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General approach to polymer chains confined by interacting boundaries. II. Flow through a cylindrical nano-tube

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The Laplace-Green's function methods of Paper I are extended to describe polymers confined in interacting, impenetrable cylindrical geometries, whose treatment is far more challenging than the slit and box geometries considered in Paper I. The general methods are illustrated with calculations (as a function of the polymer-surface interaction) of the free energy of confinement, the radial density profile, and the average of the drag force in the free draining limit, quantities that will be used elsewhere to analyze experiments of Wu and co-workers involving the flow of polymers through nanopores. All these properties are evaluated by numerical inverse Laplace transforms of closed form analytical expressions, a significant savings over the traditional eigenfunction approaches. The example of the confinement free energy for a 3-arm star polymer illustrates the treatment when a closed form expression for the Laplace transform is unavailable. © 2011 American Institute of Physics. [doi:10.1063/1.3646959]

I. INTRODUCTION

Polymer chains often suffer the effects of confinement that arise from the presence of geometric constraints introduced by interacting (i.e., adsorbing or repulsive) impenetrable boundaries. Polymer confinement phenomena influence numerous properties and processes in materials science, including rubber elasticity,¹ ultrafiltration,^{2,3} and chromatography,⁴⁻⁹ and in biology (e.g., the folding of protein chains during synthesis inside ribosome channels¹⁰ or chaperons,¹¹ the packing of the genome into viral capsids,¹² the translocation through pores,¹³⁻¹⁸ and the facilitation of protein crystallization by crowding with polymers,¹⁹ etc.).

The overwhelming majority of theoretical treatments of geometrical confinement in polymer systems follows the pioneering studies of Casassa and Tagami⁸ and of Edwards and Freed,²⁰ who employ classical eigenfunction expansion techniques for solving diffusion equations, as detailed, for example, in the classic monograph by Carslaw and Jaeger²¹ for the corresponding heat flow problems. The eigenfunction expansion methods produce analytically tractable solutions when the ratio $\delta = R_G^2/L^2$ of the squares of the radius of gyration R_G of the unconfined chain and the confinement dimension L either greatly exceeds or is much less than π^{-2} and when the interacting boundaries conform to the limiting absorbing or reflecting conditions. The mathematical expressions obtained by this classical procedure, however, become unwieldy when the polymer-boundary interaction parameter c differs from the limiting values of zero or infinity and/or the reduced

confinement scale $\pi^2\delta$ becomes on the order of unity. This unwieldy behavior arises from the necessity of determining higher order terms and eigenvalues from transcendental equations in the series expansions inherent to this approach. The intermediate range of $\delta \sim O(\pi^{-2})$ and/or $c \neq 0$ or ∞ is relevant to many practical applications,²² but these mathematically challenging “crossover regimes” have not been studied in much detail.

Our recent paper²³ develops mathematical techniques designed for treating polymer confinement phenomena for the full range of c and δ . This extension is necessary for computing the static structure factor of confined polymers, even for conditions where the “ground state dominance” approximation of retaining the lowest mode suffices for estimating the free energy of confinement. Likewise, the ground state dominance approximation is shown there to provide a rather poor approximation for the partition coefficient of a chain in a nanoscale pore and for the analysis of data from a common method used by experimentalists to characterize the dimensions of nanopores.

The approach in Ref. 22 does not employ infinite series expansions in eigenfunctions and, instead, is based on the use of Green's functions and Laplace transforms that are widely applied in quantum mechanical theories and in diffusion and heat transfer problems. These alternative methods in which the Laplace inversion can be performed analytically have only been applied to polymer systems in rather limited contexts, e.g., in renormalization group calculations of the influence of excluded volume effects on polymers near penetrable and impenetrable surfaces, between parallel surfaces, and exterior to a sphere.²⁴⁻²⁷ The extension of these methods is possible because of recent advances in numerical Laplace transform techniques.²⁸

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The Laplace/Green's function methods have hitherto been used for the simplest parallel plate and box geometries, raising questions concerning their applicability to more complicated geometries, such as cylinders and spheres. These issues are addressed by the present paper that describes the calculation of quantities required to determine the critical flow rate for transport of polymer chains through nanopores, a phenomenon studied in experiments by Wu and co-workers.² Further, their recent ground breaking experiments demonstrate that chains of different architectures but the same hydrodynamic radius can be separated by varying the flow rate through the nanopores.²⁹ Since our goal here is to illustrate the power of the Laplace/Green's function methods by evaluating quantities pertinent to describing polymer transport through nanopores, the comparisons with experiment will be presented elsewhere.

The description of polymer transport through cylindrical nanopores could, in principle, be pursued by using the traditional eigenfunction expansion approach as pursued, for instance, by Wong and co-workers.²⁹ The Laplace-Green's function methods can readily be used to compute all the probabilities determined by Wong and Muthukumar for portions of the polymer to reside in various components. However, using these methods for the case of purely repulsive walls considered by them, the probabilities are expressed as sums that are sufficiently simple that no real benefit accrues with the new approaches (apart, perhaps, for situations in which a very small portion of the chain lies in a compartment and the series expansion is slowly convergent). The classic approach, however, becomes more unwieldy when the polymer-surface interaction parameter becomes finite since the treatment of general boundary conditions would incur substantial complications associated with the need to solve transcendental equations in addition to summing terms from the eigenfunction expansion. The present work, however, demonstrates that general boundary conditions are readily handled, and all the quantities required by Wong and Muthukumar emerge from a single inverse Laplace transform of a closed form analytical expression that is readily obtained numerically from routines in MATHEMATICA.³⁰ On the other hand, when computing various averages over the conformations of confined chains, substantial and computational simplifications accrue. For example, we compute the force exerted F_{hydr} on a chain dragged through an interacting cylindrical nanopore by Poiseuille flow. The Laplace transform of the force F_{hydr} with respect to the chain length is obtained analytically for arbitrary polymer-surface interactions, and only a fairly rapid numerical Laplace inversion³⁰ is necessary to determine F_{hydr} . In contrast, the traditional eigenfunction method yields a double sum of numerical integrals involving eigenfunctions containing a parameter from the solution of a transcendental equation arising from the boundary conditions at the walls of the nanopore.

Section II provides the definitions of the Laplace transforms of the density distribution within the cylindrical nanopore and the drag force on the chain. Because the chain concentration c in the nanopore is comparable to the overlap concentration c^* , the hydrodynamic interactions are somewhat screened,³¹ and the drag force is computed in the free draining limit. Section III presents the calculation of the par-

titution function and; hence, the confinement free energy for a polymer confined by impenetrable, interacting walls, while the density profile and drag force are evaluated in Sec. IV. The treatment of more complicated systems is illustrated in Sec. V by a computation of the confinement free energy for a 3-arm star polymer. These examples illustrate in more detail various situations on which the Laplace-Green's function methods offer advantages over the eigenfunction approach and others for which there is none.

A future paper will provide comparisons of the present theory with experiment. Since the analysis of the experimental data^{2,32} considers a force balance between the confinement and drag forces, the analysis only requires the evaluation of equilibrium averages. The comparisons also serve as a partial test of the use of the free draining limit.

II. DRAG FORCE ON POLYMER IN A CYLINDER

Consider a Gaussian (theta) chain confined to a cylindrical nanopore of radius R and of length L , where L far exceeds the radius of gyration R_G of the unconfined chain. The chain-surface interaction is determined by the parameter c in units of inverse length, where $c = -\infty$ for reflecting boundary conditions for which the chain density $\rho(R)$ vanishes and $c = 0$ for adsorbing boundary conditions. Confinement of the chain to the cylinder incurs a confinement free energy A_{confine} that we wish to determine as a function of $\delta = (R_G/R)^2$ and c , noting that the regime with $\delta \sim 1$ is the most relevant for comparison with the experiments by Wu and co-workers.^{2,32} The polymer is immersed in a fluid of viscosity η that is undergoing Poiseuille flow with a pressure drop per unit length of $\Delta P/\Delta x$. The flow is assumed to be free draining, so the total drag force F_{hydr} on the chain in the free draining limit is the average of the fluid velocity $v(r)$ over the chain conformations, summed over all beads in the chain. Let $\mathbf{r}(\tau)$ denote the continuous chain conformation of the confined polymer, so F_{hydr} is expressed as the average of $v[\mathbf{r}(\tau)]$,

$$F_{\text{hydr}} = -\zeta \int_0^N d\tau \langle v[\mathbf{r}(\tau)] \rangle, \quad (1)$$

where N is the chain length and ζ is the individual bead friction coefficient.

Poiseuille flow implies that the fluid velocity in the cylinder has the radial dependence,

$$v(r) = -\frac{4}{\eta} \frac{\Delta P}{\Delta x} (R^2 - r^2). \quad (2)$$

Denoting the average chain density at the radial distance r from the center of the nanopore as $\rho(r, N, c)$, the force F_{hydr} in the free draining limit can be written as

$$F_{\text{hydr}} = -\zeta \int_0^R 2\pi r dr v(r) \rho(r, N, c).$$

The Laplace transform $\rho(r, E, c)$ of $\rho(r, N, c)$,

$$\rho(r, E, c) = \int_0^\infty dN \exp(-EN) \rho(r, N, c), \quad (3)$$

and the Laplace transform of F_{hydr} ,

$$F_{\text{hydr}}(N, c, R) = -\zeta L^{-1} \left\{ \int_0^R 2\pi r dr v(r) \rho(r, E, c) \right\}, \quad (4)$$

are evaluated in closed form in Secs. III–IV. The ability of deriving a closed form expression is one key feature facilitating the numerical inverse Laplace transform for arbitrary polymer-surface interaction parameters c . (\mathcal{L}^{-1} in Eq. (4) designates the inverse Laplace transform.) Before turning to the explicit evaluation of A_{confine} and F_{hydr} , we note that the use of the traditional eigenfunction equation method for general c would require a cumbersome series of numerical calculations: (1) First transcendental equations must be solved in order to satisfy the boundary conditions at the surface. (2) $\rho(r, N, c)$ is represented as a twofold infinite sum, with several terms required to attain numerical accuracy. (3) The radial integral $\int dr$ must be evaluated numerically for each term in the double sum. In contrast, all these complications do not plague the Laplace-Green's function methods since the boundary conditions are satisfied analytically, a single compact analytical expression for $\rho(r, E, c)$ is obtained, and the $\int dr$ in Eq. (4) is then resolved analytically.

III. PARTITION FUNCTION FOR POLYMER IN CYLINDER

The distribution function $G(\mathbf{r}, \mathbf{r}'; N)$ for the chain in a cylinder obeys the diffusion equation,

$$\left(\frac{\partial}{\partial N} - \frac{l}{6} \nabla_{\mathbf{r}}^2 \right) G(\mathbf{r}, \mathbf{r}'; N, c, R) = \delta(\mathbf{r} - \mathbf{r}') \delta(N), \quad (5)$$

where l is the Kuhn length. The presence of polymer-surface interactions at $r = R$ translates into the imposition of the boundary conditions at the walls of the nanopore that

$$\frac{\partial \ln G(\mathbf{r}, \mathbf{r}'; N, c, R)}{\partial r} \Big|_{r=R} = c. \quad (6)$$

Negative c corresponds to repulsive walls, and positive c implies attractive ones. Additionally, the boundary condition at the center of the nanopore requires that $G(0, \mathbf{r}'; N, c, R)$ is finite.

The chain partition function is evaluated from $G(\mathbf{r}, \mathbf{r}'; N, c, R)$ by

$$\begin{aligned} Z_{\text{confine}}(N, c, R) &= \exp(-\beta A_{\text{confine}}) \\ &= \iint d\mathbf{r} d\mathbf{r}' G(\mathbf{r}, \mathbf{r}'; N, c, R), \end{aligned} \quad (7)$$

where the integral is over the volume inside the cylinder.

Taking the Laplace transforms of Eqs. (5) and (6) gives,

$$\left(E - \frac{l}{6} \nabla_{\mathbf{r}}^2 \right) G(\mathbf{r}, \mathbf{r}'; E, c, R) = \delta(\mathbf{r} - \mathbf{r}'), \quad (8)$$

$$\frac{\partial \ln G(\mathbf{r}, \mathbf{r}'; E, c, R)}{\partial r} \Big|_{r=R} = c. \quad (9)$$

The Laplace transform of the chain density $\rho(\mathbf{r}; E, c, R)$ is evaluated from G as

$$\begin{aligned} \rho(\mathbf{r}; E, c, R) Z_{\text{confine}}(N, c, R) &= \iint d\mathbf{r}' d\mathbf{r}'' G(\mathbf{r}', \mathbf{r}; E, c, R) \\ &\quad \times G(\mathbf{r}, \mathbf{r}''; E, c, R). \end{aligned} \quad (10)$$

Since the length L of the nanopore is taken as very large compared to the radius of gyration of the polymer, the chain can be assumed to lie far from the ends of the cylinder (at $z = 0$ and L). Hence the boundary conditions for $z = 0, L$ are largely immaterial and are chosen as

$$G(\mathbf{r}, \mathbf{r}'; E, c, R)|_{z=0} = G(\mathbf{r}, \mathbf{r}'; E, c, R)|_{z=L} = 0. \quad (11)$$

When the expansion of $G(\mathbf{r}, \mathbf{r}'; E, c, R)$ in terms of angular (θ) and longitudinal eigenfunctions,

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'; E, c, R) &= (2\pi L)^{-1} \sum_{k=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \\ &\quad \times \exp[ik\pi(z - z')/L] \exp[im(\theta - \theta')] g_{km}(r, r'; E, c), \end{aligned} \quad (12)$$

is substituted Eqs. (4), (7), and (10), the integrals over the z and θ variables eliminate all terms in Eq. (12) apart from the single term for $k = m = 0$. Thus, the only survivor from the sum in Eq. (12) is $g_{00} \equiv (6/l)g$, which is the Green's function for zero order Bessel functions, i.e., the solution to the equations,

$$\left[a^2 + \frac{1}{r} \frac{\partial}{\partial r} r \frac{\partial}{\partial r} \right] g(r, r') = 0, \quad r' \neq r, \quad (13a)$$

$$g(r, r') \rightarrow \delta(r - r'), \quad r' \rightarrow r, \quad (13b)$$

where $a^2 = -6E/l$ and $g(r, r')$ must satisfy the same boundary condition at $r = R$ as in Eq. (9) for the full Green's function G . The solution to Eq. (13) can be written in terms of Bessel functions,

$$\begin{aligned} g(r, r') &= (\pi/2) [\lambda^{-1} J_0(ar) J_0(ar') + \theta(r - r') J_0(ar') N_0(ar) \\ &\quad + \theta(r' - r) J_0(ar) N_0(ar')]. \end{aligned} \quad (14)$$

The presence of the quantity,

$$\lambda = -\frac{a J_1(aR) + c J_0(aR)}{a N_1(aR) + c N_0(aR)}, \quad (15)$$

and the factors of $J_0(ar)$ in Eq. (14) ensure that $g(r, r')$ satisfies the boundary conditions for $r = R$ and for $r = 0$, respectively.

The traditional eigenfunction expansion method, on the other hand, would consist in an expansion of $g(r, r'; N, c, R)$ in the set of eigenfunctions $\{J_0(w_i r/R)\}$ with the $\{w_i\}$ being the infinite set of solutions to the cumbersome transcendental equation $-w J_1(w) = c R J_0(w)$ that emerges from imposition of the boundary conditions of Eq. (6).

The Laplace transform of the confinement partition function can be evaluated analytically. After changing variables to

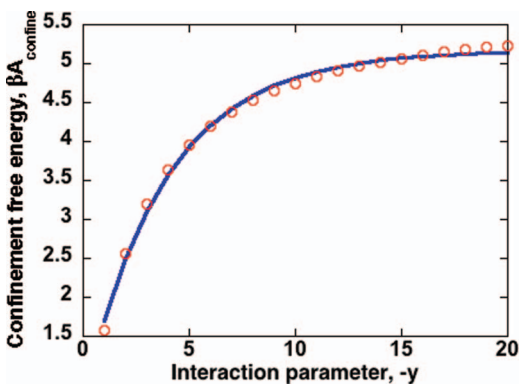


FIG. 1. βA_{confine} from Eq. (7) vs. $-y$ for a repulsive surface (symbols) and for $\delta = 1$. The line provides a fit $0.68535 + 4.48096 [1 - \exp(0.25681 y)]$ to the computed data.

$x = aR$, $x^2 = s = -6ER^2/l$, $\delta = -Nl^2/6R^2$, and $y = cR$, this procedure yields

$$Z_{\text{confine}}(\delta, y) = \frac{V}{2\pi i} \int_C \exp(s\delta) ds \times \left\{ \left(\frac{1}{s} \right) \left[\frac{-y J_1(s^{1/2})}{s^{1/2} [s^{1/2} J_1(s^{1/2}) + y J_0(s^{1/2})]} + \frac{1}{2} \right] \right\}, \quad (16)$$

where V is the volume of the cylinder and C is the standard contour for Laplace inversion. The length L of the nanopore is considered as sufficiently long, so that the contribution $kT\pi^2(R_G/L)^2$ to A_{confine} is negligible and may be ignored.

The limit $y \rightarrow -\infty$ corresponds to purely repulsive boundary conditions, where βA_{confine} scales for large δ as 5.79δ , in good agreement with the ground state dominance result of $\beta A_{\text{confine}} \rightarrow 5.78 \delta$ from the eigenfunction expansion method. However, the present approach facilitates treating the dependence of A_{confine} and F_{hydr} on the interaction parameter cR as illustrated in Figs. 1 and 2 for repulsive and attractive surfaces, respectively. Figure 1 exhibits a strong increase in the confinement free energy as the repulsive polymer-surface interaction elevates (i.e., as y goes from -1 to -8) before leveling off to the fully repulsive wall limit for $y \rightarrow -\infty$. The confinement free energy becomes favorable ($A_{\text{confine}} < 0$) and overcomes the entropy loss on

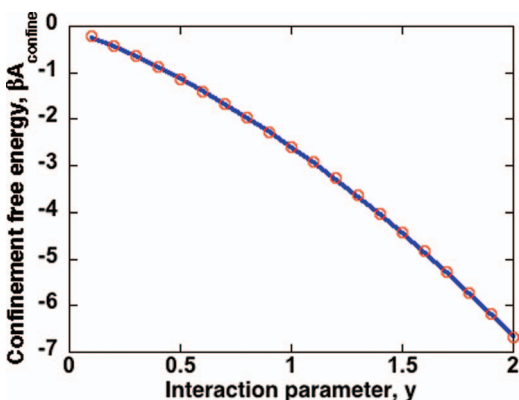


FIG. 2. βA_{confine} from Eq. (7) vs. $a = y$ for an attractive surface (symbols) and for $\delta = 1$. The line gives a fit $-0.04314 - 1.7761 y - 0.76559 y^2$ to the computed data.

confinement when the polymer-surface interaction parameter y is positive as depicted in Fig. 2.

IV. DRAG FORCE AND DENSITY PROFILE

The straightforward evaluation of the integrals in Eq. (10) produces the compact form,

$$\rho(r; E, c, R) Z(N, c, R) = V R^2 \left[\frac{l}{6(aR)^2} \right]^2 \times \left\{ \frac{-y J_0(ar)}{aR J_1(aR) + y J_0(aR)} + 1 \right\}^2. \quad (17)$$

Substituting Eq. (17) into Eq. (4) and changing variables ($w = ar$, $x = aR$) yields the radial integral required in the determination of F_{hydr} ,

$$I(x, y) = \int_0^x w (1 - (w/x)^2) \left\{ \frac{-y J_0(w)}{x J_1(x) + y J_0(x)} + 1 \right\}^2 dw. \quad (18)$$

Finally, $I(x, y)$ emerges in closed form,

$$I(x, y) = \{(-48 + 7x^2)xy^2 J_0(x)^2 + 2y[3x^4 - 48y - 2x^2(-12 + y)]J_0(x)J_1(x) + x[3x^4 + 4y(-24 + y) + 4x^2y^2]J_1(x)^2\} \times \{12[yJ_0(x) + xJ_1(x)]^2\}^{-1}. \quad (19)$$

In contrast, when using the classic eigenfunction expansion method, the corresponding average for Eq. (4) contains a double sum over the eigenfunctions $\{J_0(w_i r/R)\}$ of integrals that must be treated numerically. [Given the results in Eq. (19), use of the residue theorem enables obtaining an analytical form for the integrals, albeit in terms of a double infinite series and transcendental equations for the poles.]

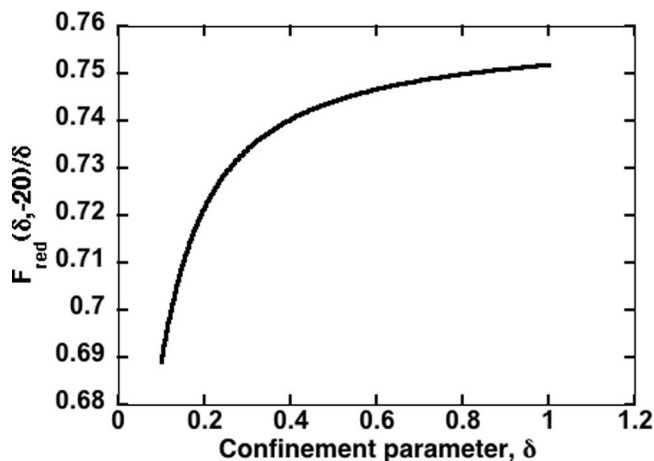
The integral $F_{\text{red}}(s, y) = s^{-3} I(x = s^{1/2}, y)$ is then numerically transformed to its counterpart $F_{\text{red}}(t, y)$ using MATHEMATICA.³⁰ Then, the drag force emerges as

$$F_{\text{hydr}} = \frac{4}{\eta} \zeta \frac{\Delta P}{\Delta x} \frac{R^2 N}{\delta} F_{\text{red}}(N, y) = \frac{24\zeta R^4}{\eta l^2} \frac{\Delta P}{\Delta x} F_{\text{red}}(N, y), \quad (20)$$

where l is the Kuhn length, $N = nl$, and n is the polymerization index.

Figure 3 demonstrates that the drag force approaches the asymptotic long chain limit for $\delta \approx 1$. Figure 4 displays F_{red} as a function $-y$, revealing that F_{red} converges towards the repulsive wall limit when $y \sim -20$ and undergoes a drop of $\sim 15\%$ as the repulsion weakens from -20 to -2 .

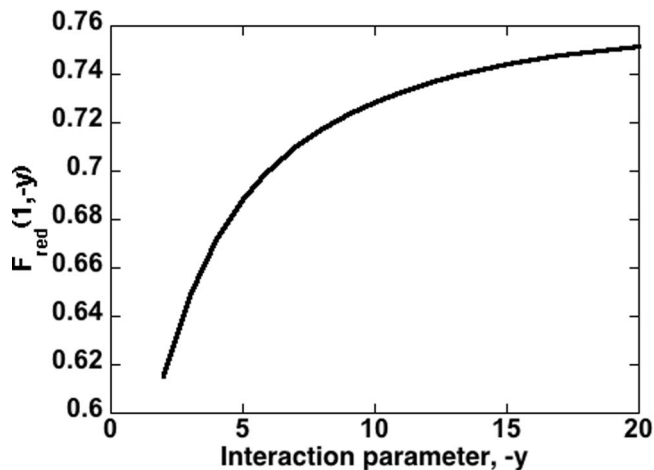
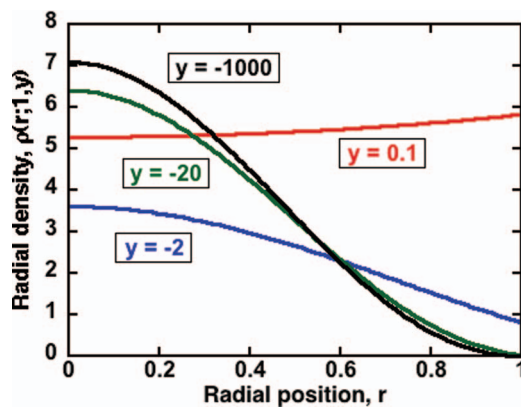
The eigenfunction expansion and Laplace-Green's function methods have been compared for properties in the simplest limit of purely repulsive walls. Curves for the confinement free energies A_{confine} are superimposed over the range from $\delta = 0.1$ (where ground state dominance is not yet established) to $\delta = 1.0$ (where ground state dominance applies) when two terms are retained in the eigenfunction expansion. Thus, no benefit emerges in this case in using the Laplace-Green's function methods. The situation alters, however, in calculations of the drag force. Convergence for $0.01 \leq \delta \leq 0.1$ requires retention of five terms from each of the

FIG. 3. $F_{\text{red}}(\delta, -20)/\delta$ from Eq. (20) as a function of δ .

two eigenfunction expansions [one for each factor of G in Eq. (10)] and, consequently, the numerical evaluation of 15 radial integrals as opposed to a *single* numerical inverse Laplace transform that is readily processed by the routines in MATHEMATICA.³⁰ Because the calculations have all been performed on a laptop, no comparative CPU times are available. Moreover, the relevant point with these types of calculations is programming time, not CPU time, and the Laplace-Green's function methods offer the greater efficiency in this regard.

A. Density profile

The radial density profile $\rho(r, N, c, R)/N$ in the nanopore is obviously sensitive to the polymer-surface interaction parameter $y = cR$, and this dependence is illustrated in Fig. 5 for both repulsive ($y < 0$) and attractive interactions ($y > 0.1$). As the repulsion diminishes in passing from $y = -1000$ to $y = -2$, the chain density increases near the walls of the nanotube. Small attractive interactions ($y = 0.1$) suffice to flatten out the radial density. [Only small attractive interactions are considered because the traditional continuous chain model becomes unphysical for large attractive y .³³]

FIG. 4. $F_{\text{red}}(1, -y)$ of Eq. (20) as a function of $-y$.FIG. 5. Density profile $\rho(r)$ vs. the radial distance from the center of the nanopore for $\delta = 1$ and $y = -2, -20, -1000$, and 0.1 (attractive).

V. FURTHER EXTENSIONS

Clearly, not all desired polymer properties can be expressed as the inverse Laplace transform of a closed form analytical expression. Thus, we use the example of the partition function (and, hence, A_{confine}) of a 3-arm star polymer to illustrate how these situations can still be treated with Laplace-Green's function methods, albeit at the expense of additional computational effort. The partition function for a 3-arm star polymer with arms of equal length N may be expressed as integrals over $G(\mathbf{r}, \mathbf{r}_1; N)$,

$$\begin{aligned} Z_{3\text{-arm}}(N) &= \int d\mathbf{r} \left[\left\{ \int d\mathbf{r}_1 G(\mathbf{r}, \mathbf{r}_1; N) \right\} \right. \\ &\quad \times \left. \left\{ \int d\mathbf{r}_2 G(\mathbf{r}, \mathbf{r}_2; N) \right\} \left\{ \int d\mathbf{r}_3 G(\mathbf{r}, \mathbf{r}_3; N) \right\} \right] \\ &= \int d\mathbf{r} \left\{ \int d\mathbf{r}_1 G(\mathbf{r}, \mathbf{r}_1; N) \right\}^3 \end{aligned} \quad (21)$$

where the second equality follows from the equivalence of the three arms. The Laplace transform of $Z_{3\text{-arm}}(N)$ with respect to N is intractable, but the transform $\int d\mathbf{r}_1 G(\mathbf{r}, \mathbf{r}_1; E)$ of $\int d\mathbf{r}_1 G(\mathbf{r}, \mathbf{r}_1; N)$ is available in closed form and may be numerically Laplace inverse transformed to obtain $\int d\mathbf{r}_1 G(\mathbf{r}, \mathbf{r}_1; N)$ as a function of r , y , and N . Specializing, for simplicity, to a system with purely repulsive walls ($y \rightarrow -\infty$), and using the variables w and x defined before Eq. (18), this integral is obtained as

$$\int d\mathbf{r}_1 G(\mathbf{r}, \mathbf{r}_1; E) = (6R^2/lx^2) \{1 - [J_0(xw)/J_0(x)]\}/x^2. \quad (22)$$

Numerical Laplace inversion of Eq. (22) for fixed N yields a numerical function $f(w, \delta)$ with $\delta = N/6r^2$. The function $f(w, \delta)$ for fixed δ can be fit quite well to the quartic function of $(w - 1)$, thus enabling the integral $\int dw w \{f(w, t)\}^3$ to be evaluated analytically. The final result yields the free energy of confinement over the range $0.1 \leq \delta \leq 1$ as

$$A_{\text{confine}} = kT[-0.1358 + 5.743d], \text{ per arm,} \quad (23)$$

with the coefficient 5.74 of δ close, as expected, to the ground state dominance limit of 5.78.

The calculations are readily performed using the same methods for surfaces with finite y and for polymers with n arms of different lengths.

VI. DISCUSSION

The benefits of the Laplace-Green's function method for describing polymer systems confined by interacting boundaries are explored further by considering more challenging systems whose boundaries have more complicated shapes than the simplest geometries (slits and boxes) treated in Paper I. Specifically, the illustrations consider cylindrical systems. The quantities evaluated (confinement free energy, drag force, chain density profile) are pertinent to describe the flow of polymers through nanopores. Because our purpose here is to illustrate the advantages of the Laplace-Green's function methods over the traditional eigenfunction expansion methods for systems with interacting boundaries, the comparison of these calculated properties with experiment will be presented elsewhere.

The evaluation of the drag force provides the most striking difference between the Laplace-Green's function and the traditional eigenfunction expansion methods for systems with general polymer-surface interactions (arbitrary y). The more complicated eigenfunction expansion methods begin by requiring the numerical solution of a transcendental equation to enable introduction of the eigenfunctions. The final results involve doubly infinite expansions in eigenfunctions for the general case, and the radial integrals in the double sum must then be evaluated numerically. In contrast, the Laplace-Green's function method simply requires a single numerical Laplace inversion of a closed form analytical function.

Prior applications of the Laplace-Green's function approach to renormalization group calculations of polymers attached to a sphere further illustrate the methods for a system where all integrals can be evaluated analytically. Numerical calculations for systems with interacting spherical boundaries are far simpler than those for cylindrical confinement since the former involve spherical Bessel functions that are analytically far more tractable than ordinary Bessel functions.

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