

The shape of a flexible polymer in a cylindrical pore

G. Morrison

Biophysics Program, Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742 and Department of Physics, University of Maryland, College Park, Maryland 20742

D. Thirumalai

Biophysics Program, Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742 and Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

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We calculate the mean end-to-end distance R of a self-avoiding polymer encapsulated in an infinitely long cylinder with radius D . A self-consistent perturbation theory is used to calculate R as a function of D for impenetrable hard walls and soft walls. In both cases, R obeys the predicted scaling behavior in the limit of large and small D . The crossover from the three-dimensional behavior ($D \rightarrow \infty$) to the fully stretched one-dimensional case ($D \rightarrow 0$) is nonmonotonic. The minimum value of R is found at $D \sim 0.46R_F$, where R_F is the Flory radius of R at $D \rightarrow \infty$. The results for soft walls map onto the hard wall case with a larger cylinder radius. © 2005 American Institute of Physics. [DOI: 10.1063/1.1903923]

I. INTRODUCTION

Beginning with the observation by Kuhn¹ that polymer coils are asymmetric even in dilute solutions, a number of studies have characterized the anisotropy of polymer chains.² Polymer molecules in good solvents, modeled using the Edwards model, are more anisotropic than Gaussian polymers because the number of ellipsoidal conformations in self-avoiding chains is far greater than spherical conformations.³ The anisotropy of polymers, which is relevant in a number of applications involving polymer dynamics,⁴ becomes even more pronounced in confined spaces. Nanopores (slits, cylinders, and gels) align the polymer coils and distort their orientations, even when the characteristic confining volume is relatively large compared to the polymer volume.^{5,6} Confinement-induced alterations in the shape of a polymer is also relevant in biological applications. For example, a newly synthesized polypeptide chain transits the ribosome through a roughly cylindrical exit tunnel. The extension is perhaps achieved by an effective stretching force⁷ $f_s \sim \alpha k_B T/D$, where T is the temperature, k_B is Boltzmann's constant, D (≈ 1 nm) is the radius of the exit tunnel, and α is a constant. The magnitude of f_s that is appropriate to the structure of the tunnel in the ribosome is between 4–10 pN, depending on α , which is large enough to unfold long stretches of proteins at low pulling speeds.⁸ Another example is the encapsulation of a protein in the roughly cylindrical cavity of the *Escherichia coli* chaperonin GroEL.⁹ In this case, substrate proteins are confined for a duration of time in a nanopore, which can enhance unfolding rates. In a very direct application, Tegenfeldt *et al.*¹⁰ have directly measured the genomic length of DNA molecules by trapping them in cylindrical nanochannels.

Motivated in part by the above observations, we consider the behavior of a self-avoiding polymer of contour

length L , confined to the interior of a cylinder of radius D . We are primarily interested in how the mean end-to-end distance R of the polymer changes as a function of D and the strength of the interaction between the cylinder and polymer. Daoud and de Gennes¹¹ obtained, using scaling arguments, R when the interaction with the cylinder is purely repulsive. As $D \rightarrow \infty$, the cylinder has no effect on the mean end-to-end distance R , which implies that $R \sim R_F \sim lN^\nu$, where l is approximately the size of one monomer, N is the number of monomers, and the Flory exponent $\nu = 3/(d+2) \approx 0.6$ in $d = 3$ dimensions. As $D \rightarrow 0$, the polymer is effectively confined to $d = 1$. In the confined environment, there are only two relevant length scales, R_F and D , so that as $D/R_F \rightarrow 0$, and using the scaling assumption, we can write¹¹

$$R \sim R_F f(R_F/D). \quad (1)$$

As $R_F/D \rightarrow \infty$, the chain is stretched in one dimension and becomes rodlike, thus resembling a one-dimensional self-avoiding walk. The scaling function $f(x)$ takes the form

$$f(x) \sim \begin{cases} 1 & x \rightarrow 0 \\ x^m & x \rightarrow \infty, \end{cases} \quad (2)$$

where the unknown exponent m is determined from the condition $R \sim N$ as $x \rightarrow \infty$, i.e., $\nu(m+1) = 1$, so that $m = 2/3$ and thus¹¹

$$R \sim lN \left(\frac{l}{D} \right)^{2/3}. \quad (3)$$

The prefactor in Eq. (3), which is a complicated function of D and the polymer-cavity interactions, is difficult to compute. In this article, we calculate R for arbitrary values of D by adapting the Edwards–Singh (ES) (Ref. 12) uniform expansion method, which has been used in a number of applications.^{5,12,13} Note that, without the inclusion of an ex-

cluded volume term, the system will converge on a one-dimensional random walk, so that $R \sim lN^{1/2}$, with no dependence on D .

The remainder of the paper is organized as follows: In Sec. II, we calculate R for a polymer confined to a cylinder with infinite polymer-cylinder repulsion. These calculations are repeated for soft walls in Sec. III, and the differences between the two systems are determined. Finally, the effect of short ranged monomer-monomer interactions is briefly described in Sec. IV.

II. HARD WALLS

A self-avoiding chain is described by the Edwards Hamiltonian¹² $\beta\mathcal{H}[\mathbf{r}(s)] = 3/2l\int_0^L ds \dot{\mathbf{r}}^2(s) + \mathcal{B}_2$, where $\mathcal{B}_2 = V_0\int_0^L\int_0^L ds ds' \delta^3[\mathbf{r}(s) - \mathbf{r}(s')]$ and V_0 is the strength of the self-avoiding interaction. Following ES,¹² we replace the true Hamiltonian by a reference Gaussian, $\beta\mathcal{H}_0 = 3/2l_1\int_0^L ds \dot{\mathbf{r}}^2(s)$, where the effective step length l_1 is determined by the ES method. We write $\beta\mathcal{H} = \beta\mathcal{H}_0 + \mathcal{B}_1 + \mathcal{B}_2$, where $\mathcal{B}_1 = 3(1/l - 1/l_1)/2\int_0^L ds \dot{\mathbf{r}}^2(s)$. We find^{5,12} $R^2 \equiv \langle \mathbf{R}^2 \rangle = \int d\mathbf{r}_0 \int d\mathbf{r}_L \int \mathcal{D}[\mathbf{r}(s)] (\mathbf{r}_L - \mathbf{r}_0)^2 \exp(-\beta\mathcal{H}[\mathbf{r}(s)]) \sim \langle \mathbf{R}^2 \rangle_0 - \Delta + O(\mathcal{B}_i^2)$, with

$$\Delta = (\langle \mathbf{R}^2 \mathcal{B}_1 \rangle_0 - \langle \mathbf{R}^2 \rangle_0 \langle \mathcal{B}_1 \rangle_0) + (\langle \mathbf{R}^2 \mathcal{B}_2 \rangle_0 - \langle \mathbf{R}^2 \rangle_0 \langle \mathcal{B}_2 \rangle_0), \quad (4)$$

and where $\langle \cdots \rangle_0$ denotes an average over the reference Hamiltonian $\beta\mathcal{H}_0$. The optimal value of l_1 is chosen to satisfy $\langle \mathbf{R}^2 \rangle \equiv \langle \mathbf{R}^2 \rangle_0$, which is possible only if $\Delta \equiv 0$. The condition $\Delta = 0$ results in a complicated self-consistent equation for l_1 . For the unconfined case, ES showed¹² that higher order terms in the \mathcal{B}_i 's merely alter the numerical coefficient of l_1 without affecting the Flory scaling laws. Thus, higher order terms will be ignored in this paper. For the remainder of the paper, all averages are taken with respect to the reference Hamiltonian \mathcal{H}_0 , so the subscripts on the brackets will be dropped. We also define $S_i \equiv \langle \mathbf{R}^2 \mathcal{B}_i \rangle - \langle \mathbf{R}^2 \rangle \langle \mathcal{B}_i \rangle$.

To calculate Δ , the Green's function for the reference Hamiltonian in a cylinder needs to be determined. Because of the infinitely repulsive polymer-cylinder interaction the Green's function vanishes at the walls of the cylinder. The resulting Green's function obeys the Heat Equation in an infinite cylinder, and the solution that satisfies the appropriate boundary conditions, in terms of the cylindrical coordinates $\mathbf{r} = (\rho, \phi, z)$, is¹⁴

$$G(\mathbf{r}_0, \mathbf{r}_L; L) = \frac{G_z(z_0, z_L)}{\pi D^2} \sum_{m=-\infty}^{\infty} \sum_{n=0}^{\infty} \cos m(\phi_L - \phi_0) \times \frac{J_m(\alpha_{mn}\rho_0/D)}{J_{m+1}(\alpha_{mn})} \frac{J_m(\alpha_{mn}\rho_L/D)}{J_{m+1}(\alpha_{mn})} e^{-\alpha_{mn}^2 l_1 L / 6D^2}, \quad (5)$$

where $G_z(z_0, z_L) = \int_{z_0}^{z_L} \mathcal{D}(z) \exp(-3/2l_1 \int_0^L ds \dot{z}^2)$, $J_m(x)$ is the m th Bessel function, and α_{mn} is its n th positive root. Using Eq. (5), $\langle \mathbf{R}^2 \rangle$ becomes

$$\langle \mathbf{R}^2 \rangle = \frac{1}{3} l L_1 + \frac{2D^2}{\mathcal{N}} \sum_n \times \left\{ \frac{1}{\alpha_{0n}^2} \left(1 - \frac{4}{\alpha_{0n}^2} \right) e^{-\alpha_{0n}^2 l_1 L / 6D^2} - \frac{1}{\alpha_{1n}^2} e^{-\alpha_{1n}^2 l_1 L / 6D^2} \right\} \equiv \frac{1}{3} l L_1 + \langle \mathbf{R}^2 \rangle_2, \quad (6)$$

where $\mathcal{N} = \sum_n \exp(-\alpha_{0n}^2 l_1 L / 6D^2) / \alpha_{0n}^2$. The transverse term of the end-to-end distance, $\langle \mathbf{R}^2 \rangle_2 = \langle x^2 \rangle + \langle y^2 \rangle$, scales as $\langle \mathbf{R}^2 \rangle_2 \sim D^2$ as $D \rightarrow 0$, implying that $\langle z^2 \rangle = l_1 L / 3 \sim D^{2/3}$ as $D \rightarrow 0$ [see Eq. (3)].

Taking a derivative of R^2 gives¹² $S_1 = l_1^2 (1/l - 1/l_1) d\langle \mathbf{R}^2 \rangle / dl_1$, and we find

$$S_1 = \frac{1}{3} l L_1^2 \left(\frac{1}{l} - \frac{1}{l_1} \right) \left\{ 1 - \frac{1}{\mathcal{N}} \sum_n \left[\left(1 - \frac{4}{\alpha_{0n}^2} - \frac{\langle \mathbf{R}^2 \rangle_2}{2D^2} \right) \times e^{-\alpha_{0n}^2 l_1 L / 6D^2} - e^{-\alpha_{1n}^2 l_1 L / 6D^2} \right] \right\}. \quad (7)$$

The second term in Eq. (4) is more complicated, but is simplified by splitting the averages into confined and unconfined terms. The unconfined z averages are calculated by completing the square in the exponent after Fourier transforming $\delta[z(s') - z(s'')]$.^{5,12} To compute S_2 we define

$$I_k(m, \{n_i\}) = \int_0^1 dx x \frac{J_k(\alpha_{kn_1} x)}{J_{k+1}(\alpha_{kn_1})} \frac{J_k(\alpha_{kn_3} x)}{J_{k+1}(\alpha_{kn_3})} \frac{J_m^2(\alpha_{mn_2} x)}{J_{m+1}^2(\alpha_{mn_2})} \text{ and} \quad (8)$$

$$E_k(m, \{n_i\}; t, t') = I_k(m, \{n_i\}) \exp \left(- \frac{l_1 L}{6D^2} [\alpha_{kn_1} t_{<} + \alpha_{mn_2} |t - t'| + \alpha_{kn_3} (1 - t_{>})] \right), \quad (9)$$

where the "time ordering" variables, $t_{<}$ and $t_{>}$, are

$$t_{<} = \begin{cases} t & t \leq t' \\ t' & t > t' \end{cases}, \quad t_{>} = \begin{cases} t' & t \leq t' \\ t & t > t' \end{cases} \quad (10)$$

with $t = s'/L$ and $t' = s''/L$. In terms of these quantities, we find

$$S_2 = \frac{2}{\mathcal{N}} \sqrt{\frac{6L^3}{\pi^3}} \frac{1}{l_1 m \{n_i\}} \int_0^1 \int_0^1 dt dt' \frac{V_0}{\sqrt{|t - t'|}} \times \left\{ - \frac{E_1(m, \{n_i\}; t, t')}{\alpha_{1n_1} \alpha_{1n_3}} + \frac{E_0(m, \{n_i\}; t, t')}{\alpha_{0n_1} \alpha_{0n_3}} \right. \\ \left. \times \left(1 - \frac{2}{\alpha_{0n_1}^2} - \frac{2}{\alpha_{0n_3}^2} - \frac{\langle \mathbf{R}^2 \rangle_2}{2D^2} - \frac{l_1 L}{6D^2} |t - t'| \right) \right\}. \quad (11)$$

In the limit $D \rightarrow \infty$, Eq. (11) converges to the Edwards-Singh self-consistent equation for the unconfined case,¹² i.e.

$$S_1 + S_2 \sim l_1^2 L \left(\frac{1}{l} - \frac{1}{l_1} \right) - 2V_0 \sqrt{\frac{6L^3}{\pi^3}} \frac{1}{l_1} = 0. \quad (12)$$

Thus, for large D , $l_1 \sim (24V_0^2 l^2 L / \pi^3)^{1/5}$ and $R \sim R_F \sim (24/\pi^3)^{1/10} (V_0 l)^{1/5} L^{3/5}$. As $D \rightarrow 0$, the ground state domi-

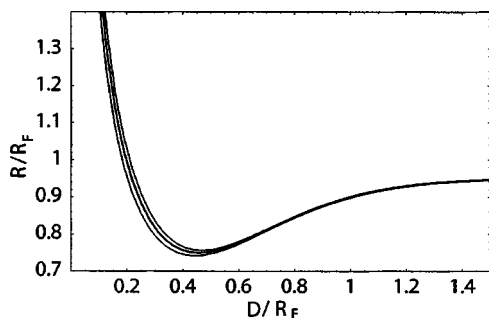


FIG. 1. Plots of R/R_F as a function of D/R_F , for various values of L and V_0 . The lowest curve corresponds to $L/l=1000$ and $V_0/l=0.1$ and the uppermost curve has $L/l=1000$ and $V_0/l=0.5$. There are two coincident curves in the middle, one with $L/l=1000$ and $V_0/l=0.1$, the other with $L/l=5000$ and $V_0/l=0.2$. The minimum for all curves occur near $D_{\min} \sim 0.46R_F$, with $R_{\min} \sim 0.75R_F$.

nates in Eq. (5). Thus, only the $(m, \{n_i\}) = (0, 0, 0, 0) \equiv \mathbf{0}$ term in Eq. (5) makes an appreciable contribution. In this case, we find that

$$S_1 + S_2 \sim \frac{1}{3} L l_1^2 \left(\frac{1}{l} - \frac{1}{l_1} \right) - \frac{16V_0}{15D^2} \sqrt{\frac{lL^5}{6\pi^3}} I_0(\mathbf{0}) = 0. \quad (13)$$

For small cylinder radius, Eq. (13) gives $l_1 \sim 0.393(V_0 l / D^2)^{2/3} L$ and $R \sim 0.627(V_0 l / D^2)^{1/3} L$, after $I_0(\mathbf{0})$ is evaluated. As predicted in Eq. (3), R has the proper scaling from $ND^{-(2/3)}$. Thus, in both the $D \rightarrow 0$ and $D \rightarrow \infty$ limits, the expected scaling form is recovered, including the predicted dependence of R on D .

To determine the behavior of R for intermediate values of the cylinder radius, the self-consistent equation ($\Delta=0$) can be numerically solved for l_1 as a function of D , and R determined using $R=(Ll_1)^{1/2}$. Figure 1 shows R/R_F for different values of L and V_0 . All of the plots are virtually identical, which implies that the only difference between the systems is the numerical value of R_F . As D/R_F exceeds unity, $R \rightarrow R_F$ from below (Fig. 1). In accordance with the scaling predictions, R/R_F increases substantially even under moderate squeezing ($D/R_F \sim 0.2$). Surprisingly, the crossover from the coil state ($D/R_F \gg 1$) to the stretched state ($D/R_F \ll 1$) is nonmonotonic. There is a minimum in $R \sim 0.75R_F$ at $D_{\min} \sim 0.46R_F$ (Fig. 1). This behavior, which has been previously observed for polymers confined to a slit,^{5,6} is due to confinement-induced anisotropy in the polymer conformations. Monte Carlo simulations by van Vliet and ten Brinke⁶ show that $R_{\min} \sim 0.8R_F$ in a slit, which shows that confinement in a cylinder squeezes the polymer somewhat more than in a slit.

III. SOFT WALLS

In real systems, the interaction between the polymer and the cylinder is not infinitely hard. It is therefore important to calculate R in the case of soft walls. By soft walls, we mean that the interaction between the polymer and the wall can be represented by a repulsive, nonhard sphere potential, which in the corresponding heat conduction problem requires radiative boundary conditions. In the hard wall case, $G(\mathbf{r}', \mathbf{r}_0; L) = G(\mathbf{r}_L, \mathbf{r}'; L) = 0$, with $\mathbf{r}' = (D, \phi, z)$. If the walls are soft then the Green's function does not vanish at the boundaries, but

satisfies¹⁵ $\partial G^S(\mathbf{r}, \mathbf{r}'; L) / \partial \rho|_{\rho=D} = C_0 G^S(\mathbf{r}, \mathbf{r}'; L)$, where $C_0 = \infty$ corresponds to the hard wall case. The Green's function in this case is

$$G^S(\mathbf{r}_L, \mathbf{r}_0; L) = \frac{G_z}{\pi D^2} \sum_{m=-\infty}^{\infty} \sum_n \frac{\beta_{mn}^2}{C^2 \gamma_{mn}^2} \times \cos m(\phi_L - \phi_0) \frac{J_m(\rho_0 \beta_{mn}/D)}{J_m(\beta_{mn})} \times \frac{J_m(\rho_L \beta_{mn}/D)}{J_m(\beta_{mn})} e^{-\beta_{mn}^2 l_1 L / 6D^2}, \quad (14)$$

where we have defined the dimensionless parameters $C = DC_0$, $\gamma_{mn} = 1 + (\beta_{mn}^2 - m^2)/C^2$, and where the β_{mn} 's are the positive roots of

$$\beta_{mn} J'_m(\beta_{mn}) + C J_m(\beta_{mn}) = 0. \quad (15)$$

When $C \gg 1$, $\beta_{mn} \sim \alpha_{mn}(1 - 1/C)$, so that $G^S \sim (1 - 1/C)G$ by a Taylor expansion. It can then be shown that, for large C , $R_{\text{soft}} \sim (1 + 4/5C)R_{\text{hard}}$. As $D \rightarrow \infty$, the results for R for the hard and soft walls coincide.

For finite C , the β_{mn} 's cannot be easily related to the α_{mn} 's, so we define

$$\mathcal{N}_S = \sum_n \frac{e^{-\beta_{0n}^2 l_1 L / 6D^2}}{\beta_{0n}^2 \gamma_{0n}^2} \quad (16)$$

$$\langle \bar{R}_2^2 \rangle = \frac{2D^2}{\mathcal{N}_S} \sum_n \frac{e^{-\beta_{0n}^2 l_1 L / 6D^2}}{\beta_{0n}^2 \gamma_{0n}^2} \times \left(1 + \frac{2}{C} - \frac{4}{\beta_{0n}^2} \right) - \frac{e^{-\beta_{1n}^2 l_1 L / 6D^2}}{\beta_{1n}^2 \gamma_{1n}^2} \left(1 + \frac{1}{C} \right)^2.$$

The \mathcal{B}_1 averages are easily computed by taking a derivative of Eq. (16), as in Eq. (7). The \mathcal{B}_2 averages are tedious to calculate, but give

$$S_2 = \frac{2}{\mathcal{N}_S} \sqrt{\frac{6L^3}{\pi^3}} \sum_{l_1 m, \{n_i\}} \frac{\beta_{mn_2}^2}{C^4 \gamma_{mn_2}^2} \int_0^1 \int_0^1 dt dt' \frac{V_0}{\sqrt{|t-t'|}} \times \left\{ -\frac{\bar{E}_1(m, \{n_i\}; t, t')}{\gamma_{1n_1}^2 \gamma_{1n_3}^2} \left(1 + \frac{1}{C} \right)^2 + \frac{\bar{E}_0(m, \{n_i\}; t, t')}{\gamma_{0n_1}^2 \gamma_{0n_3}^2} \right. \\ \left. \times \left(1 + \frac{2}{C} - \frac{2}{\beta_{0n_1}^2} - \frac{2}{\beta_{0n_3}^2} - \frac{\langle \bar{R}_2^2 \rangle}{2D^2} - \frac{l_1 L}{6D^2} |t-t'| \right) \right\}, \quad (17)$$

where $\bar{E}_k(m, \{n_i\}; t, t')$ is identical to $E_k(m, \{n_i\}; t, t')$ in Eq. (9), except that $\alpha_{mn} \rightarrow \beta_{mn}$ and $I_k(m, \{n_i\}) \rightarrow \bar{I}_k(m, \{n_i\})$, with

$$\bar{I}_k(m, \{n_i\}) = \int_0^1 dx x \frac{J_k(\beta_{kn_1} x) J_k(\beta_{kn_3} x) J_m^2(\beta_{mn_2} x)}{J_k(\beta_{kn_1}) J_k(\beta_{kn_3}) J_m^2(\beta_{mn_2})}. \quad (18)$$

As $C \rightarrow 0$, it can be shown that Eq. (15) gives $\beta_{00} \sim \sqrt{2C}$. In the small D limit, for a finite C_0 , we find S_1 converges to the first term in Eq. (13), and $S_2 \sim -8V_0/15D^2(l_1 L / 6\pi^3)^{1/2}$, implying $l_1 \sim 0.230(lV_0/D^2)^{2/3} L$ and $R \sim 0.526(V_0 l / D^2)^{1/3} L$.

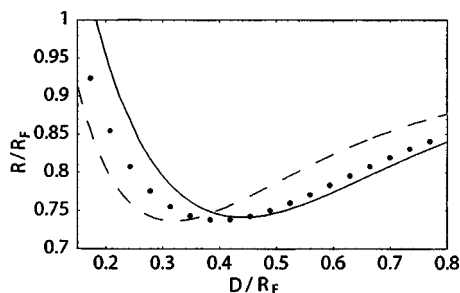


FIG. 2. Dependence of R/R_F as a function of D/R_F for various values of C_0 . The solid line corresponds to $C_0/l=10^4$, the dotted line is for $C_0/l=0.5$, and the dashed line represents $C_0/l=10^{-5}$. The values of L/l and V_0/l are 1000 and 0.1, respectively

The scaling laws are unchanged by the softness of the walls; only the numerical coefficients are altered.

The numerical solution for R as a function of D with varying C_0 shows that $R_{\min} \sim 0.75R_F$ as in the hard wall case (Fig. 2). However, as C_0 decreases, D_{\min} decreases from $\sim 0.46R_F$ to $\sim 0.32R_F$ (Fig. 2). Thus, the soft wall behaves as a hard wall with a somewhat larger effective radius, $D_{\text{eff}} = D + \delta D$. For $D \geq D_{\min}$, a shift of $\delta D \sim D_{\min}(\infty) - D_{\min}(C_0)$ causes R to coincide with the end-to-end distance in the hard wall case. If we account for this shift, we find that the values of R for both cases differ at most by 5% for $D \geq D_{\min}$. Because the scaling laws change drastically for small D , a simple shift in D is not sufficient to reduce R to the value for hard walls for $D < D_{\min}$.

IV. EFFECT OF MONOMER-MONOMER INTERACTIONS ON R

Typically, there are interactions between monomers besides the universally present excluded volume interactions. As long as these interactions are short ranged, the potential between monomers s_1 and s_2 can be modeled as $\mathcal{B}_3 = -\omega \delta[\mathbf{r}(s_2) - \mathbf{r}(s_1)]$, where $\Delta s = s_2 - s_1 > 0$. The insertion of this potential into Eq. (4) leads to $V_0 \rightarrow V_0 - \omega \delta(s' - s_1) \delta(s'' - s_2) = V_0 - \omega \delta(t - t_1) \delta(t' - t_2) / L^2$ in Eq. (11), so that for infinitely hard walls, $S_3 \sim \omega(3/8\pi^3 l_1 \Delta s)^{1/2}$ as $D \rightarrow \infty$, and $S_3 \sim 2\omega I_0(0) / D^2 (l_1 \Delta s / 6\pi^3)^{1/2}$ as $D \rightarrow 0$. Inclusion of monomer-monomer interactions for a polymer confined to soft walls yields the same scaling behavior in both limits, the only change being the numerical coefficients. Comparison of these scaling laws with Eqs. (12) and (13) shows that there is an effective shift in the strength of repulsion due to a monomer attraction, with $\Delta V_0 \sim -\omega \Delta s^{1/2} L^{-5/2}$ for small D , and $\Delta V_0 \sim -\omega \Delta s^{-1/2} L^{-3/2}$ for large D . In both regimes, the effect of S_3 is insignificant compared to S_2 for very long chains, provided that $\omega < V_0$. Short-ranged interactions between all monomers can be computed by assuming that the potential is pairwise additive. In this case, given a distribution of interactions between the i th and j th monomers ω_{ij} we find that $V_0 \rightarrow V_0 - \sum_{i,j} \omega_{ij} \delta^3[\mathbf{r}(s_i) - \mathbf{r}(s_j)]$, or $V_0 \rightarrow V_0 - \int dt dt' V_1(t, t') \delta[\mathbf{r}(t) - \mathbf{r}(t')]$, where $V_1(t, t') = \omega(s', s'') / L^2$. Because S_3 only produces a shift in V_0 , the addition of this potential will simply reproduce the results in Fig. 1 for intermediate values of D . Thus, we expect the predicted scaling form to be

unaltered for a heteropolymer confined to a cylinder, provided the effective intramolecular interaction is not strong enough to induce chain collapse.

V. CONCLUSIONS

Inspired by a number of physical situations, we have calculated the dependence of the size of a polymer molecule confined to a cylinder using the Edwards–Singh uniform expansion method. The theory presented here provides an approximate formula for the dependence of the end-to-end distance R for arbitrary values of the cylinder radius D . The major conclusions of the study are as follows.

(i) The theory yields, in the appropriate limits, the predicted scaling laws for R as a function of D . In particular, the expected scaling function is obtained in the $D \rightarrow 0$ limit. The advantage of the theory is that the numerical factors that are difficult to obtain using scaling arguments¹² have been explicitly calculated. This allows for a calculation of R for any value of D .

(ii) We have calculated R by numerically solving the self-consistent equation. Surprisingly, we found the crossover from the three-dimensional behavior ($D \rightarrow \infty$ limit) and the fully stretched limit ($D \rightarrow 0$ case) is nonmonotonic. The minimum value of $R \sim 0.75R_F$ is found at $D \sim 0.46R_F$ when the wall is infinitely hard. This is because the wall induces an orienting field that enhances the anisotropy of the polymer. This effect is greater for an encapsulated polymer in a cylinder compared to slit confinement.

(iii) A direct calculation shows that asymptotic scaling laws are the same for both hard and soft walls. Any soft wall can be replaced by an equivalent hard wall with a larger cylinder radius, provided the wall-cylinder interaction remains short ranged.

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