $a^2/\sigma = 0.25$ and $P = 20$.

is the linear superposition of the density profile in a pure solvent, $\Phi = 0$, and in a polymer melt, $\Phi = 1$, i.e., the superposition of density profiles in each of the pure components of the system. The same conclusion refers to the distribution function of free chain ends, eq 31. Hence, if there are j fractions of P chains in solution, one obtains due to this quality

$$\varphi_N(x) = (1-\Phi)[1-e^{-k^2(H_0^2-x^2)}] + \sum_{i=1}^{j}\Phi_i[1-e^{-k^2P_i(H_0^2-x^2)}] \tag{51}$$

$$g(x') = \frac{2x'\sigma}{Na^3}[(1-\Phi)kD(k(H_0^2-x'^2)^{1/2}) + \sum_{i=1}^{j}\Phi_i k\sqrt{P_i}D(k\sqrt{P_i}(H_0^2-x')^{1/2})] \tag{52}$$

where the height H_0 of the layer is now determined by the equation

$$H_0 = \frac{Na^3}{\sigma} + (1-\Phi)\frac{D(kH_0)}{k} + \sum_{i=1}^{j}\Phi_i\frac{D(k\sqrt{P_i}H_0)}{k\sqrt{P_i}} \tag{53}$$

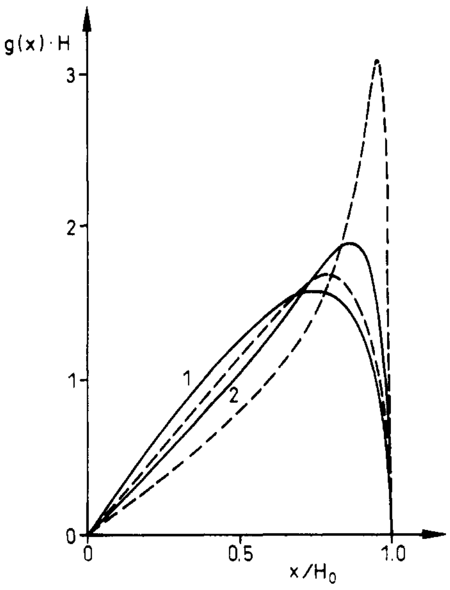

Figure 7. Distribution of free ends of grafted chains in the layer for the following values of parameters: $\Phi = 0.5$, $a^2/\sigma = 0.04$ (1) and 0.25 (2), and $P = 4$ (solid lines) and $P = 20$ (dashed lines).

The density profile of the fraction i is now given by

$$\varphi_i(x) = \Phi_i e^{-k^2P_i(H_0^2-x^2)} \tag{54}$$

(One can check that the solution of system 50 and the following application of the scheme of section II give the same results.)

Passing to the continuous distribution of mobile chains in their lengths and introducing the normalized distribution function $W(P)(\int W(P)\,\mathrm{d}P = 1)$, one obtains

$$\varphi_N(x) = (1-\Phi)[1-e^{-k^2(H_0^2-x^2)}] + \frac{\Phi}{P}\int W(P)P[1-e^{-k^2P(H_0^2-x^2)}]\,\mathrm{d}P \tag{55}$$

$$g(x') = \frac{2x'\sigma}{Na^3}\Big[(1-\Phi)kD(k(H_0^2-x'^2)^{1/2}) + \frac{\Phi}{P}\int W(P)kP^{3/2}D(k\sqrt{P_i}(H_0^2-x')^{1/2})\,\mathrm{d}P\Big] \tag{56}$$

$$\varphi_P(x) = \frac{\Phi}{P}\int W(P)P\,\mathrm{d}P\,e^{-k^2P(H_0^2-x^2)} \tag{57}$$

where H_0 is given now by the equation

$$H_0 = \frac{Na^3}{\sigma} + (1-\Phi)\frac{D(kH_0)}{k} + \frac{\Phi}{P}\int W(P)\sqrt{P}\frac{D(k\sqrt{P}H_0)}{k}\,\mathrm{d}P \tag{58}$$

Relationships 55–58 determine the characteristics of the grafted chain layer under the conditions of equilibrium with the solution of polydisperse mobile chains with arbitrary distribution function $W(P)$ in their lengths.

Let us consider now some limiting cases of relationships 55–57. If the distribution function of the mobile polymer $W(P)$ is located in the range of P values ensuring the

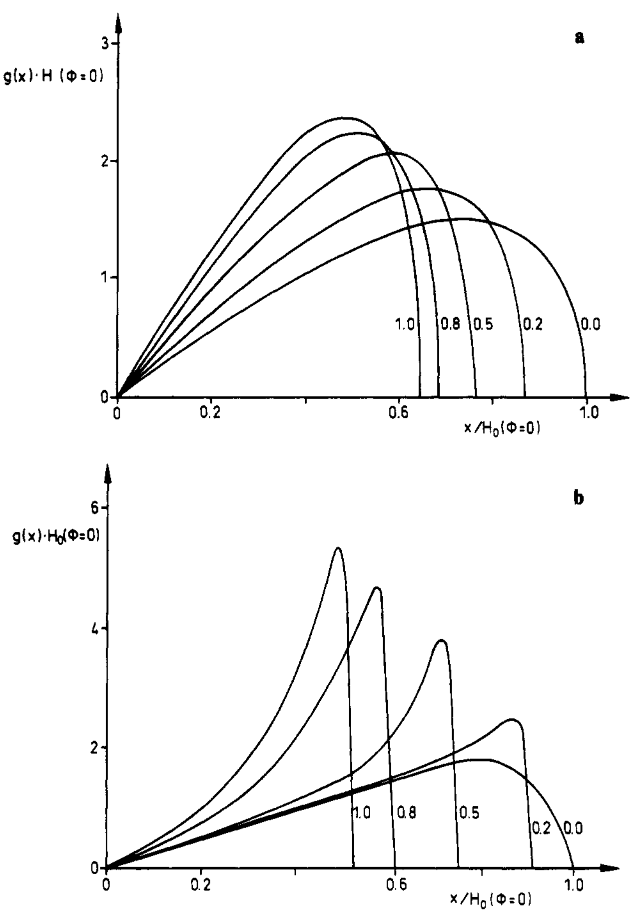

Figure 8. Profiles of the free ends of grafted chains at various values of Φ (numbers at the curves), $P = 4$, $a^2/\sigma = 0.04$ (a) and $P = 20$, $a^2/\sigma = 0.25$ (b).

condition $kH_0\sqrt{P} \ll 1$, the expansion of relationships 55, 56, and 58 to the powers of (kH_0) and ($kH_0\sqrt{P}$) give the above expressions (32) and (33) for the density profiles of N units and free chain ends where the height of the layer H_0 is now given by

$$H_0 = \left(\frac{4}{\pi^2}\right)^{1/3} aN\left(\frac{a^2}{\sigma}\right)^{1/3}\left(1 - \Phi + \frac{\overline{P^2}}{\bar{P}}\Phi\right)^{-1/3} \quad (59)$$

Here $\bar{P} = \int W(P)P\,dP$ and $\overline{P^2} = \int W(P)P^2\,dP$ are the first and the second moments of the distribution function $W(P)$. As for the density profile of P units, one obtains from (57)

$$\varphi_P(x) \approx \Phi\left[1 - k^2\frac{\overline{P^2}}{\bar{P}}(H_0^{\,2} - x^2)\right] \quad (60)$$

In the second limiting case ($kH_0 \ll 1$, $kH_0\sqrt{P} \gg 1$) the expansion of relationship 58 to the powers (kH_0) and $(kH_0\sqrt{P})^{-1}$ (with retention of the main terms only) gives the above expression (42) where P is now changed by $\bar{P}$. Hence, under the conditions of low concentration of N units in the layer, $\bar{\varphi}_N \ll \bar{P}/(1 - \Phi + (\overline{P^2}/\bar{P})\Phi)$, all characteristics of the grafted layer are determined by the ratio of the first two moments of the distribution function $W(P)$, $\overline{P^2}/\bar{P}$. And the discount of polydispersity of mobile chains is reduced to the substitution $P \rightarrow \overline{P^2}/\bar{P}$. Since $\overline{P^2}/\bar{P} \geq 1$, the polydispersity of mobile chains leads to an additional compression of the grafted chain layer with respect to the case of a monodisperse mobile polymer with the length $P = \bar{P}$. This effect, however, is not strong. It increases with the increase of the content Φ of mobile polymer in solution and is at maximum for the polymer melt, $\Phi = 1$. Here the ratio of heights of the layer in monodisperse and polydisperse melts is equal to $(\overline{P^2}/\bar{P})^{1/3} > 1$.

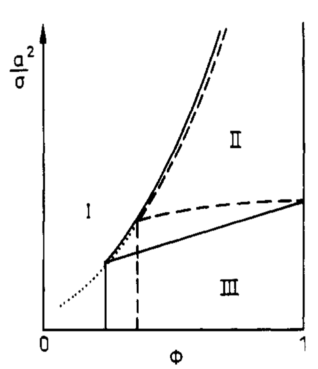

Figure 9. Diagram of state of a grafted chain layer immersed in a solution of mobile polymer in (a^2/σ, Φ) coordinates. Solid and dashed lines correspond to the SCF and scaling units, respectively. The position of the boundary between regions I and III according to the results of ref 2 is shown by dotted line.

Under the conditions of higher concentrations of N units, $\bar{P}/(1 - \Phi + (\overline{P^2}/\bar{P})\Phi) \ll \bar{\varphi}_N \ll 1$, the discount of polydispersity is reduced to the substitution $P \rightarrow \bar{P}$ in eq 42 and does not effect practically the height of the layer. Note, however, that these conclusions refer to the cases when the distribution function $W(P)$ is located in the range of P values ensuring the validity of inequalities $kH_0\sqrt{P} \gg 1$. In the intermediate case the rigorous expressions (55)–(58) should be used.

V. Discussion

The SCF theory developed in this paper makes it possible to investigate in detail the structure and properties of a grafted chain layer contacting a solution of mobile polymer. The results obtained in section III permit analysis of the dependences of the layer height H_0 and average concentrations of polymer units $\bar{\varphi}_N$ and $\bar{\varphi}_P$ on the grafting density, $1/\sigma$, the lengths of grafted and mobile chains, N and P, and the concentration of mobile polymer in solution, Φ, and investigation of the rearrangement of the layer structure caused by the variation of polymer content in solution.

In order to emphasize the main features of the system one can allot and analyze the main power dependences of the layer characteristics in various ranges of parameters, i.e., use the "scaling-type" way of analysis. The results obtained in section III show that there are three regions of values of parameters $1/\sigma$ and Φ in which the characteristics of the layer are determined by different power laws. Hence, there are three different regimes of behavior of a grafted chain layer contacting the solution of mobile polymer. Such introduction of the regimes roughens and simplifies the real picture of the system but at the same time permits an emphasis on the physical basis of the grafted layer behavior, as it was done by de Gennes in ref 2.

Figure 9 shows a diagram of the state of a grafted chain layer in (a^2/σ, Φ) coordinates (solid lines) obtained on the basis of the results (32), (39), and (42) with the retention of only main power dependences. All numerical coefficients and nonpower dependences are omitted. The characteristics of the system in various regions of the diagram are presented in Table I, the equations of the boundaries between the regions are presented in Table II.

Table I
Power Dependences of the Characteristics of a Planar Grafted Chain Layer Immersed in a Solution of Mobile Polymer

	SCF results (present paper)				scaling results[1,2]			
	H_0/a	$\bar{\varphi}_N$	$\bar{\varphi}_P$	ξ/a	H_0/a	$\bar{\varphi}_N$	$\bar{\varphi}_P$	ξ/a
I	$N(\sigma/a^2)^{-1/3}$	$(\sigma/a^2)^{-2/3}$	$\Phi^3(\sigma^2/a^4P)$	$(\sigma/a^2)^{1/3}$	$N(\sigma/a^2)^{-1/3}$	$(\sigma/a^2)^{-2/3}$		$(\sigma/a^2)^{1/2}$
II	$Na^2/\sigma\Phi$	Φ	$\Phi^3(\sigma^2/a^4P)$	$\Phi^{-1/2}$	$Na^2/\sigma\Phi$	Φ		$\Phi^{-3/4}$
III	$N(\mathrm{P}\Phi(\sigma/a^2))^{-1/3}$	$(\sigma/a^2)^{-2/3}(P\Phi)^{1/3}$	Φ	$\Phi^{-1/2}$	$N((\sigma/a^2)P)^{-1/3}\Phi^{-5/12}$	$(\sigma/a^2)^{-2/3}P^{1/3}\Phi^{5/12}$	Φ	$\Phi^{-3/4}$

Table II
Equations of Boundaries between the Regions of Figure 9

	SCF results	scaling results
I–II	$a^2/\sigma \simeq \Phi^{3/2}$	$a^2/\sigma \simeq \Phi^{3/2}$
II–III	$a^2/\sigma \simeq \Phi P^{-1/2}$	$a^2/\sigma \simeq \Phi^{7/8}P^{-1/2}$
I–III	$\Phi \simeq P^{-1}$	$\Phi \simeq P^{-4/5}$

Note that we restrict ourselves to the analysis of the *situation where the grafted chain layer consists of considerably overlapped and stretched chains and the mobile chains are much shorter than grafted chains, $P \ll N$.*

Region I in Figure 9 corresponds to the "domination" of the grafted chain layer over the solution of mobile polymer. In this region of parameters a^2/σ and Φ the penetration of mobile chains into the layer is small ($\bar{\varphi}_P \ll \bar{\varphi}_N$) and they do not effect significantly the structure and properties of the layer. Volume interactions in the layer are controlled by the pair contacts between units of grafted chains, the virial coefficient of their interaction $v/a^3 \simeq 1$. The power dependences of the characteristics of the layer are the same as in a pure low molecular weight solvent. For example, the layer height $H_0 \simeq v^{1/3}N(a^2/\sigma)^{1/3} \simeq (a^2/\sigma)^{1/3}Na$.[1]

As was already noted, these results are valid when mobile chains are much shorter than grafted chains, $P \ll N$, and partial penetration of mobile chains into the layer is totally ignored. We think, however, that in the opposite case, $P \gg N$, partial penetration of mobile chains in the layer in this regime can also be neglected. As was shown in ref 28 the characteristic length Δ of penetration of the terminal part of the outer polymer chain into the layer of thickness H can be estimated within the SCF approach as $\Delta/H = (a\sqrt{N}/H)^{4/3}$, and, hence, for strongly stretched grafted chains, $aN^{1/2} \ll H$, partial penetration of long mobile chains is negligible, $\Delta/H \ll 1$.

Note, that the regime of grafted layer "domination" was considered recently by Ligoure and Leibler[26] for the case of equilibrium adsorption of end-functionalized chains, i.e., when "grafted" (adsorbed) and mobile chains were of the same length. (In their notation this regime corresponds to $\alpha \ll 1$.) They assumed that the penetration of mobile chains into the layer does not occur on the scale of total layer thickness and showed that this approximation is valid for strongly stretched chains and relatively dilute solutions. Their estimation of penetration length Δ coincides with the result of ref 28. As for more concentrated solutions (solution domination, $\alpha \simeq 1$ in notations[26]) their model fails to predict the behavior of the grafted layer due to the penetration of mobile chains into the layer.

Let us proceed now with more concentrated systems.

Regions II and III in Figure 9 correspond to the domination of the solution over the grafted chain layer: the existence of the solution of mobile polymer leads to the rearrangement of grafted layer structure providing the leveling of densities of volume interactions in the layer and in the bulk solution.[2] This rearrangement may be achieved in two ways: by the compression of the layer and its concentrating up to the value $\bar{\varphi}_N \simeq \Phi$ (region II) or by the penetration of mobile chains into the layer and creation of the concentration $\bar{\varphi}_P \simeq \Phi$ of P units in the layer (region III). As is seen from Table I, penetration of mobile chains in the layer in region II is small, $\bar{\varphi}_P \ll \bar{\varphi}_N$, and volume interactions in the layer are controlled, as before, by pair contacts between N units. (The contributions of the interactions of higher orders are significant in the vicinity of the right boundary of region II where $\bar{\varphi}_N \simeq 1$.) The dominating of N units over P units in the layer leads immediately to the dependence $H_0 \simeq Na^3/\sigma\Phi$.

Finally, in region III, corresponding to the conditions of relatively loose grafting of N chains, penetration of mobile chains in the layer is considerable and the content of P units exceeds the content of N units, $\bar{\varphi}_P \approx \Phi \gg \bar{\varphi}_N$. Volume interactions in the layer are now controlled by the pair contacts between P units. The existence of P chains in the layer leads to the screening of volume interactions between N units and thus decreasing their effective virial coefficient $v \sim a^3/P\Phi$. Hence, the layer height $H_0 \simeq v^{1/3}N((\sigma/a^2)P\Phi)^{-1/3}$ diminishes. The decrease in polymer content Φ in solution leads to the decrease of screening in the layer. At $P\Phi \simeq 1$ (this condition corresponds within the SCF approach to the transition from a *semidilute solution to a dilute solution of mobile polymer*), the effect of mobile chains on the characteristics of the grafted chain layer disappears (left boundary of region III).

As is seen from Figure 9 and Table II, an increase in P leads to a diminishing of region III (the region of intensive penetration of mobile chains into the layer) and a corresponding increase of region II where grafted and mobile chains are separated. (Partial penetration is possible.) At $P \gg N$, region III disappears but the detailed analysis of this case is outside the framework of this paper.

As is known, the SCF approach does not take into account the fluctuation correlations of the density of polymer units in the layer and in solution. Hence, one can expect the difference in the values of the exponents obtained in the frameworks of SCF and scaling approaches. Let us analyze these differences using the results of the scaling analysis carried out by de Gennes in ref 2.

Figure 9 shows the part of scaling diagram of a grafted chain layer (dashed lines) obtained in ref 2 for the case of relatively long mobile chains, $P > \sqrt{N}$. The restriction $P > \sqrt{N}$ is significant for the analysis of the beginning of overlapping and stretching of grafted polymer coils[2] and is of no importance in the case of a stretched single layer. (Note that we consider here this particular situation.) Hence, this part of the diagram retains its validity also for short mobile chains, $P < \sqrt{N}$.

As is seen from Figure 9, a scaling diagram of a stretched grafted chain layer comprises also three regions. In two regions (I and II) scaling power dependences of H_0 and $\bar{\varphi}_N$ totally coincide with the results of the SCF approach (see Table I). In region III scaling dependences of H_0 and $\bar{\varphi}_N$ on P and σ coincide with SCF results, while the concentration dependence $H_0 = H_0(\Phi)$ is different.

The reasons for the coincidence of scaling and mean-field exponents in region I (a grafted chain layer immersed in pure solvent) were discussed in ref 3. It was shown that the SCF approach overestimates both contributions to the free energy of the layer, ΔF_{el} and ΔF_{conc}. Since the equilibrium structure of the layer in a pure solvent is determined by the balance of ΔF_{conc} and ΔF_{el}, compensation of the two errors leads to the resulting expression for layer height H_0 coinciding with the scaling result of Alexander.[1] The SCF and scaling dependences for the free energy, however, differ from each other (see ref 3 for details).

The reason for the coincidence of the SCF and scaling dependences of the layer height H_0 in region II is also clear: The leveling of the density of the free energy of volume interactions between N units in the layer and between P units in the bulk solution leads automatically to the dependence $H_0 \simeq Na^3/\sigma\Phi$ in both cases of taking or not taking into account the correlations of unit density fluctuations in the system.

Let us consider in more detail the scaling dependence of H_0 in region III where the volume interactions in the layer are controlled by the pair contacts between P units, $\bar{\varphi}_P \gg \bar{\varphi}_N$. According to the scaling concepts[15] the correlation radius of unit density fluctuations ξ (the size of concentrational blob) is given under the conditions of a semidilute athermal solution of the concentration $\bar{\varphi}_P$ by $\xi \simeq a\bar{\varphi}_P^{-3/4}$. (Note that the mean-field dependence of this characteristic of the solution is given by $\xi \simeq a\bar{\varphi}_P^{-1/2}$ [15].) Within each blob a part of a given polymer chain is slightly perturbed by the neighboring coils, while on the scale of a whole chain the intermolecular interactions lead to the renormalization of a given chain into the sequence of impermeable blobs of size ξ. Hence, each P chain in a semidilute solution is represented by the sequence $P' = P\bar{\varphi}_P^{5/4}$ blobs. The dominating of P chains in the grafted chain layer, $\bar{\varphi}_P \gg \bar{\varphi}_N$, leads also to the renormalization of each N chain into the sequence $N' = N\bar{\varphi}_P^{5/4}$ blobs of size ξ.[2] Hence, under the conditions of region III the grafted chain layer may be represented as a melt of grafted N' and mobile P' chains of blobs. According to ref 2 this leads to the decrease of the second virial coefficient of blob interaction $v_{\mathrm{B}} \simeq \xi^3/P' = \xi^3/P\bar{\varphi}_P^{5/4}$. Hence, the resulting dependence of the grafted layer height $H_0 \simeq v_{\mathrm{B}}^{1/3}(\xi^2/\sigma)^{1/3}N' \sim \bar{\varphi}_P^{-5/12} \sim \Phi^{-5/12}$ differs from the SCF result $H_0 \sim \Phi^{-1/3}$ by the factor $\Phi^{1/12}$.

Screening of volume interactions between N chains by mobile P chains decreases with the decrease of mobile chain content $\bar{\varphi}_P \simeq \Phi$ in the layer. Under the conditions $P\bar{\varphi}_P^{5/4} \simeq 1$, corresponding to the transition from a semidilute solution to the dilute solution of P chains in the layer, screening of N chain interactions disappears. Hence, the left boundary of scaling region III is determined by the concentration of overlapping P chains in the layer, $\Phi \simeq P^{-4/5}$, and here the smooth crossover between the dependences of regions I and III takes place. Note that in the original paper[2] the left boundry of region III was located in the range of lower values of Φ (dotted line in Figure 9) and was determined by the relationship $\Phi \sim (\sigma/a^2)^{-2/3}$. This location of the boundary leads to the absence of the crossover between the dependences of regions I and III and the following conclusion about the sharp character of the collapse of a grafted chain layer caused by the concentrating of the mobile polymer solution.[2] It seems to us that the natural location of the left boundary of region III, $P\Phi^{5/4} \simeq 1$, takes off the conclusion about the sharp character of the collapse of a grafted chain layer caused by an increase in a mobile chain content Φ. And, hence, both scaling and SCF approaches give qualitatively (and in many points quantitatively) similar pictures of the behavior of a grafted chain layer immersed in a solution of mobile polymer.

As was noticed above, the diagram of Figure 9 does not take into account weak, nonpower dependences of the characteristics of the system on the parameters. Contrary to the scaling method, the SCF approach makes it possible to evaluate the contributions of nonpower dependences and consider in detail the regions of crossover between the regions in Figure 9. It follows from the results of section III of this paper that under the conditions of low Φ values, $1 - \Phi \leq 1$ (region I in Figure 9), the height of the layer H_0 decreases linearly with increasing Φ, $H_0 = H_0(\Phi{=}0)(1 - b\Phi)$ (eq 35). The coefficient b increases with increasing length of mobile chains P and attains the maximal value $b \simeq (a^2/\sigma)^{-2/3}$ at $P \gg 1$ (see Figure 2c). When the increase in Φ leads to the transition from region I to region II in Figure 9, the dependence H_0 on Φ is given by (42). As is seen from (42) (see also Figure 2c) the discounting of the second addend in (42) leads at $\Phi = 1$ to an increase of H_0 with respect to pure power dependence for the value $\Delta H_0 \simeq H_0$. (At $a^2/\sigma = 0.04$ and $P = 30$ relationship 42 gives $\Delta H_0 \approx 1.25H_0$.) Hence, the discounting of nonpower dependences can change the layer height H_0 with respect to pure power dependences of Table I for the value $\Delta H_0 \simeq H_0$.

The effect of polydispersity of mobile polymer on the characteristics of the grafted layer is much weaker and manifests at small concentrations of N units in the layer only (region III and the lower part of region I, $a^2/\sigma \ll P^{-3/2}$). Here the layer height H_0 is described by eq 59 and the additional compression of the layer due to the polydispersity of mobile polymer chains is given at $\Phi \simeq 1$ by $\Delta H_0/H_0 = (\overline{P^2}/\bar{P}^2)^{1/3} - 1$. (For the values $(\overline{P^2})^{1/2}/\bar{P} \simeq M_{\mathrm{w}}/M_{\mathrm{n}} = 1.1$–$1.5$, the variation of H_0 is $\Delta H_0/H_0 = 0.1$–0.3.) In region III and the upper part of region I ($a^2/\sigma \gg P^{-3/2}$) the effect of polydispersity is negligibly small.

In conclusion it should be noted that, as was already mentioned above, the system considered in this paper (grafted chain–solution of mobile polymer) can be regarded as a basic model for various complex polymer systems. In particular, it can be used for further development of the analytical theory of steric stabilization of colloid dispersions by polymers. As is known,[29] the basis of the stabilizing effect of grafted polymers in lyophobic dispersion stabilization is the repulsion between polymer layers preventing particle aggregation due to the van der Waals attraction. The repulsive part of interparticle potential ΔV_{p}, resulting from the deformation of stabilizing layers when particles approach each other, is determined by the difference between the free energies of undeformed and compressed layers. The development of a SCF analytical theory of grafted chain layers, taking into account the equilibrium rearrangement of a grafted layer structure at its deformation, made it possible to calculate the stabilizing potential ΔV_{p} for the cases when the dispersion medium was a low molecular weight athermal solvent or Θ-solvent for stabilizing chains[30,31] or polymer melt of short mobile chains.[15] The results of this paper make it possible to calculate the stabilizing potential ΔV_{p} in a more complex, two-component dispersion medium—the solution of the mobile polymer being chemically identical with that of the stabilizing polymer. The significant difference between this case and those already considered[15,30,31] is the variation of the dispersion medium parameters in the region of particle interaction: the variation of mobile polymer content in the clearance between particles in the process of polymer layer deformation. As was shown in refs 32 and 33 under the conditions where the grafted chains are much shorter than mobile molecules, $N \ll P$, the redistribution of mobile polymer in the process of particle approach leads to a change in sign of the stabilizing potential, ΔV_p, i.e., the appearance of effective attraction instead of repulsion in the range of strong deformations and, thus, of dispersion destabilization. In the present paper the opposite case, $N \gg P$, is considered. The SCF equations obtained in section II permit analysis in the case of the effect of redistribution of mobile polymer on the structure and stabilizing properties of a grafted chain layer and, thus, extend the analytical theory of steric stabilization[15,31] for the case of a two-component dispersion medium. Our forthcoming paper will be devoted to this problem.

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