Reptation of active entangled polymers

SUPPLEMENTARY INFO

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I. ANALYTICAL SOLUTION FOR THE TUBE SEGMENT SURVIVAL FUNCTION.

In order to compute the tube segment survival function \( \psi(s, t) \), we start by calculating the function \( \Psi(\xi, t; s) \). The partial differential equation that describes the dynamics of \( \Psi(\xi, t; s) \) and the boundary and initial conditions are

\[
\frac{\partial \Psi}{\partial t} + c \frac{\partial \Psi}{\partial \xi} = D_c \frac{\partial^2 \Psi}{\partial \xi^2},
\]

\[
\Psi(\xi, 0; s) = \delta(\xi + s - L),
\]

\[
\Psi(0, t; s) = \Psi(L, t; s) = 0.
\]  

(1)

Following the procedure describe in [1], we can try solutions of the form

\[
\Psi(\xi, t; s) = \phi(\xi, t; s) \exp\left(\alpha \xi + \beta t\right).
\]  

(2)

where \( \alpha \) and \( \beta \) are arbitrary parameters. Substituting (2) in the differential equation (1), we get

\[
\frac{\partial \phi}{\partial t} + (\beta + c \alpha - D_c \alpha^2) \phi = (2D_c \alpha - c) \frac{\partial \phi}{\partial \xi} + D_c \frac{\partial^2 \phi}{\partial \xi^2}
\]

(3)

We can choose the values of \( \alpha = c/2D_c \) and \( \beta = -c^2/4D_c \) so that the differential equation (3) is simplified to

\[
\frac{\partial \phi}{\partial t} = D_c \frac{\partial^2 \phi}{\partial \xi^2},
\]  

(4)

with initial and boundary conditions given by

\[
\phi(\xi, 0; s) = \delta(\xi + s - L) \exp(-\alpha \xi),
\]

\[
\phi(0, t; s) = \phi(L, t; s) = 0.
\]  

(5)

which is a simple diffusion problem whose solution is well-known [2]:

\[
\phi(\xi, t; s) = \sum_{p=1}^{\infty} a_p \exp\left(-\frac{p^2 t}{\tau_d}\right) \sin\left(\frac{p\pi \xi}{L}\right),
\]  

(6)

where \( \tau_d \) is the terminal time defined in the main text. Enforcing the initial condition, the coefficients \( a_p(0) \) are immediately obtained:

\[
a_p = \frac{2}{L} \int_0^L \delta(\xi + s - L) e^{-\alpha \xi} \sin\left(\frac{p\pi \xi}{L}\right) d\xi
\]

\[
= \frac{2}{L} e^{-\alpha(L-s)} \sin\left(\frac{p\pi(L-s)}{L}\right).
\]  

(7)

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Substitution of the coefficients $a_p$ into Eq. (6) yields

$$
\phi(\xi, t; s) = \frac{2}{L} e^{-\alpha(L-s)} \sum_{p=1}^{\infty} \exp\left(\frac{-p^2 t}{\tau_d}\right) \sin\left(\frac{p\pi(L-s)}{L}\right) \sin\left(\frac{p\pi \xi}{L}\right), \quad \text{(8)}
$$

Substituting back $\phi(\xi, t, a)$ into Eq. (2) and reverting the first change of variables, it is easy to show that the solution to the original problem (1) yields

$$
\Psi(\xi, t; s) = \frac{2}{L} \exp\left(\frac{c\xi}{2D_c}\right) \exp\left(\frac{-c^2 t}{4D_c}\right) \sum_{p=1}^{\infty} \exp\left(\frac{-p^2 t}{\tau_d}\right) \sin\left(\frac{p\pi s}{L}\right) \sin\left(\frac{p\pi (s - \xi)}{L}\right). \quad \text{(9)}
$$

II. ANALYTICAL SOLUTION FOR THE MEAN SQUARE DISPLACEMENT.

We shall first derive a stochastic equation for reptation with drift. Let $\Delta \xi(t)$ be the distance that the primitive chain moves in a time interval $\Delta t$. We can express $R(s, t + \Delta t) = R(s + \Delta \xi(t), t)$ that relates the position of the tube segment $s$ at time $t + \Delta t$ to the position of the segment $s + \Delta \xi(t)$ at a previous time $t$. The distance $\Delta \xi(t)$ is a random Gaussian variable with mean and variance given by $\langle \Delta \xi(t) \rangle = c\Delta t$, $\langle (\Delta \xi(t))^2 \rangle = 2D_c\Delta t$. This distribution differs with pure reptation where the average of $\Delta \xi(t)$ is 0. To compute the MSD we use the stochastic equation and the definition $g_1(s, t) = \phi(s, s; t) = \langle (R(s, t) - R(s, 0))^2 \rangle$. It is easier to compute the more general correlation function $\phi(s, s'; t) = \langle (R(s, t) - R(s', 0))^2 \rangle$.

Expanding stochastic equation we get the partial differential equation

$$
\frac{\partial \phi(s, s'; t)}{\partial t} - c \frac{\partial \phi(s, s'; t)}{\partial s} = D_c \frac{\partial^2 \phi(s, s'; t)}{\partial s^2}. \quad \text{(10)}
$$

The boundary and initial conditions are preserved from the pure reptation problem:

$$
\phi(s, s'; 0) = a|s - s'|, \quad \left\{ \begin{array}{l}
\left. \frac{\partial \phi(s, s'; t)}{\partial s} \right|_{s=L} = a \\
\left. \frac{\partial \phi(s, s'; t)}{\partial s} \right|_{s=0} = -a.
\end{array} \right. \text{(11)}
$$

In order to turn the boundary conditions homogeneous, we start splitting $\phi(s, s'; t)$ into two different functions:

$$
\phi(s, s'; t) = \psi(s, s'; t) + \rho(s, s'), \quad \text{(12)}
$$

where $\rho(s, s') = a|s - s'|$. Substituting (12) into the original problem, the equation to solve for $\psi(s, s'; t)$ is written as

$$
\frac{\partial \psi}{\partial t} - c \frac{\partial \psi}{\partial s} - D_c \frac{\partial^2 \psi}{\partial s^2} = F(s, s'), \quad \text{(13)}
$$
with homogeneous both initial and boundary conditions, i.e.

\[
\psi(s, s'; t) \bigg|_{t=0} = 0, \quad \frac{\partial \psi}{\partial s} \bigg|_{s=0} = \frac{\partial \psi}{\partial s} \bigg|_{s=L} = 0,
\]

(14)

and where

\[
F(s, s') = ac[\Theta(s - s') - 1] + 2aD_c \delta(s - s'),
\]

(15)

being \(\Theta(s - s')\) the Heaviside function and \(\delta(s - s')\) the Dirac delta. Note that the non-homogeneous term \(F(s, s')\) arises from the substitution of \(\rho(s, s')\) in Eq. (10). The function \(\psi(s, s'; t)\) can be factorized as follows

\[
\psi(s, s'; t) = f(s) \cdot T(s', t).
\]

(16)

For the homogeneous problem, the segmental equation for \(f(s)\) can be expressed as

\[
\frac{\partial^2 f}{\partial s^2} + 2d \frac{\partial f}{\partial s} + \lambda_p^2 f = 0,
\]

(17)

where \(\lambda_p\) are the eigenvalues and

\[
d = \frac{c}{2D_c}.
\]

(18)

The boundary conditions for \(f(s)\) are given in Eq. (14). The solution to this problem with the homogeneous boundary conditions is the following [3]:

\[
f_p(s) = e^{-ds} \left[ \cos \left( \frac{p \pi s}{L} \right) + \frac{dL}{p \pi} \sin \left( \frac{p \pi s}{L} \right) \right] \quad \text{if} \quad p \in \mathbb{N}
\]

\[
f_0(s) = 1 \quad \text{if} \quad \lambda_0^2 = 0.
\]

(19)

Note that the eigenvalues in the first case take the form

\[
\lambda_p^2 = d^2 + \left( \frac{p \pi}{L} \right)^2.
\]

(20)

We shall now expand \(F(s, s')\) in the basis of the eigenfunctions (19):

\[
2aD_c \delta(s - s') = \sum_{p=0}^{\infty} B_p(s') f_p(s),
\]

\[
ac[2\Theta(s - s') - 1] = \sum_{p=0}^{\infty} C_p(s') f_p(s).
\]

(21)
The coefficient of the series can be computed by multiplying the sum by \(\exp(2ds) f_q(s)\) for \(p > 0\) and by \(\exp(2ds)\) for \(p = 0\) and integrating between 0 and \(L\):

\[
\begin{align*}
B_0(s') &= 4aD_c \frac{\exp(2ds')}{\exp(2dL) - 1} \\
B_p(s') &= \frac{4aD_p^2\pi^2\exp(2ds')}{L(L^2d^2 + p^2\pi^2)} f_p(s') \quad p \in \mathbb{N}, \\
C_0(s') &= \frac{2\exp(2ds') - \exp(2dL) - 1}{1 - \exp(2dL)} \\
C_p(s') &= \frac{\exp(ds') \sin \left(\frac{p\pi s'}{L}\right)}{p^2\pi^2 + L^2d^2} \quad p \in \mathbb{N}.
\end{align*}
\]  

(22)

Efforts must now be focused on solving the temporal equation which is written as

\[
\frac{\partial T}{\partial t} + D_c \lambda_p^2 T = F_p(s, s'),
\]  

(23)

where \(F_p(s, s')\) corresponds to the expansion in terms of the spatial eigenfunctions as described above. For the zero mode Eq. (23) is simplified to

\[
\frac{\partial T}{\partial t} = B_0(s') + C_0(s'),
\]  

(24)

which can be straightforwardly integrated to give in a simplified form

\[
T_0(t) = ac \coth(dL)t = \psi_0(s, s'; t).
\]  

(25)

The latter relation is valid since \(f_0(s) = 1\). Equivalently proceeding for the \(p > 0\) modes, the temporal equation (23) with the eigenvalues (20) yields

\[
T_p(t) = D_p(0) \exp(-D_c \lambda_p^2 t) + \frac{F_p(s, s')}{\lambda_p^2}.
\]  

(26)

The first term corresponds to the solution for the homogeneous equation with \(D_p(0)\) to be estimated by enforcing the initial condition (14), so that

\[
D_p(0) = -\frac{F_p(s, s')}{\lambda_p^2},
\]  

(27)

and hence, substituting the full expansion of \(F_p(s, s')\) of the positive modes we get

\[
\psi_p(s, s'; t) = e^{d(s'-s)} \sum_{p=1}^{\infty} \left(1 - e^{-D_c \lambda_p^2 t}\right) \frac{4aLp^2\pi^2}{(p^2\pi^2 + L^2d^2)^2} \\
\times \left[ \cos \left(\frac{p\pi s'}{L}\right) - \frac{dL}{p\pi} \sin \left(\frac{p\pi s'}{L}\right) \right] \left[ \cos \left(\frac{p\pi s}{L}\right) + \frac{dL}{p\pi} \sin \left(\frac{p\pi s}{L}\right) \right].
\]  

(28)
Finally, putting together both eigenfunctions (Eqs. (25), (28)) and adding the function \( \rho(s, s') \), we get the full solution for the segmental motion:

\[
\phi(s, s'; t) = a|s - s'| + \text{act} \coth \left( \frac{cL}{2D_c} \right) + e^{\left( \frac{c(s' - s)}{2D_c} \right)} \sum_{p=1}^{\infty} \left( 1 - e^{-D_c \lambda_p^2 t} \right) \frac{64aD_c^4 L p^2 \pi^2}{(4D^2 p^2 \pi^2 + L^2 c^2)²} \\
\times \left[ \cos \left( \frac{p\pi s'}{L} \right) - \frac{cL}{2D_c p \pi} \sin \left( \frac{p\pi s'}{L} \right) \right] \left[ \cos \left( \frac{p\pi s}{L} \right) + \frac{cL}{2D_c p \pi} \sin \left( \frac{p\pi s}{L} \right) \right].
\]

(29)

