Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 9155–9159 **9155**
DOI: 10.1021/ma1015402

Viscosity and Renewal Time of Polymer Reptation Models

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Received July 9, 2010; Revised Manuscript Received September 10, 2010

ABSTRACT: The viscosity η of polymer melts experimentally scales with the length L of the chains as a power law with an exponent $b \approx 3.4$ larger than the prediction $b = 3$ from de Gennes' theory of reptation. This long-standing controversy is revisited within the repton and necklace models. Exact results from the rigid chain dynamics allow us to predict the leading order viscosities and renewal times for chains with fluctuating lengths and/or center-of-mass initial position fluctuations. The corrections to scaling are determined by numerical simulations to behave as $L^{-1/2}$ in all cases. Such large effects may explain (a) the apparent exponent observed experimentally, (b) confirm the corrections due to the contour length fluctuations, and (c) highlight the importance of the relaxation of longitudinal modes.

Introduction

The reptation of a polymer in the presence of fixed obstacles, when immersed in a polymeric gel for example, was studied long ago by de Gennes,[1,2] who predicted the polymer length dependences of the curvilinear and self-diffusion coefficients as well as the renewal time. The model could also apply to the more complicated problem of the entangled polymer melts with predictions for the viscosity. The main idea is that the polymer is confined and reptates inside a tube formed by the obstacles or the other chains for the melts. The reptation is mainly one-dimensional along the confining tube, and Rubinstein introduced the so-called repton model, a lattice model for the polymer motion incorporating most of de Gennes' ideas of reptation.[3]

The theoretical prediction of the viscosity dependence $\eta \sim L^b$ on the polymer length L with $b = 3$ is in apparent conflict with the experimental observations $b \approx 3.4$.[4−6] This discrepancy is also observed in numerical simulations of the repton model.[3] The corrections to scaling as $L^{-1/2}$ is an explanation for the apparent exponent observed in viscosity experiments.[7] Such corrections are based on a reduced viscosity due to contour length fluctuations (CLF) and constraint release (CR) of the confining tube.[7−9] The longitudinal modes have been also known to affect the stress relaxation.[9] The polymer lengths experimentally accessible are however too low to detect the leading behavior without ambiguity. Thus, a lot of interest in the calculation of the self-diffusion and viscosity in reptation models focused on the long polymer limit. The next to leading order terms were long debated due to discrepancy between analytical and numerical results.[10−15]

In this paper, we will present numerical simulations for the repton and necklace models that confirm unambiguously the $b = 3$ exponent from reptation as well as the corrections to scaling behavior as $L^{-1/2}$ based on exact results for the rigid chain dynamics. The corrections to scaling are shown to depend both on the CLF and on the relaxation of longitudinal modes (LM) (even at a constrained fixed length of the chain) whereas CR are absent of the models considered. One example of LM, the center-of-mass initial position fluctuations (CMF), is shown to affect the viscosity. The importance of CMF is evident in the fixed length model where CLF are absent. The distance ΔCM between the middle of the chain and its center of mass creates forces that attract one end while repulsing the other. This fast motion of the ends has similar effects than the CLF reducing rapidly the length of the polymer inside the initial tube.

After a brief introduction of the reptation models considered in this study, we give some exact results for the curvilinear diffusion coefficients for all the models as well as for the renewal time and the viscosity of the rigid chain model. Then, numerical simulations of the renewal times and viscosities for all the models are presented with discussions of the leading order behavior and the corrections to scaling terms. Perspectives on theoretical developments and practical applications are left for the conclusion.

Models for Polymer Reptation

The models for reptation are essentially one-dimensional and consider a single chain of monomers inserted in a tube. While accounting for the longitudinal degrees of freedom like the CLF and CMF, it neglects the CR of the tube while the other chains are moving.

Repton Model. In the Rubinstein or repton model,[3] the polymer chain contains N beads. A configuration is characterized by $N - 1$ variables τ_i corresponding to the existence ($\tau_i = 0$) or not ($\tau_i = 1$) of a stored length between the two beads i and $i + 1$ along the chain. The polymer diffusion is obtained by the motion of stored lengths along the chain. Three different moves exist (see Figure 1): (a) the motion of an end bead outside its cell when this cell is occupied by the neighbor bead, (b) the motion of an end bead from its own cell to the cell of its neighbor if both cells differ, and (c) the motion of an internal bead. Cell occupancies need to be consistent with this move which means that the bead leaves a cell occupied by a neighbor and reaches the cell of the other neighbor. The moves (a) and (b) correspond to the exit and entrance of a stored length in the chain, whereas (c) is the internal motion of a stored length. The respective rates of the moves are p_a, p_b, and p_c.

In general, those rates are proportional to the number of accessible cells for the moving repton. Thus, in d dimensions and with a cubic lattice, $p_b = p_c$ and $p_a = 2dp_b$. However, the existence of larger or smaller monomers at the two ends of the chain may either reduce or increase the ratio p_b/p_c. Similarly, in the case of a polymer embedded in a gel, the gel structure in which the polymer diffuses may affect the

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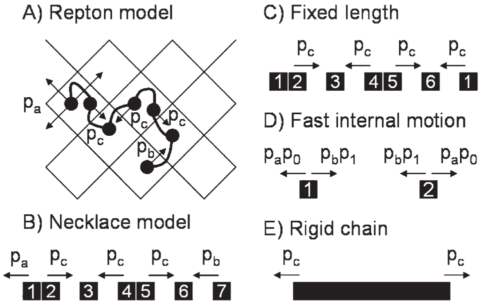

Figure 1. (A) A two-dimensional representation of a polymer chain with seven beads and the underlying cell structure in the repton model. (B) The necklace model with hardcore beads. (C) The fixed length chain with the two ends moving together. (D) The chain with fast internal motion corresponds to an infinite rate p_c. (E) The rigid chain moves as a whole.

ratio p_a/p_b. The latter ratio is responsible as we shall see to the equilibrium properties like the length of the polymer chain. The former ratio only affects the dynamics of the polymer. From a theoretical point of view, the existence of those three independent parameters gives a great flexibility in the dynamics of the polymer chain.

Necklace Model. Guidoni et al.[16] introduced recently a slightly modified model with hard-core beads. The cells may only be occupied by a single bead and two neighbor beads are either in neighbor cells ($\tau_i = 0$) or in next-neighbor cells ($\tau_i = 1$). The chains are longer than for the repton model; however, the dynamics is similar as seen in Figure 1.

Fixed Length. The CLF may be removed considering periodic boundary conditions for the motions of the end beads.[17,18] In this case, the two ends move together, and the number N_1 of nonzero variables τ_i or $N_0 = N - N_1 - 1$ of stored lengths is conserved by the dynamics leading to a fixed length of the chain. The fluctuations of the other LM than CLF are conserved, especially the CMF.

Fast Internal Motion. The chain with fast internal motion corresponds to an infinite rate p_c. The chain presents CLF with a center of mass constantly at equilibrium. In fact, all LM except CLF are instantaneously relaxed. Simplifications in the dynamics allow us to consider only the two ends motion with adapted rates p_ap_0 for increasing and p_bp_1 for decreasing the chain length. $p_1 = N_1(t)/(N - 1)$ and $p_0 = N_0(t)/(N - 1)$ are the instantaneous probabilities to have a stored length or not at proximity of the end bead. Since only the two end beads are considered, numerical simulations of longer polymers are accessible, allowing better estimations of the corrections to scaling.

Rigid Chain. Finally, we consider the trivial model of a rigid chain where the chain moves as a whole.[19,20] This simple model allows us to obtain exact results for the renewal time and viscosity. From those exact results (confirmed by numerical simulations), the leading order behaviors for the other models are deduced. Subtracting those exact behaviors from the numerical calculations allows us to obtain explicitly the corrections to scaling with great accuracy.

Exact Results and Leading Order Hypothesis

Curvilinear Diffusion Coefficient D_c. For the repton and necklace models, exact results have recently been obtained for D_c:[21-24]

$$D_c(N) = \frac{p_a p_b}{p_a + p_b} \frac{a^2}{(N-2)\Delta + 2} = \frac{D_0 P(0) P(1)}{N - 2 + 2\Delta^{-1}} \qquad (1)$$

with $D_0 = p_c a^2$ the individual diffusion coefficient of a free internal repton, a the lattice spacing, $P(0) = 1 - P(1) = p_b/(p_a + p_b)$ the probability of a stored length, and $\Delta = (p_a + p_b)/p_c$. In those models, the chain length is fluctuating with an average $L = (N - 1)(P(1)a + l_0)$ and a variance $\Delta L^2 = P(1)P(0)(N - 1)a^2$, where $l_0 = 0$ for the repton and $l_0 = a$ for the necklace models.

With periodic boundary conditions, the chain length is fixed to $L = (N - 1)(P(1)a + l_0)$ and $D_c^{pb}(N) = D_0P(0)P(1)/(N - 2)$ where we replaced $N_0/(N - 1)$ by the probability $P(0)$ to have a stored length in analogy with the open boundary case. For the fast internal motion of the beads, the limit $p_c \to +\infty$ leads to $D_c = P(0)p_a a^2/2$ with similar expressions for the average length and variance than the repton and necklace models. Finally, for the rigid chain, $D_c = D_0 = p_c a^2$ with a fixed length $L = (N - 1)a$.

Renewal Time and Viscosity for a Rigid Chain. Let us first define the length $L(t)$ of the initial tube that the polymer never quit after a time t. The renewal time τ is then defined as the first time for which the polymer completely quit the tube or $L(\tau) = 0$, whereas the viscosity, for a single chain problem, is given by[10]

$$\eta = \frac{1}{L} \int_0^{\infty} L(t)\, dt \qquad (2)$$

Because of the fluctuations of those quantities from different realizations of the dynamics and of the equilibrium initial conformation of the chain, averaged values are considered for τ and η.

For the rigid chain, the averaged renewal time and viscosity are exactly given by

$$\tau_0 = \frac{L(L+a)}{2D_0} \quad \text{and} \quad \eta_0 = \frac{(L+a)(L+2a)}{6D_0} \qquad (3)$$

Those expressions are one of the main results of this paper, and a detailed calculation is given in the Appendix. We will assume that the leading order of the renewal time τ_{lo} and viscosity η_{lo} for the repton and necklace models as well as for the fixed length and fast internal motion are simply deduced from the expressions for the rigid chain and a rescaling of the curvilinear diffusion constants as follows: $\tau_{lo} = \tau_0 D_0/D_c$ and $\eta_{lo} = \eta_0 D_0/D_c$. Both τ_0 and η_0 scale as L^2 with $b = 2$ since $D_0 \sim L^0$. Whereas, since $D_c \sim L^{-1}$, the reptation scaling for the renewal time $\tau_{lo} \sim L^3$ and viscosity $\eta_{lo} \sim L^3$ is obtained with $b = 3$. The exact result of the rigid chain leads to an explicit value of the prefactor for the leading order term in the other models. For the repton and necklace models

$$\tau_{lo} = \frac{L^3}{2A} + O(L^2) \quad \text{and} \quad \eta_{lo} = \frac{L^3}{6A} + O(L^2) \qquad (4)$$

with $A = D_0P(0)P(1)(aP(1) + l_0)$ and $l_0 = 0$ or a. The corrections to the leading behavior for those estimations scale as L^2, are positives, and are especially important at small lengths of the chains. However, those corrections are not the leading corrective terms. The later ones scale as $L^{5/2}$ and are negative. In order to amplify this next to leading term, it is easier to consider the difference between the measured values τ and η with our estimations τ_{lo} and η_{lo} rather than with the leading order behaviors in order to remove most of the L^2 terms. Thus, the corrections to scaling are easily estimated from the renewal time and viscosity as $\Delta\tau/\tau = (\tau_{lo} - \tau)/\tau$ and $\Delta\eta/\eta = (\eta_{lo} - \eta)/\eta$.

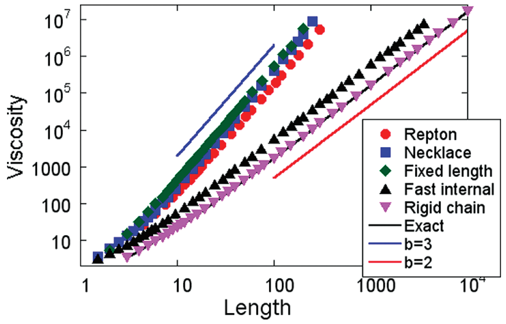

Figure 2. Viscosity as a function of the polymer length for all the reptation models in a log−log scale. The scaling behavior L^3 for the necklace and repton models is evident. The rigid chain and fast internal motion models present a scaling behavior L^2 due to curvilinear diffusion coefficient independent of the chain length. Parameters considered for the simulations correspond to $P(1) = 1/2$ and $\Delta = 1$.

Numerical Results and Discussion

We performed numerical simulations of the renewal time and viscosity for all the reptation models using a kinetic Monte Carlo algorithm.[25] Average values were obtained from 10^4 to 10^7 different equilibrium initial conditions depending on the chain lengths. For the repton, necklace, and fixed length models, we were limited to chains with few hundred beads in order to obtain small errors on the corrections to scaling. With the fast internal motion model, since only the two end dynamics are simulated, larger chains were considered up to few 10^3 beads, enabling us to characterize precisely the corrections to scaling in this case.

The leading order behavior of the viscosity as L^3 for the repton, necklace, and fixed length models is evident from Figure 2. Similar results are obtained for the renewal time and for various sets of the parameters p_a, p_b, and p_c. The rigid chain and fast internal motion models present a scaling behavior L^2 due to the polymer length independence of the curvilinear diffusion constant D_c. For rigid chains, the numerical simulations confirmed the exact results presented above.

In order to confirm the leading order estimation including the value of the prefactor, we present the corrections to scaling for the renewal time $\Delta\tau/\tau$ and the viscosity $\Delta\eta/\eta$ as a function of $\Delta L/L$ in Figure 3 for the fast internal motion model (top) and repton model (bottom). Since $\Delta L^2 \sim L$, then $\Delta L/L \sim L^{-1/2}$, and we conclude from the linear behavior for large lengths (small $L^{-1/2}$) observed in Figure 3 that the corrections to scaling behaves as $L^{-1/2}$ for the repton and fast internal motion models. For this last model, the corrections to scaling present a linear behavior with respect to $L^{-1/2}$ for nearly two decades. Furthermore, as can be seen by the collapse of the curves for various $P(1)$ values, the corrections to scaling are explicitly and identically dependent on the chain length fluctuations $\Delta L/L$. This behavior is also present for the repton and necklace model. Within those models, this corresponds to some universality in the dynamics of the polymer chains in a confining tube. In order to be more quantitative, it is possible to define α (or β) the proportionality coefficient between the corrections to scaling of the renewal time $\Delta\tau/\tau$ (or the viscosity $\Delta\eta/\eta$) and the reduced chain length fluctuations $\Delta L/L$ ($\Delta\tau/\tau = \alpha\Delta L/L + O(L^{-1})$ and $\Delta\eta/\eta = \beta\Delta L/L + O(L^{-1})$). For the fast internal motion model, $\alpha = 1.8 \pm 0.1$ and $\beta = 2.6 \pm 0.1$, whereas for the repton model $\alpha = 5.3 \pm 0.3$ and $\beta = 8.0 \pm 0.5$ and for the necklace model $\alpha = 5.4 \pm 0.7$ and $\beta = 8.1 \pm 0.5$. As can be seen, not only the parameters α and β are independent of $P(0)$, the probability of stored lengths, for each model, but it seems also independent of the hard-core size l_0 of the beads since repton and necklace models lead to similar values. This result confirms the universality behavior for the dynamics of chains confined in a tube discussed above at least within those models.

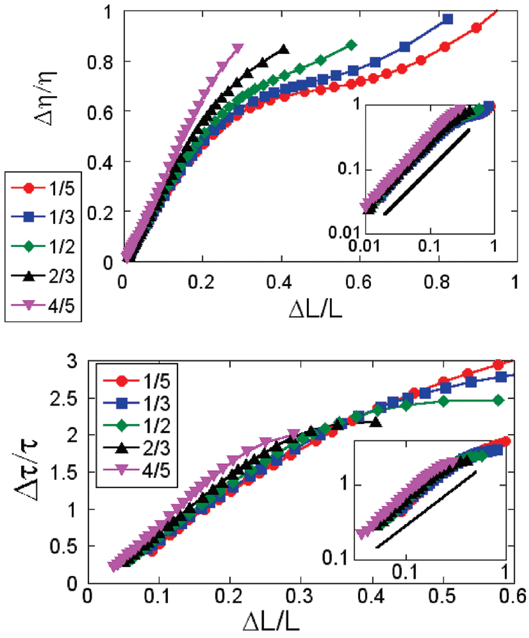

Figure 3. Corrections to scaling of the viscosity for the fast internal motion model (top) and of the renewal time for the repton model (bottom) as a function of $\Delta L/L \sim L^{-1/2}$. The linear dependence is evident for all the parameters $P(1) = p_a/(p_a + p_b)$ considered (legends) with $\Delta = 1$. The linear behavior is confirmed in a log−log scale (insets).

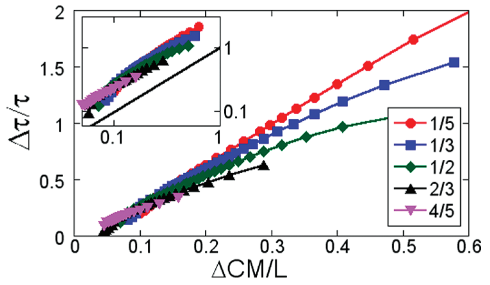

Figure 4. Corrections to scaling of the renewal time for the fixed length model as a function of $\Delta CM/L \sim L^{-1/2}$. The linear dependence is evident for all the parameters $P(1) = p_a/(p_a + p_b)$ considered (legends) with $\Delta = 1$. Inset: log−log scale.

For the fixed length model, the corrections to scaling also behave as $L^{-1/2}$, whereas the CLF are absent. However, at time $t = 0$, the center of mass is not necessarily centered at the middle of the chain. The fluctuations of those initial positions from the center drive the chain ends preferentially in one direction since one-half of the beads is compressed whereas the other half is stretched. The resulting forces exerted on the ends in the same direction rapidly reduce the length $L(t)$ remaining in the initial tube. This effect leads to similar corrections to scaling than the CLF, but they may differ in magnitude. In fact, we expect the corrections to be proportional to the relative distance $\Delta CM/L$ of the initial position of the center of mass from the middle of the chains. The variance $\Delta CM^2 = P(1)P(0)(N - 1)a^2$ is identical to the variance ΔL^2 of the length in the repton or necklace model. Thus, the corrections to scaling are expecting to scale as $\Delta CM/L \sim L^{-1/2}$. The numerical simulations confirm this assumption as shown in Figure 4. More quantitatively, $\Delta\tau/\tau = (2.5 \pm 0.3)\Delta CM/L + O(L^{-1})$ and $\Delta\eta/\eta = (4.1 \pm 0.2)\Delta CM/L + O(L^{-1})$ for the fixed length models with $l_0 = 0$ and $\Delta\tau/\tau = (2.4 \pm 0.3)\Delta CM/L + O(L^{-1})$ and $\Delta\eta/\eta = (4.0 \pm 0.2)\Delta CM/L + O(L^{-1})$ for $l_0 = a$. Similarly to the results obtained for the necklace and repton models, the corrections to scaling with the chain length constraints present some universality in the dynamics considering

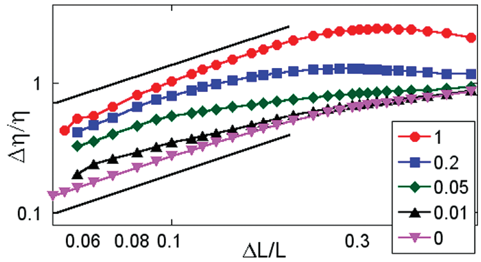

Figure 5. Corrections to scaling of the viscosity for the repton model as a function of $\Delta L/L \sim L^{-1/2}$ for various values of $\Delta = (p_a + p_b)/p_c$ considered (legends) in a log−log scale with $P(1) = 1/2$.

the independence with respect to the parameters of the models $P(1)$ and l_0.

The CMF are the simplest fluctuations of LM to interpret in term of corrections to scaling. However, it is possible that other fluctuations of LM are concerned. From our numerical results, we may deduce that either their corrections are negligible compared to the CMF ones, or they behave similarly proportional to $\Delta CM/L$.

Likhtman and McLeish considered recently the relaxation of longitudinal modes in order to improve the stress modulus expression.[9] Those modes were not considered to affect the single chain function $\mu(t) = L(t)/L$ but rather to be relaxed due to a small deformation of the tube. The dissipation of those longitudinal modes should be related to the relaxation of their fluctuations by the theorem of fluctuation−dissipation. In ref 9 all Rouse modes up to $p = Z - 1$ were affected in the stress relaxation. This parameter Z is proportional to the length of the chain L; thus, no corrections to scaling proportional to $Z^{-1/2}$ (or $L^{-1/2}$) can be expected for the viscosity, in contrast to the results presented here.

The effect of the center-of-mass position (principally CMF but possibly other LM than CLF) should be present not only in the fixed length model but also in the repton and necklace ones increasing the corrections to scaling from the pure chain length fluctuations (CLF). In the fast internal motion model, the dynamics of the ends are infinitely slow compared to the internal beads annihilating most of the LM leaving only the CLF. Considering various rates p_c for the internal motion of the beads, it is possible to increase continuously the CMF and other LM fluctuations in the presence of the CLF (Figure 5). The slopes 1 in the log−log scale confirm the linear dependence of both the CLF and CMF with $L^{-1/2}$ in the repton model. Similar results are obtained for the necklace model. Further numerical simulations would be necessary, but it seems that as soon as $p_c < +\infty$, α and β are independent of p_c (the data for $\Delta = 1$ and 0.2 seem to converge for large lengths, and similar trends are observed for lower Δ).

Conclusion and Perspectives

Considering different models for the reptation of polymers in a confining tube, we obtained explicit results on the leading behavior of the renewal time $\tau \approx L^2/2D_c$ and viscosity $\eta \approx L^2/6D_c$ with the curvilinear diffusion $D_c \approx D_0P(0)P(1)/N$ for the necklace and repton models. Those results confirm the expected leading behavior scaling with L^3 proposed by de Gennes within the reptation theory.[1] Furthermore, we obtained numerical evidence for the behavior of the corrections to scaling as $L^{-1/2}$. Those large corrections to scaling may explain the experimentally observed exponent $b \approx 3.4$ instead of the predicted value $b = 3$. In the models presented, those corrections are shown to be influenced by the chain length fluctuations (CLF) (already long ago recognized[7]) but also by the initial position of the center of mass (CMF) and more generally by the relaxation of the equilibrium fluctuations of longitudinal modes. In particular, both terms are leading to a similar behavior proportional to $L^{-1/2}$. However, the various kinetic rates p_a, p_b and p_c allow us to separate both effects explicitly. Especially, the ratio $\Delta = (p_a + p_b)/p_c$ between the rates of the ends and the internal beads plays a crucial role. Nonetheless, some universality has been observed in the dynamics of a confined chain.

On the theoretical point of view, the existence of different kinetic rates related to the internal or end beads allow us to discriminate between the relaxations of different longitudinal modes. It would be interesting to transpose those results on lattice models to off-lattice models like the usually considered bead spring (or 1D Rouse) chain.[9] Furthermore, Likhtman and McLeish discussed recently the effect of the stress relaxation due to longitudinal modes which explicitly differs from the single chain contribution.[9] Our results show the importance of the fluctuations of such longitudinal modes directly on the single chain function $L(t)/L$. It would be interesting to analyze their effects in the 1D Rouse chain. Are they already taken into account for long times by the rescaling of the renewal time and the plateau modulus or not? Certainly, the effects for short time should be different to the pure chain length fluctuations. Whereas in the case of the CLF both ends fluctuate independently and identically, the presence of CMF drives both ends in the same direction. Another important point is the possible relation between the relaxation of LM as described by Likhtmann and McLeish in[9] compared to the relaxation of the equilibrium LM fluctuations considered in this study. The fluctuation−dissipation theorem should certainly play a role but a direct quantitative link remains to be done in a particular model.

This study focused on linear chain models but the reptation theory is known to apply also to branched polymers. It would be interesting to generalize the repton or necklace models to this case. Ideas in this direction are under study.

On the experimental point of view, it is interesting to notice that chemical modifications of the polymer ends by larger monomers than the internal ones would have the effects to modify the kinetic rates. It would be interesting to observe the effects of those chemical modifications on the viscosity even though a direct comparison between chemically different polymers may be difficult to interpret.

Appendix

In this appendix we calculate the expression for the renewal time and the viscosity of the rigid chain model. This calculation is based on exact results on the span of a polymer chain by Rubin.[26] In fact, since the chain is rigid, the motion of both ends describes the same 1D random walk with an equal rate probability p_c to move to the left or right (this parameter is replaced by α in Rubin's paper). Because of the rigidity of the chain, the simple relation $L(t) = L - aM(t) + a$ relates the length $L(t)$ remaining in the tube at time t to the number of visited sites $M(t)$ by one end (note that at $t = 0$ $L(0) = L$ whereas $M(0) = 1$, which explain the additional a term). This function $M(t)$ is directly related to the span M of a polymer with N monomers considered by Rubin[26] with the simple rescaling of the time by $N = tp_c$.

From the fraction $C(M - 1, N)$ of N step random walks with a span M (eq 2.2 in ref 26), we are able to determine the probability $P(M,N) = \sum_{s=0}^{M-1} C(s,N) = c_N(M) - c_N(M - 1)$ for a span lower than M (the expression of $c_N(M)$ is given by eq A7 in ref 26). Thus, we deduce the probability $p_M(N) = P(M,N) - P(M,N-1)$ that the span increases to M at the Nth step.

The renewal time τ_0 corresponds to the first time the polymer quits completely the tube, $L(\tau_0) = 0$. Its average is given by $\tau_0 = \sum_N Np_M(N)$ with a span $M(\tau_0) = (L + a)/a$. The probability $p_M(N)$ is expressed in terms of $c_N(M)$ with an explicit definition given in Appendix A of ref 26. Simple calculations of the sums involved in τ_0 with the Mathematica software lead to the mentioned result $\tau_0 = L(L + a)/2D_0$ with the appropriate rescaling of the time.

The viscosity η_0 is given by the integral of $L(t)/L$ until $L(t)$ reaches 0. This may be expressed as $\eta_0 = (1/L)\sum_{k=1}^{L/a}\tau_0(ka)$ where we replaced the sum along the length by a sum along the time using the inverse function $\tau_0(L)$ of $L - L(t)$. From the expression of $\tau_0(L)$ follows directly $\eta_0 = (L + a)(L + 2a)/6D_0$.

Both exact results for τ_0 and η_0 are confirmed by numerical simulations. For small chain lengths, long numerical simulations allow us to obtained relative errors below 10^{-5}. For longer chain lengths, no discrepancy between analytical and numerical results may be observed (see Figure 1, for example).

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