Theory of adsorption of polymer chains at spherical surfaces: 1. Partition function: diagram of states

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The complete theory of adsorption of a Gaussian chain of finite length on the surface of a spherical adsorbent of an arbitrary radius is developed on the basis of a continual (diffusion) model of the polymer chain. The influence of the dimensions of the adsorbent on the characteristics of the adsorptional transition is analysed. The partition function of the Gaussian chain near an adsorbing impermeable sphere is obtained. The diagram of states of the system in coordinates 'radius of the adsorbent–attraction energy' is constructed.

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

INTRODUCTION

The development of a complete theory of adsorption of macromolecules on the surface of spherical particles of an arbitrary radius has many aspects of interest. In the practically important processes of the polymer flocculation of colloid dispersions and many other processes the formation of complexes between linear polymers and globular particles involves, as one of their stages, the adsorption of polymer chains on the surface of more or less spherical particles of a finite (on the chain scale) size.

Hence, apart from the development of the theory of adsorption of macromolecules on an infinite planar adsorbent, which has been mainly advanced in references 1–8, repeated attempts have been undertaken to develop the theory of adsorption of an individual macromolecule on the surface of a sphere of a finite radius r_s. However, the latter theory has not yet been completely developed even for the simplest case of individual Gaussian chain. In references 9–12, the investigation concerned only on the conditions and order of phase transition in the adsorption of an infinitely long Gaussian chain according to the dimensionality of adsorbent. The effect of volume interactions on the conformation of the polymer chain adsorbed on a sphere has been investigated by both the scaling method[13] and in the mean-field approximation[14]. However, as will be shown below, an error has been introduced in reference 14 in the determination of the dependence of the critical temperature (attraction energy) corresponding to the start of adsorption of the Gaussian chain on a sphere.

Finally, in references 15 and 16 the theory of adsorption of a Gaussian chain of a finite length on a point adsorbent was developed in connection with the problem of the random coil–globule transition in the external contracting field. The authors of references 15 and 16 have used, for this purpose, the method of a dynamic renormalization group. However, as will be shown below, the quantitative description of chain conformation given in references 15 and 16 differs from that obtained on the basis of quite reliable estimations.

The present paper deals with the development of a complete theory of adsorption of a Gaussian chain of finite length on the surface of a spherical adsorbent of an arbitrary radius (*Figure 1*). The continual (diffusion) model of the polymer chain will be used. This system makes it possible to consider the effect of not only the dimensions, but also the dimensionality, of the adsorbent on chain conformation and the character of the transition. The limits of small and large spheres correspond to different dimensionalities of the adsorbent ($d=0$ and $d=2$, respectively). The chain conformation will be investigated in detail both in the transition range and far from it.

The main part of the paper will consider the case of a rigid impermeable adsorbent: a rigid spherical core (a planar wall in the limit of an infinite radius) with a potential well on the surface (*Figure 2a*). The case of the permeable adsorbent with repulsion or attraction acting in spherical layer (*Figure 2b,c*) will be considered more briefly, and the resemblance and differences between these two types of adsorbents will be analysed.

RESULTS

Temperature and order of phase transition

In the continual model, the partition function $Z_L(\mathbf{r}', \mathbf{r})$ of a chain of the contour length L with the ends at points $\mathbf{r}'$ and $\mathbf{r}$ located in a potential field $\tilde{U}(\mathbf{r})$ obeys[16] the 'diffusion' equation

$$\left\{-\frac{a}{2D}\Delta_{\mathbf{r}}+\frac{\tilde{U}(\mathbf{r})}{T}\right\}Z_L(\mathbf{r}',\mathbf{r})=-\frac{\partial}{\partial L}Z_L(\mathbf{r}',\mathbf{r}) \qquad (1)$$

with the initial condition

$$\lim_{L\to 0} Z_L(\mathbf{r}',\mathbf{r})=\delta(\mathbf{r}'-\mathbf{r}) \qquad (2)$$

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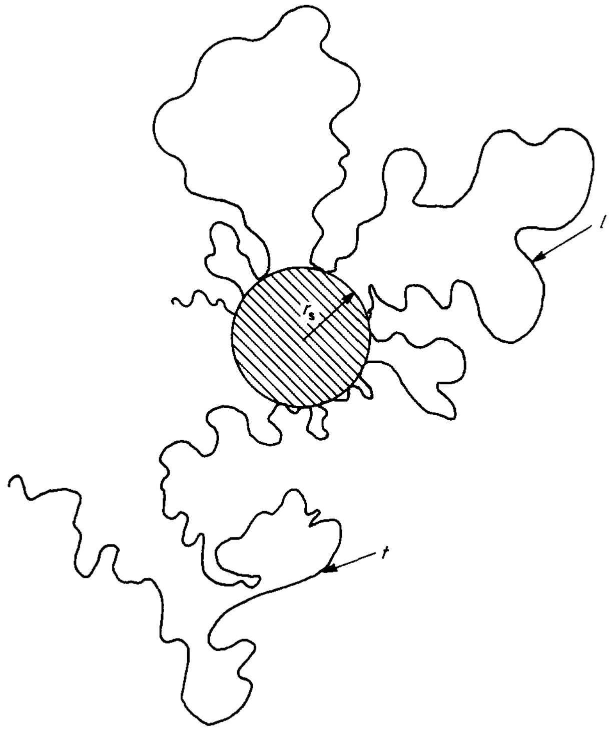

Figure 1 Polymer chain near an adsorbing sphere. Lower case letters designate the elements of structure; loops (l) and tails (t)

Here D is the dimensionality of space, Δ_r is the D-dimensional Laplacian, $a/2$ is the persistent length playing the role of diffusion coefficient (a being the segment length), $\tilde{U}(\mathbf{r})$ is the energy of unit chain length at point $\mathbf{r}$ and T is the temperature in energetic units.

In this and the following sections we will consider chain adsorption on the surface of an impermeable particle with a radius $r_s \gtreqless (La)^{1/2}$ in the potential well of width $b \ll (La)^{1/2}$ (*Figure 2a*), $(La)^{1/2}$ being the characteristic size (the mean-square end-to-end distance) of a free chain.

$$\tilde{U}(\mathbf{r}) \equiv \tilde{U}(r) = \begin{cases} \infty, & r \leqslant r_s \\ -|\tilde{U}(r)|, & r_s < r < b \\ 0, & b < r \end{cases} \tag{3}$$

The diffusion model may be applied to the description of chain conformation in those regions of space in which a is much smaller than the scale of field inhomogeneity, i.e. $b, r_s \gg a$.

The solution of equation (1) satisfying condition (2) can be expressed as

$$Z_L(\mathbf{r}', \mathbf{r}) = \sum_{\alpha} \exp(-E_\alpha N)\Psi^*_\alpha(\mathbf{r}')\Psi_\alpha(\mathbf{r}) \tag{4}$$

where the $\Psi_\alpha(\mathbf{r})$ are the orthonormalized eigenfunction of the operator on the left-hand side of equation (1)

$$\left\{-\frac{a^2}{2D}\Delta_r + \frac{U(\mathbf{r})}{T}\right\}\Psi_\alpha(\mathbf{r}) = E_\alpha \Psi_\alpha(\mathbf{r}) \tag{5}$$

where $U(\mathbf{r}) = \tilde{U}(\mathbf{r})a$ is the segment energy in the field, $N = L/a$ is the number of segments in the chain, and the sum in equation (4) contains both the summation over the discrete spectrum and the integration over the continuous spectrum.

Equation (4) is equivalent to the stationary Schrödinger equation for a quantum particle in the potential field $U(\mathbf{r})/T$. In order to determine the temperature and character of the adsorption phase transition, it is sufficient to consider the properties of the spectrum of this equation.

It is known that if $U(r \to \infty) = 0$ the eigenvalues with $E_\alpha \geqslant 0$ form a continuous spectrum, whereas these with $E_\alpha < 0$ form a discrete spectrum. For the appearance of the first ($\alpha = 0$) discrete level, E_0, corresponding to the state of the particle trapped in a well, some critical depth

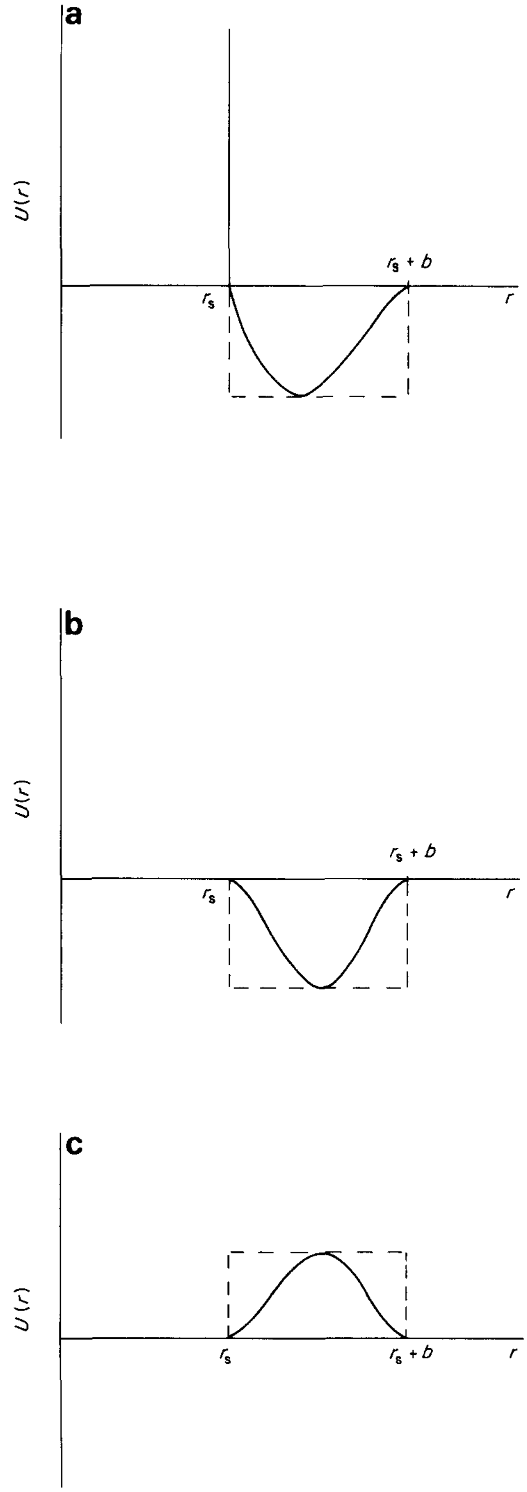

Figure 2 Potential energy $U(r)$ of a chain unit in a centrally symmetric field near (a) an impermeable adsorbing sphere; (b) an attracting; or (c) repulsing spherical layer, and its approximation by rectilinear potentials (broken line)

of this well $(U/T)_c$ different from zero and depending on its shape (in particular, on the width b) is necessary. If the parameter being varied is the temperature T, this implies that the discrete level is absent at high temperatures and appears at $T \leqslant T_c$. In the case of a rectilinear well (dashed line on the (*Figure 2a*)), we have[8]

$$T_c = \left(\frac{24}{\pi^2}\right) U \left(\frac{b}{a}\right)^2 \tag{6}$$

and at $\tau \equiv (T - T_c)/T < 0$, $|\tau| \ll 1$ we have

$$E_0 = -\frac{\pi^2}{16}\tau^2\left(\frac{U}{T_c}\right) = -\frac{1}{6}\left(\frac{\pi^2}{8}\frac{a}{b}\tau\right)^2 \tag{7}$$

At $\tau < 0$, the discrete level $E_0 < 0$ is separated from the continuous spectrum ($E_\alpha \geqslant 0$) by a finite interval. Hence, at $|E_0|N \gg 1$, the bound state provides an exponentially large contribution to the partition function comparing to the contribution of the total continuous spectrum (ground state dominance, GSD). In this case the value of E_0 is the free energy of the segment. At $N \to \infty$, the GSD conditions are obeyed at any small distance from $T = T_c$. Hence, the point $\tau = 0$ is the point of the phase transition of the chain from the free into the adsorbed state. The quadratic dependence of E_0 on the transition parameter τ in equation (7) corresponds to the second order phase transition. For finite chains, the admixture of the states of continuous spectrum below T_c leads to the appearance of the finite transition range $\Delta\tau \sim N^{-1/2}$.

Chain partition function

Determination of the partition function requires the knowledge of eigenfunctions in equation (5). The spherical symmetry of the system ($U(\mathbf{r}) = U(r)$) makes it possible to separate the variables in equation (5) representing $\Psi_\alpha(\mathbf{r})$ in the form

$$\Psi_\alpha(\mathbf{r}) = \frac{1}{r}\chi_{El}(r) Y_{lm}(\mathbf{n}) \tag{8}$$

where $l = 0, 1, \ldots$; $m = -l, \ldots, l$; $\alpha = \{E, l, m\}$, $\mathbf{n} = \mathbf{r}/r$, $Y_{lm}(\mathbf{n})$ are spherical functions. The continuously differentiated at $r > r_s$ radical functions $\chi_{El}(r)$ satisfy the equation

$$\frac{d^2}{dr^2}\chi_{El}(r) + \left[\frac{6}{a^2}(E - U(r)) - \frac{l(l+1)}{r^2}\right]\chi_{El}(r) = 0 \tag{9}$$

with the boundary conditions

$$\chi|_{r=r_s} = 0 \qquad \chi|_{r\to\infty} \text{ is limited} \tag{10}$$

Substituting equation (8) into equation (4) and applying the theorem of summation for spherical functions, we find

$$Z_L(\mathbf{r}', \mathbf{r}) = (rr')^{-1}\sum_E \exp(-EN) \times \sum_{l=0}^{\infty}\frac{(2l+1)}{4\pi} P_l(\mathbf{n}', \mathbf{n})\chi^*_{El}(r')\chi_{El}(r) \tag{11}$$

where $P_l(\mathbf{n}'\mathbf{n})$ is Legendre's polynomial.

In the particular case of a free chain at $U(r) = 0$, the solution of equation (9) obeying the conditions in equation (10) is given by

$$\chi_{El}(r) = (kr)^{1/2} J_{l+1/2}(kr) \tag{12}$$

where $J_\nu(x)$ are Bessel's functions of ν order and $k^2 = 6E/a^2$. In this case equation (11) leads to the evident result: the Gaussian function

$$Z_{Lf}(\mathbf{r}', \mathbf{r}) = \left(\frac{3}{2\pi La}\right)^{3/2}\exp\left(-\frac{3(\mathbf{r}' - \mathbf{r})^2}{2La}\right) \tag{13}$$

(Here and in subsequent considerations the subscript f refers to the free chain, and all partition functions are normalized in such a manner that the total number of states of a free chain of length L is taken to be unity).

In a centrally symmetrical field $U(r)$, it is convenient to avoid angular variables by introducing a centrally symmetrical partition function, $Z_L(r', r)$ of the chain beginning at point $\mathbf{r}'$ and ending in a spherical layer of radius r and unit thickness. The contributions to this partition function provide only s-states (with $l = 0$)

$$Z_L(r', r) = r^2\int Z_L(\mathbf{r}', \mathbf{r})\,d\Omega_{\mathbf{n}'\mathbf{n}} = \frac{r}{r'}\sum_E \exp(-EN)\chi_{E0}(r)\chi^*_{E0}(r') \tag{14}$$

Now let us consider the case of weak adsorption $|\tau| \ll 1$. At $N \gg 1$, when a considerable contribution to the partition function is provided only by weakly excited states of the continuous spectrum ($EN \sim a^2k^2N = k^2La \lesssim 1$), our problem of weak chain adsorption is equivalent to the well known[8] problem of resonance scattering of slow particles in an attractive field having a shallow level in a discrete spectrum.

For the values of r and r' belonging to the external range, $r, r' > (r_s + b)$, in which $U(r) = 0$, the solutions of equation (9) referring to discrete and continuous spectra are given by

$$\chi_{E0}(r) = (2k)^{1/2}\exp[-k(r - r_s)], \qquad E < 0, \qquad k = \left(\frac{6|E|}{a^2}\right)^{1/2} \tag{15a}$$

$$\chi_{E0}(r) = \left(\frac{2}{\pi}\right)^{1/2}\sin[k(r - r_s) + \delta_K], \qquad E \geqslant 0, \qquad k = \left(\frac{6E}{a^2}\right)^{1/2} \tag{15b}$$

The phase shift δ_K in equation (15b) is determined by the crossover of solutions of equation (15b) to those in the inner range $r_s < r < r_s + b$ where

$$\chi_{E0} \approx \sin\left[\left(k^2 + \frac{6|U|}{a^2}\right)^{1/2}(r - r_s)\right] \tag{16}$$

Instead of this crossover the corresponding boundary condition at $r = r_s + b$ may be introduced. At $|\tau| \ll 1$, the solutions in equation (16) relating to the weakly excited states are virtually independent of E (and of k) because the width of the well is much smaller than the chain size ($b \ll (La)^{1/2}$). Consequently, the boundary conditions should not depend on k. Moreover, the fulfilment of the condition $kb \ll 1$ implies that the boundary condition may be ascribed to the adsorbent surface $r = r_s$ and presented in the form

$$\frac{d}{dr}\ln\chi_{E0}(r)|_{r=r_s} = c \tag{17}$$

This condition should be obeyed by all eigenfunctions corresponding to energies close to zero including (at $T \lesssim T_c$) the eigenfunction $\chi_0(r)$ of the bound state determined by equation (15a) at $E = E_0$. Hence, it is possible to find the value of the constant C in equation (17)

$$c = -k_0 = -\left(\frac{6|E_0|}{a^2}\right)^{1/2} \simeq \frac{\pi^2}{8b}\tau \tag{18}$$

where the last ratio applies equation (7) valid at $|\tau| \ll 1$. The analytical continuation of equation (18) to the range $T \geqslant T_c$ makes it possible to take into account the surface effect on the eigenfunctions of the continuous spectrum in the precritical range also (virtual level in the well). For the phase shift δ_K we obtain from equations (16) and (17)

$$\cot \delta_K = c/k \tag{19}$$

It should be noted that the numerical coefficients in equations (7) and (18) refer to the case of the rectangular well. However, the character of the dependences on τ at $|\tau| \ll 1$ is universal and independent of the form of the attractive part of the potential. As to the constant c, it is important that it changes its sign passing through zero at the critical point, near where it depends linearly on the transition parameter ($c \sim \tau$) and tends to infinity at $T \to \infty$ or at $U = 0$ when the potential well is absent.

Using the eigenfunctions (15) of discrete and continuous spectra after integration in equation (14) for the continuous spectrum, we find the partition function of the chain near the spherical particle

$$\begin{aligned}Z_{Lc}(z', z) = \frac{z + r_s}{z' + r_s}\Bigg\{\left(\frac{1}{4\pi R^2}\right)^{1/2}\left[\exp\left(-\frac{(z-z')^2}{4R^2}\right)\right.\\ \left. + \exp\left(-\frac{(z+z')^2}{4R^2}\right)\right] - c\exp(c^2R^2 + c(z+z'))\\ \times \operatorname{erfc}\left(cR + \frac{z+z'}{2R}\right)\Bigg\}\end{aligned} \tag{20}$$

where $R^2 = Na^2/6$ is the mean-square radius of gyration of a random coil, $z = r - r_s$ and $z' = r' - r_s'$ are the distances from chain ends to the surface of the particle and

$$\operatorname{erfc}(x) = 1 - \operatorname{erf}(x) = \frac{2}{\pi^{1/2}}\int_x^\infty \exp(-t^2)\,dt \tag{21}$$

is the error function.

It can be seen from equation (20) that the partition function of the chain near the spherical surface of radius r_s is related by a simple equation to the partition function of the chain near the impermeable plane $Z_{Lc}^\infty(z', z)$ to which it passes at $r_s \to \infty$ and which has been obtained previously in references 7 and 8:

$$Z_{Lc}(z', z) = \frac{z + r_s}{z' + r_s} Z_{Lc}^\infty(z', z) \tag{22}$$

Note that the partition function $Z_{Lf}(r', r)$ of the free chain may also be formally represented in the form $Z_{Lf}(z', z)$ where z' and z are the distances between the chain ends and a phantom spherical surface of radius $r_f = r - z = r' - z' > 0$. Substitution of equation (13) into equation (14) gives

$$\begin{aligned}Z_{Lf}(z', z) &= \frac{z + r_f}{z' + r_f}\left(\frac{1}{4\pi R^2}\right)^{1/2}\left[\exp\left(-\frac{(z-z')^2}{4R^2}\right) - \exp\left(-\frac{(z+z'+2r_f)^2}{4R^2}\right)\right]\\ &= \frac{z + r_f}{z' + r_f} Z_{Lf}^\infty(z', z)\left[1 - \exp\left(-\frac{(z+r_f)(z'+r_f)}{R^2}\right)\right]\end{aligned} \tag{23}$$

where $Z_{Lf}^\infty(z', z)$ is obtained from equation (23) at $r_f \to \infty$.

The dependence of $Z_{Lf}(r', r)$ on r_f follows directly from the definition of the centrally symmetrical partition function of the free chain and in this sense is trivial in contrast to equation (22) describing the dependence of the conformation of a chain interacting with the spherical surface on the radius r_s of this surface. These dependences differ markedly. Thus, at $z', z \ll r_f$, the partition function of the free chain strongly depends on r_f, in particular at $r_f \ll R$, decreasing with r_f. This dependence is due to the enthropy disadvantage of a chain return to the small region (of the size $r_f \ll R$). In contrast, partition function (22) at $z, z' \ll r_s$ is virtually independent of r_s: with decreasing r_s steric restrictions imposed by the particle also decrease thus compensating for the entropy disadvantage of the return.

Subsequently we will compare the expressions corresponding to the real and phantom spheres for different conformational chain characteristics.

Apart from partition function (20) it is possible to consider the partition function of a chain with one fixed end obtained by the integration of $Z_{Lc}(z', z)$ over z

$$Z_{Lc}(z') = \int_0^\infty Z_{Lc}(z', z)\,dz = 1 + [Z_{Lc}^\infty(z') - 1]\frac{cr_s - 1}{c(r_s + z')} \tag{24}$$

where $Z_{Lc}^\infty(z')$ is the known[8] partition function of a chain one end of which is fixed at a distance z' from the planar surface

$$Z_{Lc}^\infty(z') = \operatorname{erf}\left(\frac{z'}{2R}\right) + \exp(c^2R^2 + cz')\operatorname{erfc}\left(cR + \frac{z'}{2R}\right) \tag{25}$$

And $Z_{Lc}(z')$ passes into $Z_{Lc}^\infty(z')$ at $r_s \to \infty$. It is evident that for a free chain near the phantom sphere we have $Z_{Lf}(z') = 1$ independent of z'.

Using partition functions (2) and (24) it is possible to find various conformational characteristics of the chain with one fixed end: firstly, the number of chain contacts with the surface

$$N_s \sim -\frac{1}{a}\frac{\partial}{\partial c}\ln Z_{Lc}(z') \tag{26}$$

And secondly, the mean-square distance of the free chain end from the spherical surface

$$\bar{z}_N^2 = Z_{Lc}^{-1}(z')\int_0^\infty Z_{Lc}(z', z)z^2\,dz \tag{27}$$

Thirdly, the number of chain units in a spherical layer of radius $r = r_s + z$ and unit thickness

$$M_{Lc}(z) = \frac{1}{a}Z_{Lc}^{-1}(z')\int_0^L Z_{lc}(z', z)Z_{(L-l)c}(z)\,dl \tag{28}$$

and

$$m_{Lc}(z) = M_{Lc}(z)[4\pi(r_s + z)^2]^{-1} \tag{29}$$

the mean density in a layer of radius $r = r_s + z$.

Fourthly, the mean-square thickness of a layer formed by the chain above the surface (mean-square distance of chain units from the surface)

$$\overline{H^2_{Lc}} = N^{-1}\int_0^{\infty} \mu_{Lc}(z) z^2\, dz \qquad (30)$$

The expressions obtained above will be used below for the analysis of the conformation of a chain grafted onto a sphere ($z' = 0$).

Diagram of state of a chain grafted onto a sphere

The conformation of the Gaussian chain grafted onto a sphere is determined by the sign and the relationship between three parameters having the dimensionality of length: $|c|^{-1}$, r_s and the size of the free chain R, or (at $|\tau| \ll 1$) of two scaling variables cR and r_s/R.

For infinitely long chains, the point $c = 0$ is the point of adsorption phase transition. For finite chains, the transition occurs in the range $\Delta c \sim \Delta\tau \sim N^{-1/2}$ near $c = 0$. Beyond the transition range (far from the critical point) at $c < 0$ and $|c|R \gg 1$, the conditions of GSD are fulfilled, and the chain is adsorbed (the bonded state provides the main contribution to the partition function). At $c > 0$ and $cR \gg 1$ the effect of the attracting part of the potential on the chain conformation as a whole is not important. In further discussion, these limiting states will be called the adsorption (A) and the precritical (B) regimes, respectively. The partition function and all the conformational characteristics introduced by us for finite chains have two asymptotics each, corresponding to these regimes. The achievement of the corresponding asymptotics takes place for relatively long ($R \gg |c|^{-1}$) chains. The intermediate asymptotics correspond to the tricritical point $c = 0$. At $|c|R \simeq |c|N^{1/2}a \approx 1$ a crossover occurs between them and the dependences corresponding to regimes A and B. The transition range (crossover range) will be called regime C (at $N \to \infty$ it reduces to point $c = 0$).

The particle size r_s determines the measure of steric restrictions imposed by the adsorbent surface on the chain conformation. If r_s greatly exceeds the characteristic chain size, then on the chain scale a spherical adsorbent is equivalent to an infinite plane adsorbent. Hence, the dependence of conformational characteristics on r_s should be strong at low r_s (regime s of a small sphere) and be absent in the asymptotics of large r_s (regime p of a large sphere equivalent to a plane). The characteristic size r_{so} separating the regimes s and p is peculiar to each adsorption regime.

For the determination of r_{so}, the partition function of a chain grafted at one end onto a sphere of radius r_s will be considered (equation (24) at $z' = 0$)

$$Z_{Lc}(0) = \frac{1}{cr_s} + \left(1 - \frac{1}{cr_s}\right) Z^{\infty}_{Lc}(0) \simeq \begin{cases} \dfrac{1}{cr_s}(1 - Z^{\infty}_{Lc}(0)) & r_s \ll r_{so} \\ Z^{\infty}_{Lc}(0) & r_s \gg r_{so} \end{cases} \qquad (31)$$

where

$$Z^{\infty}_{Lc}(0) = \exp(c^2R^2)\,\mathrm{erfc}(cR) \qquad (32)$$

is the partition function of a chain grafted onto a plane and

$$r_{so} \sim (1 - Z^{\infty}_{Lc}(0))(cZ^{\infty}_{Lc}(0))^{-1} \sim \begin{cases} R & \text{regimes B and C} \\ |c|^{-1} & \text{regime A} \end{cases} \qquad (33)$$

As will be shown below, r_{s0} coincides with an accuracy of the coefficient with the thickness of the adsorption layer $(\overline{H^2_{Lc}})^{1/2}$.

Hence, taking into account three adsorption (A, C, B) and two 'geometrical' (s and p) regimes we have six regimes (different asymptotics) for the conformational characteristics of the chain. *Figure 3* shows the $c - r_s^{-1}$ diagram of state for a chain grafted onto a sphere, and *Table 1* gives the asymptotics of the partition function $Z_{Lc}(0)$, in different regimes. At the boundaries of regions in the diagram in *Figure 3*, a crossover takes place between the dependences in the neighbouring regions.

It can be seen from *Table 1* and equation (31) that at all values of r_s the partition function $Z_{Lc}(0)$ increases with decreasing temperature $\tau \sim c$. The minimum value of $Z_{Lc}(0)$ corresponds to $T \to \infty$ (regime B, the limit of an inert surface). It may be obtained from equation (24) in

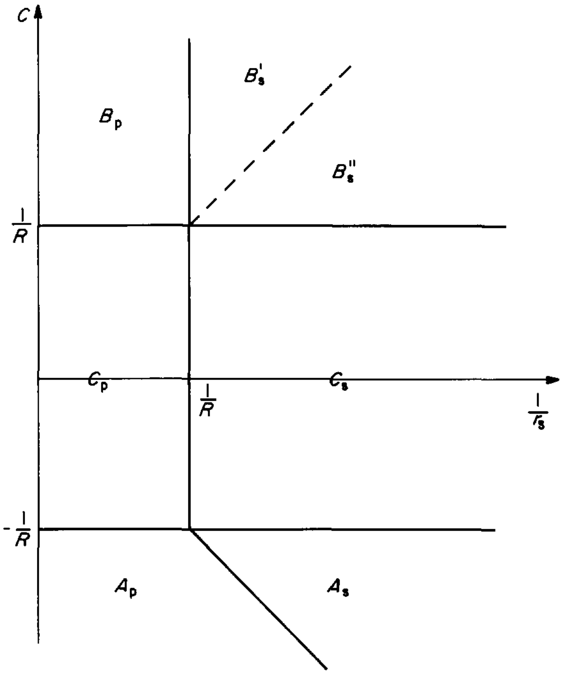

Figure 3 Diagram of state of a chain grafted onto a spherical surface of radius r_s in a system of coordinates $(c - r_s^{-1})$. Capital letters A, B and C designate adsorption regimes and lower case letters s and p designate the regimes of a small and a large sphere, respectively

Table 1 Asymptotics of the partition function $Z_{Lc}(0)$ in different regimes (r_{s0} from equation (33))

Geometric regimes	Adsorption 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 $r_s \gg r_{s0}$	$(cr_s)^{-1}$	$2R/(r_s\pi^{1/2})$	$2\exp(c^2R^2)/(\lvert c\rvert r_s)$
s $r_s \ll r_{s0}$	$(cR\pi^{1/2})^{-1}$	1	$2\exp(c^2R^2)$

the limit $c \to \infty$ (at $z' = a$)

$$Z_{Lc=\infty}(0) = (a + r_s)^{-1}\left(a + r_s \operatorname{erf}\left(\frac{a}{2R}\right)\right)$$
$$\simeq \begin{cases} a/r_s & r_s \ll R \\ a/(R\pi^{1/2}) & r_s \gg R \end{cases} \tag{34}$$

For the free energy of a chain segment at $N \to \infty$ we have from *Table 1*

$$N^{-1}F_{Lc} = -TN^{-1}\ln Z_{Lc}(0) \xrightarrow[N\to\infty]{} \begin{cases} 0 & c \geqslant 0 \\ -\frac{1}{6}a^2c^2T & c < 0 \end{cases} \tag{35}$$

It is clear that in complete agreement with conclusions drawn here, the point $c = 0$ is the point of the phase transition between states B and A. At $N \to \infty$ the boundaries of regimes A–C and B–C in *Figure 3* become one and are transformed into the line of adsorption second order phase transition.

Strong adsorption

So far we limited ourselves to the conditions of weak ($\tau < 0$, $|\tau| \ll 1$) adsorption under which the fraction of bonded units is small $\phi \approx |\tau| \ll 1$, and most units are in loops. In the opposite limiting case of strong adsorption ($|\tau| \to 1$), the chain is completely localized in the attraction range $z < b$ near the surface. In a deep potential well, the first discrete level is near its bottom and under the conditions of GSD ($(a/b)^2N \gg 1$) free energy per unit of the adsorbed chain is given by

$$-F/N \simeq -U + (\pi^2/6)(a/b)^2T \tag{36}$$

Figure 4 shows the temperature dependence of free energy per unit of an infinitely long chain. The range of quadratic dependence $-F/N \sim (T - T_c)^2$ near T_c corresponds to the range of weak adsorption, and in that of strong adsorption the free energy varies depending linearly on T and tends to $-U$ at $T \to 0$ (equation 36).

Adsorption in a spherical layer (*'ditch'*)

In preceding sections adsorption on the surface of an impermeable adsorbent has been considered (*Figure 2a*). Let us now consider the adsorption in a marked out spherical layer in the absence of an impermeable core (adsorption on the surface of a phantom sphere), i.e. in a field of the form (*Figure 2b*)

$$U(r) = \begin{cases} 0, & r < r_s \quad \text{or} \quad r > r_s + b \\ -U, & r_s < r < r_s + b \end{cases} \tag{37}$$

This problem is solved by the method analogous to the above procedure. For the critical adsorption temperature T_c which, as before, corresponds to the second-order phase transition point, from the condition of the appearance of the first discrete level in the hole of the form of equation (37) one obtains

$$\kappa_c r_s \operatorname{tg} \kappa_c b = 1 \tag{38}$$

where

$$\kappa_c^2 = (6/a)^2(U/T)_c \tag{39}$$

to give

$$T_c \simeq 6U\left\{\frac{br_s}{a^2} + \frac{4}{\pi^2}\left(\frac{b}{a}\right)^2\right\} \simeq \begin{cases} \dfrac{24}{\pi^2}U(b/a)^2, & r_s \ll b \\ 6U\dfrac{r_s b}{a^2}, & r_s \gg b \end{cases} \tag{40}$$

It is clear that at small $r_s \ll b$ the value of T_c from equation (40) coincides with that obtained previously for adsorption on the surface of an impermeable particle, i.e. the impermeability of the core of a small particle does not affect the position of the transition. In contrast, at $r_s \gg b$, the value of T_c increases (or (U/T_c) decreases) proportionally to r_s so that $T_c \to \infty$ (or $(U/T_c) = 0$) at $r_s \to \infty$, i.e. on passing to the case of a plane permeable adsorbent. In this case the beginning of adsorption does not require any large scale change in the conformation of the free chain reliably returning to the phantom plane. In contrast to adsorption in the potential well near the wall (*Figure 1a*), in this case the perturbing action of the impermeable surface is absent.

Analysis shows that in the case of a potential (equation 37), all adsorption regimes described above still exist. In these regimes, large scale conformational and thermodynamic characteristics of the chain coincide with those obtained above. The difference is only in the renormalization of the interaction parameter c, in the dependence $T_c = T_c(r_s)$ and in the fact that at $r_s \gg R$ the precritical regime B_p exists only under the conditions of the repulsing spherical layer $U < 0$ in equation (37) (*Figure 2c*). At $U > 0$ the regime B_p may exist only at $T < 0$.

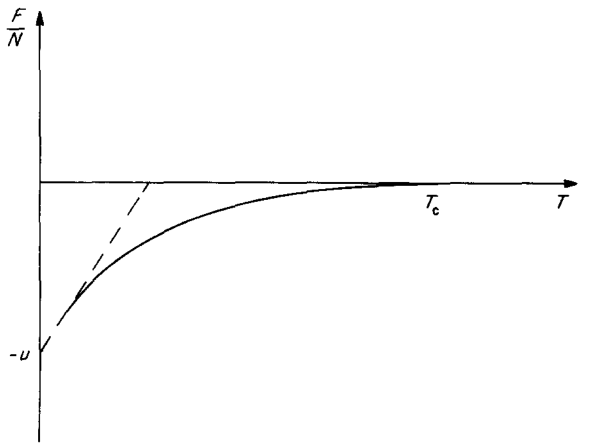

Figure 4 Temperature dependence of free energy per unit of an infinitely long chain interacting with a spherical particle

CONCLUSION

In the first part of the paper the analytical expressions for the partition function of the chain near an adsorbing spherical surface are obtained and the diagram of states of the system is constructed. In Part 2 of this paper we shall perform the full analysis of the conformation of the chain in all regions of the diagram of states.

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