Effects of length fluctuations on the viscosity exponent in the necklace model

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Abstract
It is commonly accepted that contour length fluctuations increase the viscosity exponent for chains that diffuse by reptation. We found that length fluctuations in the necklace model can play an unexpected role as they can also decrease this exponent. A detailed analysis of the interplay between the discrete character of the model and how the fluctuations take place is presented in this work. Basically, we found that when fluctuations are symmetric their influence is the expected one; when fluctuations are not symmetric new effects can appear.

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1. Introduction

The dynamics of entangled linear polymers has been successfully described by reptation theory [1, 2]. Reptation considers a single snakelike linear chain trapped in a network of permanent entanglements. This network hinders lateral movements of the chain confining its motion within a one-dimensional curvilinear path, called the tube. The model predicts that diffusivity scales with the molecular weight as $M^{-\alpha}$, where $\alpha = 2$ in three dimensions, and that the zero-shear-rate viscosity scales as $\eta_0 \sim M^\beta$, with $\beta = 3$. However, experiments show deviations from these scalings. The challenge has been to identify the origin of these deviations from the original predicted scaling [3].

Doi proposed that the observed scaling could be attributed to a chain springlike motion, or contour length fluctuations (CLFs), that speed up relaxation in such a way that the viscosity including fluctuations is smaller than the viscosity when fluctuations are not incorporated [4]. He argued that the fraction of the tube that is relaxed by fluctuations scales as $M^{-1/2}$. Thus, as M gets larger, this effect vanishes so that the viscosity increases faster than expected, meeting the asymptotic regime from below. More recent theoretical work also supports CLFs as the major source for scaling deviations [5].

A second modification of the original theory comes from the fact that all the chains are mobile and then entanglements are not permanent on the time scale of reptation. The tube motion or constrain release (CR) is a collective effect as opposed to fluctuations which are a single chain effect [6–12]. In experiments, tube motions can mostly be suppressed by studying the dynamics of a small fraction of short entangled probe chains (tracer diffusion) in a high-*M* matrix of low diffusivity [13–15].

Rubinstein proposed the first discretized version of the reptation model more than 20 years ago [16]. This model can predict an effective exponent for the viscosity larger than 3, demonstrating that a simple discrete model of a single-chain dynamics can present nontrivial behavior. Since then, other models, including different modifications of the Rubinstein model, have been introduced. This is the case of the Duke model [17], which describes gel electrophoresis or the fast extron model of Leegwater [18].

In this work, we study the reptation scaling in the necklace model. This is a one-dimensional discretized model that mimics the diffusion of a chain including CLFs. We avoid a number of complications that can arise in a realistic model. We do not focus on reproducing experiments but on presenting a very simple model with rich behavior. Extending our previous work [19, 20], we especially focus on cases in which diffusion shows the original reptation scaling with the chain length, so the viscosity scaling is not affected by the diffusivity scaling. It is shown that chain-length fluctuations can affect viscosity in an unexpected way. Also, comparison with the resulting viscosity of a rigid-length chain indicates that fluctuations can increase or decrease the viscosity exponent. These results show that the manner in which fluctuations behave can be crucial in discretized models such as the necklace model.

2. Model

The discretized version of reptation known as the necklace model, in which hardcore interactions are included, will be studied [19, 20]. The model consists of a one-dimensional chain with *N* beads or particles. The hardcore interactions are incorporated by considering that beads can hop to a nearest site only if this site is empty. Particles can hop to the right or left but no more than one site can be empty between two particles which preserves chain integrity. If allowed by these rules, the probability for a hopping is the same for all the particles except for those at the ends. Indeed, a middle particle jumps with a probability per unit time p_c while end particles are allowed to jump with probabilities per unit time p_a and p_b when jumping stretches or compresses the chain, respectively (see figure 1) (for more details, see [19, 20]). Hence, p_a, p_b and p_c are the free parameters in the necklace model. In the following, we use that the distances between the adjacent sites of the lattice and the unit time are both equal to 1.

3. Theoretical considerations

Reptation scaling can readily be derived by resorting to the Einstein relation [1]. If all beads have the same behavior, the frictional force is proportional to the number of beads in the chain, *N*. Then, the mobility μ must be equal to μ_1/N, where μ_1, independent of *N*, is the mobility of a single bead. The Einstein relation states that mobility and diffusion are proportional, therefore the one-dimensional diffusion coefficient or tube diffusivity, D_{tube}, must be equal to D_1/N, where D_1 is the diffusion coefficient of a single bead; i.e., $D_{\text{tube}} \propto 1/N$. To escape from the original tube, the chain must progress along the tube a distance *L*, which is proportional to
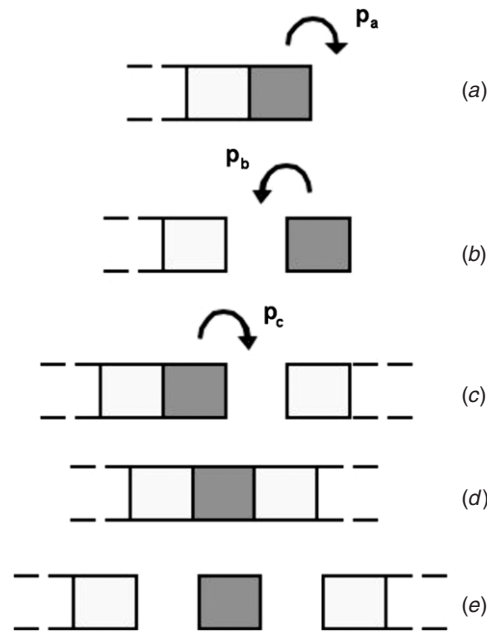
Figure 1. Configurations for end ((*a*), (*b*)) and middle particles ((*c*)–(*e*)), and their hops. In configurations (*d*) and (*e*), jumps are not possible because there is not a neighboring hole and only one hole is allowed between particles.

N. The time required for this is

$$\tau \propto \frac{L^2}{D_{\text{tube}}} = \frac{NL^2}{D_1} \propto N^3. \tag{1}$$

Let us stress that, at this point, we assume the absence of length fluctuations. As the zero-shear-rate viscosity is proportional to τ, the original reptation theory predicts an exponent $\beta = 3$.

While a reptating chain moves a length L along its tube, in space this motion corresponds to a much smaller displacement because the tube is contoured. More specifically [21], after a given time, the chain diffuses out of its initial tube and is in a new configuration confined in a new tube, which is uncorrelated with the initial one. To do this, the chain must diffuse a distance of the order of its length. In its new configuration, the center of mass of the chain is displaced from the initial position by an amount proportional to the chain's span, which goes as $N^{1/2}$ for a Gaussian chain. Then one obtains

$$D_{\text{rep}} \propto \frac{D_{\text{tube}}}{N}, \tag{2}$$

and thus, D_{rep} is proportional to N^{-2}. Deviations of the diffusion coefficient from the N^{-2} scaling could be due to the failure of equation (2). However, the extension of the necklace model in two and three dimensions in the case $p_a + p_b = p_c$ scales as N^{-2}, for $N \geqslant 10$, as shown in [22]. Anyway, these details do not affect our conclusions because we focus on viscosity through the manner a chain abandons its original tube.

In the necklace model, an empty site in the chain is named a hole. The probability of having a hole between two particles can easily be calculated as shown in [19]:

$$P_h = \frac{p_a}{p_a + p_b}. \tag{3}$$

Note that P_h is independent of p_c. The average number of holes in a chain is $P_h(N-1)$ since there are $(N-1)$ positions available for holes. Then the average length of a chain and its fluctuation amplitude are given by

$$\langle L \rangle = N + P_h(N-1), \tag{4}$$

$$\langle (L - \langle L \rangle)^2 \rangle = (N-1)P_h(1-P_h). \tag{5}$$

Recently, the exact analytical expression for the diffusion coefficient for the one-dimensional necklace model has been obtained [23, 24] (see also [25] where related results were obtained), and it is given by

$$D = \frac{p_a p_b p_c}{(p_a + p_b)\left[(N-2)(p_a + p_b) + 2p_c\right]}. \tag{6}$$

The mean jumping frequencies of an end particle (k_e) and a middle particle (k_m) can be calculated (see [23]). The ratio between these jumping frequencies is

$$\frac{k_e}{k_m} = \frac{p_a + p_b}{p_c}. \tag{7}$$

If $p_a + p_b = p_c$, the probability of jumping is the same for every particle of the chain. Under this condition, all particles behave similarly and then the diffusivity presents the scaling originally predicted for reptation, namely $D_{\text{tube}} \propto 1/N$. Indeed, in this case equation (6) simplifies as follows:

$$D = \frac{p_a p_b}{p_c} \frac{1}{N}. \tag{8}$$

This means that for $p_a + p_b = p_c$, the effective friction at the end particles is the same as that at the rest of the particles in the chain. This is also confirmed in [26], where we particularly studied the consequences of applying an external force to every particle of the chain. We found that, when $p_a + p_b = p_c$, the chains are dragged without deforming and the Einstein relation is always valid, for chains with any number of beads and for any applied force strength. This means that, for any N, there is a linear dependence between the drift velocity and the applied force.

The relaxation process can be studied by following the rates at which the chain vacates the initially occupied sites [16, 27]. The number of these sites will be denoted as $l(t)$, that is, the part of the original tube that has not met the chain ends during the time interval between 0 and t [4]. The zero-shear-rate viscosity is calculated by integrating the stress, which is proportional to $l(t)$, i.e.

$$\eta_0 = \frac{1}{\langle L \rangle} \int_0^\infty \langle l(t) \rangle \, dt, \tag{9}$$

where L is the chain length and the brackets denote the ensemble average. Defining $x_R(t)$ as the leftmost propagation of the bead of the right end at time t and, similarly, $x_L(t)$ as the rightmost propagation of the bead of the left end, for the necklace model $l(t) = x_R(t) - x_L(t) + 1$, provided that $x_R(t) - x_L(t) + 1 \geqslant 0$, $l(t) = 0$ otherwise.

Contour length fluctuations and constrain release or tube reorganization are not included in the original reptation model. This model considers the random walk of a fixed length object
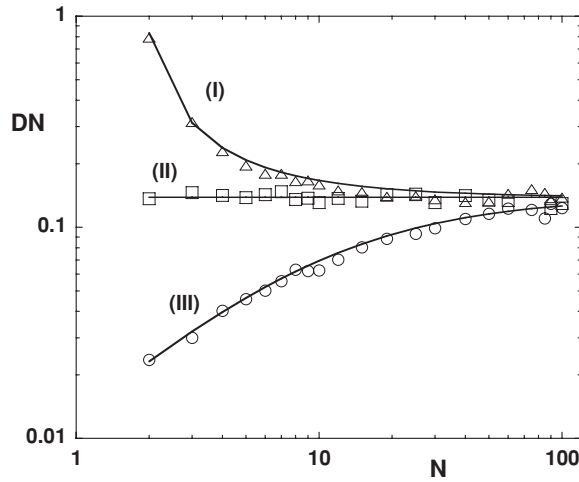
Figure 2. Diffusion coefficient of the center of mass *D*, plotted as *DN*, as a function of the number of beads *N*. The parameters of the model (p_a, p_b, p_c) are (1, 1/5, 1/5) for case I, (5/6, 1/6, 1) for case II and (5/36, 1/36, 1) for case III. Lines correspond to the analytical values of equation (6). For the sake of clarity, results for case I were multiplied by 5 so the diffusivities for the three cases converge to the same value for large *N*.

with a curvilinear (or tube) diffusion coefficient inversely proportional to its molecular weight. Experimentally, the CR effects can be minimized in tracer diffusion because the matrix of high molecular weight provides obstacles that confine for a larger time the reptation of tracer chains. It is found that when the matrix molecular weight is sufficiently high, the tracer diffusivity scales with the probe chain's molecular weight as predicted by the original reptation theory, i.e., $D_{rep} \propto 1/N^2$ [13, 14]. Note that in these experiments CLFs are present.

The necklace model does not include CR, but chains are free to stretch and compress as they diffuse. Indeed, a chain within the necklace model is not considered to be a rigid object as one end moves independently of the other one. However, independent of similitudes and differences with experiments, the main goal of the present work is to study, from a theoretical point of view, the effects of chain-length fluctuations on viscosity in the necklace model.

4. Results and discussions

With the Monte Carlo simulation, the diffusivity of the center of mass is determined through

$$D = \frac{\langle [R_m(t) - R_m(0)]^2 \rangle}{2t}, \qquad (10)$$

where R_m is the position of the center of mass. In figure 2, numerically calculated diffusion coefficients for some given parameters are presented. We have chosen three groups of values for the parameters (p_a, p_b, p_c), specifically (1, 1/5, 1/5), case I; (5/6, 1/6, 1), case II and (5/36, 1/36, 1), case III. Parameters have been chosen to always have the same average number of holes ($P_h = 5/6$) and then the same average length and length fluctuations (see equations (4) and (5)). To highlight deviations from the reptation scaling, *DN* is plotted. For the sake of clarity, results for case I were multiplied by 5 so the diffusivity for the three cases converges to the same value with *N*. In the asymptotic regime, *D* always presents a slope 1/*N*, which is the expected diffusivity dependence for reptation in a one-dimensional model that
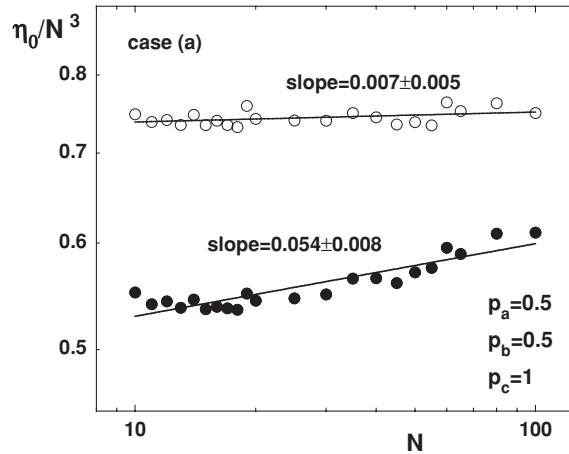
Figure 3. The viscosity as a function of the number of beads N plotted as η_0/N^3 in a log–log plot. The parameters of the model (p_a, p_b, p_c) are (0.5, 0.5, 1). Full symbols represent the viscosity for chains that follow the rules of our model. Open symbols represent the viscosity for chains of constant length, $\langle L \rangle$, for which their centers of mass move as dictated by the centers of mass of chains that follow our model dynamics during diffusion. Note that, as a consequence of fluctuations, the viscosity exponent becomes larger.

corresponds to the tube diffusivity. The exponent α (in one dimension) for relatively small N becomes larger (case I) or smaller (case III) than 1 because end particles present larger (case I) or smaller (case III) jumping frequencies than middle particles. For large enough values of N, the influence of end particles vanishes and then D always presents a slope $1/N$. In case II, in accord with equation (8), DN shows no dependence with N. In what follows, we will restrict our analysis to cases in which $p_a + p_b = p_c$ for which $D_{\text{tube}} \propto 1/N$, see equation (8), as is predicted by the original reptation theory.

Note that the model has in principle three parameters: p_a, p_b and p_c. However, what is relevant in our studies is the ratio among them and thus we chose $p_c = 1$. This reduces the number of free parameters to 2. Finally, since we will only study the cases for which $p_a + p_b = p_c$, the model has only a single parameter, say $p_a = P_h$. Even though we do not attempt to reproduce experimental findings, we will work with $10 \leqslant N \leqslant 100$, which approximately corresponds to the range of molecular weights used in experiment to obtain the viscosity exponent (N in the model plays the role of Z in [14]).

In figure 3, the numerically calculated values of the viscosity through equation (9) for a case with $p_a = p_b = 0.5$ and $p_c = 1$, case (a), are presented (full symbols). In order to stress how far from 3 the exponent β is, η_0/N^3 is plotted. Note that even for $N = 100$, the steady state viscosity values are apparently far from reaching the asymptotic behavior. The slope found in the double logarithmic scale is not exactly equal to 3. In fact, the viscosity presents a dependence of $N^{3.05}$ that one would attribute to a CLF effect.

To check the influence of length fluctuations, we took a chain of constant length, equal to $\langle L \rangle$, and made its center of mass move as dictated by the center of mass of a chain during its diffusion within the necklace model. Note that this is very close to the original model of de Gennes in which there are no length fluctuations. Specifically, in the simulation we use two chains. The first one corresponds to the necklace chain and the second one to the constant length chain. Every time the center of mass of the first chain moves, due to the hop of a
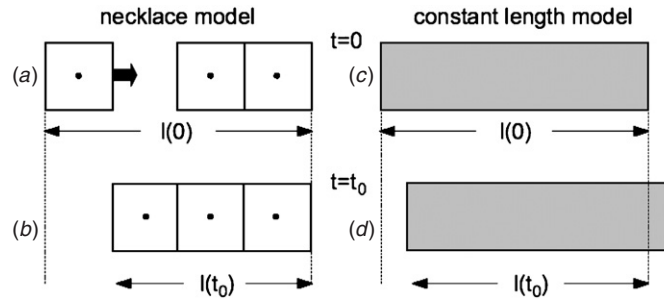
Figure 4. Example for a chain with $N = 3$ and $P_h = 0.5$ for the necklace and constant length models; points correspond to the positions of the beads. (*a*) Initial chain configuration within the necklace model; the number of occupied sites is $l(0) = 4$. (*b*) Chain configuration after the hop of the left bead; the number of sites that were originally occupied is $l(t_0) = 3$. (*c*) Chain in the constant length model for which $l(0) = \langle L \rangle = 4$. (*d*) The hop of a bead to the right in the necklace model reflects as a move of $1/3$ in the same direction; $l(t_0) = 11/3$.

particle, the rigid chain is moved $1/N$ in the same direction the particle jumped in the first chain.

Figure 4 shows an example for a chain with $N = 3$ and $P_h = 0.5$ in which the jumping of a bead is described. The average chain length is $\langle L \rangle = 4$ (see equation (4)). In (*a*) we depict an initial chain configuration, arbitrarily chosen, within the necklace model. $l(t)$ is the part of the original tube that has not met the chain ends during the time intervals between 0 and t used in the computation of the viscosity (see equation (9)). In the example of figure 4, $l(0) = 4$. At $t = t_0$, after the left bead jumped to the right, the resulting configuration is that shown in (*b*) and $l(t_0) = 3$. In the constant length model, $l(0) = \langle L \rangle = 4$, as shown in (*c*). The hop of a bead to the right in the necklace model reflects in the constant length model as a move of $1/3$ in the same direction. As a consequence, $l(t_0) = 11/3$ as shown in (*d*). Note that the viscosity is directly related to the integral of $l(t)$.

The resulting viscosity as a function of N for rigid chains is shown in figure 3 (empty symbols). We found that the viscosity of the rigid chain is always larger than that of the flexible chain. This is the expected effect, as fluctuations imply an extending and compressing chain while diffusing and then an acceleration of the stress relaxation. Since fluctuations are less important for long chains relatively to their lengths—see equations (4) and (5)—eventually, for large enough values of N, their effects vanish and thus the viscosities of the flexible and the rigid chains converge. As a consequence of this, the rigid chain presents a smaller viscosity exponent. Indeed, β reduces to almost 3, that is, the value predicted in the original reptation model.

In figure 5, the numerically calculated values of the viscosity for a case with $p_a = 0.9$, $p_b = 0.1$ and $p_c = 1$, case (b), are shown. Now, the viscosity presents a dependence of $N^{3.09}$, with a larger exponent β than in case (a). It is also found that for the rigid chain, when fluctuations are not included, case (b) behaves as expected, as the viscosity is always larger than that of the flexible chain. These findings apparently agree with the generalized idea that CLFs can significantly speed up chain relaxation and thus the viscosity exponent becomes larger than expected from the reptation theory. However, there is something that is not consistent with the regular interpretation. Indeed, the fluctuation amplitude in case (b) is smaller than that in case (a) and the average length of the chains in case (b) is larger than that in case (a) (see equations (4) and (5)). Then, one would expect a smaller effect of the
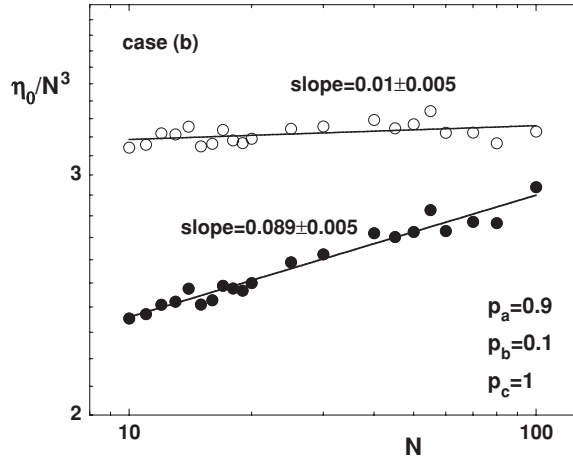
Figure 5. The viscosity as a function of the number of beads N plotted as η_0/N^3 in a log–log plot. The parameters of the model (p_a, p_b, p_c) are $(0.9, 0.1, 1)$. Full symbols represent the viscosity for chains that follow the rules of our model. Open symbols represent the viscosity for chains of constant length, $\langle L \rangle$, for which their centers of mass move as dictated by the centers of mass of chains that follow our model dynamics during diffusion. Note that, as a consequence of fluctuations, the viscosity exponent becomes larger, even larger than that in case (a).

fluctuations in case (b) than in case (a) but the opposite takes place. The next case is even more surprising.

Similar studies for chains in which $p_a = 0.1$, $p_b = 0.9$ and $p_c = 1$, case (c), show striking results. For this choice of parameters, the diffusivity and the amplitude of fluctuations are the same as those of case (b) (see equations (8) and (5)). However, for the same value of N, the chains in case (c) are shorter because the number of holes is smaller. Figure 6 shows that in the range $10 \leqslant N \leqslant 100$, $\beta \sim 2.9$ is smaller than 3. As before, we also studied the consequences of eliminating length fluctuations. Unexpectedly, in case (c) fluctuations have the effect of reducing β. Indeed if fluctuations are eliminated, β increases to 2.98.

The configuration of a chain is determined by the sequence of holes and the lack of holes (no-holes). The probability P of a chain configuration is simply given by multiplying the probabilities of having or not having a hole between every couple of particles of the chain, i.e.

$$P = P_h^n (1 - P_h)^m, \tag{11}$$

where n is the number of holes and m is the number of no-holes. Note that $n + m = N - 1$. There are different possible ways to arrange a determined number of holes along a chain. Indeed, the total number of configurations of a chain of N particles with n holes is $(N-1)!/(n!m!)$. Hence, the probability $P_N(n)$ of having n holes in a chain with N particles is

$$P_N(n) = \frac{(N-1)!}{n!m!} P_h^n (1 - P_h)^m, \tag{12}$$

which is a binomial distribution. For $P_h = 0.5$, the binomial distribution is symmetric around the average number of holes $P_h(N-1)$. Conversely, for $P_h \neq 0.5$ the distribution is asymmetric. For large values of N, the distribution loses its asymmetry and tends to exhibit a neat maximum and to decrease rapidly as one goes away from it. Eventually, as $N \to \infty$, the binomial distribution becomes the so-called Gaussian distribution. From this analysis, we see that, in general, the probability distribution of the chain lengths is asymmetric. The
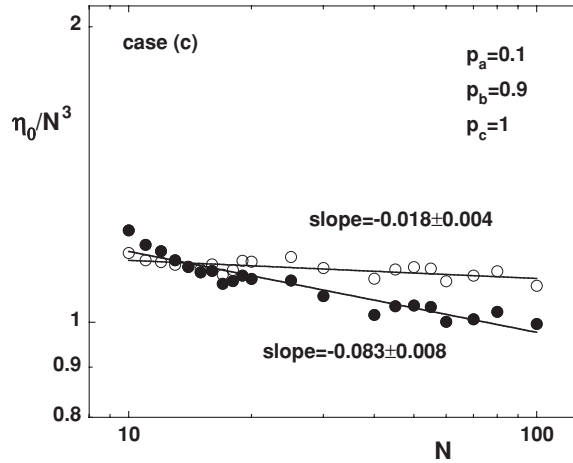
Figure 6. The viscosity as a function of the number of beads N plotted as η_0/N^3 in a log–log plot. The parameters of the model (p_a, p_b, p_c) are (0.1, 0.9, 1). Full symbols represent the viscosity for chains that follow the rules of our model. Open symbols represent the viscosity for chains of constant length, $\langle L \rangle$, for which their centers of mass move as dictated by the centers of mass of chains that follow our model dynamics during diffusion. Note that, as a consequence of fluctuations, the viscosity exponent becomes smaller.

distribution is symmetric only for the case $P_h = 0.5$. On the other hand, a chain diffuses by evolving from one configuration to other. It is important to note that the average time that a chain spends with a given configuration is proportional to P (see equation (11)).

Thus, for $P_h \neq 0.5$, the chain length distribution is asymmetric with respect to the average length, and the chain does not spend the same time in every configuration. These 'details' in the dynamics of an evolving chain can have important consequences in the resulting viscosity as discussed below.

The anomalous results found can be understood by analyzing the behavior of a chain with a small number of beads, as discussed in [20]. If $p_a > p_b$, the chain is said to be *long* ($P_h > 1/2$) and if $p_a < p_b$, the chain is said to be *short* ($P_h < 1/2$). For $N = 3$, for example, $\langle L \rangle \cong 5$ for a very long chain and $\langle L \rangle \cong 3$ for a very short chain. As discussed above, the viscosity is calculated by integrating the function $\xi(t)$,

$$\xi(t) = \frac{1}{\langle L \rangle} \langle l(t) \rangle. \tag{13}$$

It could be expected that $\xi(t)$ reduces exponentially with time, say proportional to $\exp(-t/\tau)$. In this case, the viscosity, i.e. the integral of ξ, would be proportional to τ. However, the behavior of the function ξ is not so simple, $\xi(t)$ is not exactly an exponential function. Since a long chain has the preference of having many holes, the first jump very probably reduces the value of ξ. On the other hand, a short chain presents very few holes, if any, and thus first jumps very probably do not affect ξ. This explains why, at short times, ξ reduces faster than expected for long chains and slower than expected for short chains affecting significantly the integral of ξ and the determined viscosity. Thus, η_0 for long chains is smaller than expected and for short chains larger than expected. Since eventually for large N, viscosities converge to their values as originally predicted in the reptation theory, β tends to be larger for chains with a great number of holes and smaller for chains with a small number of holes.

The effect of eliminating fluctuations (shown in figures 3, 5 and 6) can be explained with a similar argument. Since fluctuations imply an extending and compressing chain while diffusing, an acceleration of the stress relaxation should occur. Results for cases (a) and (b) show this trend. This is also observed in case (c) for large values of N. However, for small values of N the viscosity in case (c) is smaller for the chains with rigid length. As commented above, short chains tend to present a larger value of viscosity than expected because first jumps do not affect ξ. Conversely, ξ for a rigid chain is reduced since the first jump leads to a lower viscosity. As a consequence of these mechanisms, the resulting exponent β in case (c) is larger for rigid chains.

It is very counterintuitive that contour length fluctuations can increase the viscosity. The key point here is to realize how fluctuations take place in the model. In case (a), fluctuations are symmetric, in the sense that chains stretch and compress symmetrically in space and all configurations are equally probable. Thus, in case (a) we can attribute a value of β larger than 3 to the expected effect of fluctuations. The long chains of case (b) can compress more than they stretch; as a consequence of their uneven evolution, the viscosity of chains with small N is strongly reduced and thus β results larger in case (b) than in case (a), the opposite of what would be expected if only the fluctuation amplitude were considered. Case (c) is the most surprising one as the elimination of fluctuations can reduce the viscosity; a chain of case (c), on average, needs stretching before compressing which retards the reduction of $\xi(t)$. The anomalies described here are due to the discrete character of the model. For large enough values of N, these details in the dynamics become less and less relevant as fluctuations become more symmetric. Eventually, for any values of the parameters, β converges to 3.

Similar effects to those reported here were observed in the Duke–Rubinstein model as the ratio between stretching and shrinking rates is changed. This ratio is that between p_a and p_b in the necklace model and is given through the parameter d in [28, 29]. In both models, for small values of this ratio and not very large values of N, the $\beta < 3$ regime is found.

5. Conclusions

It is commonly accepted that contour length fluctuations increase the viscosity exponent in reptation models of entangled linear polymers. It is argued that when fluctuations are present the chain is compressed and stretched, which facilitates the chain escape from the tube. In other words, for a given chain length, the viscosity is smaller. Since it is expected that this effect decreases with N, the viscosity exponent is greater than that for the case in which there are no fluctuations. As we have shown, these arguments are not always valid.

We have analyzed a computer model, the necklace model, which simulates the diffusion of a chain of particles in one dimension. The free parameters of the model were chosen in order to reproduce the diffusivity exponent of the original reptation model (and that found in experiments). We found that the behavior of the exponents depends on the model parameters in a non-trivial manner. As a consequence of the details in chain dynamics, the viscosity exponent for chains of rigid length can be larger or smaller than that for chains with fluctuating lengths. The origin of the resulting scaling was shown not to be due directly to the amplitude of the chain length fluctuations but a consequence of how fluctuations take place in the model. The observed behavior points to the relevance of the chain movements due to the bead dynamics and the discrete character of the model. The conclusions of this paper are not in contradiction with previous work (for example, [4, 5] because we are dealing with a model that presents some details in its dynamics not previously studied. In short, when fluctuations are symmetric their influence is the expected one; when fluctuations are not symmetric new effects, which have not been considered before in discretized versions of the reptation model,

can appear. Let us finally stress that, even for simple models, such as the necklace model, very rich and non-trivial behavior appears that can help us to understand the reality.

Acknowledgments

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