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LETTER TO THE EDITOR

Adsorption of a free polymer chain interacting with an interface

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Abstract. We present the average conformational properties of a polymer chain interacting with a surface and free to move in a space of size L perpendicular to the surface. The properties are found solving the problem by means of integral equations.

The study of adsorption of polymers at a surface, due to its great technological importance [1, 2], was given considerable attention over the last few decades [1-10]. The interactions between the polymer chains and the interface either of liquid-solid, liquid-liquid, or liquid-gas nature, change the conformational behaviour of the chains relative to those in the bulk away from the surface. The presence of the surface leads to anisotropy and differentiates the z -direction perpendicular and the directions parallel to it. If the area of the available interface is S and the larger perpendicular distance on each side of the interface along which the chain can move is $(L/2)$ then the volume of the available space is $V = S \times L$. The chain generally is free to belong either to the solution or to the neighbourhood of the interface; the situation is more general than that described by chains fixed with one of their ends at the interface. The anchored chain has been studied before by means of the continuous model [5] and results in agreement with the results from lattice models [3] were found. When the chains do not interact among themselves the problem of the n chains is separable and equivalent to the problem of an isolated chain interacting with the interface.

The continuous model used before [5], with one end of the chain fixed at the surface, can be extended to the study of chains free to move in the whole space of volume V . The surface is approximated by the xy plane and a general configuration of the flexible polymer chain is represented with a continuous curve $\mathbf{R}(s)$ ($0 < s < Nl$), where $\mathbf{R}(s)$ are the position vectors of the points of the chain. The contour length s varies from zero to the total length Nl of the chain made of N units each one of length l . The probability distribution $P[\mathbf{R}(s)]$ of a specific configuration is given by

$$P[\mathbf{R}(s)] = P_0[\mathbf{R}(s)] \exp\left\{-u_a \int_0^{Nl} ds \delta[z(s)]\right\} \quad (1a)$$

where

$$P_0[\mathbf{R}(s)] = \left(\frac{3}{2\pi l^2}\right)^{3N/2} \exp\left\{-\frac{3}{2l} \int_0^{Nl} ds [\dot{\mathbf{R}}(s)]^2\right\} \quad (1b)$$

is the probability of the non-interacting ideal chain representing a connectivity term, and u_a is a dimensionless parameter proportional to the intensity of the interactions

between the monomers and the interface. Varying the magnitude of u_a from negative to positive values, a systematic study of the nature of the mean interactions between the interface and the polymer, either of attractive or repulsive character, can be done.

The configurational partition function C is defined by means of the path integral [11, 12]

$$C = \int D[\mathbf{R}(s)] P_0[\mathbf{R}(s)] \exp\left\{-u_a \int_0^{Nl} ds \delta[z(s)]\right\} \quad (2)$$

equivalent to an integration of all position vectors of the points of the chain over the whole available volume V . From the expansion of (2) with respect to u_a , it is seen that C can be written as

$$C = V \left[1 - \frac{l u_a}{L} \int_0^N di g(u_a, N-i) \right] \quad (3)$$

where the function $g(u_a, N-i)$ obeys the integral equation

$$g(u_a, N-i) = 1 - u_a \sqrt{\frac{3}{2\pi}} \int_0^{N-i} dj \frac{1}{\sqrt{j}} g(u_a, N-j-i). \quad (4)$$

The volume V in front of (3) comes from the integration of the position vector of the last point of the free chain over the whole volume V , while the factor $1/L$ appears because chains attached to the surface are prevented from moving along the L distance away from the surface. Equation (4) can be solved by means of Laplace transforms. The final expression of C is given by

$$C = V(1 - F_2) \quad F_2 = \frac{2l\sqrt{N}}{L\sqrt{6}} \left[\frac{2}{\sqrt{\pi}} - \frac{1}{U} + \frac{1}{U} \exp(U^2) \operatorname{erfc}(U) \right] \quad (5)$$

where $U = u_a \sqrt{6N}/2$ is a reduced dimensionless interaction parameter. C depends explicitly on the perpendicular size L of the available volume V . It is a function with normal behaviour and in the limit $L \rightarrow \infty$, C goes to V expressing the fact that the huge size of the available volume in this limit over dominates the effects happening at the neighbourhood of the surface.

Other characteristic properties are the density profile and the size of the coil. The density profile ρ is defined as the density of monomers at any point \mathbf{R} and is a function of the absolute value of the component z of \mathbf{R} along the perpendicular axis. It is given by

$$\rho(Z, U, L) = \int D[\mathbf{R}(s)] P[\mathbf{R}(s)] \int_0^{Nl} ds \delta[\mathbf{R}(s) - \mathbf{R}] \left(\int D[\mathbf{R}(s)] P[\mathbf{R}(s)] \right)^{-1} \quad (6)$$

with $Z = |z| \sqrt{6}/l \sqrt{N}$ a reduced dimensionless distance. The mean end to end square distance, which varies as the square of the size of the coil, is given by

$$\langle [\mathbf{R}(N) - \mathbf{R}(0)]^2 \rangle = \int D[\mathbf{R}(s)] P[\mathbf{R}(s)] [\mathbf{R}(N) - \mathbf{R}(0)]^2 \left(\int D[\mathbf{R}(s)] P[\mathbf{R}(s)] \right)^{-1}. \quad (7)$$

In a similar fashion as C , the density profile $\rho(Z, U, L)$ and the second moment $\langle [\mathbf{R}(N) - \mathbf{R}(0)]^2 \rangle$ can be found. Their final expressions are given by

$$\rho(Z, U, L) = \rho_0 \left\{ \frac{1 + F_1}{1 - F_2} \right\} \quad \rho_0 = \frac{N}{V} = \rho(Z, 0, L) \quad (8a)$$

$$\langle [\mathbf{R}(N) - \mathbf{R}(0)]^2 \rangle = Nl^2 \left\{ 1 + \frac{F_3}{1 - F_2} \right\} \quad (8b)$$

with

$$\begin{aligned}
 F_1 = & -2 \frac{UZ+3}{U\sqrt{\pi}} \exp(-Z^2) + \frac{2U^2+2UZ-3}{U^2} \exp(U^2+2UZ) \operatorname{erfc}(U+Z) \\
 & + \frac{U^2(1+2Z^2)+4UZ+3}{U^2} \operatorname{erfc}(Z) + 2 \frac{UZ+2}{U\sqrt{\pi}} \exp\left(-\frac{Z^2}{4}\right) \\
 & + \frac{2}{U^2} \exp(U^2+UZ) \operatorname{erfc}\left(U+\frac{Z}{2}\right) - \frac{U^2(2+Z^2)+2UZ+2}{U^2} \operatorname{erfc}\left(\frac{Z}{2}\right) \quad (9a)
 \end{aligned}$$

$$\begin{aligned}
 F_3 = & \frac{2L\sqrt{N}}{3L\sqrt{6}} \left[\frac{2}{U^3} - \frac{2}{U^3} \exp(U^2) \operatorname{erfc}(U) - \frac{4}{U^2\sqrt{\pi}} + \frac{1}{U} \right. \\
 & \left. + \frac{1}{U} \exp(U^2) \operatorname{erfc}(U) - \frac{2}{3\sqrt{\pi}} \right] \quad (9b)
 \end{aligned}$$

and F_2 taken from (5).

A comparison with known results at special limits provides a check on the correctness of the present results. The numerator for example, of (8a) agrees with that found by Eisenriegler [7] who employed the magnetic field model [6] to study an impenetrable surface in the limit $L \rightarrow \infty$. For $U \rightarrow \infty$, $\rho(Z, U, L)$ is also the same as that given in the treatment of the adsorption of a free chain from an impenetrable surface [10] by means of the Edwards model [11] and the ground state approximation of de Gennes [1]. The results of the impenetrable surface can be taken from the present results of a penetrable surface if the proper normalization condition is applied which consists of a multiplication of the space variable Z by 2 and of C , (5), by 1/2. The inclusion of the size L of the available volume describes the behaviour of the chain in a complete manner, ensuring for example that the law of conservation of mass is obeyed, according to which

$$\int_{\text{all space}} \rho \, dV = N. \quad (10)$$

A study of the whole range of U from negative (attractions) to positive (repulsions) values is possible in this way. For repulsions, ρ and $\langle [\mathbf{R}(N) - \mathbf{R}(0)]^2 \rangle$ behave as predicted. Monomers are pushed away from the surface so that ρ is reduced to smaller values than those of ρ_0 for $Z \rightarrow 0$, while it obtains slightly bigger values than ρ_0 at large Z , because of the law of conservation of mass. In this regime the dependence on L is negligible. For $U \rightarrow \infty$, the density on the surface tends to zero and its graph as a function of Z , figure 1, is of the same structure as that found experimentally by Ausserre *et al* [8, 9].

$\langle [\mathbf{R}(N) - \mathbf{R}(0)]^2 \rangle$ for positive values of U tends to the value Nl^2 of the free chain, as shown in figure 4. For attractions (negative U) though, the study of ρ and $\langle [\mathbf{R}(N) - \mathbf{R}(0)]^2 \rangle$ reveals some new features in the behaviour of the chain, arising mainly from the inclusion in the treatment of the size L of the available space. We plot eight different graphs of ρ as a function of Z for two different values of L in figure 2. Due to the conservation of mass, in all graphs the area above $\rho/\rho_0 = 1$, representing the mass accumulated at the neighbourhood of the surface, is equal to the area between $\rho/\rho_0 = 1$ and the graph below it representing the mass reduction from the space further away from the surface. For small negative values of U (slight attractions) the probability of the chain being closer to the surface is increased. Equivalently, in an ensemble of

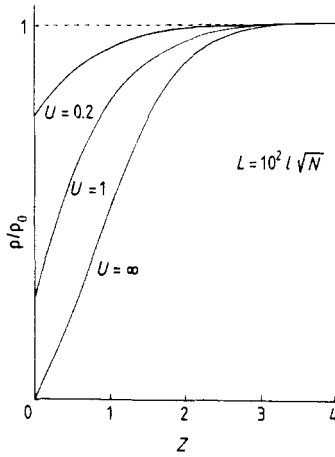


Figure 1. The dependence of the density profile ρ as a function of Z for various positive U 's (repulsions).

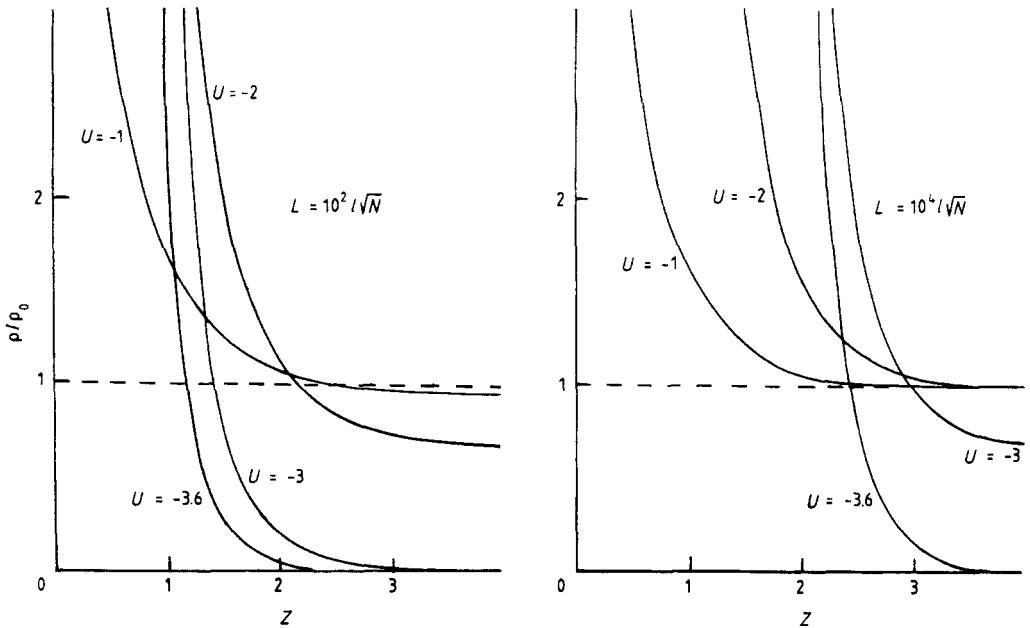


Figure 2. For attractions (U negative) there are critical values of U where the widths of the distributions start decreasing.

many chains an increase in the concentration of chains at the surface takes place because more chains, mainly unperturbed, approach the surface. Increasing the attractions, the accumulation of unperturbed chains increases and this is realized by the wider values which the distribution obtains at the significant area above $\rho/\rho_0 = 1$. This continues until a critical value of U is reached. For stronger attractions than this critical value, a reduction of the width of the distribution is observed. This is the onset of the alteration of the conformation of the chains themselves. The strong attractions

in this regime make the chains more compact, changing the three-dimensional objects to two-dimensional adsorbed chains [4].

More illustrative of the phenomenon is the plot of ρ as a function of U for various Z 's as it is shown in figure 3. When the attractions increase (decreasing U) we observe

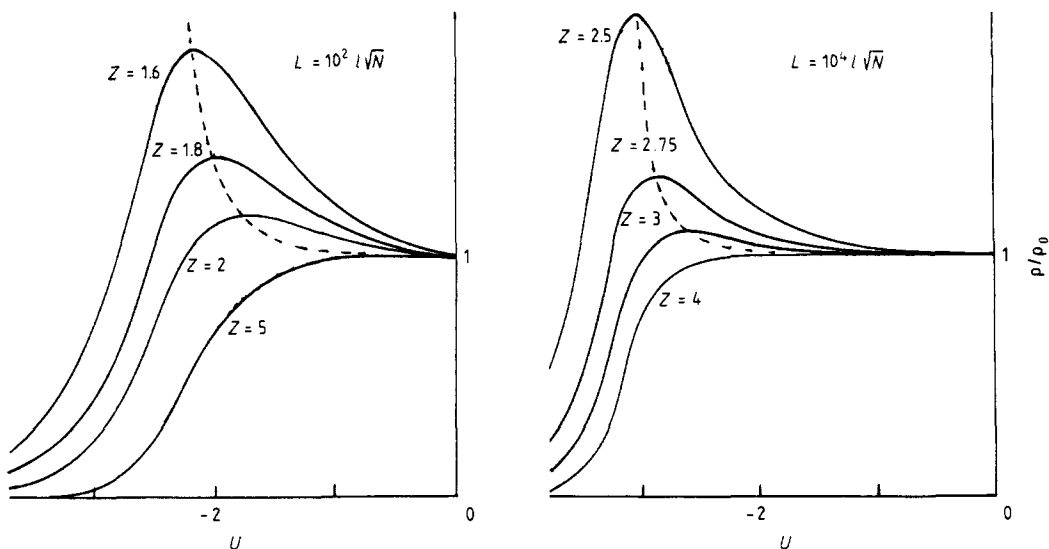


Figure 3. The distributions as functions of U obtain maxima at the points where the onset of the change of the dimensions of the coils take place.

an initial increase in the density ρ because of the accumulation of chains. ρ passes through a maximum and then decreases because of the change of the three-dimensional chains to the more compact two-dimensional adsorbed chains. For smaller Z 's ρ is larger indicating that the adsorbed layer is denser closer to the surface. This explanation is strongly supported by the U dependence of $\langle [\mathbf{R}(N) - \mathbf{R}(0)]^2 \rangle$, figure 4. Indeed, we see from this figure that by decreasing U we go from three-dimensional behaviour of

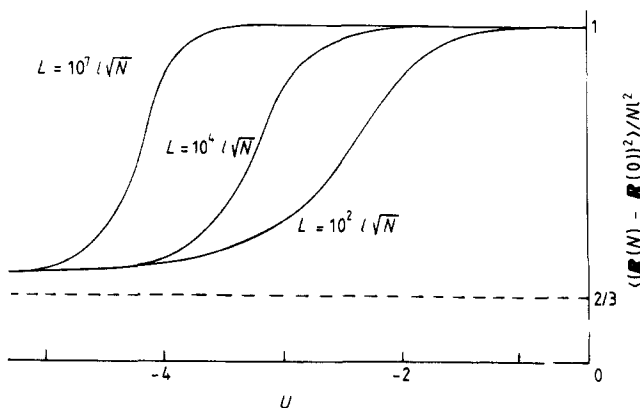


Figure 4. The critical values of U for each L , about which the transitions from three-dimensional behaviour of the coil to two-dimensional take place, are the same as those where the distributions obtain maxima.

the chain with $\langle [\mathbf{R}(N) - \mathbf{R}(0)]^2 \rangle \approx Nl^2$ to two-dimensional behaviour with $\langle [\mathbf{R}(N) - \mathbf{R}(0)]^2 \rangle \approx \frac{2}{3}Nl^2$. The critical values of U about -2 for $L = 10^2 l\sqrt{N}$, and U about -3 for $L = 10^4 l\sqrt{N}$, where these transitions take place, are the same with the values of U for each L ; at this point the beginning of the reduction of the width of the distribution ρ takes place.

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