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Theory of Adsorption of Macromolecules. 2. Phase Transitions in Adsorption: General Approach

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ABSTRACT: A general procedure for the analysis of the phase transition order in various cases of polymer chain adsorption is proposed. It is shown that the phase transition order is connected with the molecular weight dependence of the mean number of the intersections of the segments of the free chain with some phantom surface geometrically equivalent to the adsorbent surface and penetrable for the macromolecules.

The principal aim of this series of papers is to present a general theory of adsorption of a single polymer chain. The approaches thus far developed usually describe the behavior of rather simple (frequently lattice) model systems[1-10] (see, however, ref 11 and 12). The well-known theory of conformational transitions in macromolecules based on sequence-generating functions[13,14] gives the possibility of studying transitions in a general case, provided that the thermodynamic properties of single intramolecular sequences are known. Adsorption can be considered as a conformational transition, with the thermodynamics of single sequences determined, in many respects, by the geometry of the polymer–adsorbent system.

In our previous publication (paper 1;[15a] see also ref 15b), we have obtained the basic equation for the transition point and analyzed its dependence on the conformational properties of a chain and on the shape of the adsorbent. Our current aim is to extend the general approach to the investigation of the transition order at the adsorption of infinitely long chains ($N \to \infty$). The applications of this approach will be realized mainly in the next paper.

I. Desorption–Adsorption Transition

Our purposes in this section are (a) to demonstrate that the adsorption of a chain on a solid adsorbent of any form always shows a phase transition and (b) to relate the conformation of a macromolecule at the transition point to that of a free macromolecule.

Let us first outline the derivation of starting equations.[13-15]

The adsorbed chain appears as a linear sequence of adsorbed segments S and loops L. Its free energy μ (per monomer unit) may be found from the equation

$$\Xi_S(\lambda)\Xi_L(\lambda) = 1 \tag{1}$$

Here

$$\lambda = \exp(-\mu) \tag{2}$$

is the largest root of eq 1, and

$$\Xi_S(\lambda) = \sum_{n=1}^{\infty} Z_S(n,\epsilon)\lambda^{-n} = \sum_{n=1}^{\infty} Z_S^0(n)e^{-n\epsilon}\lambda^{-n} \tag{3}$$

$$\Xi_L(\lambda) = \sum_{n=1}^{\infty} Z_L(n)\lambda^{-n} = \sum_{n=1}^{\infty} Z_v(n)W_L(n)\lambda^{-n} \tag{4}$$

are the generating functions for the adsorbed segments and the loops.

The partition function $Z_S(n,\epsilon)$ of an adsorbed segment of n units contains the conformational contribution $Z_S^0(n)$ and a factor depending on the monomer–surface interaction energy ϵ (the energetic quantities ϵ and μ are expressed in kT units).

The partition function $Z_L(n)$ of a loop of n units may be divided into two factors. $Z_v(n)$ is the partition function of an n-unit portion in a free chain (in a solution in the absence of a surface)

$$Z_v(n) = \lambda_v^n = \exp(-n\mu_v) \tag{5}$$

$W_L(n)$ characterizes conformational entropy limitations in the loop.

In some special cases[16,17] it is also necessary to include in $Z_L(n)$ the additional factor $Q_L(n)$ resulting from the external fields. Here we assume $Q_L(n) = 1$.

A similar treatment is extensively used for investigating a broad class of intramaolecular order–disorder transitions in linear polymer chains.[14,18-20] In each case the thermodynamically stable state is selected by the competition between λ_v and λ (increasing with the attraction energy $-\epsilon$ in ordered sequences), where λ_v corresponds to a completely unordered state and λ to a partly ordered state (in our case to the adsorbed state).

(In principle, one should also take into account the fully ordered state to complete the system of hypothetically possible states. However, this state is reached[14] only if the partition function $Z_S(n)$ of an ordered sequence has some special form, as it has in the case of the β structure–coil transition.[18-20] If $Z_S(n)$ is a simple exponential function, as it is in the processes of adsorption (see eq 15) or helix–coil transition, the roots λ and λ_v are sufficient to describe the system.)

Equations 1 and 5 describe the two fundamentally different cases of order–disorder transitions, namely, the existence of either a true phase transition or a cooperative non phase transition. The first case takes place if $\lambda < \lambda_v$ at $-\epsilon$ is lower than some "critical" value $-\epsilon_c \geq 0$ and $\lambda > \lambda_v$ at $-\epsilon > -\epsilon_c$. The equilibrium states of a long macromolecule are different in these two ϵ regions, and there is a true phase transition at the point ϵ_c determined by the crossover condition

$$\lambda(\epsilon_c) = \lambda_v \tag{6}$$

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Another case takes place if $\lambda > \lambda_v$ over the whole range $-\epsilon < \infty$. Now the equilibrium state is always a partly ordered one (with the degree of ordering depending on ϵ), and there is no crossover (6) and no true phase transition. The hypothetical completely unordered state, presented by eq 5, is never reached in this case ($-\epsilon_c \to -\infty$).

As remarked by Poland and Scheraga whether a phase transition exists or not depends on the behavior of the function $W_L(n)$; only if the infinite series $W_L(n)$ ($n = 1, 2, ...$) is convergent is there a true phase transition (if $\alpha > 1$ for $W_L(n) \sim n^{-\alpha}$). Well-known examples[14] are the helix–coil transitions, which are cooperative non phase transitions in polypeptides ($\alpha = 0$) and in DNA with imperfect matching loops ($\alpha = {}^1/_2$) but resemble a true phase transition in DNA with perfect matching loops ($\alpha = {}^3/_2$).

For the problem under study, i.e., adsorption of a macromolecule on a solid surface, the necessary information about the behavior of $W_L(n)$ can be obtained from simple considerations. $W_L(n)$ in eq 4 is measured by that fraction of the free chain states which can be realized in the n-unit loops terminating on the surface. Summing $W_L(n)$ over all n, we obtain the *probability* $\mathcal{W}_L$ that a free chain, starting at the surface, returns to it after walking in space. Obviously, $\mathcal{W}_L \leq 1$; i.e., the infinite series $W_L(n)$ is convergent. Therefore *the adsorption of a macromolecule on the solid adsorbent occurs always as a true phase transition.*

According to eq 4–6 the loop-generating function at the transition point

$$\Xi_L(\lambda_v) = \sum_{n=1}^{\infty} W_L(n) = \mathcal{W}_L \leq 1 \tag{7}$$

is connected with the probability of loop formation in a free chain with reference to the "virtual" surface (drawn through a free macromolecule). Equation 7 serves as a basis for a further treatment.

Two cases should be distinguished, depending on whether the return of the free chain to the virtual surface is a certainty ($\mathcal{W}_L = 1$) or not ($\mathcal{W}_L < 1$). The realization of either of the two cases is governed only by such a general property of the virtual (and adsorbing) surface as its extent in various dimensions, as was shown in part 1 by using the analogy with Pólya random walk problem.[21] The infinitely long Gaussian chain always returns to the surface which is infinitely extended at least in one dimension (infinite plane, $d = 2$; infinite rod, $d = 1$), but the return to a surface finite in all dimensions (small particle, point, $d = 0$) is uncertain, $\mathcal{W}_L < 1$.

A characteristic property of the case $\mathcal{W}_L = 1$ is *the identity of conformations of both the adsorbed chain at the critical point and the free chain* (with respect to the virtual surface). Both conformations contain a large (infinite at $N \to \infty$) number of loops with the same distribution $W_L(n)$ of the loop lengths. The differences are only local in nature and reduce to the replacement of each passing through the virtual surface (free chain) by the reflection of the chain from the impenetrable adsorbent following the adsorption of a certain number of units (on average $\bar{n}_S(\epsilon_c)$) on the surface.

If $\mathcal{W}_L = 1$ the basic equation for the phase transition point obtained from eq 1 and 7 acquires the simplest form

$$\Xi_S(\lambda_v,\epsilon_c) = \sum_{n=1}^{\infty} \frac{Z_S(n,\epsilon_c)}{Z_v(n)} = 1 \tag{8}$$

Consequently, the critical energy ϵ_c ensures the compensation for only the local conformation restrictions produced by adsorbent. Equation 8 was discussed in great detail in part 1.

At $\mathcal{W}_L < 1$ the free chain returns to the virtual surface only a few times, mainly forming a tail. As a result *the beginning of the adsorption is related to a drastic rearrangement of the chain conformation to* one with a great number of loops.

The basic equation for the phase transition point

$$\Xi_S(\lambda_v,\epsilon_c) = \sum_{n=1}^{\infty} \frac{Z_S(n,\epsilon_c)}{Z_v(n)} = \frac{1}{\mathcal{W}_L} \tag{9}$$

shows that as $\mathcal{W}_L$ decreases, the critical adsorption energy increases and, hence, the chain rearrangement produces additional difficulties for adsorption. It should be noted that according to eq 7 the loop length distribution does not vary with the chain rearrangement at the critical point and is the same for both a small number of loops in the free chain and many loops of the adsorbed chain.

All previous analyses started from eq 1, which is strictly applicable only to Gaussian chains without long-range excluded volume interactions. The chain segments (adsorbed segments and loops in eq 1) are independent in such chains. In principle, it is possible to extend eq 1 to interdependent segments in non-Gaussian chains with volume interactions considering each segment in the average field generated by the remaining chain part. Now, however, any change in the chain conformation leads to a change in the average field.

From this it follows that the possibility to preserve the key relationship, eq 7, for non-Gaussian chains is principally limited to the case $\mathcal{W}_L = 1$, wherein the beginning of adsorption does not cause a fundamental rearrangement of the free chain conformation. It is believed that the local reflecting action of the surface in this case does not change the distribution of loop lengths, so at the critical point it remains the same as in the free non-Gaussian chain. In the following study the same procedure will be applied to Gaussian chains for the cases $\mathcal{W}_L = 1$ and $\mathcal{W}_L < 1$ and to non-Gaussian chains for the case $\mathcal{W}_L = 1$.

II. Thermodynamics of the Phase Transition and the Moments of the Loop Length Distribution

The order of the phase transition is determined, according to Ehrenfest, by the lowest free energy–temperature derivative which is discontinuous at the transition point.

The temperature is not a separate variable within the framework of the present approach but it is included in all energetic parameters, in particular in the energy ϵ, which serves as an external variable parameter. The first free energy derivative on ϵ

$$\vartheta = d\mu/d\epsilon = -d \ln \lambda/d\epsilon \tag{10}$$

determines the degree of adsorption of a single macromolecule, i.e., the mean fraction of units attached to the surface $\vartheta = N_s/N$. Evidently ϑ determines the adsorption component of the chain energy (if ϵ is completely energetic in nature, this adsorption energy of the chain is $E = N\vartheta\epsilon$). Similarly, $d^2\mu/d\epsilon^2$ determines the adsorption heat capacity etc. Hence, according to our formalism, the order of the phase transition is dictated by the behavior of $d^k\mu/d\epsilon^k$ at the critical point (Figure 2).

In the pretransition region, $-\epsilon < -\epsilon_c$, the long polymer chain ($N \to \infty$) at equilibrium is situated in a solution, its free energy μ_v is independent of ϵ, and $d^k\mu/d\epsilon^k = 0$ at any k. At $-\epsilon > -\epsilon_c$ the chain is adsorbed and its free energy μ is determined by eq 1 and 2. The phase transition order k_0 is determined as the value satisfying the conditions

$$d^k\mu/d\epsilon^k = 0 \qquad k < k_0, \quad -\epsilon = -\epsilon_c + 0 \tag{11a}$$

$$d^k\mu/d\epsilon^k \neq 0 \qquad k = k_0, \quad -\epsilon = -\epsilon_c + 0 \tag{11b}$$

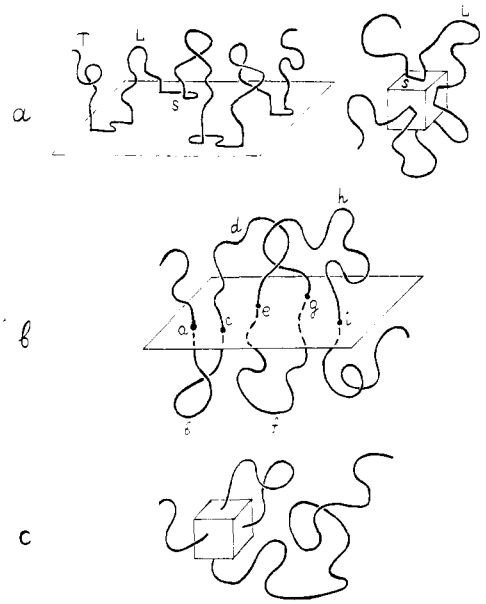

Figure 1. Conformation of (a) an adsorbed chain (L = loop, S = adsorbed segment, and T = tail) and (b, c) that of a chain at the virtual surface at (b) $\mathcal{W}_L = 1$ and (c) $\mathcal{W}_L < 1$ (L = simple loop and $\tilde{L}$ = complex loop). L: abc, cde, efg...; $\tilde{L}$: abcde, abcdefg, abcdefghi, cdefg, cdefghi...

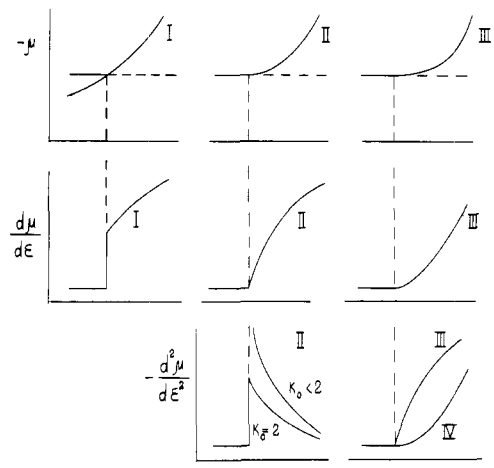

Figure 2. Thermodynamic functions near phase transition points: I, II, III, ..., phase transition order.

Let us consider the first derivative obtained by differentiation of eq 1

$$\frac{d\mu}{d\epsilon} = \vartheta = \frac{\partial \ln \Xi_S/\partial\epsilon}{\partial \ln \Xi_S/\partial \ln \lambda + \partial \ln \Xi_L/\partial \ln \lambda} = \frac{\bar{n}_S}{\bar{n}_S + \bar{n}_L} \tag{12}$$

where

$$\bar{n}_S = -\partial \ln \Xi_S/\partial\epsilon = -\partial \ln \Xi_S/\partial \ln \lambda \tag{13}$$

and

$$\bar{n}_L = -\partial \ln \Xi_L/\partial \ln \lambda \tag{14}$$

are the mean lengths of adsorbed segments and loops. From the right-hand side of eq 12 we have omitted the factor $1 - \vartheta_T$ (ϑ_T is the fraction of units in the chain tails) because ϑ_T, being nonzero at $-\epsilon = -\epsilon_c$ and zero at $-\epsilon > -\epsilon_c$ does not affect the behavior of the derivatives we are interested in.

In the Gaussian chains the partition function of adsorbed segments, $Z_S(n,\epsilon)$ in eq 3 is determined by the short-range interactions only and is given by (at least if n is not too small; see part 1)

$$Z_S(n,\epsilon) = \sigma_S z_S^{n-1} z_L e^{-n\epsilon} \tag{15}$$

Here, $\sigma_S z_S$, z_S, and z_L are conformational partition functions for the first, next, and first starting off units in the adsorbed segment, respectively. Substitution of eq 15 in eq 3 and 13 shows $\bar{n}_S$ to be a limited value at all ϵ, in particular, at $\epsilon = \epsilon_c$. As an example, in the simplest case when eq 15 is valid at all $n \geq 1$ and $\sigma_S = 1$, we obtain $\bar{n}_S(\epsilon_c) = (z_S + z_L)/z_L$; for the random walks on the simple cubic lattice $z_S = 4$, $z_L = 1$, $-\epsilon_c = \ln {}^6/_5$, and $\bar{n}_S(\epsilon_c) = 5$. Obviously, the higher averages $\overline{n_S^\kappa}$ are also limited in value. Moreover, it is possible to extend this conclusion to non-Gaussian chains with volume interactions.

Hence the behavior of the free energy derivative, eq 12, is governed by the mean length of loops at the transition point

$$\vartheta = d\mu/d\epsilon \sim \bar{n}_S/\bar{n}_L \qquad -\epsilon = -\epsilon_c + 0 \tag{16}$$

Providing $\bar{n}_L(\epsilon_c)$ is limited, $\vartheta(\epsilon_c) > 0$ and the adsorption appears as a first-order ($k_0 = 1$) phase transition (Figure 2). If this is not the case and $\bar{n}_L(\epsilon_c) \to \infty$, the derivative in eq 16 is zero, and the transition order is higher than unity, $k_0 > 1$. To obtain a more definite conclusion in the latter case it is necessary to analyze the second free energy derivative at $\epsilon = \epsilon_c$. After differentiating eq 12 and 16 and omitting zero components, we obtain

$$\left|\frac{d^2\mu}{d\epsilon^2}\right| \sim \left|\frac{\partial}{\partial\mu}\left(\frac{\bar{n}_S}{\bar{n}_L}\right)\right|\left|\frac{d\mu}{d\epsilon}\right| \sim \bar{n}_S{}^2\frac{\overline{n_L{}^2}}{\bar{n}_L{}^3} \qquad -\epsilon = -\epsilon_c + 0 \tag{17}$$

(the relation $|\partial\bar{n}_L/\partial\mu| \sim \overline{n_L{}^2} - \bar{n}_L{}^2$, which follows from eq 2 and 4, is taken into account).

If this derivative also becomes zero at ϵ_c, differentiation should be continued until the nonzero k_0-th derivative will be obtained. As in eq 16 and 17, the form of k-th derivatives at ϵ_c is $k \leq k_0$.

$$\frac{d^k\mu}{d\epsilon^k} \sim \bar{n}_S{}^k\frac{\overline{n_L{}^k}}{\bar{n}_L{}^{k+1}} \tag{18}$$

Hence the problem of the phase transition order at adsorption reduces to the analysis of the loops moments $\overline{n_L{}^k}$ at the transition point.

III. Distribution of Loop Lengths

Let us now suppose the distribution function of loop lengths at the transition point to be the terms of a power series

$$W_L(n) \sim 1/n^{1+\delta} \tag{19}$$

Then it is easy to obtain the loop moments in the macromolecule of $N \gg 1$ units

$$\overline{n_L{}^k} \sim \int_1^N n^{k-1-\delta}\,dn \sim N^{k-\delta} \tag{20}$$

in particular

$$\bar{n}_L \sim N^{1-\delta} \tag{20'}$$

Hence eq 18 becomes

$$|d^k\mu/d\epsilon^k| \sim \frac{\overline{n_L{}^k}}{\bar{n}_L{}^k} \sim N^{-(1-k\delta)} \tag{21}$$

From this it follows that the order k_0 of the desorption–adsorption phase transition for infinitely long chains ($N \to \infty$) is according to eq 11

$$k_0 = 1/\delta \tag{22}$$

It should be noted that $1/\delta$ may be nonintegral. In this

case the integer order of the lowest nonzero derivative is $k_0^1 = [1/\delta + 1]$ (the square brackets symbolizing the integer part), and this derivative exhibits an infinite jump at the transition point (because $k_0^1\delta > 1$; see eq 21). For integer $1/\delta$, the k_0-th derivative undergoes a jump limited in value. In the general case $k_0^1 = -[-1/\delta]$. As will be seen in eq 27, not k_0^1 but $k_0 = 1/\delta$ determines the chain free energy near the transition point. Consequently, we will describe precisely $k_0 = 1/\delta$ as the phase transition order, irrespective of its value (integral or not).

Equation 22 relates the phase transition order k_0 at adsorption to the single parameter δ of the loop length distribution.

As follows from eq 19–21, only the asymptotic behavior of this distribution is of importance. The broader the distribution, i.e., the lower δ is, the higher the order of the desorption–adsorption transition. If $\delta \geq 1$, the first-order phase transition occurs, $k_0 = 1$; if $\delta \to 0$, $k_0 \to \infty$.

IV. Free Energy of the Adsorbed Macromolecule near the Transition Point

Equation 21 expresses the free energy derivatives in terms of a small quantity $1/N$. We need to obtain the dependence of the free energy on another small positive quantity $\Delta\epsilon = -(\epsilon - \epsilon_c)$, measuring the deviation from the transition point. The infinitesimal replacement conditions $1/N \sim \Delta\epsilon^{1/\delta}$ may be obtained from eq 6, 11, and 21 if we bear in mind that each differentiation of μ with respect to ϵ diminishes by unity the $\Delta\epsilon$ power in the μ–$\Delta\epsilon$ relation.

Hence the first term of the free energy expansion in $\Delta\epsilon$ is

$$-(\mu - \mu_v) \sim \Delta\epsilon^{1/\delta} \tag{23}$$

A number of different thermodynamical and conformational characteristics of the chain near the transition point can also be obtained in the same approximation, for example, the mean loop length (the chain dimensions normal to surface)

$$\bar{n}_L \sim \Delta\epsilon^{-(1-\delta)/\delta} \tag{24}$$

the degree of the adsorption

$$\vartheta \sim \Delta\epsilon^{(1-\delta)/\delta} \tag{25}$$

and others.

We now direct our attention to the coefficients in eq 23–25 and their dependences on the chain features. As is clear from eq 12 and 17 each differentiation of μ with respect to ϵ produces a factor $\bar{n}_S$ (the mean length of adsorbed segment at the transition point). Hence in the particular case $\delta = {}^1/_2$, the lowest nonzero derivative (the initial slope of the degree of the adsorption) is

$$\left|\frac{d^2\mu}{d\epsilon^2}\right| = \left|\frac{d\vartheta}{d\epsilon}\right| \simeq \bar{n}_S{}^2\frac{\overline{n_L{}^2}}{\bar{n}_L{}^3} \sim \frac{\bar{n}_S{}^2}{a} \tag{26}$$

where a is the persistence length of the chain. The factor a^{-1} on the right-hand side of eq 26 is due to the discrepancy between the powers of loop length moments in the numerator and the denominator of the expression in the middle part of eq 26. The moments are found to depend on the chain flexibility as $\overline{n_L{}^k} \sim a^k$, where a is the invariant measure of chain flexibility, for example, the persistence length or the Kuhn segment. Consequently, the ratio of moments varies inversely with the persistence length. It should be emphasized that the loop length moments in eq 26 refer to the transition point and hence to the free chain (see section I). Thus the flexibility parameter a also refers just to a free chain.

For this particular case $\delta = {}^1/_2$ the combination of eq 23 and 26 yields the coefficient in eq 23. In a similar manner we obtain at any δ

$$-(\mu - \mu_v) = \kappa\frac{(\bar{n}_S\Delta\epsilon)^{1/\delta}}{a} \tag{27}$$

where $\kappa > 0$ is a numerical factor, $\bar{n}_S$ refers to the point $\Delta\epsilon = 0$, and a is the flexibility characteristic of a free chain. The value $\bar{n}_S$ increases with the stiffness of the chain a, because the chain should bend to leave the surface.

Equation 27 is invariant with respect to the chain subdivision into "monomer units" interacting with the adsorbent. It contains the free energy change per persistence length $a(\mu - \mu_v)$, resulting from the adsorption, and the excess energy of adsorption per adsorbed segment $\bar{n}_S\Delta\epsilon$ ($\Delta\epsilon$ is the excess energy, because we subtract from ϵ the part ϵ_c, which ensures compensation of the conformational entropy restrictions on adsorption; see section I).

Equation 27 opens the way for a detailed quantitative analysis of the effects of chain stiffness on the $\Delta\mu$–$\Delta\epsilon$ relation. In the present paper we will restrict ourselves only to one general conclusion. As can be seen from eq 27, the chain stiffness always acts as a scaling factor in the $\Delta\mu$–$\Delta\epsilon$ relation. The order of the transition is unaffected by chain stiffness, being dependent only on the asymptotic behavior of the loop length distribution in a free chain.

V. Simple and Complex Loops at the Virtual Surface

The distribution $W_L(n)$ deals with the elementary or simple loops formed by the first return of a chain on the surface. Now it is advantageous to introduce the distribution function $\tilde{W}_L(n)$ for complex loops formed by any return of a chain to the surface, not necessarily the first one (Figure 1).

Distributions similar to $W_L(n)$ and $\tilde{W}_L(n)$ are widely used in probability theory. These functions are interdependent through their generating functions[22]

$$\tilde{W}_L(s) = [1 - W_L(s)]^{-1} \tag{28}$$

where

$$W_L(s) = \sum_{n=1}^{\infty} W_L(n)s^n \tag{29}$$

$$\tilde{W}_L(s) = \sum_{n=1}^{\infty} \tilde{W}_L(n)s^n \tag{30}$$

Equation 28 gives also the relationship between $W_L(s = 1) = \mathcal{W}_L$ and $\tilde{W}_L(s = 1) = \tilde{\mathcal{W}}_L$.

There is a one-to-one correspondence between the probability of return and the divergence of the $\tilde{W}_L(n)$ series. The latter diverges in the case of certain return, $\mathcal{W}_L = 1$, and converges if the return is uncertain, $\mathcal{W}_L < 1$; and, vice versa, the behavior of the $\tilde{W}_L(n)$ series determines the $\mathcal{W}_L$ value.

The single-parameter form of the distribution $W_L(n)$, eq 19, enables us to obtain the distribution $\tilde{W}_L(n)$.

Let us begin with the case $\mathcal{W}_L = 1$. Then at $N \gg 1$

$$\mathcal{W}_L \sim 1 - \sum_{n=N+1}^{\infty} n^{(1-\delta)} \sim 1 - N^{-\delta}$$

and according to eq 28 at $s = 1$

$$\tilde{\mathcal{W}}_L \sim N^{\delta} \tag{31}$$

This sum of the $\tilde{W}_L(n)$ series is a measure of the number of event realizations; in our case it is equal to the mean number N_s of the chain returns to the virtual surface. Hence, the asymptotic dependence of N_s is

$$N_s \sim \tilde{\mathcal{W}}_L \sim N^{\delta} \tag{32}$$

and N_s increases infinitely with N as $\delta > 0$.

From eq 31 it is possible to obtain the terms of the $\tilde{W}_L(n)$ series

$$\tilde{W}_L(n) \sim 1/n^{1-\delta} \tag{33}$$

In the case $\mathcal{W}_L < 1$, when the return is uncertain, $\tilde{\mathcal{W}}_L$ and N_s do not grow indefinitely with N, tending to some finite limits as $N \to \infty$. Differentiating eq 28 with respect to s, we obtain at $s = 1$ the relation between the mean lengths of complex and simple loops:

$$\tilde{n}_L = \bar{n}_L \frac{\mathcal{W}_L}{1 - \mathcal{W}_L} \tag{34}$$

It indicates that the asymptotic behavior of the complex loops is similar to that of the simple loops. From this it follows the equivalence of the $W_L(n)$ and $\tilde{W}_L(n)$ series. Therefore at $\mathcal{W}_L < 1$

$$\tilde{W}_L(n) \sim W_L(n) \sim 1/n^{1+\delta} \tag{35}$$

Thus the problem of the phase transition order is reduced to the analysis of the complex loop distribution $\tilde{W}_L(n)$ for a free chain with respect to the virtual surface.

It is evident that $\tilde{W}_L(n)$ depends on the properties of both the free chain and the surface. It is possible to separate these dependences by using the well-known distribution function $W_n(\vec{r})$ of the intersegment vector $\vec{r}$ connecting units i and $i + n$ in the free chain.

VI. Loops and Distribution of Intrachain Vectors

Let us draw the virtual surface (geometrically equivalent to an adsorbent surface) through the i-th unit of a free chain in the origin of the coordinate system. The probability of the $(i + n)$-th unit to reach this surface forming an n-unit loop (it may be a complex loop in a general case) is determined as

$$\tilde{W}_L(n) \sim \int W_n(\vec{r})\, dS(\vec{r}) \tag{36}$$

where the integral is taken over the virtual surface. According to eq 36, the probability for a loop to be closed somewhere on the surface is equal to a sum of the products of the probabilities $W_n(\vec{r})$ and $dS(\vec{r})$ of finding both the last unit of the loop and the surface element at the same point $\vec{r}$.

As pointed out above, we are interested only in the asymptotic behavior of the distribution $\tilde{W}_L(n)$, i.e., in the components with $n \gg 1$. This permits us to simplify the integration over the adsorbent surface. It is easy to understand that the integration over coordinates corresponding to limited adsorbent sizes is not essential for sufficiently large n. Indeed, for example, let $W_n(\vec{r})$ have a Gaussian form

$$W_n(\vec{r}) \sim \frac{1}{(\overline{r_n^2})^{3/2}} \exp[-3(r_{nx}^2 + r_{ny}^2 + r_{nz}^2)/2\overline{r_n^2}] \tag{37}$$

and the adsorbent dimension be limited in the x direction. Hence the integration in eq 36 must be performed over $|x| \leq x_0$. For sufficiently large n, $\overline{r_n^2} \sim n \gg x_0$, and as a result of the integration of the exponential factor, we obtain only the numerical coefficient $\sim x_0$, which does not affect the behavior of $\tilde{W}_L(n)$.

Thus to determine the asymptotic behavior of $\tilde{W}_L(n)$, it is sufficient to integrate in eq 36 only over the coordinates corresponding to the unlimited adsorbent sizes. Moreover, since $W_n(\vec{r})$ is a function only of $r = |\vec{r}|$, the surface elements can be expressed as

$$dS(r) \sim r^{d-1}\, dr \tag{38}$$

Table I
Phase Transition Order in Adsorption of Macromolecules as a Function of the Chain Conformation Exponent and of the Dimensionality d of the Surface[a]

	d		
ν_D	2	1	0
$^1/_3$	$^3/_2$	3	
$^1/_2$	2	∞	2
$^3/_5$	$^5/_2$		

[a] ν_D is equal to $^1/_3$, $^1/_2$, and $^3/_5$ for the globular state, the Gaussian coil, and the expanded coil, respectively.

where d = 1–3 refers to the one-, two-, and three-dimensionally unlimited adsorbents (d-dimensional adsorbents); for quasi-zero-dimensional, $d = 0$, adsorbents (limited in size in all direction), $r \sim 0$ and $\tilde{W}_L(n) \sim W_n(0)$.

It should be noted that this result does not depend on the other pecularities of the adsorbent structure. For example, expression 38 is directly applicable without alteration to a case where instead of a continuous adsorbent we have an infinite sequence of small (point) adsorbents, situated in the d-dimensional order. Of course, the replacement of the continuous adsorbent by the discrete one leads to a decrease in the numerical value of the integral (36), but it has no effect on its asymptotic behavior at $n \to \infty$.

VII. Results and Discussion

We have shown that the information about the order of the phase transition at adsorption of long polymer chains is contained in the distribution $W_n(\vec{r})$ of the intrachain vectors in a free chain. To extract this information only the dimensionality d of the adsorbent is required. Calculating the distribution $\tilde{W}_L(n)$ from eq 36 and 38, we obtain δ either from eq 33 if $\tilde{W}_L(n)$ is divergent with n or from eq 35 if it is convergent. Then the order of the phase transition is given by eq 22.

There is also a simpler way of determining the transition order based on the assumption that the distributions $W_L(n)$ and $\tilde{W}_L(n)$ exhibit single-parameter forms. To obtain this single parameter δ, one should know the molecular weight dependence on only one average characteristic of a free chain. It is advantageous to use the $N_s(N)$ dependence for determining δ from eq 32.

Let us draw an imaginary virtual d-dimensional surface through a free macromolecule. Knowing the molecular weight dependences of the mean dimension and the density of the polymer chain, we can easily find the required dependence for the number of intersections N_s between the virtual surface and the chain.

Evidently, this simplest method is suitable only if the number of intersections N_s increases indefinitely with N, i.e., if $\mathcal{W}_L = 1$. Then

$$\tilde{\mathcal{W}}_L \sim N_s \sim \frac{N}{V} S \sim N R^{-(D-d)} \sim N^{1-\nu_D(D-d)} \tag{39}$$

where $V \sim R^D$ and $R \sim N^{\nu_D}$ are the volume and the radius of a free chain in a D-dimensional space; $S \sim R^d$ is the dimension of the intrachain part of the d-dimensional virtual surface. For $D = 3$ the exponent ν_D is equal to $^3/_5$, $^1/_2$, and $^1/_3$ for an expanded coil in a good solvent, a Gaussian coil, and a globule (at $T < \Theta$), respectively.

The transition orders obtained according to eq 22, 32, and 39 are collected in Table I. We find here a great variety of phase transitions in the adsorption of macromolecules. We will discuss these results extensively in part 3. Note here only the regularities in Table I: the order of transition increases with increasing ν_D and decreasing

d up to the conformation of a chain and the geometry of a surface ensure the return of a free chain to the virtual surface, $\mathcal{W}_L = 1$. This condition holds in the upper left part of the table, which is divided by the dashed line into the regions $\mathcal{W}_L = 1$ and $\mathcal{W}_L < 1$ (the lower right part of the table).

Note that the proposed formalism is strict for Gaussian chains for any $\mathcal{W}_L \leq 1$ but is not applicable for non-Gaussian chains if $\mathcal{W}_L < 1$. In the case of expanded coils it remains approximately correct if $\mathcal{W}_L = 1$, because the density of a free coil scales as $\rho \sim N^{-4/5}$ and the reflection from an adsorbing surface in the transition point does not change the scaling law. The applicability of eq 22 and the whole scheme of definition of the transition order in adsorption to globular structures needs further analysis.

Summary

A general method for investigating the transition type during adsorption of polymer chains on various solid surfaces has been developed. It is shown that a decisive part is played by the asymptotic behavior of length distribution functions for loops formed by the return of free chains to the virtual surface geometrically equivalent to the adsorbent surface. The dependence of the chain free energy on the adsorption energy near the desorption–adsorption transition point is obtained in general form.

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Study of the Surface Tension of Polymer Solutions: Theory and Experiments. 1. Good Solvent Conditions

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ABSTRACT: A study of the surface tension of semidilute polymer solutions in good solvent conditions is presented. Theoretical predictions are given for the two cases when the interface is attractive or repulsive for the polymer, for the cases of both weak and strong adsorption. The Cahn approach for the interfacial tension is used and the concentration profile is calculated in mean field theory. The measurements were performed on two polymer good solvent systems: poly(dimethylsiloxane)–toluene and polystyrene–toluene for the attractive and repulsive cases, respectively. The well-known ring method was used. The agreement between theory and experiments is good and indicates that the two systems are strong-adsorption cases.

Recently, much effort has been devoted to the study of the interfacial properties of solutions. In particular, the behavior of polymers at liquid surfaces (melt or solution) has raised much interest, both theoretically and experimentally.

One can distinguish two different situations. The first one is the contact between two liquid phases with no discontinuity in the concentration of the constituents in the interface.[1-4] The second one concerns the presence of a wall (either at a solid–liquid or a liquid–gas interface) leading to a discontinuity of the concentrations.[5-8] We are interested in that second case since the liquid–gas surface of the solution is sharply defined.

It was observed long ago that some polymers exhibit surface activity in organic solvents. On the other hand, adsorption phenomena are frequently of great amplitude for polymer solutions in contact with surfaces.[9]

From the theoretical point of view the approach of Cahn[7] for the interfacial tension and wetting properties of fluid–solid interfaces and some recent calculations[8,10,11] of the profiles of polymer concentration in the vicinity of attractive or repulsive interfaces seem good building blocks for new predictions of interfacial behavior. This paper presents such predictions for the surface tension of semidilute solutions of polymers in good solvents. Both attractive and repulsive interfaces are examined, leading to different behaviors.

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