Macromolecules 1991, *24*, 6754-6758

On the Density Profile of Ring Chains Interacting with a Surface

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Received March 26, 1991; Revised Manuscript Received July 8, 1991

ABSTRACT: The density profile of ring chains interacting with a surface and free to belong in a space of size L perpendicular to the surface is found as a function of the intensity of the polymer-surface interactions and the molecular weight of the chains. We work in the frame of the continuous model, and exact analytic expressions are given by means of integral equations and Laplace transforms. The density profiles of rings for the adsorption and depletion cases are described and compared with those of linear chains of the same molecular weight under similar conditions. The ring polymers which have more compact structures due to the closure of their chains are found to be more affected by the surface.

1. Introduction

The study of the behavior of polymers interacting with surfaces is of large technological interest because it finds application in numerous fields like the stability of colloids after adsorption of polymers,[1] chromatography involving polymers,[2] and adhesion of different polymeric phases,[3] the strength of which depends on the amount of interpenetration of the different species. The study of chains interacting with a surface also has theoretical interest because of the anisotropy due to the presence of the surface, which alters the isotropic properties of the chains in the bulk.[4-7] Both experimental methods based on the surface quasi-elastic light scattering,[8] the evanescent-wave-induced fluorescence,[9] and the small-angle neutron scattering[10] techniques and theoretical methods by means of Lattice models,[11] the Magnetic model,[4] and the continuous model[5,7] have been employed for the study of such systems, and the majority of these works mainly concern the adsorption of linear polymers but not chains of other architectures like rings, stars, or combs. Though the solution properties of polymer of various architectures like the average size of their coils, their osmotic pressure, sedimentation coefficients, and intrinsic viscosities have received much attention,[12] their description near an interface has only recently been started.[13-15] Ring polymers are a special class of chains with a different architecture than that of linear chains, and a theoretical estimate of their sedimentation coefficient and intrinsic viscosity has been used for the description of the molecular parameters of the circular DNA.[16] Concerning the adsorption of rings, a mean-field, numerical lattice approach[13] has been used and slightly higher adsorption has been determined compared to that of linear chains. The closure of the chains of the rings yields more compact structures which give a higher density of coils than the corresponding density of linear chains. This leads to smaller second virial coefficients of osmotic pressure,[17] smaller limiting viscosity numbers,[16,18] and larger adsorption at a surface.[15] In a good solvent the excluded-volume effects expand the chains and reduce their adsorption; the effects of this expansion and reduction of adsorbance are expected to be larger in rings than in linear chains because of the higher density of the former. A systematic description of the density profiles of ring chains interacting with a surface is missing from the literature, and we present here such a systematic study based on techniques which we have applied recently on linear chains[7] providing at the same time a challenge to experimentalists to determine density profiles of polymers of various architectures. In this paper we deal with ideal chains interacting with the surface as a first step toward studying excluded-volume and concentration effects, keeping in mind that at least two real situations can be described by this study: the Θ state of the chains where excluded-volume effects are absent and more dense systems where intra- and interchain excluded-volume effects cancel.

Free ring chains interacting with a surface may belong either to the surface region or to the bulk. The surface, penetrable or impenetrable, can be represented by the XY plane while the perpendicular size of the available volume V is extended to $L/2$ in each side for the penetrable or to $L/2$ in one side for the impenetrable plane (Figure 1). The chain is made of N units each of an effective length l, and in the continuous model it is represented with a continuous line of length Nl. The probability of any configuration $\mathbf{R}(s)$ $(0 \le s \le Nl)$ is given by

$$P[\mathbf{R}(s)] = P_0[\mathbf{R}(s)] \exp(-u_a \int_0^{Nl} ds\, \delta[z(s)]) \times \delta[\mathbf{R}(Nl)-\mathbf{R}(0)] \quad (1.1)$$

where

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

is the probability of the noninteracting ideal chain representing a connectivity term, while the exponential term of eq 1.1, with u_a the binary cluster integral, describes the interactions between the monomers and the surface.[5,7,19] The properties of the rings are taken from those of the linear chains if we held the two ends of the chain together. The last δ function of eq 1.1 brings the two ends of the chain together and describes this closure. $P[\mathbf{R}(s)]$ is the basic quantity, and the properties of the system can be found as averages over $P[\mathbf{R}(s)]$. In the continuous-line representation the averages over all position vectors of the points of the chain are equivalent to path integrals,[20] and a property $X[\mathbf{R}(s)]$ depending on the configuration $\mathbf{R}(s)$ takes the average value

$$X = \int D[\mathbf{R}(s)]\, P[\mathbf{R}(s)]\, X[\mathbf{R}(s)] / \int D[\mathbf{R}(s)]\, P[\mathbf{R}(s)] \quad (1.2)$$

2. Total Number C_r of Weighted Configurations

The total number of configurations of the ensemble of n chains noninteracting among themselves is equal to the nth power of the total number C_r of weighted configurations of a single chain given by

$$C_r = \int D[\mathbf{R}(s)]\, P[\mathbf{R}(s)] \quad (2.1)$$

and its study is the first step toward understanding the

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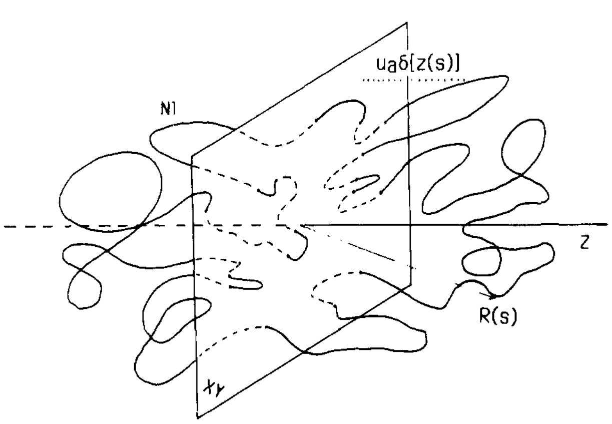


Figure 1. Ring polymer chain of length Nl interacting with a penetrable XY plane via a potential of the form $u_a\delta[z(s)]$.

behavior of ring chains interacting with the surface. From the expansion of eq 2.1 in powers of u_a it is seen that C_r can be written as

$$C_r = \left(\frac{3}{2\pi l^2 N}\right)^{3/2} V\left[1 - \frac{u_a l N}{L} + \frac{u_a{}^2 l^2 N}{L}\left(\frac{3}{2\pi l^2 N}\right)^{1/2}\int_0^N \mathrm{d}i\, f(N-i,N)\right] \quad (2.2)$$

where the function $f(x,N)$ obeys the integral equation

$$f(x,N) = \int_0^x \mathrm{d}j \frac{1}{[j(N-j)]^{1/2}} - u_a\left(\frac{3}{2\pi}\right)^{1/2}\int_0^x \mathrm{d}j \frac{1}{\sqrt{j} f(x-j,N)} \quad (2.3)$$

and can be found by means of Laplace transforms. The V term comes from the integration of the position of the last point of the chain over the whole volume V, and the $1/L$ factor ($L \gg l\sqrt{N}$) is due to the action of the δ function which sticks a chain point at the surface and prevents it from belonging to any point along the z axis. The final expression of C_r is

$$C_r = \left(\frac{3}{2\pi l^2 N}\right)^{3/2} V[1 - F_{2r}(U)] \quad \text{with } F_{2r}(U) = \frac{l(N\pi)^{1/2}}{L\sqrt{6}} \times [\,1 - \exp(U^2)\ \mathrm{erfc}\,(U)],\quad U = \frac{u_a(6N)^{1/2}}{2} \quad (2.4)$$

where U is a reduced dimensionless interaction parameter and the prefactor $(3/2\pi l^2 N)^{3/2}V$ is the number of configurations of a free chain in the absence of the surface. Equation 2.4 describes the case with the penetrable surface, but it can also give C_r of an impenetrable surface if the impenetrability of the surface is achieved by means of the reflecting boundary conditions.[19] The conversion to the impenetrable surface can be done after the adjustment of the normalization constant by multiplying C_r of eq 2.4 by $^1/_2$. For $U = 0$, $F_{2r} = 0$ and the ideal behavior of the chain is recovered. F_{2r} is a normal increasing function of U, negative for $U < 0$ and positive for $U > 0$, and for $U \rightarrow -\infty$, $F_{2r} \rightarrow -\infty$. C_r therefore is larger for larger attractions at smaller negative values of U, and for $U \rightarrow -\infty$ it obtains hugh values. This happens because larger attractions cause a larger gathering of chains at the surface area and an increase of the weights of the configurations of the adsorbed chains. Two different behaviors of the chains can be realized, that of adsorbed chains at attractions (negative values of U) and that of desorbed chains for positive values of U. Of interest is the plot of $(3/2\pi l^2 N)^{3/2}(V/C_r) = 1/(1 - F_{2r})$ as a function of U given in Figure 2 from which a first physical insight to the macroscopic behavior of the chain is obtained: the two distinct states of the adsorption and the repulsion of chains are clearly observed as the two limiting horizontal parts of the S-shaped curves for $U \rightarrow -\infty$ and $U \rightarrow 0$, respectively. Further description of the two states will be given later in the section, based on the behavior of the density profile $\rho_r(z)$. C_r depends also through F_{2r} on the perpendicular size L of the available volume V ($L \gg l\sqrt{N}$), and the following physical insight can be obtained from this dependence. For attractions (U negative) where F_{2r} is negative, the large C_r decreases with L and this is because larger L means larger freedom and larger chances for the chains to be away from the surface missing so the large weights of the adsorbed chains. For repulsions (U positive) where F_{2r} is positive, the small C_r increases with L, and this dependence is also expected since the chains are away from the surface and behave almost ideally, increasing their numbers of configurations in larger available spaces. For $U \rightarrow \infty$, $F_{2r} \rightarrow l(\pi N)^{1/2}/\sqrt{6}L$ and $C_r = (3/2\pi l^2 N)^{3/2} V[1 - l(\pi N)^{1/2}/\sqrt{6}L]$ obtains slightly smaller values than that of the ideal chain because of the confinement. This small reduction disappears as $L \rightarrow \infty$.

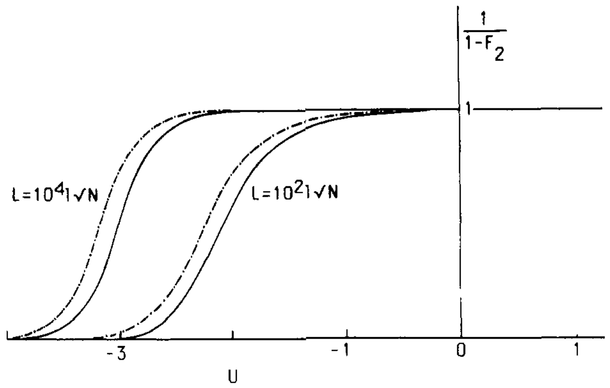


Figure 2. Function $1/(1-F_2)$ as function of U for ring (—) and for linear (- • -).

C_r has structure and behavior similar to that of the linear chains[7] (dotted lines in Figure 2). In Figure 2 two sets of plots are given for linear and ring chains for two different values of L. We see that $1 - F_2$ of rings is larger than that of linear chains which means that the compactness of the rings coming from their closure has as a result the larger influence on them of the attractions of the interacting surface. For repulsions the factors $1 - F_2$ go to the limits of almost free chains which is slightly larger for rings.

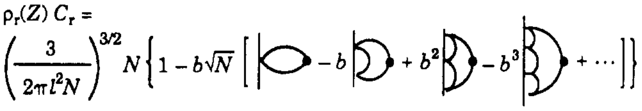
3. Density Profile

The density profile $\rho_r(\mathbf{R})$ of interacting nonlocalized rings is defined as the density of the monomers of the chain at any point $\mathbf{R}$. It has the symmetry of the system which is translational invariant along the XY plane, and it is thus a function of the absolute value $|z|$ of the z component of $\mathbf{R}$ along the axis perpendicular to the plane (Figure 1). For n chains noninteracting among themselves the problem is separable and $\rho_r(z)$ can be determined from the behavior of a single chain. It is given by

$$\rho_r(z) = \frac{n}{C_r}\int D[\mathbf{R}(s)]\, P[\mathbf{R}(s)] \int_0^{Nl} \mathrm{d}s\, \delta[\mathbf{R}(s) - \mathbf{R}] \quad (3.1)$$

where the denominator of eq 3.1 is the already found and analyzed configurational partition function which expresses the total number of weighted configurations.

The density profile $\rho_r(z)$ of rings can be found after the evaluation of the numerator of eq 3.1 as well. Expanding the term $\exp\{-u_a\int_0^{Nl}\mathrm{d}s\, \delta[z(s)]\}$ of the numerator of this equation, the produced diagrams are characterized by the number of bridges they have and a dot which represents the point of the study of the density



(3.2)

with $b = u_a\sqrt{6}/2\sqrt{\pi}$. The diagram with i bridge is equal to

$$= \int_0^N dx_1 \int_0^{N-x_1} dx_2 \ldots \int_0^{N-x_1-x_2-\cdots x_{i-1}} dx_i \times \frac{\exp\left[-\frac{k^2}{4}\left(\frac{1}{x_1} + \frac{1}{N - x_1 - x_2 - \cdots x_i}\right)\right]}{\sqrt{x_1 x_2 \cdots x_i (N - x_1 - x_2 - \cdots x_i)}} \quad (3.3)$$

where $k = |z|\sqrt{6}/l$. The Laplace transforms of the terms of eq 3.2 can then be summed, and finally eq 3.2 can be written by means of the inverse Laplace transform L_s^{-1} as

$$\rho_r(z)\,C_r = \left(\frac{3}{2\pi l^2 N}\right)^{3/2} N\left[1 - b\sqrt{N} L_s^{-1}\left\{\frac{\pi \exp(-2k\sqrt{s})}{\sqrt{s}(\sqrt{s} + b\sqrt{\pi})}\right\}\right] \quad (3.4)$$

The inverse Laplace transform of eq 3.4 is trivial, and the final expression of $\rho_r(z)$ becomes

$$\rho_r(Z) = \rho_0 \frac{1 - U\sqrt{\pi}\,\exp(U^2 + 2UZ)\,\mathrm{erfc}\,(U + Z)}{1 - \frac{l(N\pi)^{1/2}}{L\sqrt{6}}[1 - \exp(U^2)\,\mathrm{erfc}\,(U)]},$$

$$Z = \frac{|z|\sqrt{6}}{l\sqrt{N}} \quad (3.5)$$

where Z is a reduced positive distance from the surface and $\rho_0 = nN/V$ is the homogeneous density of the solution obtained for $U = 0$. Though eq 3.5 as well as eq 2.4 can also be taken from the three- and two-point propagators[21] of the linear chain by forcing the two ends of the chain to coincide, the method of diagrams employed here attacks straightforwardly the properties of the ring which are more simply determined because of the symmetry of the ring. For the impenetrable surface when the impenetrability is achieved by the reflecting boundary conditions,[19] eq 3.5 must be multiplied by 2, making $\rho_r(Z)$ of the impenetrable case double to that of the penetrable case. $\rho_r(Z)$ depends on both U and L, and it obeys the law of conservation of mass according to which the integral of $\rho_r(Z)$ over the whole volume

$$\int_{\text{all space}} \rho_r(Z)\,dV = nN \quad (3.6)$$

is equal to the total mass nN of all the n chains. This is the reason that in all graphs of $\rho_r(Z)$ the areas between the $\rho/\rho_0 = 1$ line and the parts of the graphs above it representing an excess of mass are equal to the areas between $\rho/\rho_0 = 1$ and the parts of the graphs below it representing a reduction of mass from the equilibrium homogeneous distribution (Figures 3a and 5a). For $U = 0$ the surface is absent and $\rho_r = \rho_0$ as expected since in the absence of the surface the homogeneity of the solution is spread out in the whole space.

A. The Case of Adsorption. For negative U's (attractions), adsorption of chains takes place and adsorption density profiles $\rho_r(Z)$ taking larger values at the vicinity of the surface are observed (Figure 3). In the strong adsorption limit, $U \rightarrow -\infty$, the form of the density profile becomes a δ function, $\lim_{U\rightarrow-\infty} \rho_r(Z,U) = \delta(Z)$ and the chain lies flat on the surface. Notice from the graphs of Figure 3a that the amount of mass taken from the solution represented by the areas between the $\rho/\rho_0 = 1$ line and the parts of the graphs below it, being equal to the excess amount of mass gathered at the vicinity of the surface, is larger for larger attractions at more negative U's. The form though of the profiles near the surface is not monotonous, indicating a change in the behavior of the interacting chains. Increasing the attractions (decreasing U from $U = -1$ to $U = -1.8$ for the example of the ring of Figure 3a), wider distributions are observed above the $\rho/\rho_0 = 1$ line, which means that more chains are gathered at the surface area mainly unperturbed. Increasing further the attractions (decreasing U), going, for example, to $U = -3$ of the ring case of Figure 3a, a decrease of the size of the adsorbed layer occurs again, though the number of chains is larger and this is because of the change of the macroscopic behavior of the chains themselves. From a three-dimensional character of the desorbed chains we go to a two-dimensional character of adsorbed chains which are denser, giving smaller width to the adsorbed layer. In this finite system the existence of a critical value of U for

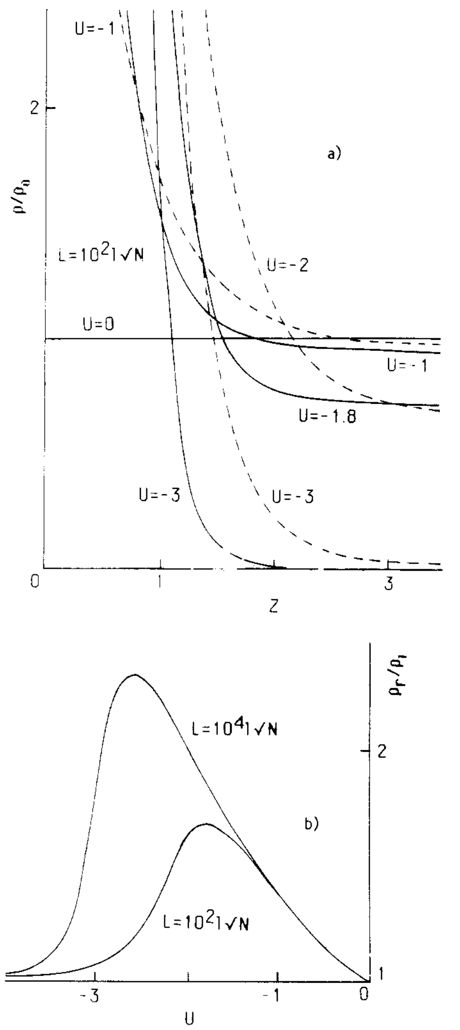


Figure 3. (a) Critical values of the adsorption parameter U for attractions (U negative) for ring chains (—) as for linear chains (- -): −1.8 for the ring and −2 for the linear chain where the widths of the distributions start decreasing. (b) Ratio ρ_r/ρ_l of densities of ring and linear chains, on the surface (Z = 0) for attractions when $L = 10^2 l\sqrt{N}$ and $L = 10^4 l\sqrt{N}$. These ratios become maximum between the critical energies of adsorption, closer to that of rings with the stronger adsorption.

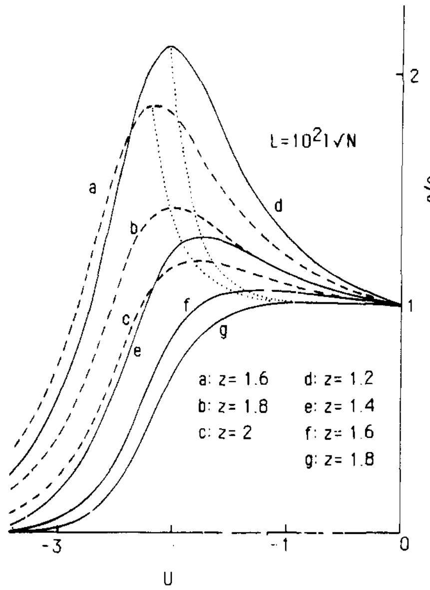


Figure 4. Density ρ/ρ_0 as function of U for attractions ($U < 0$) for ring (—) and linear (- -) chains.

each L, where the change of the character of the chains takes place,[7] is further supported from the plot of $\rho_r(Z)$ as a function of U (Figure 4). Following the density profile $\rho_r(Z)$ as a function of U, we see that on decreasing U (increasing the attractions) it increases, reaches a maximum, and then starts decreasing again though the number of chains in the vicinity of the surface increases and this is because the character of the adsorbed chains begins to change into a two-dimensional one for energies more attractive than the critical one. The density profile $\rho_r(Z)$ of rings shows a behavior similar to that of linear chains;[7] see Figures 2–5. Similar phenomena happen with linear chains, the difference being now that for the case of rings the change to the two-dimensional character starts earlier at smaller attraction, supporting the general rule that the influence of the surface is larger on rings than on linear chains. In Figure 3b we show the ratio ρ_r/ρ_l of the densities of the ring and linear chains for attractions at $Z = 0$. The density of the ring polymer on the surface is larger than that of the linear polymer in accordance with the rule that ring chains are more affected by the surface interactions. Maximum values of the ratio ρ_r/ρ_l are observed between the critical energies of adsorption of the chains at the following values of U: -1.8 (-2) and -2.6 (-3) for rings (linears) and for $L = 10^2 l\sqrt{N}$ and $L = 10^4 l\sqrt{N}$, respectively, and are closer to that of rings with the stronger adsorption. Reduction of the ratio ρ_r/ρ_l for more attractive energies is observed, tending to 1 for $U \rightarrow -\infty$ because all the monomers are adsorbed at the surface for both cases (for both ring and linear polymers in the limit of $U \rightarrow -\infty$, ρ_r becomes the Dirac δ function). For less attractive energies than the critical energies the ratio ρ_r/ρ_l is also reduced, going to 1 for $U \rightarrow 0$ where the two densities ρ_r and ρ_l become equal to ρ_0. According to the results of the present work (Figure 3a), rings decay more rapidly than linear chains. Comparing these results with previous results, we see that though they are of a decaying nature they are not of the simple form of an exponential decay.[22] Notice also that for larger L the chain has larger freedom and larger attractions are necessary for the adsorption.

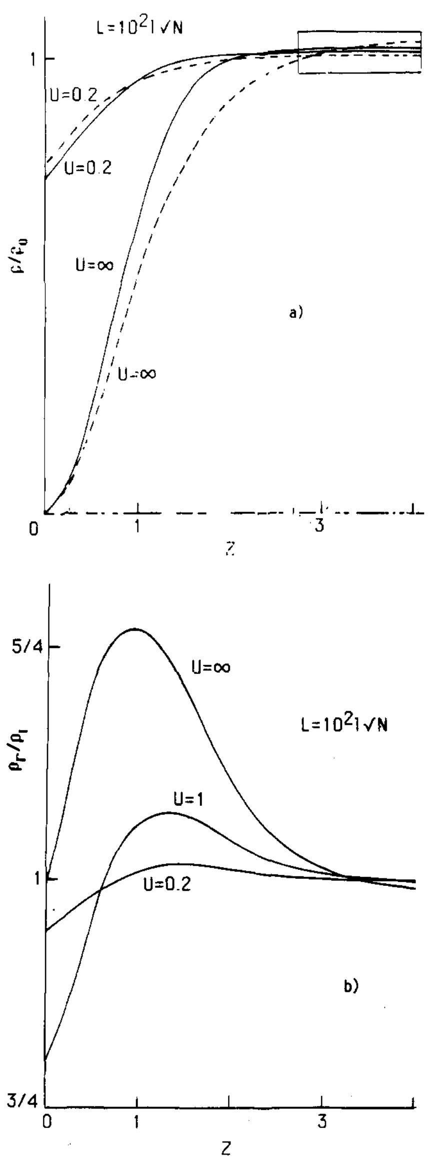


Figure 5. Density profile ρ/ρ_0 as function of Z for ring (—) and linear (- -) chains for repulsions (positive U). For a better representation the perpendicular distances between the graphs in the window have been enlarged; they all end above the $\rho/\rho_0 = 1$ line. (b) Ratio $\rho_r(Z)/\rho_l(Z)$ of densities of ring and linear chains as a function of Z for repulsions.

B. The Case of Depletion. For positive U the repulsions between the surface and the monomers lead to depletion layers with values of $\rho_r(Z)$ at the vicinity of the surface smaller than the average bulk density (Figure 5a). Increasing the repulsions, the mass near the surface decreases, and as $U \rightarrow \infty$ the density on the surface $\rho_r(Z=0)$ tends to zero and no monomeric units remain on the surface. As U increases more mass is pushed away from the surface and so the graphs are steeper and end up at larger limits above $\rho/\rho_0 = 1$. In the strong depletion limit the density profile becomes

$$\lim_{U \rightarrow \infty} \rho_r(Z,U) = \rho_0 \frac{1 - \exp(-Z^2)}{1 - \dfrac{l(\pi N)^{1/2}}{L\sqrt{6}}} \qquad (3.7)$$

Of interest is the comparison of ring and linear chains[7] based on the graphs of their density profiles (Figure 5), which provides a physical insight to the macroscopic behavior of these two macromolecules. For the same repulsions at the same values of positive U for small Z when the chains are near the surface, the density of rings is smaller than the corresponding density of linear chains, $\rho_r/\rho_l < 1$, and this is in accord with the observation that the effects of the surface are larger on rings than on linear chains of the same molecular weight because of the denser structure of rings. The larger pushing effects on rings lead larger masses of rings away from the surface, making their graphs close to the surface steeper than those of the linear chains. Due to the conservation of mass, eq 3.6, these large masses are taken to larger distances from the surface, making the densities of rings larger at larger distances. This inversion has as a result the crossing of the graphs of the density profiles of rings and linear chains (Figure 5a). The crossing with $\rho_r/\rho_l = 1$ moves to smaller distances as U increases and ends at $Z = 0$ for $U \to \infty$ (Figure 5b).

4. Conclusions

Density profiles of a ring, in Θ state without excluded-volume interactions, but interacting with a surface, are determined and studied in the frame of the continuous model by means of exact analytic solutions. The profiles for both the adsorption and depletion cases are described and compared with those of linear chains under the same conditions. We find that the effects of the surface are larger on rings with denser structures than on linear chains, leading to larger adsorption and depletion for the former case.

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