Study of polymer chain in a solution of colloidal particles

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Formation of a complex between a long polymer chain and several spherical particles with surface attractive adsorption layers is studied using scaling arguments. It is shown that if the spatial position of particles is fixed, the polymer chain in the complex becomes highly stretched. In this case the polymer is adsorbed on many particles and adopts an extended conformation; its dimensions substantially exceed those of a free coil. Complex formation (adsorption) is a first order phase transition. By contrast, if adsorption on mobile particles is considered, additional stretching vanishes and the dimensions of the adsorbed polymer chain are of the same order as those of a corresponding free coil. In this case adsorption of polymer macromolecule remains a first order phase transition. However, its features are similar to those of the second order phase transition, because the approach to the critical point of adsorption results in considerable swelling of adsorption layers of particles involved in the complex.

(Keywords: adsorption; colloidal particle; complex; adsorption layer)

INTRODUCTION

The interaction of colloidal particles and polymer chains has been studied using the methods of statistical physics of macromolecules[1-4]. Investigations in this field are constantly stimulated by various applications to the problems of stabilization and aggregation of colloidal solutions. The topic of most of the studies[1-4] is the theoretical description of the process of complex formation of a single colloidal particle with several macromolecules from polymer solution. This approach can be used if the dimensions of colloidal particles substantially exceed those of the free polymer coil. Meanwhile, an opposing limiting case is possible, for example, if adsorption on protein molecules or micelles is considered. In this case the polymer chain is adsorbed on many particles simultaneously (*Figure 1*). Several problems associated with the theoretical treatment of such complexes have been discussed[5-9]. In the present paper we perform simple analyses of these complexes using scaling arguments[9], and present some new results concerning the structure and properties of these complexes.

We will also consider an analogous system which differs from the initial one (*Figure 1*) in only one respect: the particles are fixed in space. The study of properties of adsorption of a polymer chain in this system is not only of fundamental interest, but is also connected with some practical applications (for instance, the description of conformations of macromolecule in a gel with spatially distributed adsorbing centres). We will start our analysis with this latter problem, because this is a necessary step in solving the problem of mobile colloidal particles.

POLYMER CHAIN IN A SYSTEM OF FIXED PARTICLES

Let us suppose that a polymer chain with degree of polymerization N and monomer link dimension α is trapped in a system of immobile spherical particles of radius R (*Figure 2*); we assume that the particles are randomly distributed in space. Let c be the concentration of particles and $l = c^{-1/3}$ the average distance between them. We suppose that interactions of colloidal particles and monomer links are connected with the facts that links cannot penetrate inside particles (steric repulsion) and that each particle is surrounded by a thin attractive potential well of thickness $\delta \sim \alpha$. Thus, if a monomer link is in this potential well, it acquires negative energy $-\Delta\varepsilon = \varepsilon - \varepsilon^*$, where $\varepsilon^* \sim T\alpha^2/\delta^2$ is the critical energy of adsorption on the plane (T is the temperature).

Let us consider the free energy, F, of the complex formed by the polymer chain and colloidal particles, assuming that the total number of particles attached to the chain is k (zero level of free energy is associated with unadsorbed state). According to standard scaling theory[9] it is possible to write:

$$F = F_1 + F_2 + F_3 + F_4 + F_5 \qquad (1)$$

Here $F_1 \sim -\Delta\varepsilon$ is the energy of a monomer link captured by potential wells of colloidal particles, F_2 is the confinement energy of adsorbed chain associated with surface adsorption layers[9,10] of thickness Δ (*Figure 2*). We will assume that $\Delta \ll R$, and this will be confirmed. Let N_g be the average number of monomer links inside the adsorption layer of each particle; in this case for the terms F_1 and F_2 one can write the following estimates[9]:

$$F_1 \sim -k\,\Delta\varepsilon \frac{\delta}{\Delta} N_g \qquad (2)$$

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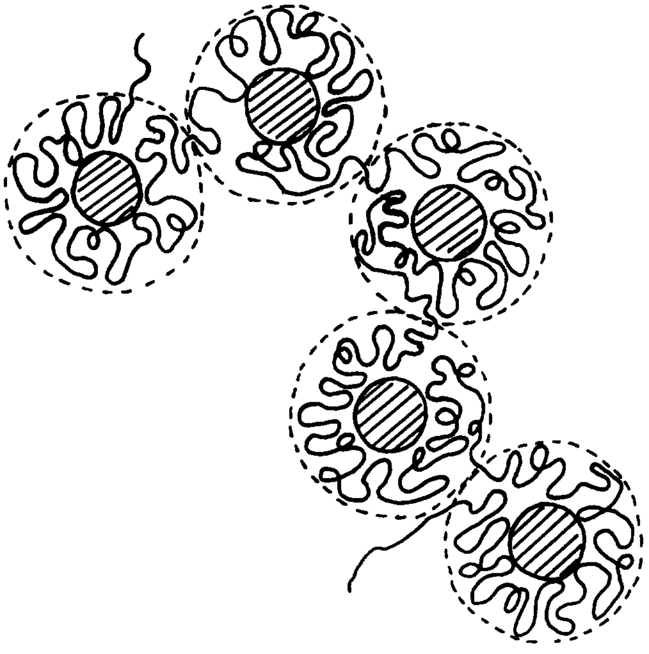

Figure 1 Complex of a polymer chain and k colloidal particles

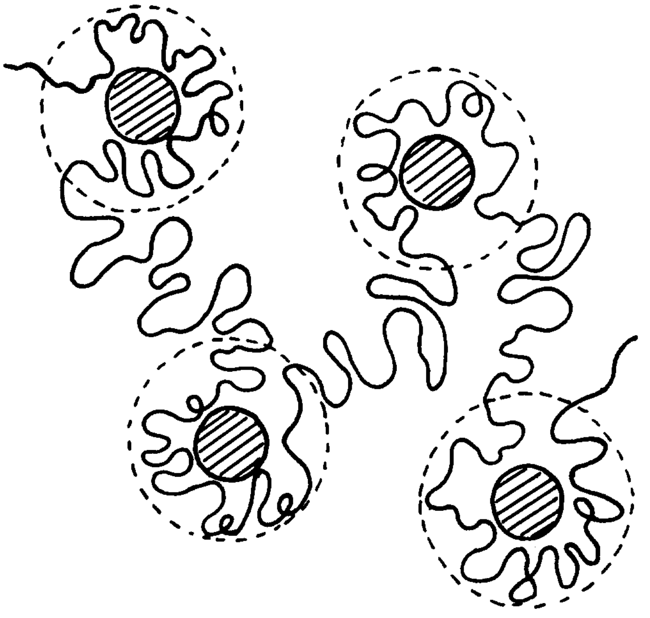

Figure 2 Polymer chain in a system of immobile colloidal particles with surface potential wells

$$F_2 \sim kTN_g \frac{\alpha^2}{\Delta^2} \tag{3}$$

Temperature T is taken in energy units here and below. To obtain exact expressions one has to multiply equations (2) and (3) by constants of order unity. We will imply this fact without indicating it explicitly, and with this in mind, instead of equations (2) and (3) we can write:

$$F_1 = -k\,\Delta\varepsilon \frac{\delta}{\Delta} N_g$$

$$F_2 = kTN_g \frac{\alpha^2}{\Delta^2} \tag{4}$$

The term F_3 in equation (1) accounts for excluded volume interactions of segments in adsorption layers. We suppose that the solvent for the polymer chain is good and polymer volume fraction in adsorption layers ϕ is small (weak adsorption limit)[9]; the generalization of this theory for the case $\phi \sim 1$ can be performed easily. Thus only the second term of virial expansion should be taken into account:

$$F_3 \sim kTB \frac{N_g^2}{R^2\Delta} \tag{5}$$

since at $\Delta \ll R$, the volume of the adsorption layer is of the order $R^2\Delta$, and B is the second virial coefficient of the interaction of links. For flexible chains in good solvent $B \sim \alpha^3$, therefore, taking into account the arguments presented after equation (3) we find that:

$$F_3 = kT\alpha^3 \frac{N_g^2}{R^2\Delta} \tag{6}$$

The term F_4 in equation (1) corresponds to the fragments of the chain between adsorption layers of neighbouring particles. We will show that in equilibrium these fragments are highly stretched; F_4 is the free energy which accounts for this stretching. Let N_f be the average number of monomer links per fragment of the chain connecting neighbouring adsorption layers. Since the total number of links is N, the values of N_g and N_f are connected by the expression:

$$kN_g + (k-1)N_f = N \tag{7}$$

Obviously, the distance between the ends of the chain fragment consisting of N_f bonds is of the order of the distance l between neighbouring colloidal particles, thus we have:

$$F_4 = (k-1)T \frac{l^2}{N_f\alpha^2} \tag{8}$$

Equation (8) is valid if $N_f\alpha \gg l$, but it should be modified if the limit of complete stretching ($N_f\alpha \sim l$) is approached.

Finally, the term F_5 is due to the fact that not only chain fragments between adsorption layers, but also the fragments within these layers (which are adsorbed on colloidal particles) can be stretched. This stretching can take place along the surface of the particles, and in complete analogy to equation (8) we write:

$$F_5 = kT \frac{R^2}{N_g\alpha^2} \tag{9}$$

because the distance between the ends of the chain of N_g segments is of the order R. It should be noted that if $R^2 > N_g\alpha^2$, adsorbed chain does not completely cover the colloidal particles.

Equations (1), (4), (6), (8) and (9) define completely the total free energy of the complex of polymer chain and k colloidal particles. In order to determine the structure of this complex one has to minimize the free energy F with respect to the parameters k, Δ, N_f and N_g, taking into account the additional condition, equation (7) (therefore the total number of minimization parameters is three). The results of this minimization are presented below.

At high temperatures the free energy F is always positive, thus there is no adsorption of polymer chain on colloidal particles. As temperature decreases the complex is formed for the first time at:

$$T_c \sim \varepsilon \frac{\delta^2}{\alpha^2} \frac{1}{1+\dfrac{\delta}{(\alpha R)^{1/2}}} \tag{10}$$

Evidently, T_c is the temperature of capture of polymer chain by surface potential wells of colloidal particles.

The formation of the complex is a first order phase transition; at this point all conformational characteristics of the polymer molecule are changed dramatically. At the transition point $T = T_c$ parameters of the complex are:

$$\begin{aligned} \Delta &\sim (\alpha R)^{1/2} \\ k &\sim N(\alpha R)^{1/2} \alpha l^{-2} \\ N_g &\sim \left(\frac{R}{\alpha}\right)^{3/2} \ll N_f \sim \frac{N}{k} \end{aligned} \tag{11}$$

It can be seen that if $R \gg \alpha$ then $\alpha \ll \Delta \ll R$, i.e. the weak adsorption limit takes place and at the same time the thickness of adsorption layers is essentially smaller than R. At the transition point only a small fraction of polymer links are located in adsorption layers ($N_g \ll N_f$) while the others remain in free fragments of the chain.

The most unexpected result can be obtained if one calculates the radius of gyration $\langle s^2 \rangle$ of adsorbed chain. Since fragments of the chain of N_f links that connect adsorption layers of colloidal particles are statistically independent, we get (*Figure 2*):

$$\langle s^2 \rangle \sim k l^2 \tag{12}$$

At $T = T_c$ this gives:

$$\frac{\langle s^2 \rangle}{\langle s^2 \rangle_0} \sim \left(\frac{R}{\alpha}\right)^{1/2} \gg 1 \tag{13}$$

where $\langle s^2 \rangle_0 \sim N\alpha^2$ is the radius of gyration of a free chain. Thus, after adsorption the radius of gyration is not decreased (as one might expect), but is substantially increased. This result can be explained as follows: for a polymer chain in a complex it is preferable that the maximum possible fraction of links is located in surface potential wells of colloidal particles. But the 'capacity' of these wells is finite, thus the chain tends to adsorb on the maximum possible number of colloidal particles by stretching the chain fragments of N_f bonds between them. In fact, it is easily found that at $T = T_c$:

$$\frac{l^2}{N_f \alpha^2} \sim \frac{R^2}{N_g \alpha^2} \sim \left(\frac{R}{\alpha}\right)^{1/2} \gg 1 \tag{14}$$

i.e. the chain is highly stretched. It is due to the entropy loss associated with this stretching that the complex is destroyed at $T = T_c$.

Now let us consider changes in conformation of adsorbed macromolecule as the temperature decreases (at $T < T_c$). In the interval $T' < T < T_c$ (the definition of T' is given below) parameters of the complex are:

$$\begin{aligned} \Delta &\sim \frac{\alpha}{u} \\ k &\sim N u^3 \frac{R^2}{l^2} \\ N_g &\sim u \frac{R^2}{\alpha^2} \ll N_f \sim \frac{N}{k} \end{aligned} \tag{15}$$

$$\frac{\langle s^2 \rangle}{\langle s^2 \rangle_0} \sim u^3 \frac{R^2}{\alpha^2} \tag{16}$$

$$\frac{F}{T} \sim -N u^6 \frac{R^4}{l^2 \alpha^2} + N u^2 \frac{R^2}{l^2} \tag{17}$$

where $u \equiv \Delta\varepsilon\delta/\alpha T$ is a characteristic dimensionless ratio connected with the depth of surface potential wells of colloidal particles. It can be seen that the thickness of adsorption layers Δ becomes smaller as temperature decreases. At the same time the number of chain segments per adsorption layer N_g and the number of colloidal particles k in the complex is increased. Increase of k is associated with the fact that as temperature decreases it is more advantageous for monomer link to be located in an adsorption layer, therefore the chain tends to create new adsorption layers on the maximum possible number of colloidal particles. Due to essential chain stretching the radius of gyration of the macromolecule is increased in this process (as seen from equation (16)).

The stretching of the chain, caused by including new colloidal particles in the complex terminates when temperature reaches the value

$$T' \sim \varepsilon \frac{\delta^2}{\alpha^2} \frac{1}{1+\dfrac{\delta}{R}\left(\dfrac{l}{\alpha}\right)^{1/2}}$$

($u' \sim (\alpha l)^{1/2}/R$). At $T < T'$ we enter a new regime: in this case the number of segments in adsorption layers exceeds the number of segments in the fragments of the chain which connect these layers ($N_g \gg N_f$). The characteristics of the complex are given by the following expressions:

$$\begin{aligned} \Delta &\sim \frac{\alpha}{u} \\ k &\sim N \frac{\alpha^{3/2}}{R l^{1/2}} \\ N_f &\sim \frac{l}{\alpha u} \ll N_g \sim \frac{N}{k} \\ \frac{\langle s^2 \rangle}{\langle s^2 \rangle_0} &\sim \frac{l}{R}\left(\frac{l}{\alpha}\right)^{1/2} \gg 1 \end{aligned} \tag{18}$$

i.e. the number of colloidal particles in the complex k and its radius of gyration remain constant in this temperature range. At the same time if the temperature is further lowered (below T') the thickness of adsorption layers Δ is decreased and the stretching of the chain fragments that connect neighbouring adsorption layers is increased. At $u \sim 1$ we achieve the limit of complete stretching of these chain fragments. Simultaneously Δ becomes of the order of α. Thus, for this case weak adsorption approximation can no longer be used.

In conclusion, it should be noted that according to our analysis the term F_3, which describes excluded volume interactions in adsorption layers, is not essential in the entire temperature range. Thus, various modifications of equation (6) (for instance, taking into account chain stretching along adsorption layers) do not change the results obtained above.

POLYMER CHAIN IN A SYSTEM OF MOBILE PARTICLES

We now consider a solution of colloidal, protein or micellar particles with surface adsorption potential wells. We keep the model of interactions adopted in the previous section; the only essential difference is the fact that now the particles are not fixed and are free to move in space. We assume that the solution of particles in the absence of macromolecules is dilute, thus its chemical potential has the form:

$$\mu_0 = T \ln(cR^3) < 0$$

Being adsorbed on k colloidal particles, the macromolecule forms a complex with these particles (*Figure 1*). It is evident that in principle all the contributions to the free energy F_1–F_5 (see equations (4), (6), (8) and (9)) will still be present for this case. Additionally, the contribution

$$F_6 = -k\mu_0 \qquad (19)$$

connected with the loss in translational entropy due to the incorporation of k independent particles in one complex, should be taken into account.

The fact that the particles are now free to move essentially simplifies the analysis. First of all, one can argue that the chain fragments of N_f segments that connect neighbouring adsorption layers are absent ($N_f = 0$, $N_g = N/k$). In fact, let us fix for a moment all colloidal particles in the system, i.e. let us return to the situation shown in *Figure 2*. Suppose now that we gradually decrease the average distance l between the particles of the complex. From equation (17) one can conclude that the free energy F will decrease in the course of this process. This means that there is attractive force between neighbouring particles involved in the complex (*Figure 2*) (this force is caused by stretching of the chains of N_f links that connect adsorption layers). If the particles are now free to move due to the presence of this force, they will approach each other up to direct contact of their adsorption layers (i.e. up to the situation shown in *Figure 1*). Thus highly stretched chain fragments of N_f segments will disappear and the term F_4 in the free energy is omitted.

Another simplification is that for an equilibrium complex one can immediately write the following estimate for the number of particles k:

$$k \sim N\frac{\alpha^2}{R^2} \qquad (20)$$

Equation (20) means that the number of particles in the complex is such that adsorption layers completely cover colloidal particles and that the chains inside these layers are not stretched. Indeed, suppose that the equilibrium value of k exceeds $N\alpha^2/R^2$. From the analysis of equations (4), (6), (9) and (19) it is possible to conclude that this assumption leads to the loss of entropy associated with chain stretching (equation (9)) and with adsorption of additional particles (equation (19)). At the same time the reasons for such an increase in k being favourable, from the point of view of the free energy, are absent. Let us suppose now that $k < N\alpha^2/R^2$; in this case a small gain of entropy is achieved which is connected with translational entropy of colloidal particles. However, a more considerable loss of free energy takes place which is due to the growth of excluded volume effects in adsorption layers (equation (6)). Therefore, equation (20) provides the equilibrium value of k.

The estimate (20) can also be formally obtained by minimization of the free energy defined by equations (10), (4), (6), (9) and (19) if one takes into account that the free energy of volume interactions can be written in the form of equation (6) only if $N_g\alpha^2 > R^2$. If $N_g\alpha^2 \ll R^2$, i.e. for highly stretched chains, the term F_3 drops more quickly than according to equation (6) (equation (6) is written in the mean field approximation[10]). The estimate obtained on the basis of scaling treatment indicates that at $N_g\alpha^2 \ll R^2$ the term F_3 in free energy of the complex can be neglected.

Equation (20) is crucial for the proper understanding of equilibrium structure of the complex. A priori, the 'necklace' structure shown in *Figure 1* is not the only possible structure. An alternative hypothetical variant corresponds to the case where a polymer chain visits the adsorption layer of a given particle several times. The arguments presented above are useful in explaining why this situation is less favourable. First, for the structure involving several visits of a polymer chain to a given adsorption layer, some parts of the chain are subjected to essential stretching (note that if polymer chain enters a given adsorption layer several times the number of segments of each of these fragments is substantially less than N/k). This leads to considerable loss in entropy. Finally, chain conformation in the case of many returns to a given adsorption layer is more compact, thus free energy of excluded volume repulsion in this case is larger.

To calculate the thickness of adsorption layers Δ in equilibrium one now has to substitute equation (20) into the expression for F and perform minimization of this expression with respect to Δ. The result does not depend on μ_0 and R and has the form:

$$\Delta \sim \frac{\alpha}{u-1} \qquad (21)$$

where $u \equiv \Delta\varepsilon\delta/\alpha T$. Obviously, equation (20) makes sense only if the denominator is positive, i.e. for low enough temperature: $T < T^*$, where

$$T^* \sim \varepsilon\frac{\delta^2}{\alpha^2}\frac{1}{1+\frac{\delta}{\alpha}}$$

As the temperature approaches T^*, the thickness Δ is proportional to τ^{-1}, where $\tau \equiv (T - T^*)/T^*$. This behaviour is characteristic for the thickness of adsorption layer in the course of the approach to the adsorption point[10].

However, due to the existence of the term $F_6 > 0$ in free energy the complex is destroyed at a temperature somewhat below T^*. Free energy of the complex becomes zero at $T_{tr} < T^*$ (recall that at T^* the sum $F_1 + F_2 + F_3 = 0$):

$$T_{tr} \sim \varepsilon\frac{\delta^2}{\alpha^2}\frac{1}{1+\frac{\delta}{R}|\ln cR^3|^{1/2}+\frac{\delta}{\alpha}} \qquad (22)$$

It is easy to understand that the formation of a complex is a first order phase transition. At $T = T_{tr}$ the value of Δ is equal to $R|\ln cR^3|^{-1/2}$. Therefore, at the transition point, $\Delta < R$, and the thickness of adsorption layers is decreased with decrease in the concentration of the solution of colloidal particles. When the temperature is further lowered the value of Δ is diminished and finally we abandon the weak adsorption regime. Thus to describe excluded volume effects in adsorption layers it becomes necessary to take into account the next terms in the virial expansion.

Although phase transition (formation of the complex) is of the first order, it can be close to second order phase transition if the parameter $(\delta/R)|\ln cR^3|^{1/2}$ is small. In fact, in this case T_{tr} is close to T^* (see equation (21)) and one can conclude that as the temperature approaches T_{tr}, essential swelling of adsorption layers should be observed. This situation is typical for second order adsorption phase transitions in the usual cases[10].

An important characteristic of the complex which can be experimentally measured is its radius of gyration $\langle s^2 \rangle$. According to *Figure 1*:

$$\langle s^2 \rangle \sim kR^2 \tag{23}$$

Taking into account equation (20) the result is:

$$\langle s^2 \rangle \sim N\alpha^2 \tag{24}$$

i.e. the radius of gyration of the macromolecule in the complex is of the same order as that of a free chain. Equations (23) and (24) need to be somewhat modified if some violations of Gaussian statistics of polymer chain due to the excluded volume effects are taken into account. However, the basic result remains the same: formation of the complex is not accompanied by significant changes of dimensions of polymer chain. This fact has indeed been experimentally observed for situations similar to that studied in the present paper[11]. Thus the theory presented above provides a natural explanation for this fact.

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