Theory of adsorption of polymer chains at spherical surfaces: 2. Conformation of macromolecule in different regions of the diagram of states

T. M. Birshtein and O. V. Borisov
Institute of Macromolecular Compounds, Academy of Sciences of the USSR, Leningrad 199004, USSR
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The chain conformation near an impermeable adsorbing sphere is investigated over a wide range of temperatures (attractive energy). Analytical expressions for various conformational characteristics of the chain with one fixed end (the number of chain contacts with the surface, the mean-square distance between the free chain end and the surface, the profile of monomer unit density etc.) are obtained. The influence of the dimensions and dimensionality of the adsorbent on the characteristics of the conformational transition related to the chain adsorption is analysed.

(Keywords: polymer chain adsorption; chain conformation; conformational transition; spherical adsorbent)

INTRODUCTION

In Part 1 of this paper the analytical expressions for the partition function of the Gaussian chain near a spherical adsorbent (equations (20) and (24) in Part 1) were obtained and the diagram of states of the system was constructed. In this paper we will consider the change in the thermodynamic and conformational characteristics of a grafted chain upon adsorption, i.e. during the transition B → C → A due to a decrease in temperature. For this purpose we will use the expressions for the partition function, equations (31)–(35) in Part 1, and for conformational characteristics of the chain in different regimes obtained from equations (26)–(30) in Part 1 and reported in Appendixes 1 and 2 and Tables 1 and 2 in Part 1 (omitting further references to these equations).

RESULTS

Chain grafted onto a plane. Regimes B_p–C_p–A_p

It is known that an infinitely long free chain reliably returns to the phantom plane, and the number of its returns is $\sim N^{1/2}$. For this reason, the impermeable plane appreciably affects the conformation of the grafted chain even at $T \to \infty$ because of purely steric restrictions. The impermeability of the plane makes a large number of conformations impossible leaving permitted only the fraction $\sim N^{-1/2}$ of conformations of the free chain (addition to free energy $\sim \ln N$). The number of chain returns to the impermeable plane decreases drastically as compared to those to the phantom plane and virtually becomes independent of N (i.e. the returns take place mainly at the chain part near the grafted end). The components of the mean-square chain dimensions perpendicular to the plane increase (by a factor of $2^{1/2}$ in the case of the end-to-end dimensions). Finally, the concentration of units near the surface decreases (at $z \ll R$ we have $M(z) \approx z$ *Figure 1*) and passes through a maximum at $z_{\max} \simeq 0.96R$.

With decreasing temperature (decreasing c), this situation is maintained over the entire region B ($c > 0$, $cR \gg 1$), though the attraction of units to the surface increases. Hence, increases also the statistical weight of those among the permitted conformations which correspond to chain contacts with the surface and the mean number of these contacts, which, however, remain

Table 1 Asymptotic expressions for the number of chain contacts with the surface in different regimes

	Adsorption regimes		
	B	C	A
Geometric regimes	$c > 0$, $cR \gg 1$	$c \simeq 0$, $\lvert c\rvert R \ll 1$	$c < 0$, $\lvert c\rvert R \gg 1$
p $r_s \gg r_{s0}$	$(ac)^{-1}$	$2R/(a\pi^{1/2})$	$2R^2\lvert c\rvert a^{-1}$
s $r_s \ll r_{s0}$		$R\pi^{1/2}/(2a)$	

Table 2 Asymptotic expressions for the mean-square distance between the free chain end and the spherical surface in different regimes (from equation A1.2)

	Adsorption regimes		
Geometric regimes	B $c > 0$, $cR \gg 1$	C $c \simeq 0$, $\lvert c\rvert R \ll 1$	A $c < 0$, $\lvert c\rvert R \gg 1$
p $r_s \gg r_{so}$	$4R^2$	$2R^2$	$2\lvert c\rvert^{-2}$
s $r_s \gg r_{s0}$	$6R^2$	$4R^2$	$6\lvert c\rvert^{-2}$

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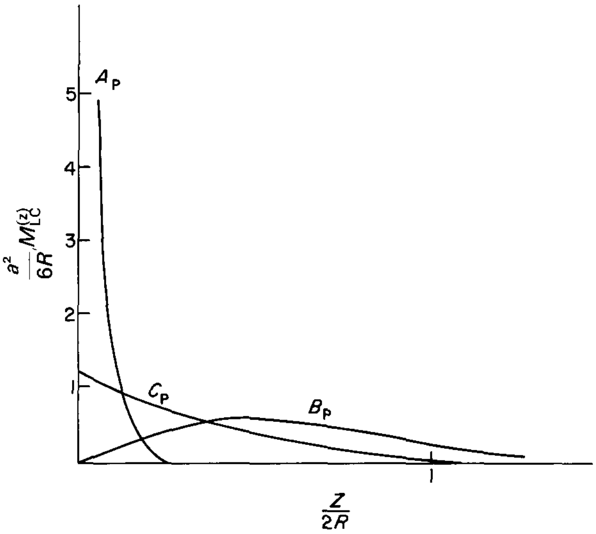

Figure 1 Distribution of units of a chain grafted onto a plane in the direction normal to the plane in different adsorption regimes

independent of N. The partition function of the chain

$$Z^{\infty}_{Lc}(0) \simeq \frac{1}{ac} Z^{\infty}_{Lc=\infty}(0)$$

increases too (remaining less than unity). Density distribution retains a maximum displaced towards the surface with decreasing temperature but retains the dependence $z_{\max} \sim R \sim (La)^{1/2}$.

Upon further decrease in temperature to $T \sim T_c$, the system passes to regime $C(|c|R \lesssim 1)$ where steric restrictions introduced by the surface are compensated for by attraction to it. The chain characteristics in this region are close to those of a free chain 'grafted' onto a phantom plane. The partition function is $Z_{Lc=0}(0) = 1$ just as for a free coil; the number of contacts with the surface is $N_s \sim N^{1/2}$; the size $\overline{z_N^2}$ is close to the corresponding size of the free chain; and the distribution of unit density in the direction normal to the plane is the same as for a free chain grafted onto the phantom plane with a maximum at $z = 0$. (The unit density in the semispace $z > 0$ is twice higher than that for a free chain, *Figure 1*).

Further decrease in temperature leads to a transition to absorption regime $A(c < 0, |c|R \gg 1)$, into conditions of GSD where the chain (even at $N \to \infty$) contacts the surface of a certain fraction of its units $\Theta \equiv N_s/N \sim |c|a$ increasing with decreasing T. The partition function $Z_{Lc}(0) \gg 1$, and the main contribution to the free energy of the chain is provided by the interaction of units with the surface. The unit density has maximum near the surface and decreases exponentially with the distance from it (correlation length of density fluctuations in the normal direction is $\sim |c|^{-1}$). The height of the chain end above the surface $(\overline{z_N^2})^{1/2}$ and the thickness of the adsorption layer $(\overline{H_N^2})^{1/2}$ are proportional to $|c|^{-1}$ (*Figure 1*). It should be borne in mind that only weak adsorption $b|c| \sim |\tau| \ll 1$ has been considered so far.

Chain grafted onto a small particle. Regimes $B_s(B_s', B_s'')$–C_s–A_s–A_p

The decrease in particle size to $r_s < R$ leads to a decrease in steric restrictions imposed by the particle. At $T \to \infty$, since the return of the free chain to the region limited in three directions (zero-dimensional) is not certain, the chain grafting onto a small particle affects the array of conformations and conformational characteristics of a long chain only in the form of independent of N end effects. The number of allowed conformations is found to be less than that for a free chain only by a factor of $\sim (r_s/a)$ (addition to the free energy which is independent of N), the chain size coincides (with an accuracy of the terms $\sim r_s/R$) with that of the free chain, and the number of contacts is independent of N just as for the free chain 'grafted' onto a small phantom sphere. Near the surface of the sphere, the unit density $m(z)$, just as in the case of a plane, decreases to zero but this effect is limited by the scale $z \sim r_s$. At $z_{\max} \sim r_s$ the density $m(z)$ passes through the maximum and at $r_s \ll z \ll R$ decreases as $m(z) \sim 1/(z + r_s)$ as in the free chain (with respect to one end) (*Figure 2*).

The overall picture of the perturbing action of a small particle only on the conformation of the grafted chain end is also retained with decreasing temperature (decreasing c) over the entire regime B_s. However, two cases existing successively may be singled out with respect to the character of this action (subregimes B_s' and B_s''). The partition function of the grafted chain in the region B_s is determined by the equation (the first equality is obeyed at all r_s)

$$Z_{Lc}(0) = 1/(ac)Z_{Lc=\infty}(0) = 1/cr_s \qquad (1)$$

and takes the values less than unity at $c^{-1} < r_s$ (subregime B_s') and greater than unity at $c^{-1} > r_s$ (subregime B_s''). This fact implies that in subregime B_s', just as at $T \to \infty$, the repulsion of units from the particles continues to play the prevailing role, whereas in subregime B_s'' the end effects acquire the character of attraction. Correspondingly, in subregime B_s', the dimensions and the concentration profile retain the same form as at $T \to \infty$, but with decreasing temperature the density maximum approaches the surface, and the near-surface density increases. In subregime B_s'', the unit density is maximum at the surface, decreases as $m(z) \sim 1/(z + r_s)^2$ $(M(z) = \text{const}(z)$ at distances $z \lesssim c^{-1})$, and the decrease in density characteristic of the free chain: $m(z) \approx 1/(z + r_s) \times (M(z) \sim (z + r_s))$ is established at distances $c^{-1} \ll z \lesssim R$ (*Figure 2*).

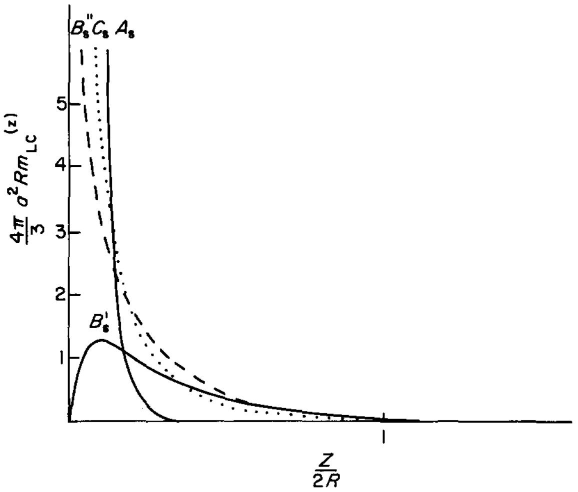

Figure 2 Radial distribution of units of a chain grafted onto a spherical particle with a radius $r_s = 0.2R$ in different adsorption regimes

Further decrease in temperature transforms the chain into the critical regime C. The partition function increases with decreasing T attaining the value of $Z_{Lc}(0) \sim R/r_s \gg 1$ at the boundary of regimes B and C and retains this value over the entire regime C_s (with an accuracy of the value of the coefficient slightly increasing with decreasing T). In this regime the polymer chain forms $\sim N^{1/2}$ loops of return to the surface (the number of contacts with the surface $N_s \sim N^{1/2}$), and the value of r_s influences only the coefficient increasing with r_s. The height of the chain end above the surface $(\overline{z_N^2})^{1/2} = 2R$, i.e. it is less by a factor of $(3/2)^{1/2}$ than that for the free chain. Unit concentration is at a maximum near the surface and decreases as $m(z) \approx (z + r_s)^{-2}$ with the distance from it ($M(z) \simeq \text{const}(z)$, *Figure 2*), which greatly differs from the concentration profile in the free chain.

Upon further decrease in temperature, the chain passes into the adsorption regime A ($c < 0$, $|c|R \gg 1$). A term increasing exponentially with N appears in the partition function: the chain contacts with the surface by a finite (even at $N \to \infty$) fraction of its units $\Theta \sim |c|a$ forming $\sim N$ loops the length of which is independent of N. The height of the chain end above the surface and the thickness of the adsorption layer are also independent of N and are proportional to $|c|^{-1}$. Unit concentration is at a maximum at the surface, and the number of units in the spherical layer $M(z)$ decreases exponentially with increasing distance from the surface with the correlation length $\approx |c|^{-1}$. At $|c|^{-1} \gtrsim r_s$, the conformational characteristics retain a certain dependence on r_s (regime A_s). As the temperature decreases further, at $|c|^{-1} \ll r_s$ the dependence on r_s disappears: the chain passes to regime A_p.

Interaction radius of coil with a spherical particle

Let us now consider the effect of a particle with a radius r_s on the conformation of the macromolecule, one end of which is fixed at a distance z' from the surface. It is evident that at $z' \to \infty$ the chain does not 'feel' the surface at any T and r_s retaining the conformation of a free coil $(Z_{Lc}(z') \to_{Z' \to \infty} 1)$.

In the general case of an arbitrary z' value at $T \to \infty$ we have

$$Z_{Lc=\infty}(z') = (z' + r_s)^{-1}\left(z' + r_s \operatorname{erf}\left(\frac{z'}{2R}\right)\right)$$

$$\simeq \begin{cases} 1 & z' \gg \min(R, r_s) \\ \operatorname{erf}\left(\dfrac{z'}{2R}\right) & z' \ll R \ll r_s \\ z'/r_s & z' \ll r_s \ll R \end{cases} \tag{2}$$

When the temperature decreases, and z' is not very great the system passes successively through regimes B, C and A. Partition functions and numbers of contacts with the surface in these regimes calculated from equations (24)–(26) in Part 1 are given in Appendix 2. Let us discuss these results and establish the distances z' at which the effect of surface on chain conformation is important.

It can be seen from equation (2) that at $T \to \infty$ the small sphere ($r_s \ll R$) no longer restricts the array of chain conformations even at $z' \gg r_s$, whereas the restrictions imposed by the plane are considerable up to $z' \approx R$. With decreasing temperature, the steric effects remain predominant in regime B_p and subregime B'_s (where $c^{-1} < r_s \ll R$) and the surface affects the chain conformation up to $z' \approx R$ or $z' \approx r_s$, respectively. A different situation is observed in subregime B''_s in which $r_s < c^{-1} \ll R$. As at $z' = 0$, the end effects in this regime have the character of attraction which is manifested up to $z' \approx c^{-1}$ (the characteristic scale c^{-1}, increases with decreasing distance from the critical point). The number of contacts between the chain and the sphere in regimes B is independent of r_s and N and at $z' \ll c^{-1}$ is independent of the position of the fixed end z'. At $z' \gg c^{-1}$, the number of contacts decreases with increasing z' according to the power law $N_s \sim c^{-1}(c^{-1}/z')$.

In the critical range, the existence of the sphere influences coil conformation at $z' \lessgtr R$. Moreover, the number of contacts with its surface is $\sim N^{1/2}$ and is approximately the same as for a chain grafted onto a sphere of the same radius r_s. At $z' > R$, the number of contacts decreases exponentially with increasing z'.

Finally, in the adsorption regime $A(c < 0;\ |c|R \gg 1)$, the surface influences the coil conformation at any r_s if its end is fixed at a distance $z' < |c|R^2 \sim L|c|a$ from it. In this case the conditions of GSD are obeyed, and the chain is attached to the surface by a finite fraction $\Theta \sim (Na)^{-1}(2R^2|c| - z')$ of its units, just as the chain grafted onto the surface. As already mentioned in this regime another characteristic scale $|c|^{-1}$ exists, determining the correlation radius $\zeta \sim |c|^{-1}$. When z' changes near the limiting value, $|c|R^2$, by the value of $\pm\zeta$, the chain passes from the state of the bonded chain to that of a chain which virtually does not interact with the surface. The contribution of the ground state to the partition function decreases to the value of approximately 0(1), i.e. of the order of magnitude of the contribution of a continuous spectrum, and the number of chain contacts with the particle decreases to zero.

DISCUSSION

Order of adsorption phase transition

As already mentioned, the variation in r_s makes it possible to study the effect of not only the size but also the dimensionality of the adsorbent on the relationships of adsorption. At $r_s \ll R$, the spherical particle is a quasi-zero-dimensional ($d = 0$) adsorbent, i.e. the adsorbent limited in all dimensions on the chain scale, and in the limit $r_s \to \infty$ (it is sufficient if $r_s \gg R$) is transformed into an adsorbing plane, $d = 2$. It is essential that the increase in the adsorbent size with the maintenance of spherical symmetry leads to a direct transition from $d = 0$ to $d = 2$ without passing $d = 1$. It follows from the results of this work that at any r_s the adsorption of infinitely long Gaussian chains on a spherical particle is performed by the second-order phase transition. This result is in complete agreement with the expression obtained previously[1–3] for the order K_0 of phase transition in the adsorption of Gaussian chains from the D-dimensional space on the d-dimensional adsorbent

$$K_0 = |1 - \tfrac{1}{2}(D - d)|^{-1} \tag{3}$$

It can be seen that at $D = 3$ the value of $K_0 = 2$ both at $d = 2$ and at $d = 0$. It is noteworthy that for the intermediate case $d = 1$ (adsorption on an infinite cylinder) the order of phase transition $K_0 = \infty$.

The similarity of the cases $d = 0$ and $d = 2$ and the possibility of a continuous transition between them are associated[1–3] with the fundamental properties of random walks in a three-dimensional space. Although the return to the infinite phantom plane is reliable and that to a point is unreliable, the asymptotic distribution functions of the lengths of return loops coincide.

At the same time, the difference in the reliability of a return causes the difference between the cases $d = 0$ and $d = 2$. Thus, there is a considerable difference between the character of the conformational reconstruction of a free chain at the beginning of adsorption for these two cases. The beginning of adsorption is associated with the formation of a large ($\sim N^{1/2}$) number of loops of return to the surface. For a chain adsorbed on a plane, this fact implies that the global conformation of a free coil is retained. In contrast, in adsorption on a point or a small particle, a large-scale change in conformation is required with entropy loss $\sim N^{1/2}$. It is of interest that in adsorption on a small particle in the regime B_s where the free chain conformation is still retained on the whole, near the boundary with regime C_s a specific marginal subregime B_s'' appears. In this regime, the end effects are of the attractive type, and the change in chain conformation in regime C_s is prepared.

Position of phase transition

As shown above, the value of $(U/T)_c$ is virtually independent of the presence or absence of the impermeable core in adsorption on a limitingly small ($r_s \ll b$) particle. In the case of its presence, this value does not depend on r_s and retains the same value as that for adsorption on a planar wall. In the case of its absence it decreases with increasing r_s reducing to zero for adsorption in a planar ditch.

The first and third results have the simplest explanation. In the critical range, the chain forms a large, $\sim N^{1/2}$, number of contacts with the surface. The reduced energy of these contacts $\sim N^{1/2}(U/T)_c$ compensates for the entropy disadvantage of this chain conformation. Under these conditions two sources of loss in the conformational entropy of the chain exist: global chain reconstruction occurring, as already indicated, only at small $r_s \ll R$ and leading to entropy losses $\sim (aN/r_s)^{1/2}$; and local conformational restrictions occurring for $\sim N^{1/2}$ adsorbed units when an impermeable wall exists.

The third result confirms the conclusion about the absence of global change in chain conformation in adsorption on a planar adsorbent. In the case of adsorption on a ditch when the local perturbing action of the wall is absent, adsorption begins at any virtually small depth of the ditch, i.e. adsorption begins on a phantom plane. The presence of an impermeable plane wall behind the potential well leads to the appearance of local conformational restrictions for adsorbed units. The beginning of adsorption requires the compensation for the corresponding entropy losses, and, hence, the critical depth of potential well differs from zero.

The first result shows that the case of small sphere ($r_s \ll b \ll R$) is the opposite limiting case when the entropy losses at the beginning of adsorption are related only to the large-scale change in chain conformation, and the impermeability of the core does not lead to local entropy losses.

The second result is related to a great extent to the diffusion model used. In fact, both the large scale reconstruction of free chain conformation in adsorption on a small particle and the local restrictions of conformations of adsorbed units at the beginning of adsorption lead to entropy losses of the same order of magnitude $\sim N^{1/2}$. Moreover, with increasing r_s the former of these contributions decreases (as $1/r_s$, see equation (40) in Part 1) and the latter increases. In this case the value of $(U/T)_c N^{1/2}$ compensating for the total entropy loss is independent of r_s, which indicates that the increase in local and decrease in global entropy losses with increasing r_s are exactly (in the framework of the diffusion model) mutually compensated for. Other models may lead to the dependence of T_c on the dimensionality, $d = 0$ or $d = 2$, of the impermeable adsorbent. Thus, on lattice models[1–4] (under the conditions of a narrow wall potential hole $r_s \geqslant b$), local conformational losses do not decrease with r_s down to the limiting small r_s so that T_c becomes an increasing function of r_s.

Boundary conditions in adsorption (equation (17) in Part 1)

In Part 1 of this paper, the absence of the dependence of T_c on r_s in the adsorption of a Gaussian chain on a spherical surface has been considered. This result was obtained in the framework of the diffusion model used. However, in a recently published paper by Pinkus *et al.*[5] the same model has been considered and the dependence $T_c = T_c(r_s)$ has been suggested. Our analysis showed that this erroneous conclusion in reference 5 is a result of incorrect transfer to the spherical model of some results grounded previously for a planar model.

The problem of adsorption of a Gaussian chain on an impermeable planar surface in the framework of a diffusion model has been first solved by de Gennes[6]. In this case the symmetry of the system does not require the transition from eigenfunctions in equation (4) in Part 1 to other functions, and it is these functions that must satisfy the boundary condition

$$\frac{\partial}{\partial x} \ln \Psi_\alpha(x) = c \qquad (4)$$

where the parameter c passes through zero at the critical point changing its sign ($c \sim \tau$). In reference 5, the same condition has been extended without additional analysis to eigenfunctions in the problem of chain adsorption on a spherical surface of a finite radius.

The rigorous consideration carried out in our paper showed that in adsorption on a sphere the boundary condition should be superposed on functions $\chi_\alpha(r) = r\Psi_\alpha(r)$ rather than on functions $\Psi_\alpha(r)$. For adsorption on the surface of an impermeable sphere, the correct expression of boundary conditions leads to the absence of the dependence of T_c on r_s. It should be emphasized that, generally speaking, this result is well known for another but completely equivalent problem: the capture of the quantum particle by the potential well[7].

The analogy of ensembles of chain conformations near the adsorbing surface and the trajectories of random walk of a particle near a surface with the same geometry has been repeatedly considered in the literature. It has been shown that in the case of a planar surface, the precritical range corresponds to the partial absorption of particles by the surface, and the critical point corresponds to complete reflection, which is described in equation (4).

The results of our work show that in the case of a spherical adsorbent of a finite radius, the critical point does not correspond to the condition of reflection from the surface. According to equations (8) and (17) in Part 1, the behaviour of functions near the spherical surface is determined by its radius, and the conditions of reflection are obeyed only at $r_s \to \infty$.

Conformations of a chain grafted onto a surface

The results of the present paper show that the arrangement of a Gaussian chain grafted onto a spherical surface with respect to this surface is determined by the 'adsorption' regime in which the system exists and is virtually independent of the size of r_s and the degree of permeability of the adsorbent (under the condition that the system is in the same adsorption regime). This independence is caused by the superposition and mutual compensation of a number of effects. Thus, in precritical regime B, grafted chains virtually do not return to the surface regardless of r_s and of whether this surface is an impermeable sphere (Figure 2a in Part 1) or a singled out spherical layer (let us bear in mind that in a planar variant, the regime B_p exists at a positive energy acquired by a chain unit upon arrival in this layer, i.e. when a 'ditch' is replaced by a barrier, 'mountain ridge'; Figure 2c in Part 1). This absence of the return results, however, from different reasons: the unreliability of the return of a free chain into a limited region at small r_s (regime B_s) and the local perturbing action of the surface at large r_s (the impossibility of the passage through the plane or an energy loss occurring on passing over the barrier) in regime B_p. The increase in r_s leads to an increase in both the probability of the return and in the perturbing action of the surface so that the number of chain contacts with the surface does not change (i.e. remains $\sim N^{\circ}$).

In the critical range, the chain forms a great ($\sim N^{1/2}$) number of contacts with the surface regardless of r_s. At large r_s (regime C_p), as already mentioned, for this purpose it is sufficient for the chain to adopt the conformation of a free coil near the phantom surface (in the case of an impermeable plane, with the replacement of passages through the plane by reflections). At small r_s (regime C_s), a marked change in the conformation of the free chain is necessary.

In regimes B and C, a certain dependence of the conformational characteristics of the chain on r_s is retained in the form of the difference between the numerical coefficients in the dependences of these characteristics on N. In adsorption regime A when the number of chain contacts with the surface is $\sim N$, the dependence of these coefficients on r_s becomes weaker and, as can be seen from the diagram of state (Figure 3 in Part 1), at relatively low temperatures the chain passes from regime A_s to regime A_p at any r_s.

In all regimes, a chain grafted onto the surface at one end consists of a part attached to the surface (this part may contain and contains the alternating sequence of adsorbed parts and loops) and a tail walking away from the surface and never returning to it (Figure 1 in Part 1). In precritical regimes B_p and B_s, a long chain ($N \gg 1$) consists almost entirely of the tail, and the mean-square height of the free end above the surface is determined by

$$\overline{z_N^2} = \begin{cases} 2/3La = 4R^2 & B_p \\ La = 6R^2 & B_s \end{cases} \tag{5}$$

In regime B_p, the value of $\overline{z_N^2}$ coincides with the component of the square of the end-to-end dimension normal to the surface. In the case of an impermeable surface, this component increases twice as compared to the free chain. In regime B_s, the value of $\overline{z_N^2}$ coincides with the square of the end-to-end dimension of the free chain (cf. equation (A1.2) in Appendix 1).

In contrast, in regimes A_p and A_s, the tail length is independent of N and $\overline{z_N^2} \sim |c|^{-2}$. In intermediate (critical) regimes, C_p and C_s, the tail contains a certain finite fraction of units, and another part of the chain is a sequence of adsorbed parts and loops or, according to terminology in reference 2, a composite loop. The average fraction q of units in the tail under critical conditions, may be found from the values of $\overline{z_N^2}$ obtained in equation (A1.2) in Appendix 1 which are the square of the height of the tail end above the surface. It is evident that

$$q = (\overline{z_N^2}|_{c=0})(\overline{z_N^2}|_{c\to\infty})^{-1} \tag{6}$$

which gives the fraction of units in the tail $q = 1/2$ and 2/3 in chain adsorption on a plane and on a small sphere, respectively. The other fraction of units, $1 - q$, forms a composite loop.

It is of interest that these values of q are directly related to the fundamental properties of random walks in free space, which also determine the order of adsorption phase transition. We mean the probability of the formation of loops and tails during these walks (cf. references 2 and 3).

Let us consider a grafted chain under critical conditions at $N \gg 1$. Let $f(q') = f_{\text{loop}}(1 - q')f_{\text{tail}}(q')$ be the probability of a chain state in which $N(1 - q')$ units are in the composite loop and the others, Nq' units are in the tail. It is known[1–3] that loop distribution at the critical point is the same as in the free chain near the phantom plane. For composite loops we have

$$f_{\text{loop}}(q') \approx \frac{1}{q'^{\alpha}} \tag{7}$$

where $\alpha = 1/2$ for composite loops of return to both a small particle and an infinite plane. Let us bear in mind that $f_{\text{loop}}(q')$ is proportional to the probability of a return to the small particle or to the plane after exactly $q'N$ steps, and the value of the exponent α determines the order of adsorption phase transition. However, the cases of grafting onto the plane and the small particle differ in the function

$$f_{\text{tail}}(q') \approx \frac{1}{q'^{\beta}} \tag{8}$$

where $\beta = 1/2$ for a tail grafted onto a plane and $\beta = 0$ for a tail at a small particle. For the average tail length at the critical point

$$q = \frac{\int_0^1 q' f_{\text{tail}}(q') f_{\text{loop}}(1 - q')\,\mathrm{d}q'}{\int_0^1 f_{\text{tail}}(q') f_{\text{loop}}(1 - q')\,\mathrm{d}q'} \tag{9}$$

we obtain from equations (7) and (8): $q = 1/2$ and $q = 2/3$ in the cases of a chain at the plane and at the small particle, respectively. *Figure 3* shows the distribution functions $f(q')$ of tail length at the critical point indicating that for a chain grafted onto a plane, the distribution is enriched with very long and very short tails, and for a

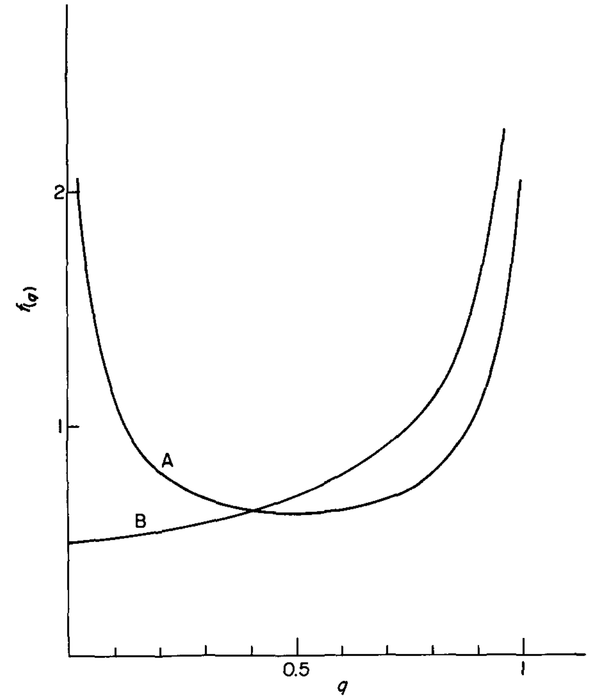

Figure 3 Distribution function of chain tails at the critical point for a chain grafted onto a plane (curve A) and a small particle (curve B)

chain grafted onto a small particle, long tails predominate. These values of q are in complete agreement with those found above by successive calculation.

We draw special attention to these values of q and to their relationship to the fundamental properties of random walks in the three-dimensional space because in a recent paper by Grosberg and Schakhnovich[8] in which adsorption at a point has been investigated by the method of dynamic renorm group, and alternative values of $q = 3/4$ and $\overline{z_N^2}|_{c=0} = 9/2R^2$ have been obtained. In a similar manner, for a more general case of adsorption at a point $d = 0$ from the D-dimensional space it has been obtained in reference 8 that $q = D/(2D - 2)$. However, in accordance with the above scheme we have $\alpha = 1 - |1 - \frac{1}{2}(D - d)|$ and $q = 2/D$. On the basis of these considerations we suppose that the results of reference 8 and its generalizations to the case of a heteropolymer[9] based on the suggested methods are not completely valid.

CONCLUDING REMARKS

The present paper considered the adsorption of a Gaussian chain on a spherical particle. Although this model system is an idealized system and, generally speaking, it is impossible to carry it out in practice, its successive consideration seems to us important for passing to real systems. Let us briefly state some features of real systems leading to essential differences from the above picture and being particularly important at $r_s < R$. First, the adsorbent at $d = 0$ can be saturated, and hence only $\sim (r_s/R)^2$ part of the chain can be adsorbed on it. As a result, at $d = 0$ the adsorption transition loses the phase character. Further, the volume interactions in real chains preventing chain compactization in adsorption are important. The authors hope to study further the adsorption of polymer chains on a small particle taking into account these factors on the basis of the theory developed above.

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APPENDIX 1. CONFORMATIONAL CHARACTERISTICS OF A CHAIN GRAFTED ONTO A SPHERE

The average number of chain contacts with the surface is given in *Table 1*.

It appears independent of the sphere radius r_s in regimes B and A, but increases with r_s in regime C. For the chain dimensions (mean-square distance from the free end to the surface) we obtain from equation (27) in Part 1

$$\overline{z_N^2} = Z_{Lc}^{-1}(0)\left\{\frac{6R^2}{cr_s} - 2\left(\frac{3}{cr_s} - 1\right)\right. \\ \left. \times \left[\frac{2R}{c\pi^{1/2}} - \frac{1}{c^2}(1 - \exp(c^2R^2)\,\mathrm{erf}c(cR))\right]\right\} \quad \text{(A1.1)}$$

The asymptotics of this dependence corresponding to different adsorption and geometrical regimes are given in *Table 2*. It should be noted that at $\overline{z_N^2} \gg r_S^2$ the value of $\overline{z_N^2}$ is the square of the end-to-end dimension and at $\overline{z_N^2} \ll r_S^2$ is the square of the projection of this dimension on a fixed axis. Thus, for a free chain 'grafted' onto a phantom sphere of radius r_f (i.e. in the absence of the effects related to the interaction and steric restrictions) we have

$$\overline{z_N^2} = 2R^2\left\{1 + 2\left[2\left(\frac{r_f}{2R}\right)^2 + 1\right]\mathrm{erf}c\left(\frac{r_f}{2R}\right)\right. \\ \left. - \frac{2r_f}{R\pi^{1/2}}\exp\left(-\frac{r_f^2}{4R^2}\right)\right\} \simeq \begin{cases} 6R^2, & r_f \ll R \\ 2R^2, & r_f \gg R \end{cases} \quad \text{(A1.2)}$$

The complete expression for the distribution $M_{Lc}(z)$ of chain units above the surface (the number of units in a layer of unit thickness located at a distance z from the surface) is very cumbersome, and only the asymptotic expressions for all adsorption regimes will be reported.

Regime B (c > 0, cR ≫ 1)

$$M_{Lc}(z) \simeq \frac{6}{a^2}\frac{(r_s + z)}{cr_s} Z_{Lc}^{-1}(0) \\ \times \left\{\left[1 + \frac{1}{c(r_s + z)}\right]\mathrm{erf}c\left(\frac{z}{2R}\right) - \frac{r_s}{r_s + z}\mathrm{erf}c\left(\frac{z}{R}\right)\right\}$$

$$\simeq \frac{6}{a^2}\begin{cases} R\pi^{1/2}\left[\operatorname{erfc}\left(\frac{z}{2R}\right)-\operatorname{erfc}\left(\frac{z}{R}\right)\right] & r_s \gg R \gg c^{-1} \\ (r_s+z)\left\{\left[1+\frac{1}{c(r_s+z)}\right]\operatorname{erfc}\left(\frac{z}{2R}\right) - \frac{r_s}{r_s+z}\operatorname{erfc}\left(\frac{z}{R}\right)\right\} & r_s \ll c^{-1} \ll R \\ (r_s+z)\left[\operatorname{erfc}\left(\frac{z}{2R}\right)-\frac{r_s}{r_s+z}\operatorname{erfc}\left(\frac{z}{R}\right)\right] & c^{-1} \ll r_s \ll R \end{cases} \quad \text{(A1.3)}$$

(The last relationship describes the distribution of chain units near an inert sphere.)

Regime C (c ≃ 0, |c|R ≪ 1)

$$M_{Lc}(z) = \frac{6}{a^2}\left(\frac{2R}{r_s\pi^{1/2}}\right)Z_{Lc}^{-1}(0)\left\{\frac{R\pi^{1/2}}{2}\operatorname{erfc}\left(\frac{z}{R}\right) + z\left[\exp\left(-\frac{z^2}{4R^2}\right)-\exp\left(-\frac{z^2}{R^2}\right) + \frac{z\pi^{1/2}}{2R}\left(2\operatorname{erfc}\left(\frac{z}{R}\right)-\operatorname{erfc}\left(\frac{z}{2R}\right)\right)\right] + r_s\left[\exp\left(-\frac{z^2}{4R^2}\right)-\frac{z\pi^{1/2}}{2R}\operatorname{erfc}\left(\frac{z}{2R}\right)\right]\right\}$$

$$\simeq \frac{6}{a^2}\begin{cases} \left\{\frac{R\pi^{1/2}}{2}\operatorname{erfc}\left(\frac{z}{R}\right) + z\left[\exp\left(-\frac{z^2}{4R^2}\right) - \exp\left(-\frac{z^2}{R^2}\right) + \frac{z\pi^{1/2}}{2R}\left(2\operatorname{erfc}\left(\frac{z}{R}\right) - \operatorname{erfc}\left(\frac{z}{2R}\right)\right)\right]\right\} & r_s \ll R \\ \frac{2R}{\pi^{1/2}}\left[\exp\left(-\frac{z^2}{4R^2}\right)-\frac{z\pi^{1/2}}{2R}\operatorname{erfc}\left(\frac{z}{2R}\right)\right] & r_s \gg R \end{cases} \quad \text{(A1.4)}$$

Regime A (c < 0, |c|R ≫ 1)

$$M_{Lc}(z) \simeq (12/a^2)R^2|c|\exp(-2|c|z) \quad \text{(A1.5)}$$

The mean-square distance of units from the surface is found to be equal to Regime B.

Regime B

$$\overline{H_{Lc}^2} \simeq Z_{Lc}^{-1}(0)\frac{1}{cr_s}\left(3R^2 + \frac{7Rr_s}{3\pi^{1/2}}\right) \simeq \begin{cases} 3R^2 & r_s \ll R \\ 7R^2/3 & r_s \gg R \end{cases} \quad \text{(A1.6)}$$

Regime C

$$\overline{H_{Lc}^2} \simeq Z_{Lc}^{-1}(0)\frac{2R}{r_s\pi^{1/2}}\left(\frac{5}{3}R^2 + \frac{Rr_s\pi^{1/2}}{2}\right) \simeq \begin{cases} 5R^2/3 & r_s \ll R \\ R^2 & r_s \gg R \end{cases} \quad \text{(A1.7)}$$

Regime A

$$\overline{H_{Lc}^2} \simeq \frac{1}{2}|c|^{-2} \quad \text{(A1.8)}$$

whereas for a free chain 'grafted' onto a phantom plane we have $\overline{H^2} = R^2/2$ (and for a chain grafted onto a point $\overline{H^2} = 3R^2$).

APPENDIX 2. CONFORMATIONAL CHARACTERISTICS OF A CHAIN WITH ONE END FIXED AT A DISTANCE Z′ FROM THE SURFACE

Regime B (c > 0, cR ≫ 1)

$$Z_{Lc}(z') \simeq \left(z' + r_s\operatorname{erf}\left(\frac{z}{2R}\right)\right)(z'+r_s)^{-1} + \operatorname{erfc}\left(\frac{z'}{2R}\right)[c(z'+r_s)]^{-1}\Big) \quad \text{(A2.1)}$$

$$N_s \sim (ac)^{-1}\left[c\left(z' + r_s\operatorname{erf}\left(\frac{z'}{2R}\right)\right)+1\right]^{-1} \simeq \begin{cases} (ac)^{-1} & z' \ll c^{-1} \\ (ac)^{-1}\frac{c^{-1}}{z'} & z' \gg c^{-1} \end{cases} \quad \text{(A2.2)}$$

Regime C (c ≃ 0, |c|R ≪ 1)

$$Z_{Lc}(z') \simeq 2R\exp\left(-\frac{z'^2}{4R^2}\right)(z'+r_s)^{-1}\pi^{-1/2} + 1 - z'(z'+r_s)^{-1}\operatorname{erfc}\left(\frac{z'}{2R}\right)$$

$$\simeq \begin{cases} 2R(z'+r_s)^{-1}\pi^{-1/2} & r_s, z' \ll R \\ 1+\left(\frac{2R}{z'}\right)^2 R\exp\left(-\frac{z'^2}{4R^2}\right)(z'+r_s)^{-1} & r_s \ll R \lessgtr z' \\ 1 & r_s \gg R \end{cases} \quad \text{(A2.3)}$$

$$N_s \sim \begin{cases} \frac{R\pi^{1/2}}{2a} & r_s, z' \ll R \\ \frac{2R}{a\pi^{1/2}} & z' \ll R \ll r_s \\ \frac{R}{a}\left(\frac{2R}{z'}\right)^2\exp\left(-\frac{z'^2}{4R^2}\right) & z' \gtrsim R \end{cases} \quad \text{(A2.4)}$$

Regime A (c < 0, |c|R ≫ 1)

$$Z_{Lc}(z') \simeq 2\exp(c^2R^2 + cz')(|c|^{-1} + r_s)(z'+r_s)^{-1} \quad \text{(A2.5)}$$

$$N_s \sim \begin{cases} 0 & z' > R^2|c| \\ (2R^2|c| - z')a^{-1} & z' < R^2|c| \end{cases} \quad \text{(A2.6)}$$