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Chain Dimensions of a Polymer Confined between Two Interacting Plates

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ABSTRACT: The chain dimensions of a polymer confined between two plates, and interacting with them, are herein studied. The contribution of the excluded volume interaction is evaluated using the mean field theory as originated by Flory. The expansion factor perpendicular to the plate, α_z increases monotonously with the distance between the plates, D, when the polymer plate interaction, W, is repellent. However α_z decreases abruptly with increasing D when W is attractive. This transition corresponds to the conformational change between the bridge type and the loop type of conformation. The parallel component of the expansion factor, α_x decreases with increasing D when W is repellent. At the transition, α_x increases abruptly.

KEY WORDS Chain Dimension / Confined Polymer / Slit / Slab / Excluded Volume / Mean Field Theory / Adsorption /

The behavior of a polymer chain interacting with a surface is interesting not only theoretically but also for its role in such practical problems as adhesion and reinforcement. Many theoretical investigations have been carried out.[1] A polymer confined between two interacting plates has also been studied for its role in stabilization of colloidal suspension.

Segment concentration profiles and free energies of polymer chains confined between two adsorbing plates were studied by Levine, Thomlinson and Robinson[2] using a lattice model and by de Gennes[3] using a continuum model. Ishinabe[4] studied the free energies of the self-avoiding lattice chain confined between two adsorbing plates using the exact enumeration method.

The chain dimension of a polymer confined between two perfectly repellent plates has been studied in depth. Both Daoud and de Gennes[5] and Turban[6] discussed the dimensions of a confined chain using scaling arguments. Wang, Nemirovsky, and Freed[7] investigated chain dimensions using the ε expansion method. The present author derived the full dependence of the chain dimensions of a confined chain on the distance between the plates, using both the homotopy parameter expansion method[8] and the mean field theory.[9] However, few studies on the effect of polymer plate interaction on chain dimension have been carried out. Wang *et al.* studied the case of reflecting plates,[7] while we reported the mean end-to-end distance of a chain confined between two interacting plates.[10]

In this paper, we studied the full dependence of the chain dimension of a confined polymer on the distance between the plates, on the polymer surface interaction, and on the strength of the excluded volume. The polymer surface interaction was included exactly within the distribution functions of the unperturbed polymer confined between two plates. The contribution of the excluded volume interaction was introduced under the assumption that the segments were distributed uniformly in an

equivalent ellipsoid whose principal axes were proportional to the components of the mean end-to-end distance. The closed expression was obtained for expansion factors parallel and perpendicular to the plates. It predicts the transition when the polymer plate interaction is attractive.

MODEL

A model chain consists of N free rotating bonds of a unit length. The distance between the plates, D, is much larger than unity. The z axis is taken perpendicular to the plates and the x and y axes are taken parallel to the plates. The polymer chain is confined between $z=-D/2$ and $D/2$.

The probability distribution function of an unperturbed chain which starts at $\boldsymbol{R}'$ and ends at $\boldsymbol{R}$, $G_0(\boldsymbol{R}, \boldsymbol{R}'; N)$ can be decomposed as

$$G_0(\boldsymbol{R}, \boldsymbol{R}'; N) = G_{0x}(R_x; N)G_{0y}(R_y; N)G_{0z}(z, z'; N) \quad (1)$$

where R_x and R_y are the components of the end-to-end vector parallel to the plates. For an unperturbed chain, G_{0x} and G_{0y} are Gaussian functions.

As was shown in one of our previous papers,[10] we can obtain the component of distribution function perpendicular to the plates, G_{0z} as follows:

$$G_{0z}(z, z'; N)=(2/D)\{\sum_k A_k \cos(a_k z/D)\cos(a_k z'/D)\exp(-a_k^2 d) + \sum_k B_k \sin(b_k z/D)\sin(b_k z'/D)\exp(-b_k^2 d)\} \quad (2)$$

where $d=N/6D^2$. The coefficients a_k and b_k are determined by the following transcendental equations, where A_k and B_k are normalization constants:

$$\tan(a_k/2)=DW/a_k\,; \quad A_k=1/(1+\sin(a_k)/a_k) \quad (3a)$$

$$\cot(b_k/2)=-DW/b_k\,; \quad B_k=1/(1-\sin(b_k)/b_k) \quad (3b)$$

a_0 is imaginary when $DW<0$, and b_1 is imaginary when $DW<-2$. The nature of the roots, a_k and b_k was demonstrated in the same paper.[10]

The z component of the end-to-end vector $\boldsymbol{R}$ is $R_z=z-z'$. The utilizable range of z is $[-D/2+R_z, D/2]$ for $z>z'$ and $[-D/2, D/2+R_z]$ for $z<z'$. Equation 2 is averaged with respect to z. Then we get

$$G_0(\boldsymbol{R}, N)= (3/2\pi N)\exp(-3(R_x^2+R_y^2)/2N)E(d, R_z/D)/4D \quad (4)$$

where E is given as

$$E(x, y)=\{\sum_k A_k[(1-y)\cos(a_k y) + \sin(a_k(1-y))/a_k]\exp(-a_k^2 x) + \sum_k B_k[(1-y)\cos(b_k y) - \sin(b_k(1-y))/b_k]\exp(-b_k^2 x)\} /\{\sum_k A_k[(1-\cos(a_k))/a_k^2]\exp(-a_k^2 x)\} \quad (5)$$

The distribution function for the end-to-end distance of a perturbed chain is assumed to be[9]

$$G(\boldsymbol{R}, N)=G_0(\boldsymbol{R}, N)\exp(-vZ_2(\boldsymbol{R})) \quad (6)$$

where Z_2 is the number of two-body contacts between segments and v is the excluded volume of a segment. As in another of our previous papers,[9] Z_2 is evaluated assuming that the segments are distributed uniformly in an equivalent ellipsoid, whose principal axes are proportional to R_x, R_y, and R_z respectively. We can then obtain the distribution function of a perturbed chain as

$$G(\boldsymbol{R}, N)=G_0(\boldsymbol{R}, N)\exp(-vc'N^2/R_xR_yR_z) \quad (7)$$

where c' is a numerical constant.

MEAN DIMENSION

It is impossible to calculate analytically the mean square values of R_x, R_y, and R_z using eq 7. The roots of the mean square of R_x, R_y, and R_z can be evaluated approximately fol-

lowing the procedure by Hermans and Overbeek.[11] The maximizing condition is

$$\frac{\partial}{\partial R_x}(\ln R_x + \ln G_0(\boldsymbol{R}, N) - vc'N^2/R_xR_yR_z) = 1/R_x - 3R_x/N + vc'N^2/R_x^2R_yR_z = 0 \quad (8)$$

The parallel component of linear expansion factor, $\alpha_x = R_x/(N/3)^{1/2}$ (hereafter R_x, R_y, and R_z denote the mean values) is given as

$$\alpha_x^2 - 1 = cz/\alpha_x\alpha_y\alpha_z \quad (9a)$$

where c is a numerical constant and z is the excluded volume parameter defined as $z = (3/2\pi)^{3/2}\, vN^{1/2}$. In the same manner, we get

$$\alpha_y^2 - 1 = cz/\alpha_x\alpha_y\alpha_z \quad (9b)$$

$$F(d, R_z/D) - 1 = cz/\alpha_x\alpha_y\alpha_z \quad (10)$$

where $F(x, y)$ is defined as

$$\begin{aligned} F(x,y) = y\{&\textstyle\sum_k A_k[2\cos(a_k/2)\cos(a_k(y-1/2)) \\ &+ a_k(1-y)\sin(a_ky)]\exp(-a_k^2x) \\ &+ \textstyle\sum_k B_k[-2\sin(b_k/2)\cos(b_k(y-1/2)) \\ &+ b_k(1-y)\sin(b_ky)]\exp(-b_k^2x)\} \\ &/\{\textstyle\sum_k A_k[(1-y)\cos(a_ky) \\ &+ \sin(a_k(1-y))/a_k]\exp(-a_k^2x) \\ &+ \textstyle\sum_k B_k[(1-y)\cos(b_ky) \\ &- \sin(b_k(1-y))/b_k]\exp(-b_k^2x)\} \end{aligned} \quad (11)$$

As easily seen from eq 9 and 10, $F(x, y)$ corresponds with the square of the expansion factor perpendicular to the plates. $F(x, y)$ is illustrated as a function of y in Figure 1. The solid curves represent the case where DW is infinite and the dotted curves represent the case where $DW = 0$. As y increases from 0 to 1, $F(x, y)$ increases rapidly from 0 to infinity for all values of x. The values of $F(x, y)$ are independent of DW for small x, however they depend on DW as the value of x increases. The physical interpretation is as follows. The contribution of polymer plate interaction can be disregarded when the chain dimension is much smaller than D. However the contribution becomes dominant when the chain dimension approaches D. Dot-dash curves show the case where $DW = -10$. In this case, the value of $F(x, y)$ increases monotonously with D, for small values of x and y. However, it shows a depression in the case where the values of x or y increase. Finally, it increases rapidly with y.

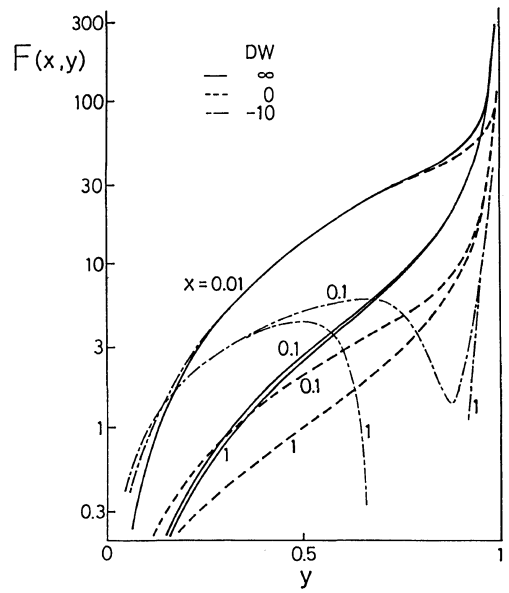

Figure 1. $F(x, y)$ as a function of y for various values of x: Solid curves, DW being infinite; dotted curves, $DW = 0$; dot-dash curves, $DW = -10$.

The values of $F(1/2, y)$ are shown as a function of y in Figure 2 for various values of DW. They increase with y for $DW > -2$. In the case where $DW < -3$, $F(1/2, y)$ has a depression, as in the case where $DW = -10$ in Figure 1. The depth increases with decreasing DW. This suggests that phase transition occurs at an appropriate negative value of DW, as explained later.

The left hand side of eq 10 corresponds to α_z^2. Linear expansion factors become $\alpha_x = \alpha_y = \alpha_z = \alpha_\infty$ as $D \to \infty$ limit. Introducing them into eq 9 gives us

$$\alpha_\infty^5 - \alpha_\infty^3 = cz \quad (12)$$

This is the well-known Flory equation for the unconfined chain.

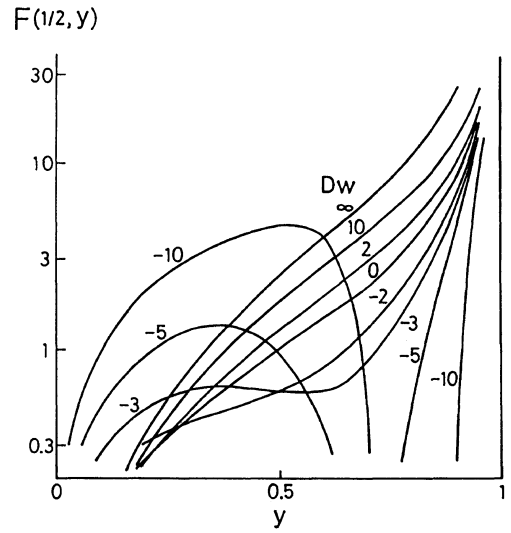

Figure 2. $F(1/2, y)$ as a function of y for various values of DW. Numerical values in the figure indicate DW.

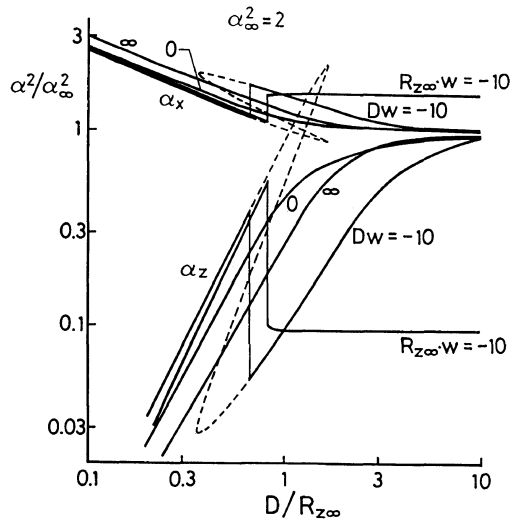

Figure 3. The reduced expansion factor as a function of DW. Numerical values indicate W. The dotted curves indicate unstable states.

Substituting eq 12 into eq 9a, we get

$$\alpha_x^4 - \alpha_x^2 = (\alpha_\infty^5 - \alpha_\infty^3)/\alpha_z \tag{13}$$

Solving eq 13 for α_z and substituting it into eq 10 we get

$$F\left(\frac{R_{z\infty}^2}{2D^2\alpha_\infty^2}, \frac{R_{z\infty}(\alpha_\infty^4 - \alpha_\infty^2)}{D(\alpha_x^4 - \alpha_x^2)}\right) = \alpha_x^2 \tag{14}$$

using the relation $R_{z\infty} = (N/3)^{1/2}\alpha_\infty$. Equation 14 can be solved numerically for α_x at given $D/R_{z\infty}$, α_∞^2, and DW, and then α_z can be obtained using eq 13.

DISCUSSION

The reduced expansion factors, $\alpha_x^2/\alpha_\infty^2$ and $\alpha_z^2/\alpha_\infty^2$ calculated using eq 13 and 14 are plotted against $D/R_{z\infty}$ in Figure 3. In this calculation, the value of α_∞^2 is fixed at 2. For small values of $D/R_{z\infty}$, the values of $\alpha_z^2/\alpha_\infty^2$ increase in proportion to D^2 with increasing $D/R_{z\infty}$, and these values increase with decreasing DW. This is interpreted as the chain ends and segments approaching and being adsorbed onto plates as the polymer plate interaction becomes more attractive. The value of $\alpha_z^2/\alpha_\infty^2$ increases monotonously towards 1 with increasing $D/R_{z\infty}$, when the polymer plate interaction is non-attractive. However, when the interaction is attractive, the values of $\alpha_z^2/\alpha_\infty^2$ decrease abruptly as the chain dimension in free space approaches almost the same as the distance between the plates. This transition is interpreted as the conformation change between the bridge type and the loop type of conformation, whose ends and segments are adsorbed onto the same plate. The loop type of conformation is more stable than the bridge type because the chain is less elongated. In the case where the value of $R_{z\infty}W$ is constant ($= -10$), the value of $\alpha_x^2/\alpha_\infty^2$ remains constant with increasing $D/R_{z\infty}$. Some parts of the chain are adsorbed onto one of the plates and remain there, while D is much larger than $R_{z\infty}$, with the chain shape then being independent of D. However, in the case where the value of DW is constant ($= -10$), the value of $\alpha_z^2/\alpha_\infty^2$ increases gradually with increasing $D/R_{z\infty}$. This is because in this case the polymer plate interaction becomes less attractive with increasing D.

The values of $\alpha_x^2/\alpha_\infty^2$ decrease in proportion to $D^{-1/2}$ with increasing $D/R_{z\infty}$ for small values of $D/R_{z\infty}$. They are less dependent on DW than

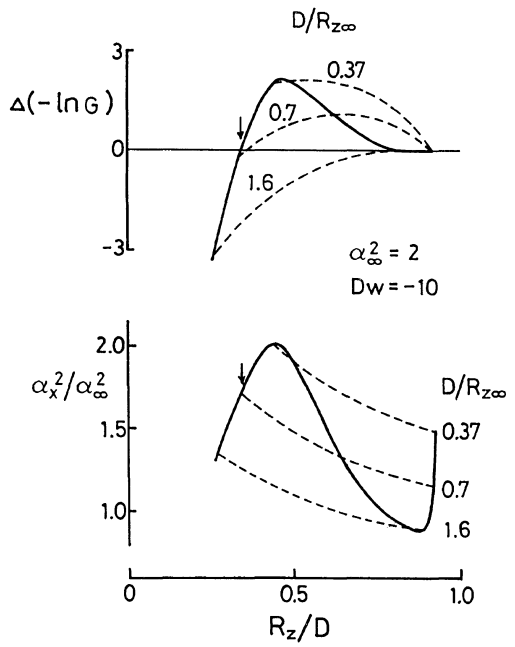

Figure 4. $\Delta(-\ln G)$ and $\alpha_x^2/\alpha_\infty^2$ as functions of R_z/D. Dotted lines represent the cases where $D/R_{z\infty}$ is constant. Numerical values in the figure represent the values of $D/R_{z\infty}$.

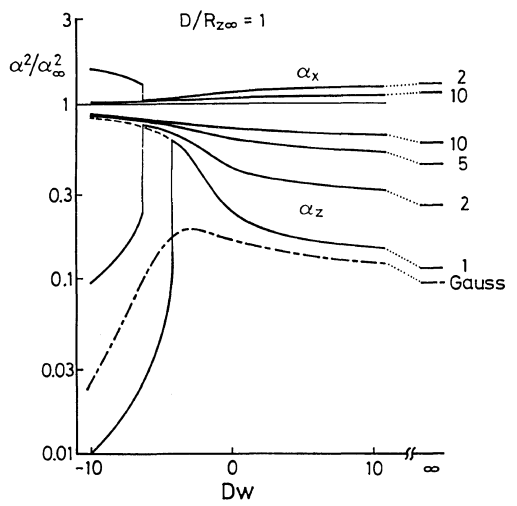

Figure 5. Reduced expansion factor as a function of DW. Numerical values on the right hand side of the figure indicate α_∞^2. The dot-dash curve represents the exact solution for an unperturbed chain.

are the z components. The transition between the bridge type and the loop type of conformation occurs when the polymer plate interaction is attractive, as shown in the case of $\alpha_z^2/\alpha_\infty^2$.

The dotted curves in Figure 3 indicate the quasi stable states calculated using eq 14. As easily seen in Figure 2, three solutions can be obtained for a suitable range of α_z^2 at given DW and $D/R_{z\infty}$. The stable branch is estimated as follows. The values of $\Delta(-\ln G)$ and $\alpha_x^2/\alpha_\infty^2$ are plotted against R_z/D in Figure 4, where the value of G is approximated by the corresponding value of the mean value of $\boldsymbol{R}$ using eq 7. The reference value of $\Delta(-\ln G)$ is the value at about $R_{z\infty}/D \simeq 0.9$. The value of $-\ln G$ corresponds to the free energy of the chain. Then, transition occurs between two points at which the values of $-\ln G$ are identical. The stable form is the one whose value of $\Delta(-\ln G)$ is negative. The dotted curves in Figure 4 indicate the lines for which $D/R_{z\infty}$ are constant. For example, the solutions are $R_z/D=0.92$, 0.65, and 0.34 for the case where $D/R_{z\infty}=0.7$. The point at $R_z/D=0.65$ is an unstable one, while the others are stable. The point at $R_z/D=0.34$ is slightly more stable than that at $R_z/D=0.92$. Then the value of $\alpha_z^2/\alpha_\infty^2$ for stable conformation can be found as $(0.34\times 0.7)^2=0.057$. The value of $D/R_{z\infty}$ at which transition between the bridge type and the loop type of conformation occurs, is slightly less than 0.7.

The values of $\alpha_z^2/\alpha_\infty^2$ and $\alpha_x^2/\alpha_\infty^2$ are plotted against DW in Figure 5, where the value of $D/R_{z\infty}$ is fixed as 1. The numbers on the right hand side in the figure indicate the values of α_∞^2. The values of $\alpha_z^2/\alpha_\infty^2$ increase with decreasing DW. This indicates that the chain segments are compressed into the central part of two plates when the polymer plate interaction is repellant, while they spread out and approach the plates as the polymer plate interaction becomes more attractive. When the polymer plate interaction is attractive, the bridge type of conformation is stable, and then the value of $\alpha_z^2/\alpha_\infty^2$ approaches 1. However, the transition between the bridge type and the loop type of conformation occurs and the value of

$\alpha_z^2/\alpha_\infty^2$ becomes very small when the polymer plate interaction becomes more attractive. Finally if the chain is adsorbed onto one of the plates, α_z may tend towards zero. In the present calculation, we assume that the segments are distributed uniformly in an equivalent ellipsoid. This assumption may be invalid when a large part of the segments are adsorbed on the plates. The contribution of the segment–segment repulsion on the plates does not take into consideration, except eq 7. Then the results for the chain confined between very strong adsorbing plates are doubtful.

As shown in Figure 5, the chain where $\alpha_\infty^2 = 1$ shows the transition. It corresponds to the unperturbed chain. The dot-dash curve in Figure 5 indicates the exact solution of the unperturbed chain. The exact solution indicates that the value of $\alpha_z^2/\alpha_\infty^2$ has a maximum, that it decreases rapidly with DW. This behavior seems crossover rather than transition. More detailed analysis is desired concerning this transition.

The values of $\alpha_x^2/\alpha_\infty^2$ decrease slightly with decreasing DW. Transition occurs when DW is negative and the value of α_∞^2 is small, as in the case of α_z^2.

CONCLUSION

In this paper we studied the chain dimension of a perturbed chain confined between two interacting plates using the mean field theory originated by Flory. Segments are assumed to be distributed uniformly in an equivalent ellipsoid whose principal axes are proportional to the component of the mean end-to-end distance. The components of expansion factors perpendicular and parallel to the plates are derived as functions of $D/R_{z\infty}$, α_∞^2, and DW. When the polymer plate interaction is attractive, transition between the bridge type and the loop type of conformation occurs, and the value of $\alpha_z^2/\alpha_\infty^2$ decreases abruptly with increasing D.

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