Confinement of a polymer chain in a tube

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Abstract. We have adapted the transfer matrix method to the confinement of a single polymer molecule in tube-like cavities. The method is exact and numerically efficient for realistic polymer models such as the freely rotating chain and the rotational isomeric chain models. It allows us to calculate the chain end distribution function from which the longitudinal end-to-end distance and the free energy are obtained. The confinement is modelled as a cylindrical potential with soft walls or as a harmonic potential. Known scaling laws are recovered for long chains and strong confinement and new scaling behaviour is found in the intermediate regime. The effect of anchoring one chain end to a base plate of a semi-infinite tube is also studied.

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1. Introduction

The static and dynamic properties of single polymer molecules subject to external forces have become accessible to direct experimental investigation, such as the measurement of their mechanical equation of state or force–extension curve, with the atomic force microscope [1]. The confinement of single macromolecules or of polymer solutions in pores, represented by external potential walls, is of great significance in fields as diverse as lubrication, filtration, enhanced oil recovery, transport through membranes, and the structure of polymer brushes and of polymeric liquid crystals, if transverse fluctuations are accounted for.

An early discussion of the confinement of single polymers in pores and tubes can be found in de Gennes’ work [2]–[5], where he advances simple scaling ideas for the free energy and the longitudinal extension in a tube as a function of the confinement cross-section. The concept of the blob was created to characterize the structure of a confined polymer. These ideas were further elaborated over the years for simple polymer models such as the Gaussian chain [6, 7], polymers in θ-solvent [8], semiflexible or worm-like chains [9]–[14], bead–spring models [15]–[18], the reference interaction site approximation [19], and self-avoiding walk (SAW) models [20]–[23]. The attraction of these models is that many results can be obtained by analytical methods, although several authors have relied on Monte Carlo simulations to get explicit results. Their drawback is well known, namely that they are ‘realistic’ only in limiting situations; for instance, the Gaussian and worm-like chains only apply in the limit of very long chains and in the absence of external forces, while lattice models do not capture the small-scale details of real molecules. Similarly the bead–spring and Gaussian models do not account for such important features as bond and dihedral angles, which, for instance, have an important effect on the properties of polymers in external fields [24]–[26]. Besides their intrinsic contribution to the scientific development, these studies are of great help in the understanding of the reptation model for entangled polymer solutions formulated by Doi and Edwards [9], de Gennes [2]–[5], and recently observed for DNA molecules [27]. Application of their ideas to the statistical mechanics of entangled solutions of semiflexible chains can be found, for example, in [10]–[12].

We briefly summarize the main scaling laws discovered for the confinement of polymers in a tube-like cavity in the regime $b < D < \langle R \rangle_0$, where $b$ is the average monomer size, $\langle R \rangle_0$ is the mean end-to-end distance of the polymer in the absence of confinement, and $D$ is the cross-sectional dimension of the cavity. For the ideal (or Gaussian) chain [2], [28]–[30] the free energy change per monomer, $\Delta F/N$, of the confinement, as a function of $D$, obeys the relation

$$\frac{\Delta F}{Nk_B T} \propto D^{-2},$$

(1)

where $N$ is the number of monomers. The longitudinal dimension of the chain, $R_\parallel$, does not change with $D$ for this chain model. For a polymer in the θ-condition [8], the free energy displays the same functional dependence, but the chain size changes with $D$ as

$$R_\parallel \propto N D^{-1}.$$

(2)

In the case of a chain in a good solvent [2, 31] the scaling behaviour is altered:

$$\frac{\Delta F}{Nk_B T} \propto D^{-5/3},$$

(3)

$$R_\parallel \propto N D^{-2/3}.$$

(4)
For the bead–spring model \cite{15} and for the SAW on a cubic lattice \cite{21,22}, Monte Carlo simulations have confirmed the same scaling laws as for the chain in a good solvent.

For a semiflexible polymer \cite{10,11} the confinement can be characterized in terms of its contour length $L$, persistence length $P$, and the deflection length $\lambda \approx (D^2 P)^{1/3}$. The corresponding scaling laws for the free energy in different regimes are

\begin{align}
\frac{\Delta F}{k_B T} &\simeq \ln(L/D)^2 \quad \text{for } L \lesssim \lambda/2, \quad (5) \\
\frac{\Delta F}{k_B T} &\simeq (L/\lambda) \ln(P/\lambda) \quad \text{for } L = P, P \gg \lambda, \quad (6) \\
\frac{\Delta F}{k_B T} &\simeq L/\lambda \quad \text{for } L > P, P \gg \lambda, \quad (7) \\
\frac{\Delta F}{k_B T} &\simeq L P / D^2 \quad \text{for } D \gg P. \quad (8)
\end{align}

The last relation recovers the ideal chain limit. The semiflexible chain behaviour upon confinement was also studied by computer simulations \cite{13}; the findings are consistent with the above scaling laws. These techniques also determined the numerical prefactors entering the free energy expression for various confinement geometries (cross-sectional shapes) \cite{32}.

In this paper we present an adaptation of the transfer matrix method to the confinement of a polymer chain in a tube for more ‘realistic’ polymer models such as the freely rotating chain (FRC) and rotational isomeric state models. We consider different confinement potentials and give detailed results on the free energy and longitudinal extent of the polymer. This method also allows us to calculate the end-to-end distributions and the average end-to-end distance.

In the next section we define the confinement by choosing two axially symmetrical potentials with simple forms. For our numerical work we use the FRC, which accounts for the geometrical structure of polymers, such as fixed bond lengths and bond angles. We also endow our model with an appropriate monomer volume, represented by its van der Waals radius.

In section 3 we describe the transfer matrix method and we adapt it to the study of polymer confinement. We show how this method is implemented numerically to render the various quantities of relevance for this problem. In section 4 we present and discuss extensive results for two forms of confinement potential. A detailed comparison between our calculations and existing scaling laws is also given.

\section{Model}

The confinement of a polymer molecule in a tube is achieved by an external potential acting on the polymer. We assume the tube to be a cylinder of circular cross-section. For the potential itself we study two models. Our first choice is to assume that the potential is zero up to a radius $R_c$ after which it rises linearly. This deviation from a hard wall is to mimic the possible penetration of the polymer into the wall over a distance of the atomic roughness of the wall material:

\begin{equation}
\frac{V(r)}{k_B T} = \begin{cases} 
0 & \text{for } r < R_c \\
(r - R_c)/s & \text{for } r \geq R_c.
\end{cases}
\end{equation}

Here $s^{-1}$ is the slope of the potential function beyond the radial distance $R_c$ and is a measure of its rigidity, i.e. $s$ is the ‘softness’. Our second choice is a harmonic wall potential.
in which the parameter $R_h$ controls the rate of potential increase. Such a potential is more appropriate for pores and channels in soft, flexible materials such as polymeric bilayers [33].

We will consider two different ‘boundary conditions’, namely

(i) a tube extending indefinitely in the axial direction and

(ii) a semi-infinite tube with one end sealed by a bottom plate in the centre of which we anchor one end of the polymer.

This is a simple model for the confinement of a polymer by the surrounding molecules in a polymer brush.

In this paper we will consider simple hydrocarbon chains such as $n$-alkanes, for which the FRC is a realistic model. It describes such molecules as a sequence of $N$ monomers of equal length, $b$, joined together by fixed bond angles, $\gamma$, with the rotations around the dihedral angle assumed unhindered. For $n$-alkanes we have $b = 1.53$ Å and $\gamma = 68^\circ$ [34]. The excluded volume interaction and the action of the solvent are neglected, so our model is essentially an ideal chain with some ‘realistic’ features incorporated. We further associate with each monomer a repulsive hard-core sphere whose radius is taken as its van der Waals radius, $R_m$. For the CH$_2$ monomer and the methyl end-group this radius is about 2 Å [35]. This hard-core radius is introduced in our model in order to describe the contact between the chain monomers and the confining tube, and does not intervene in the intrachain interactions. A sketch of the FRC with five monomers is given in figure 1.

The contour length of the FRC is $L = Nb\cos(\gamma/2)$, while the minimum radius of confinement is achieved when the chain is completely stretched and is given by $R_{\text{min}} = R_m + b\sin\{\tan^{-1}[\sin(\gamma/2 + \cos\gamma)]\}$. In the absence of an external force or a confinement potential the mean square radius of gyration is known analytically [36]:

$$\frac{\langle R_g^2 \rangle}{N b^2} = \frac{1}{6} \frac{(N + 2) (1 + \cos \gamma)}{(N + 1)(1 - \cos \gamma)^2} - \frac{\cos \gamma}{(N + 1)(1 - \cos \gamma)^2},$$

and also the mean square end-to-end distance

$$\langle R^2 \rangle_0 = Nb^2 \left( \frac{1 + \cos \gamma}{1 - \cos \gamma} - \frac{2 \cos \gamma}{N} \frac{1 - (\cos \gamma)^N}{(1 - \cos \gamma)^2} \right).$$
For large degrees of polymerization and for small bond angles the FRC can also be regarded as a semiflexible chain with a persistence length

\[ P = b \frac{\cos(\gamma/2)}{|\ln \cos \gamma|}. \]  

(13)

For a bond angle of 68° the persistence length is \( P = 0.85b \). The Helmholtz and Gibbs free energies can be obtained exactly also in the presence of an external force, using the transfer matrix method, or the polymer Green function [24]–[26].

3. Transfer matrix method

To obtain the statistical mechanics of a single polymer confined in a tube we employ the transfer matrix, or Green function method. We introduce the Green function or probability distribution function (PDF) \( G(i, S) \) that gives the probability that monomer \( i \) is found at position and orientation \( S \) (a set of appropriate coordinates to be specified below). The ‘propagation’ of the PDF from one monomer to the next along the polymer’s contour is controlled by an integral equation

\[ G(i + 1; S') = \int dS G(i; S) T(S'; S), \]  

(14)

where \( T \) is the transfer operator. It describes the conditional probability that monomer \( i + 1 \) is found at \( S' \) if monomer \( i \) is at \( S \). Discretizing the coordinates in \( S \) (for numerical evaluation) turns \( T \) into the transfer matrix. In figure 2 we depict the relevant coordinates of a chain bond in a convenient frame. In order to predict the PDF of say monomer 2, indicated by point \( P_2 \), we need to know the PDF of monomer 1, located at \( P_1 \). The geometrical connection between the two is the bond vector \( b \). Owing to the axial symmetry, the azimuthal angle for the ends of the chain can be ignored, so the position and the orientation of the bond in this geometry is given by the coordinates \( r, z, \theta, \phi \).

A review of the transfer matrix approach for polymers can be found in classical polymer texts by Flory [36] and Grosberg [37]; extensive applications to configurational properties were recently demonstrated for simple models, such as the freely jointed chain, the FRC, rotational isomeric state approximation, and the interacting chain model, also in the presence of an external force [24]–[26].

The transfer matrix can be written in the form

\[ T(r', z', \theta', \phi'; r, z, \theta, \phi) = C(r', z', \theta', \phi'; r, z, \theta, \phi) \exp(-V(r', z', \theta', \phi')/kT), \]  

(15)

with

\[ C(r', z', \theta', \phi'; r, z, \theta, \phi) = \int_0^\pi d\psi \delta(r' - g_r(r, \theta, \phi, \psi))\delta(z' - g_z(z, \theta, \psi)) \cdot \delta(\theta' - g_\theta(\theta, \psi))\delta(\phi' - g_\phi(r, \theta, \phi, \psi)), \]  

(16)

where the functions \( g_r, g_z, g_\theta, \) and \( g_\phi \) are determined by the geometrical restrictions between two successive bonds. For the FRC these functions are given by

\[ g_r(r, \theta, \phi, \psi) = [(r + b \cos \phi (\sin \gamma \cos \psi \cos \theta + \cos \gamma \sin \theta) - b \sin \gamma \sin \psi \sin \phi) + b^2(\sin \phi (\sin \gamma \cos \psi \cos \theta + \cos \gamma \sin \theta) + \sin \gamma \sin \psi \cos \theta)^2]^{1/2} \]  

(17)
Figure 2. Geometrical parameters describing the location and orientation of a bond $b$ with respect to the axis of symmetry $Oz$.

\[ g_z(z, \theta, \psi) = z + b(-\sin \gamma \cos \psi \sin \theta + \cos \gamma \cos \theta) \]  
\[ \cos[g_\theta(\theta, \psi)] = -\sin \gamma \cos \psi \sin \theta + \cos \gamma \cos \theta \]  
\[ \cos[g_\varphi(r, \theta, \varphi, \psi)] = \frac{[g_r(r, \theta, \varphi, \psi)]^2 + b^2[(\sin \gamma \cos \psi \cos \theta + \cos \gamma \sin \theta)^2 + (\sin \gamma \sin \psi)^2] - r^2}{2g_r(r, \theta, \varphi, \psi)b[(\sin \gamma \cos \psi \cos \theta + \cos \gamma \sin \theta)^2 + (\sin \gamma \sin \psi)^2]^{1/2}}. \]  

Once we know the PDF for the $N$th chain monomer, we can calculate all statistical and thermodynamic quantities of interest for the polymer. For instance, the (unnormalized) probability that the chain ends at a distance $z$ from its beginning, or the chain end distribution, is given by

\[ G_z(z) = G_z(N; z) = \int_0^\infty dr \int_0^\pi d\theta \int_{-\pi}^\pi d\varphi G(N; r, z, \theta, \varphi). \]  

A measure for the chain stretching along the tube axis $Oz$ is given by the longitudinal mean square end-to-end distance:

\[ \langle R_z^2 \rangle = \langle (z_N - z_0)^2 \rangle \]  
\[ = \frac{\int z^2 G_z(z) \, dz}{\int G_z(z) \, dz}. \]  

where $\langle \cdots \rangle$ denotes the ensemble average. Similarly, the longitudinal mean square radius of gyration (the chain dimension along the $Oz$ axis) can be calculated according to
\[ R_\parallel^2 = \frac{1}{N + 1} \left\{ \sum_{i=0}^{N} (z_i - z_{cm})^2 \right\} \]  

(24)

\[ = \frac{1}{N + 1} \left\{ \sum_{0 \leq i < j \leq N} z_{ij}^2 \right\}, \]  

(25)

where \( z_{ij} = z_i - z_j \) and \( z_{cm} \) is the coordinate of the polymer’s centre of mass. This yields

\[ R_\parallel^2 = \frac{1}{N + 1} \sum_{0 \leq i < j \leq N} \int \frac{z^2 G_z(|i - j|; z) \, dz}{\int G_z(|i - j|; z) \, dz}, \]  

(26)

where \( G_z(|i - j|; z) \) is defined as in equation (21), after replacing \( N \) with \( |i - j| \).

The canonical partition function is obtained by integrating the PDF of the last monomer over all its coordinates:

\[ Z_N = \int dS G(N; S), \]  

(27)

so the Helmholtz free energy difference with respect to the free coil state is

\[ \Delta F = -k_B T \ln Z_N. \]  

(28)

To solve the integral equation for the PDF of any chain monomer, as given by (14), we must resort to a numerical procedure which, in the first step, involves the discretization of the (continuous) spatial coordinates in \( S \). For instance, the range \([0, \pi]\) of the angular coordinate \( \theta \) will be sampled by \( M_\theta \) uniformly distributed points. Similarly, we divide the range \([0, R_c]\) of the radial coordinate \( r \) into \( M_r \) intervals and the length of the occupied confinement tube \( \Lambda \) into \( M_\Lambda \) intervals. For \( \Lambda \) larger than the contour length of the polymer the confinement tube is ‘infinitely’ long, while for \( \Lambda \) less than that, end effects play a role. The total number of discrete values for \( S \) is \( M_S = M_\theta \times M_r \times M_\theta \times M_\psi \). The transfer operator \( T(S_i, S_{i+1}) \) in equation (14) thus becomes an \( M_S \times M_S \) transfer matrix and the numerical solution involves its diagonalization. It is clear that the mesh parameters must be chosen large enough that the numerical discretization does not affect the results.

4. Results

In this section we present numerical results for the confinement of a polymer in a tube. We will discuss the effects of changing the size of the tube and the rigidity of its walls. We will vary the degree of polymerization, or the length, \( N \), of the chain and the bond angle where relevant. We will also analyse the effects of anchoring the polymer to the bottom of the tube. The bond angle \( \gamma \) is fixed at \( 68^\circ \) and the van der Waals radius at \( 1.3b \). The bond length \( b \) will serve as the length scale in the problem.

Numerical convergence within a few per cent in the solution of the discretized version of the integral equation (14) is assured for mesh parameters \( M_\theta = 20, M_\psi = 2N + 20 \), for a chain with \( N \) monomers\(^1\).

\(^1\) For a chain length \( N = 100 \), with the mesh parameters chosen here, it takes about 5 h on a 1 GHz Pentium III to calculate all properties for a tube with a given radius \( R_c \).

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4.1. Confinement in tubes with walls of variable rigidity

We first consider the confinement of a polymer in an infinite tube and the effects of decreasing its cross-sectional area. The chain end distribution functions for various degrees of confinement are represented in figure 3 as solid curves. For $R_c$ larger than the contour length $L$ of the unconfined polymer, there is no effect of confinement. The chain end distribution $G_z(z)$ has a maximum at $z = 0$ and is symmetrical with respect to this point. As $R_c$ reaches values comparable to the radius of gyration of the unconfined polymer, its chain end distribution broadens, panel (b), because it starts to develop a second maximum (c). The latter grows and shifts to larger $z$-values as the confining tube narrows. In the final stages of confinement the chain end distribution is narrowly peaked at the contour length, $z = L$, indicating that the chain is maximally stretched, panel (f).

To analyse the effect of the wall rigidity we varied the rigidity parameter in equation (9) using three choices: $s/b = 1, 10^{-1}, 10^{-2}$. The quantities studied were the longitudinal mean square radius and the Helmholtz free energy, plotted in figure 4 as a function of tube radius. For large $R_c$, confinement is minimal and the rigidity of the walls has no effect. For $R_c \lesssim 5b$, the wall rigidity comes into play, such that for $s/b \lesssim 0.1$ the limit of confinement by an impenetrable hard wall is reached, both in the longitudinal mean square radius and in the free energy; see figure 4.

In figure 5(a) we show the Helmholtz free energy as a function of the tube radius for confinement for different degrees of polymerization. In the regime $b < R_c < R_g$ the free energy
Figure 4. The effect of the wall rigidity on the properties of the confined polymer: the longitudinal mean square radius (a), and the Helmholtz free energy (b). The chain length is $N = 50$.

is inversely proportional to the base area of confinement, as in equation (1). This behaviour is similar to that of the ideal chain [2], polymers under the $\theta$-condition [8], and the semiflexible chain in the limit $R_c \gg P$ [10]; see equation (8). For the FRC, and even more so for interacting chains, such an argument would ignore the fact that more than one length scale, $R_c$ and $b$ for the FRC, and more than one energy scale, interaction energies in addition to $k_BT$, control the system. An optimal power law fit of the free energy for strong confinement ($R_c$ a few bond lengths) yields an exponent $-3$, instead of $-2$, and this is plotted as a second (steeper) thin solid curve in figure 5(a). It offers an appropriate description only over a narrow range of the confinement radius, $2b < R_c < 4b$. This indicates a more pronounced resistance to confinement, which is a consequence of the fact that, for tight confinement, the behaviour of a polymer depends on the specific details of its geometrical structure (and the energy landscape for interacting chains). For instance, the fixed bond angle in the FRC makes U-turns very improbable as $R_c$ approaches a few bond lengths. Also, in contrast to the cases for the Gaussian chain and the freely jointed chain, where folding of consecutive bonds can occur, this effect is completely forbidden for the FRC.

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Considerable deviations from the scaling law appear for less confinement, $R_c \gtrsim 5b$, in that the energy per monomer is larger for longer chains. This is simple to understand when one recalls that for the FRC the Helmholtz free energy variation is just $-T \Delta S$, where $\Delta S$ is the entropy difference between the confined and free coil states.

The longitudinal rms end-to-end distance, $R_{\parallel}' = \sqrt{\langle R_z^2 \rangle}$, and the longitudinal radius of gyration, $R_{\parallel}$, of confined polymers of various degrees of polymerization are shown in figures 5(b) and (c) respectively. The two quantities have similar dependences on the tube radius. In the strong-confinement regime (when $R_c$ is a few bond lengths), the data are well fitted by a power law $R_{\parallel}' \propto N R_c^{-3}$.

The slope in the strong confinement varies with the degree of polymerization. As expected, for $R_c > R_g$, where the effect of confinement fades, the longitudinal dimensions rapidly approach
their unperturbed limits; that is, $R_\parallel \to R_g/\sqrt{3}$, $R'_\parallel \to \langle R \rangle_0/\sqrt{3}$. In the other extreme, at maximum confinement, the polymer assumes a rod-like conformation and has an end-to-end distance equal to $L$.

These behaviours are typical for the finite FRC, and were not encountered in the case of other models previously studied in the literature, such as the Gaussian chain and freely jointed chain. One can expect even more pronounced deviations for the rotational isomeric state models that incorporate more structural details of the polymer.

To further clarify the importance of the model parameter in the polymer behaviour upon confinement, we performed the same statistical study on a model with different particulars, namely different bond angles and chain lengths. Reducing the bond angle causes the FRC to resemble a stiff polymer, like the worm-like or rod-like chain. This enables us to compare our results to the known scaling laws for semiflexible chains of this type [10].

In figure 6 we present the free energy of confinement (solid curves) for two chains with small bond angles, 10° and 20°, and with chain lengths equal to their respective persistence lengths. For $\gamma = 10^\circ$ one obtains according to equation (13) a persistence length $P \simeq 65b$, and for $\gamma = 20^\circ$, $P \simeq 16b$. This allows us to compare our work to scaling results for semiflexible polymers, plotted as dashed curves in figure 6. The numerical factor of proportionality needed in equation (6) for fitting our data is of the order of unity, more precisely 2.5 for $\gamma = 20^\circ$ and 1.3 for $\gamma = 10^\circ$. The chain with a smaller bond angle is better approximated by a semiflexible chain since the latter model is obtainable from the FRC model by taking the limit $\gamma \to 0$. For comparison we also show the free energy for $N = 10$, $\gamma = 68^\circ$ (dash–dotted curve) which is much steeper, i.e. less flexible.
4.2. Confinement in a harmonic potential

In this section we present and discuss the confinement of a polymer chain in a harmonic potential; see equation (10). The degree of confinement is represented in this case by the parameter $R_h$ controlling the softness of the wall. We first look at the modification of the chain end probability distribution with respect to the $z$-coordinate for various degrees of confinement. Numerical results for $N = 10$ and six values of the parameter $R_h$ are displayed in figure 7. As in figure 3, we note the trend of this distribution to change from its unconfined form (left uppermost panel) with a broad peak for small $z$ to an extremely localized function (the right lowermost panel) at large $z$, corresponding to almost complete stretching of the chain. Note that the chain is already strongly stretched for $R_h = 0.4b$ and, from this point on, the confinement increases very slowly with the decrease in $R_h$. The free energy change due to confinement as a function of $R_h$ for various chain lengths is presented in figure 8(c). The long-chain limit is effectively reached for $N > 20$.

Although this confining potential does not have a characteristic length scale, a scaling law for long chains can be derived: to have a base area $\pi r^2$ available for confinement, an energy has to be expended that is given by equation (10) with $\Delta F = V(r)$, so $r^2 = R_h^2 \Delta F / k_B T$. Thus, assuming that $\Delta F$ is proportional to the inverse area, see equation (1), we get $\Delta F \propto 1 / \pi r^2 \propto 1 / (R_h^2 \Delta F)$ or

$$\frac{\Delta F}{Nk_BT} = a_0(b/R_h).$$

(29)
Figure 8. (a) The longitudinal mean end-to-end distance as a function of the degree of confinement, $R_h$, for chain lengths $N = 10, 20, 50, 100$ as indicated in the key. Inset: the negative of the maximum slope of the graph as a function of $N$. Circles: our data. Solid curve: the fitting curve according to equation (33). (b) The longitudinal mean radius of gyration for the same chain lengths. (c) The Helmholtz free energy. The straight solid curve is the function $1/R_h$.

This new scaling law for confinement in a parabolic potential is plotted in figure 8(c) as a straight solid line and fits the overall trend rather well. It breaks down for short chains because they cannot stretch as far up the parabolic wall potential. Corrective terms in $R_h$ give a better fit:

$$\frac{\Delta F}{Nk_BT} = \left(\frac{R_h}{b}\right)^{-1} + \alpha_2 \left(\frac{R_h}{b}\right)^{-2} + \alpha_3 \left(\frac{R_h}{b}\right)^{-3},$$

(30)
with $\alpha_2 = -0.1$ and $\alpha_3 = 0.01$. Recalling the results in the previous section, we note a significant difference between the confinement in the two types of potential. In a rigid tube the free energy scales with the radius as $R_c^{-2}$, while in a harmonic potential it varies like $R_h^{-1}$. The two radial distances, $R_c$ and $R_h$, albeit having a different mathematical significance, play a similar role in the physical picture—both dictate the degree of confinement for the polymer chain.

To study the longitudinal dimensions for this type of confinement we plot in figure 8(a) the rms longitudinal end-to-end distance versus the degree of confinement. For all chain lengths we get the values $R'_\parallel = \langle R \rangle_0 / \sqrt{3}$ in the $R_h \to \infty$ limit, and $L$ in the strong-confinement limit. Generally the slope of decrease varies with $N$ and, in all cases, the maximum of $R'_\parallel$ is attained at about $R_h = b/2$. In the intermediate-confinement regime, the slope of the curve $R'_\parallel$ versus $R_h$ can be roughly evaluated from the condition that the ‘drop’ in this quantity occurs entirely over an $R_h$-interval of a few $b$, as seen from our data:

$$\frac{\Delta R'_\parallel}{\Delta R_h} \sim -\frac{L - \langle R \rangle_0 / \sqrt{3}}{b}. \quad (31)$$

If $N \gg 1$, $\gamma = 68^\circ$, the unperturbed size according to equation (12) can be approximated as

$$\frac{\langle R \rangle_0}{b} \simeq \sqrt{\frac{(1 + \cos \gamma)}{(1 - \cos \gamma)}} N \simeq 1.5\sqrt{N}. \quad (32)$$

From equations (31) and (32) one gets

$$\frac{\Delta R'_\parallel}{\Delta R_h} \sim \beta_0 \sqrt{N} - \beta_1 N. \quad (33)$$

In the inset in figure 8(a) we plot the negative of the slope of the graph in the region of most pronounced variation ($R_h \sim b$) as a function of $N$, for the four values indicated in the key. We found that this curve follows closely the dependence in equation (33) with coefficients $\beta_0 = 2.04$ and $\beta_1 = 1.13$ (solid curve). Accordingly, the dependence of $R'_\parallel/Nb$ on $R_h$ in the above region has a slope linear in $N^{-1/2}$ and, as a consequence, the curves for very large $N$ will be close to each other.

We also studied the variation of the longitudinal mean radius of gyration with the degree of confinement in figure 8(b). This dependence is very similar to that in figure 8(a) for the rms end-to-end distance.

4.3. Anchoring the chain on a grafting surface

So far, we studied the polymer confinement in a tube with axial symmetry that extends to infinity in the longitudinal directions. The transfer matrix method can easily be adapted to the situation where one end of the chain is anchored on a bottom plate of a semi-infinite tube. For simplicity, we choose the anchoring point to be in the centre of the bottom plate and insist that the first bond is perpendicular to the surface.

The effect of chain grafting on the end-to-end distribution function under confinement conditions is illustrated in figure 3; dashed curves. At small confinement, the presence of the surface forces the maximum to shift away from the surface plane and for the second maximum to develop earlier. In the regime of large confinement, grafting effects become negligible since the chain is completely stretched in any case.
In figure 9 we show the effect of anchoring in a tube-like potential, equation (9), for a relatively long chain $N = 100$. The solid and dashed curves correspond to the free end chain and the anchored end chain, respectively. There is little change in the longitudinal end-to-end distance dependence; see panel (a). However, one can see differences in the free energy curves in figure 9(b), especially in the weak-confinement regime, $R_c > R_g$. The dashed curve represents the free energy difference with respect to the anchored, but unconfined polymer restricted to a half-space. The dash–dotted curve is the free energy difference with respect to the completely free coil. The energy change due to anchoring amounts to about $0.02 k_BT$ per monomer. Anchoring the polymer in the centre of the tube by the tethered bond results in the loss of translational degrees of freedom, and restricting it to a half-space reduces its rotational degrees of freedom. Thus the anchored chain does not need any significant adjustment of configuration for confinement up to its radius of gyration. Also note that these differences are very small overall and certainly irrelevant for strong confinement.

For confinement in a harmonic potential, equation (10), anchoring effects both on the longitudinal end-to-end distance and on the free energy are displayed in figure 10. Anchoring obviously confines the chain to the lower part of the potential and prevents it from slipping up to a radial region where the tube is wider, thus increasing the end-to-end distance and the free energy by a more or less uniform shift.

5. Conclusions

We have adapted the transfer matrix method to the confinement of single polymer molecules in tube-like cavities. The method is exact and numerically efficient for realistic polymer models such as the rotational isomeric chain models. It allows us to calculate the chain end distribution function from which the longitudinal end-to-end distance and the free energy are obtained. The confinement is modelled as a cylindrical potential with soft walls and as a harmonic potential. Known scaling laws are recovered for long chains and strong confinement, and new scaling behaviour is found in the intermediate regime. The effect of anchoring one chain end to a base plate of a semi-infinite tube is also studied.

For confinement in a rigid tube we recover known scaling laws in the appropriate limits: the Helmholtz free energy is inversely proportional to the square of the radius $R_c$; see equation (1). However, for the longitudinal dimension of the polymer the simple scaling laws obtained for the ideal chain or the polymer in the $\theta$-condition do not hold for realistic values of bond angles in the FRC.

In a harmonic potential a simple scaling law applies: the free energy is inversely proportional to the potential radius $R_h$; see equation (29). As in a tube with rigid walls, the variation of the longitudinal extent of the polymer is dramatic when $R_h$ reaches a few bond lengths. For various degrees of polymerization, the slope of the curve $R'_\parallel/Nb$ versus $R_h$ in the quasi-linear region of maximum increase is approximately linear in $N^{-1/2}$. Also, the present model allows us to explore the limit of stiff polymers, by reducing the bond angle appropriately. In this limit our results verify the scaling behaviour for this model given by equation (6). An important factor in the functional form of these quantities, especially in the regime of tight confinement, is the imposition of the $\theta$-condition. In a solvent where the excluded volume interaction and the action of the solvent molecules do not mutually cancel each other, the behaviour would certainly be altered.

The transfer matrix approach to the problem of confinement is not restricted to a tube-like geometry or to the FRC model. We intend to look at other types of confinement—in spherical
Figure 9. The effect of a grafting surface on the longitudinal dimension and on the confinement free energy curves of a chain confined in a tube. Chain length: $N = 100$. Solid curve: free end chain. Dashed curve: with the end anchored to a grafting surface. Dash–dotted curve: the free energy variation of the anchored chain with respect to the free coil state.

cavities, parallel plates, channels, etc—and other polymer models as well. Specific applications will include:

(i) the confinement of the rotational isomeric state model in various geometries;
(ii) incorporation of the excluded volume interaction and the action of the solvent;
(iii) translocation of polymers through pores in membranes; and
(iv) the confinement of polymer solutions.

Within the framework of this method, it is quite feasible to design schemes for the study of polymers with any type of primary structure and under a wide variety of conditions.

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Figure 10. The effect of a grafting surface on the longitudinal dimension and on the confinement free energy curves of the chain confined in a harmonic potential. Chain length: \( N = 100 \). Solid curve: free end chain. Dashed curve: with the end anchored to a grafting surface.

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