

**Discretized model for diffusion of a chain in one dimension**S. E. Guidoni,<sup>1</sup> H. O. Martín,<sup>2</sup> and C. M. Aldao<sup>1</sup><sup>1</sup>*Institute of Materials Science and Technology (INTEMA), Universidad Nacional de Mar del Plata–CONICET, Juan B. Justo 4302, 7600 Mar del Plata, Argentina*<sup>2</sup>*Physics Department, School of Exact and Natural Sciences, Universidad Nacional de Mar del Plata, Deán Funes 3350, 7600 Mar del Plata, Argentina*

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With the help of Monte Carlo simulations, the one-dimensional diffusion motion of a chain of  $N$  beads is studied to determine its diffusion coefficient and viscosity. We found that the end bead movements with respect to that of the central beads play a key role. There is no memory between bead hops but they become correlated as a consequence of the chain dynamics. This determines the scaling exponents and the relation connecting them. In particular, the scaling exponent for the viscosity can be smaller or greater than 3 but it must scale as  $N^3$  in the asymptotic regime ( $N \rightarrow \infty$ ). We analyze in detail the dynamics of a chain with three beads to explain why the expected relation between diffusivity and viscosity exponents is not satisfied.

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**I. INTRODUCTION**

Diffusion mechanisms can be much more complex than those for single-particle diffusion on a frozen potential energy landscape. In particular, the presence of interactions among diffusing particles imparts a collective character to the process that can dramatically affect diffusivity. To date, a variety of mechanisms has been proposed to describe the migration of clusters. They include the sequential displacement of individual particles, the successive shearing of some compact blocks, dislocation mechanisms, and gliding of the whole cluster [1,2].

If only single-jump mechanisms are considered, cluster dynamics results from the sequential motion of individual atoms. For example, self-diffusion of large Ag and Cu clusters on the (100) surface takes place by adatom edge diffusion and evaporation and condensation of adatoms [3]. If we restrict ourselves to one dimension, the cluster is reduced to a chain and possible mechanisms for migration are essentially of a single kind. A chain in one dimension can only move by contracting and stretching in a wormlike fashion. This mechanism, called reptation in polymer physics, plays a key role in the dynamics of entangled polymer melts [4]. In the dynamics of entangled polymers, neighboring chains constrain a given chain to diffuse only along a confining tube and then the chain executes a one-dimensional random walk [5,6]. Thus, a chain can progress by leaving part of the initial tube and creating a new part as it reptates. The tube model successfully explains many characteristic features experimentally observed but certain discrepancies between theory and experiment remain controversial.

Reptation, as originally introduced, predicts that diffusivity scales with the molecular weight as  $M^{-\alpha}$ , where  $\alpha=2$  in three dimensions, and the time to escape completely from the initial tube and therefore the zero-shear-rate viscosity scales with molecular weight as  $\eta_0 \sim M^\beta$ , with  $\beta=3$ . These results can be readily derived by resorting to the Einstein relation [6]. If all beads have the same behavior, the frictional force is proportional to the number of beads in the chain,  $N$ . Then, the mobility  $\mu$  must be equal to  $\mu_1/N$ , where  $\mu_1$ , indepen-

dent of  $N$ , is the mobility of a single bead. The Einstein relation states that if the system under study obeys a Boltzmann distribution, mobility and diffusion are proportional; therefore, the one-dimensional diffusion coefficient or tube diffusion,  $D_{\text{tube}}$ , must be equal to  $D_1/N$ , where  $D_1$  is the diffusion coefficient of a single bead. To escape from the original tube, the chain must progress a distance  $L$  proportional to  $N$ . The time needed for that is

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

While a reptating chain moves along its tube a length  $L$ , in space this motion corresponds to a much smaller displacement because the tube is contoured; it can be shown that  $D_{\text{rep}} = D_1/N^2$ . Despite some scatter in the experimentally found values, the viscosity is experimentally found to scale as  $M^{3.4}$ . There have been several explanations for these results, most of them consisting of modifications of the reptation theory [7]. Nevertheless, the disagreement between the predictions of theoretical models and experimental results should not be surprising since the dynamics of real entangled polymer melts is still controversial.

In this paper we discuss in some detail a model we recently introduced that describes a chain diffusing in one dimension [8]. The dynamics is similar to that found in the original work of de Gennes [5] in which the constraints in the dynamics due to other chains are only reflected in the trapping of the chain in a certain tube. The chain progresses by reptating, leaving some parts of the tube and creating new ones as it diffuses. Our model, however, can exhibit a scaling exponent for the viscosity *larger or smaller* than 3. Here we show that the anomalous viscosity scaling is the consequence of the whole chain dynamics during diffusion in which the dynamics of end beads plays a central role. Specifically, we focus on a chain consisting of three particles. The detailed analysis of this simple cluster sheds new light on a problem of enduring interest: the fact that the molecular-weight dependence of the viscosity is different than the original reptation

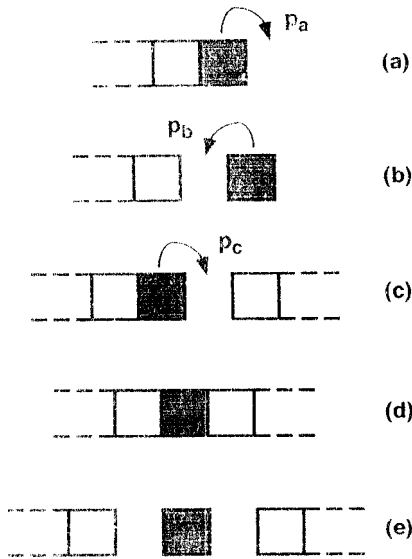


FIG. 1. Configurations for end [(a),(b)] and middle [(c),(d),(e)] particles and their possible hops.

tion model prediction. We found that the bead hops are correlated and that this is crucial in the resulting values for  $\alpha$  and  $\beta$ .

## II. MODEL

Let us consider a chain in a one-dimensional lattice consisting of  $N$  particles or beads that can hop to the nearest site only if this site is empty. Hops are accomplished by picking a particle at random and attempting to move it. There can be only one particle per site. Particles can hop to the right or left but no more than one site can be empty between two of them. In Fig. 1 hoppings for particles in all possible configurations are shown. In configuration (a) the end particle, if selected, can only jump to the right and the resulting configuration is that of (b). This jump probability is called  $p_a$ . In configuration (b) the end particle can only jump to the left and, if selected, the attempted jump succeeds with probability  $p_b$ . A particle not at one of the ends—a middle particle—can be in any of the configurations shown in Fig. 1(c), 1(d), or 1(e). If it is in configuration (c), the particle can jump and after being randomly selected the probability of hopping is taken to be  $p_c$ . Particles in configurations (d) and (e) are unable to move. Hence,  $p_a$ ,  $p_b$ , and  $p_c$  are the free parameters in our model ( $0 \leq p_a, p_b, p_c \leq 1$ ).

Thus, the computer model is based on a random walk in a one-dimensional lattice of  $N$  particles forming a chain with the restrictions described above. At time  $t$  one particle of the chain is randomly selected. Then, the probability of jumping is dictated by the rules described for middle and end particles and the time is increased by  $\delta t = 1/N$ . Every time a particle jumps, the center of mass moves  $1/N$  of the distance  $l$  between adjacent sites of the lattice. In the following we use  $l = 1$ . The repetition of this procedure simulates the random motion of the chain.

A simple way to see that the viscosity is directly related to the time needed for the chain to escape from the initial tube

can be found in Refs. [6] and [9]. The Maxwell model is of use in predicting the response of a polymer during stress relaxation. In this case, if a constant strain is imposed on the system, the stress as a function of time behaves as  $\sigma = \sigma_0 \exp(-Et/\eta)$ . Then, its relaxation time would be  $\eta/E$ , where  $E$  is the Young modulus.

According to the reptation model, after a step strain, the resulting stress decays as the chain reptates into an undeformed configuration. Consider a small change in stress  $\sigma$  due to a change in strain  $\gamma$ ,

$$d\sigma = G(t)d\gamma = G(t)\dot{\gamma}dt, \quad (2)$$

where  $G(t)$  is called the relaxation modulus. Integrating this expression gives

$$\sigma = \int_{-\infty}^t G(t-t')\dot{\gamma}dt'. \quad (3)$$

Thus, the stress is an integral, over all past time, of the relaxation modulus times the rate of strain. For a constant value of the rate of strain, we can write

$$\sigma = \dot{\gamma} \int_{-\infty}^t G(t-t')dt' = \dot{\gamma} \int_0^{\infty} G(t)dt. \quad (4)$$

The ratio  $\sigma/\dot{\gamma}$  in steady shearing flow is independent of  $\dot{\gamma}$  if  $\dot{\gamma}$  is vanishingly small. This ratio is known as  $\eta_0$ , the zero-shear-rate viscosity. Therefore,

$$\eta_0 = \int_0^{\infty} G(t)dt. \quad (5)$$

Let  $x_R(t)$  be the leftmost propagation position of the right end of the chain and  $x_L(t)$  be the rightmost propagation position of the left end of the cluster. The zero-shear-rate viscosity  $\eta_0$  is then calculated by integrating the stress [10,11] which is proportional to the number of initially occupied sites, i.e.,

$$\eta_0 = \frac{1}{\langle L \rangle} \int_0^{\infty} \langle x_R(t) - x_L(t) + 1 \rangle dt, \quad (6)$$

where  $L$  is the chain length, the brackets denote the ensemble average, and the integral is evaluated only for positive values of the integrand.

A related model, the repton model, was originally proposed by Rubinstein [11]. This model consists of  $N$  random walkers (reptons) in one dimension. The reptons move in such a way as to not break the connectivity of the cluster. A site in the middle of the chain cannot be vacated and the original order of the reptons is preserved. The model contains a parameter,  $z$ , which is the number of possible gates for an end repton to move to. Then there are  $z-1$  possible gates through which to enter into an empty cell and only one gate through which to move into an already occupied one. Accordingly, the probability of a move that lengthens the configuration is  $(z-1)$  times the probability of a move in the middle of the chain. Rubinstein found that the viscosity scales with the cluster size with exponents greater than 3

with the exact value depending on the parameter  $z$ ; for the case  $z = 6$ , which can be understood to correspond to a three-dimensional cubic lattice, the exponent takes a value of 3.36, predicting what is observed in experiments. Although at first glance the rules of our model look different than those of the reptation model, there is a direct correspondence between both models regarding diffusion. However, since in the reptation model particles can be at the same site, viscosity does not present the same behavior. Operatively, the main difference between both models is the flexibility we adopted regarding the possible different jump probabilities for particles at the ends of chains relative to those for the central ones.

The question now is what is the difference in essence between the de Gennes original reptation model and a reptating real polymeric chain. It has been proposed that the basic difference is that in the de Gennes solution the fluctuations of the chain length are not considered. De Gennes assumes reptation to be the random walk of a fixed length object with a curvilinear diffusion coefficient inversely proportional to its molecular weight (see, for example, Refs. [4,12,13]). In the reptation model and ours this assumption is not made because chains are free to stretch and compress as they diffuse. Indeed, it is possible for one end to move independently of the other and the length of the chain can vary. The effect of length fluctuation was expressed analytically quite simply as a factor  $[1 - k/M^{1/2}]^3$  with  $k$  being a constant [12]. This is not a power law with an exponent of 3.4 but it approximates the viscosity over the range of molecular weights used in experiments. This explanation fails for our model because we found that resulting values for the viscosity exponent can be *larger but also smaller* than 3. We also found chains with the same diffusivity and length fluctuation amplitude that show viscosities larger or smaller than the value consistent with the diffusivity exponent. Furthermore, we specifically show that fluctuations can increase or decrease viscosity.

### III. THEORETICAL CONSIDERATIONS

An empty site in the chain will be called a *hole*. The average number of holes in a chain can be easily calculated as follows. A hole is created or annihilated every time an end particle jumps away from the chain or toward the chain, respectively. An end particle jumping attempt that creates a hole is successful with probability  $p_a(1 - P_h)$ , where  $P_h$  is the hole probability. Similarly, an end particle jumping attempt that annihilates a hole succeeds with probability  $p_b P_h$ . In equilibrium we expect the same probability for creation and annihilation. Then,  $P_h$  can be expressed as

$$P_h = \frac{p_a}{p_a + p_b}. \quad (7)$$

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 chain length  $\langle L \rangle$  and its fluctuation amplitude are given by

$$\langle L \rangle = N + P_h(N-1), \quad (8)$$

$$\langle (L - \langle L \rangle)^2 \rangle = (N-1)P_h(1 - P_h). \quad (9)$$

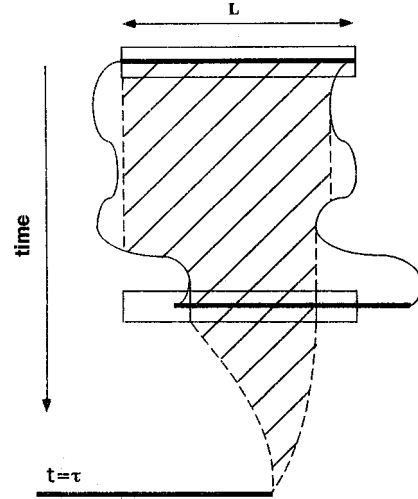


FIG. 2. Stress relaxation as a function of time. The striped area is proportional to viscosity. The rectangle represents the original tube and the thick lines represent the chain.

Monte Carlo simulations verify these results.

The extreme case, in which the chain needs to diffuse the longest distance to escape from the tube, occurs when the chain is deformed in a such a way as to have the center of mass close to one end. Let us first consider a chain of average length  $L$  and fluctuations  $\Delta L$ ;  $x_M$  is the position of the center of mass and  $\tau$  the time at which the chain leaves the original tube. Hence, the following relation must be valid:

$$|x_M(\tau) - x_M(0)| \leq 2L + 2\Delta L < 4L. \quad (10)$$

This equation indicates that the distance traveled by the center of mass at the moment the chain leaves the tube must scale at most as  $N$ , since  $L$  scales with  $N$ . Then, we can write

$$\langle [x_M(\tau) - x_M(0)]^2 \rangle < 16L^2 \sim N^2 \quad (11)$$

and it is well known that for a given time  $t = \tau$

$$\langle [x_M(\tau) - x_M(0)]^2 \rangle = 2D\tau. \quad (12)$$

If  $D \sim 1/N$  and  $\tau$  does not scale as  $N^3$ , say  $\tau \sim N^{\beta'}$  with  $\beta' > 3$ , Eq. (12) becomes

$$\langle [x_M(\tau) - x_M(0)]^2 \rangle \sim N^{\beta' - 1}, \quad (13)$$

where  $\beta' - 1 > 2$ . Equation (13) contradicts Eq. (11) and implies that, for values of  $N$  large enough, the center of mass would end up outside the chain. This analysis shows that eventually if  $D \sim 1/N$ , for large enough values of  $N$ ,  $\tau$  must eventually scale at most as  $N^3$ .

In Fig. 2 we present a scheme that shows a chain vacating the initial occupied sites. Viscosity is proportional to the integral of  $x_R(t) - x_L(t)$  [see Eq. (6)] and then to the striped area in Fig. 2. This area must be smaller than  $L\tau$  which is smaller than  $L_{\max}\tau$ . Hence, the following relations for the viscosity follows:

$$\eta_0 < \frac{1}{\langle L \rangle} L_{\max} \langle \tau \rangle. \quad (14)$$

Since the ratio  $L_{\max}/\langle L \rangle$  is a constant in the asymptotic limit [see Eq. (8)], it can be seen that if  $\langle \tau \rangle$  scales at most as  $N^3$  then  $\eta_0$  also must scale at most as  $N^3$  for  $N \rightarrow \infty$ . Similar arguments can be used in other related models. Previous results of  $\beta > 3$  correspond then to values of  $N$  not large enough; the value  $\beta = 3$  must be recovered in the asymptotic regime.

In what follows we will discuss how the diffusion coefficient can be derived. The probability of success for an attempted jump can be expressed as

$$J = P_h(1 - P_h)p_c \frac{N-2}{N} + \frac{(1 - P_h)p_a + P_h p_b}{N}. \quad (15)$$

Equation (15) shows that  $J$  presents two terms. The first one refers to the possible jump of a middle particle while the second term reflects the possible jump of one of the end particles. With Eq. (7), Eq. (15) takes the form

$$J = \frac{p_a p_b p_c}{(p_a + p_b)^2} + \frac{2p_a p_b}{N(p_a + p_b)} \left( 1 - \frac{p_c}{p_a + p_b} \right). \quad (16)$$

It is well known that for an ordinary random walk the diffusion coefficient can be expressed in terms of the mean jump frequency  $\Gamma$  and step length  $a$  as

$$D = \Gamma a^2. \quad (17)$$

For a chain with  $N$  beads,  $\Gamma$  is  $NJ$  per time unit and the motion of the center of mass is  $1/N$ , since  $l = 1$ . Hence, the diffusion coefficient of the center of mass would be given by

$$D = \frac{p_a p_b p_c}{N(p_a + p_b)^2} \left( 1 + \frac{2}{N} \frac{p_a + p_b - p_c}{p_c} \right). \quad (18)$$

It is apparent that this approach leads to incorrect results. For example, for  $p_c = 0$  Eq. (18) predicts  $D \neq 0$  which is not correct because immobile central beads imply a null diffusivity. In this case, only end beads can jump and after a hop they can only jump in the opposite direction, so hopping is extremely correlated. The derivation of Eq. (18) is wrong because it is assumed that hops are not correlated. In general, Eq. (16) is valid but Eq. (17) cannot be applied.

Correct expressions for the diffusivity for small values of  $N$  can be derived as follows. We will focus on  $N = 3$ . In Fig. 3 different configurations for a chain with three beads and its evolution are presented. The scheme also shows the probabilities for the possible transitions among configurations. To determine the diffusion coefficient we will use an alternative approach, not regularly applied in the literature, that simplifies the calculations. With this method this problem can be solved using only algebra [14,15].

The method consists in applying Fick's law to a hypothetical system consisting of a large number of noninteracting chains of three beads. After some time the system is assumed to reach steady state at which the average number of chains in each configuration and the number of chains per

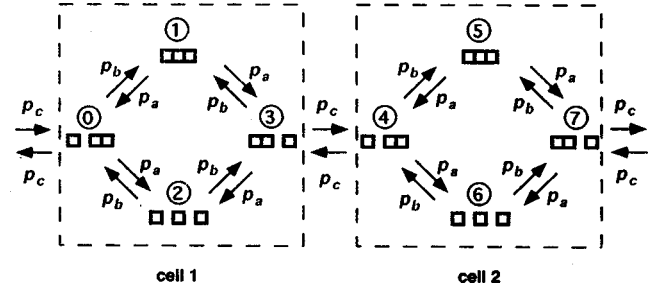


FIG. 3. Representation of the possible configurations for a chain with three beads, transitions among configurations, and jumping probabilities.

unit of time evolving among configurations remain constant. A gradient in the number of chains is needed. To do so, the number of chains with configuration (0),  $n_0$ , is imposed to be null, which implies an ideal sink at that place. At some point, a reservoir or a source of chains is necessary to maintain the chain flux. Then, under steady-state conditions, the number of chains  $n_i$  in each configuration  $i$  must remain constant. Therefore, we can write the following:

$$p_b n_3 = 2p_a n_1,$$

$$p_a n_3 = 2p_b n_2,$$

$$p_a n_1 + p_b n_2 + p_c n_4 = (p_a + p_b + p_c) n_3,$$

$$p_c n_3 + p_a n_5 + p_b n_6 = (p_a + p_b + p_c) n_4,$$

$$p_b n_4 + p_b n_7 = 2p_a n_5,$$

$$p_b n_4 + p_b n_7 = 2p_a n_5,$$

$$p_b n_4 + p_b n_7 = 2p_a n_5,$$

$$p_a n_4 + p_a n_7 = 2p_b n_6,$$

$$p_a n_5 + p_b n_6 + p_c n_8 = (p_a + p_b + p_c) n_7. \quad (19)$$

From this set of equations, the total number of particles in cells 1 and 2 can be determined (see Fig. 3). The net flux is given by  $p_a n_1 + p_b n_2$ , and then, by applying Fick's first law, the diffusion coefficient can be found to be

$$D_{N=3} = \frac{p_a p_b p_c}{(p_a + p_b)(p_a + p_b + 2p_c)}. \quad (20)$$

Except when the condition  $p_a + p_b = p_c$  holds, this result differs from Eq. (18). Monte Carlo results are in agreement with Eq. (20). Note that the diffusion of the center of mass of a chain is similar to the diffusion of a particle in a complex lattice with inequivalent sites.

#### IV. RESULTS AND DISCUSSION

With Monte Carlo simulations, the diffusivity of the center of mass is calculated through

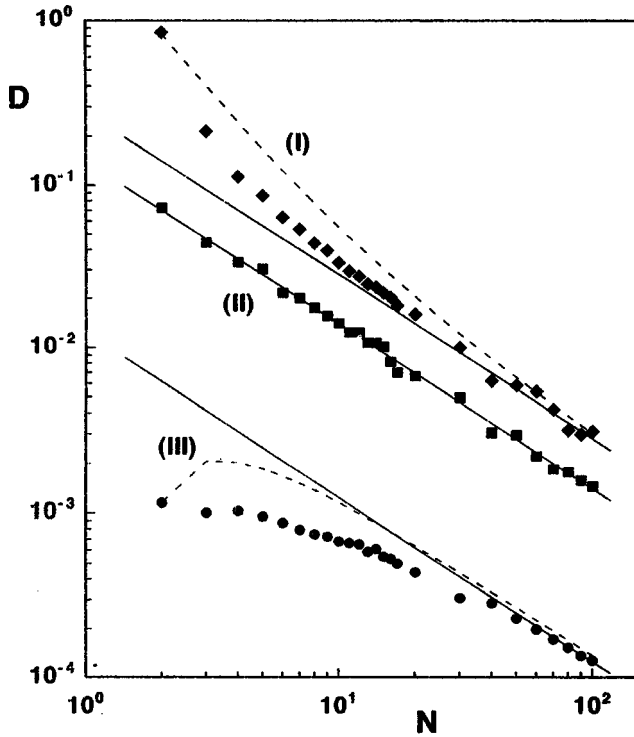


FIG. 4. Diffusion coefficient of the center of mass for chains consisting of  $N$  beads. The parameters of the model ( $p_a, p_b, p_c$ ) are (1, 1/5, 1/5) for case I, (5/6, 1/6, 1) for case II, and (5/36, 1/36, 1) for case III. Dashed lines correspond to theoretical results according to Eq. (18). Note that Eq. (18) should only be applied in case II, when hops are not correlated. Straight lines correspond to the asymptotic behavior with slope  $-1$ . In case II dashed and straight lines are coincident. For the sake of clarity, diffusivity values for case I were multiplied by 10 and those for case III by 0.1. The evolutions of at least 100 chains were averaged.

$$D = \frac{\langle [x_M(t) - x_M(0)]^2 \rangle}{2t}. \quad (21)$$

In Fig. 4, 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) for case I, (5/6, 1/6, 1) for case II, and (5/36, 1/36, 1) for case III. Parameters have been chosen to always have the same average number of holes ( $P_h = 5/6$ ) and the same average length and length fluctuation [see Eqs. (8) and (9)]. In the asymptotic regime  $D$  always presents a slope

$1/N$ . This is the expected diffusivity dependence for a one-dimensional model corresponding to the curvilinear diffusivity of a chain in a three-dimensional tube (i.e.,  $\alpha = 1$ ). The exponent  $\alpha$  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 probabilities than middle particles, as discussed below. For large values of  $N$  the influence of end particles vanishes (see Table I). Theoretical results corresponding to Eq. (18) are also presented. They are asymptotically correct for  $N \rightarrow \infty$  but differ considerably from those obtained with the model in the range of  $N$  studied. Equation (18) and Monte Carlo results are in agreement for case II, for which  $p_a + p_b = p_c$ , when bead hops are not correlated, as shown below.

Note that all the particles forming the chain have the same chance to be chosen to perform a hop but, in general, end and middle particles do not have the same chance to hop. In average, the probability that, once chosen, an end particle performs a jump to the right or left is

$$J_e = (1 - P_h)p_a = P_h p_b, \quad (22)$$

while for a middle particle, once chosen, the probability of making a jump to the right or left is

$$J_m = (1 - P_h)P_h p_c. \quad (23)$$

Using Eq. (7), the ratio between expressions of Eqs. (22) and (23) can be written as

$$\frac{J_e}{J_m} = \frac{p_a + p_b}{p_c}. \quad (24)$$

If  $p_a + p_b = p_c$  the probability of jumping is the same for every particle of the chain. Under this condition, if a jump to the right occurred, any of the particles in the chain has the same probability of having made that jump. As a consequence, on average, the resulting configuration of the chain does not change and then the chain center of mass executes an ordinary random walk diffusion. This is satisfied in case II but not in cases I and III for which hops become *correlated*. The past move is not directly taken into account in the following step but hops become correlated as a consequence of the established rules through the resulting configurations. A hop being to the right or left does not causally depend on the previous move, i.e., the chain does not have memory. However, if  $p_a + p_b \neq p_c$ , in many configurations the probability to hop in one direction can be different than in the other one.

TABLE I. Exponents  $\alpha$  and  $\beta$  for different values of the free parameters  $p_a$ ,  $p_b$ , and  $p_c$ .  $\beta = 2 + \alpha$  is the expected relation between diffusivity and viscosity exponents. Relative errors are around 5% for  $\alpha$  and 1% for  $\beta$ . The evolutions of at least 100 chains were averaged.

Case	$p_a$	$p_b$	$p_c$	$P_h$	$4 \leq N \leq 20$			$20 \leq N \leq 100$		
					$\alpha$	$\beta$	$2 + \alpha$	$\alpha$	$\beta$	$2 + \alpha$
I	1	1/5	1/5	5/6	1.22	3.46	3.22	1.05	3.16	3.05
II	5/6	1/6	1	5/6	1.01	3.07	3.01	0.98	3.09	2.98
III	5/36	1/36	1	5/6	0.50	2.51	2.50	0.77	2.87	2.77
I'	1/5	1	1/5	1/6	1.22	3.05	3.22	1.05	3.05	3.05

Conversely, if the  $p_a + p_b = p_c$  condition is satisfied, in all possible configurations the next hop has the same probability to be to the right or left.

If  $p_a + p_b > p_c$ , the end particles are more likely to jump than those in the middle of the chain. Then, if a jump to the right occurs, a hole creation at the right end of the chain or a hole annihilation at the left end of the chain is more likely to occur than a specific hole movement related to middle particle hops. Then, after a jump to the right, the probability of finding a hole on the right end will be greater than  $P_h$ , and the probability of finding a hole on the left end will be smaller than  $P_h$  (the opposite happens for  $p_a + p_b < p_c$ ). Thus, the resulting average configuration changes after a particle hop and, as a consequence, hops become *correlated*. This is the reason why Eq. (18), in which jumps were assumed to be uncorrelated, is not correct except in the asymptotic case that corresponds to  $N \rightarrow \infty$  when the influence of the end particles becomes negligible. Obviously, if the condition  $p_a + p_b = p_c$  is satisfied, the hops of the center of mass of the chain become uncorrelated and the discrepancies between results from Monte Carlo simulations and those obtained applying Eq. (18) disappear. In short, it is not correct to apply Eq. (17) with  $\Gamma = NJ$  and  $a = 1/N$  if hopping to the right and left are not equally probable.

The above discussion becomes clear analyzing a small chain of three beads. In Fig. 3 we see that configurations 1 and 2, since they are symmetric, have the same probability of evolving towards configurations 0 or 3. Conversely, if the chain adopts configuration 3, the probability of jumping to the right is  $p_c$  and to the left is  $p_a + p_b$  per unit time. If  $p_a + p_b > p_c$ , the probability of jumping to configuration 1 or 2 is larger than a jump towards configuration 4. Due to this asymmetry, it is more likely for the chain to adopt configuration 3 from configurations 1 and 2 than from configuration 4. As a consequence the probability that a chain hops back to the previous configuration is greater than  $\frac{1}{2}$ . Thus, on average, the chain has the tendency to move in the opposite direction of the previous jump. The smaller  $N$  is, the stronger the correlation is. For long chains this effect eventually becomes negligible.

To check that indeed the chain hops are correlated, we analyze the behavior of a chain by devising the following algorithm. Let us define a variable  $Z$  that can take only the value  $+1$  or  $-1$ . We wait for a successful hopping. If a hop  $i$  is to the right then  $Z(i) = 1$  and if the hop is to the left  $Z(i) = -1$ . The unsuccessful trials between one hop and the next one are not taken into account. Eventually a hop  $i+1$  occurs and then  $Z(i+1) = 1$  if the hop is to the right or  $Z(i+1) = -1$  if the hop is to the left. Correlation will be determined with the function  $C(n)$ , defined as

$$C(n) = \frac{1}{n} \sum_{i=1}^n Z(i)Z(i+1), \quad (25)$$

where  $n+1$  is the number of successful hops. If jumps are not correlated, a hop in one direction is followed by a hop in the same or a different direction indistinctly and then  $C(n)$  converges to 0 as  $n$  increases. This happens in case II, as discussed above. Negative correlations are found for any

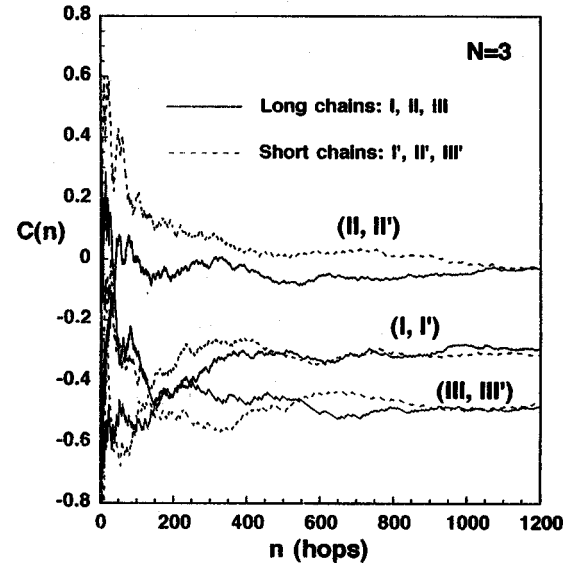


FIG. 5. Correlation defined in Eq. (25) for a chain of three beads. In cases I', II', and III' parameters  $p_a$  and  $p_b$  were interchanged for case I, II, and III, respectively. For  $n \rightarrow \infty$ ,  $C(n)$  converges to  $-0.275 \pm 0.05$  for cases I and I', to  $0 \pm 0.05$  for cases II and II', and to  $-0.450 \pm 0.05$  for cases III and III'. Exact results can be obtained with Eq. (29).

case for which  $p_a + p_b \neq p_c$ , such as in cases I and III. In Fig. 5 we present Monte Carlo results for  $C(n)$  and  $N=3$  as a function of  $n$ . We also present three other cases, (I', II', and III'), for which  $p_a$  and  $p_b$  were interchanged. Interestingly, the value of the function  $C(n)$  for  $n \rightarrow \infty$  is invariant under this interchange.

An analytical expression of  $C(n)$  for  $N=3$  can be deduced. With the help of Fig. 3, the probability of having two successive hops with the same direction can be shown to be

$$C^+ = k \left( \frac{p_a + p_b}{2(p_a + p_b + p_c)} + \frac{2(p_a + p_b)p_c}{(p_a + p_b + p_c)^2} \right), \quad (26)$$

and of having two successive hops with different directions,

$$C^- = k \left( \frac{p_a + p_b}{2(p_a + p_b + p_c)} + \frac{(p_a + p_b)^2}{(p_a + p_b + p_c)^2} + \frac{p_c^2}{(p_a + p_b + p_c)^2} \right), \quad (27)$$

where  $k$  is a normalization constant. Then,  $C(n)$  after an infinite number of hops can be calculated through

$$C(n \rightarrow \infty) = \frac{C^+ - C^-}{C^+ + C^-}. \quad (28)$$

With Eqs. (26) and (27), it can be found that

$$C(n)_{n \rightarrow \infty} = - \frac{(p_a + p_b - p_c)^2}{(p_a + p_b + p_c)[2(p_a + p_b) + p_c]}. \quad (29)$$

Results obtained through Monte Carlo simulations converge to those using Eq. (29); see Fig. 5. For example, in cases III

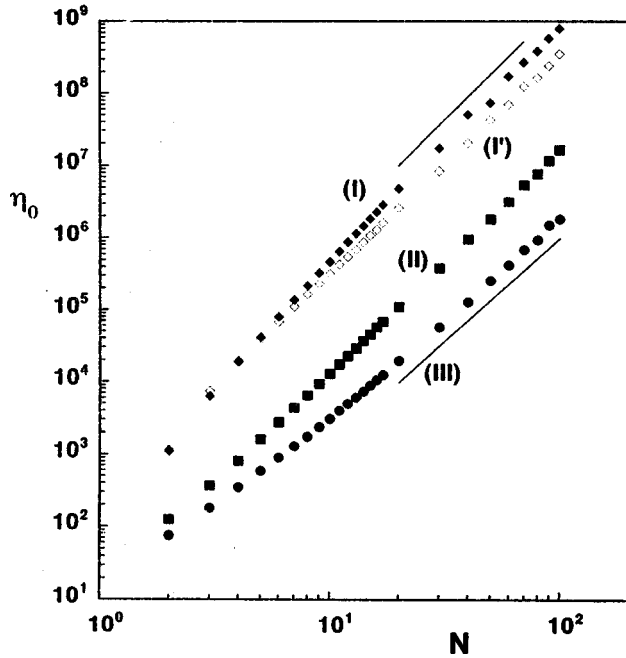


FIG. 6. Viscosity as a function of the number of beads  $N$  for the three cases in Fig. 4 and that for case I' for which the parameters of the model ( $p_a, p_b, p_c$ ) are  $(1/5, 1, 1/5)$ . For the sake of clarity, viscosity values for cases I and I' were multiplied by 100 and those for case II by 10. The straight lines have the slopes of cases I and III for  $20 \leq N \leq 100$  and were drawn as a guide to the eye (see Table I). The evolutions of at least 50 chains were averaged.

and III'  $C(n \rightarrow \infty)$  converges to  $-0.45$ . Correlation decreases with the chain length, for example  $C(n \rightarrow \infty)$  reduces to  $-0.16$  for  $N=5$ , and to  $-0.04$  for  $N=10$ . Note that Eq. (29) is invariant under an interchange of  $p_a$  and  $p_b$ .

In Fig. 6 the numerically calculated values of  $\eta_0$  through Eq. (6) are presented (see Table I). The found slopes in the double logarithmic scale converge to three as  $N$  increases for all the cases studied. However, case I presents a larger slope at low  $N$  as found in Ref. [11]. Values of  $\eta_0$  for a fourth case (I') corresponding to  $p_a=1/5$ ,  $p_b=1$ , and  $p_c=1/5$  are also shown. Note that the diffusivity for case I' is exactly the same as that for case I because  $p_c$  is the same in both cases and values for  $p_a$  and  $p_b$  have been interchanged. This can be easily seen with the help of Eqs. (7), (22), and (23). The probabilities that, once chosen, an end particle and a middle particle make a jump to the right or to the left are  $p_a p_b / (p_a + p_b)$  and  $p_a p_b p_c / (p_a + p_b)^2$ , respectively. Consequently, since these expressions are invariant under the interchange of  $p_a$  and  $p_b$ , the jumping probabilities in cases I and I' are the same and hence diffusivities have the same value, a result that is confirmed in the simulations. Also, the fluctuation amplitudes are coincident [see Eq. (9)] but the number of holes are very different [see Eq. (7)]. Interestingly, chains with the same diffusivity and fluctuation amplitude present different viscosities. Furthermore,  $\beta$  can be larger (case I) or smaller (case I') than expected from the diffusivity exponent ( $\beta_{\text{expected}} = 2 + \alpha$ ). Indeed, the diffusivity exponent is 1.22 for  $4 \leq N \leq 20$  and viscosity exponents are 3.46 and 3.05 for cases I and I', respectively. These results show

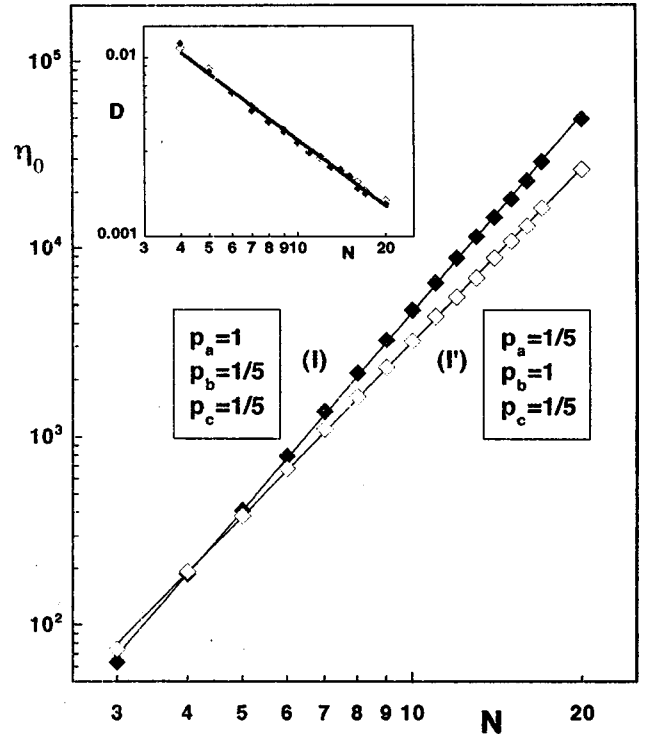


FIG. 7. Viscosity as a function of the number of beads  $N$  for cases I and I' for a small number of beads. Diffusivities for these cases are coincident and are shown in the inset. The straight line has a slope of  $-1.22$ . The viscosity exponent  $\beta$  is larger (case I) or smaller (case I') than expected from the diffusivity exponent.

that  $\beta$  also depends on  $P_h$ . Figure 7 shows in detail the viscosity and diffusivity for cases I and I'. A viscosity exponent lower than 3 is obtained for case III when the central beads are more mobile than the end ones. Usually, this condition is not fulfilled in polymer melts which is consistent with experimental findings.

The above results can be understood by analyzing the behavior of a chain consisting of three beads, the simplest chain having a central bead. If  $p_a = p_b$ , all configurations are equally likely and the average length of the chain is  $\langle L \rangle = 4$ , see Eq. (8). If  $p_a > p_b$ , the chain is said to be long, the most likely configuration is the stretched one (configuration 2 in Fig. 3), and  $\langle L \rangle > 4$ . If  $p_a < p_b$ , the chain is said to be short since  $\langle L \rangle < 4$  and configuration 1 of Fig. 3 is the most likely.

As discussed above, viscosity is calculated by integrating the function  $\mu(t)$ ,

$$\mu(t) = \frac{1}{\langle L \rangle} \langle x_R(t) - x_L(t) + 1 \rangle. \quad (30)$$

It could be expected that  $\mu(t)$  reduces exponentially with time, say, proportionally to  $\exp(-t/\tau')$ . In that case, the average time needed to escape from the initial tube and also the viscosity, i.e., the integral of  $\mu$ , would just be proportional to  $\tau'$ . However, the behavior of function  $\mu$  is not so simple. In Fig. 8 we present two plots of  $\mu(t)$  for  $N=3$  that shows that  $\mu$  does not exactly behave as an exponential function. In this

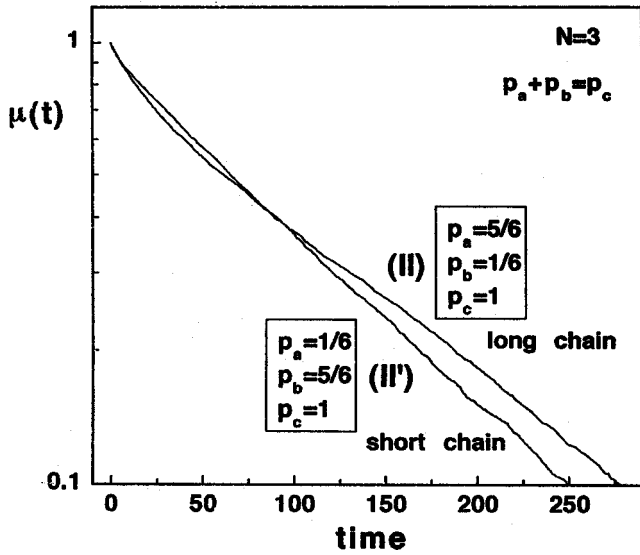


FIG. 8. Function  $\mu(t)$ , see Eq. (30), for a long and a short chain, cases II and II'.  $\mu$  for the long chain reduces faster in the beginning and eventually slower than for the short chain. Results correspond to the average of 1000 trials.

figure we present results for a short and a long chain that diffuses through noncorrelated hops of their beads, i.e.,  $p_a + p_b = p_c$ .  $\mu$  for the long chain reduces faster at the beginning and eventually slower than for the short chain. This result can be interpreted with the help of Fig. 9 (we maintain the configuration names given in Fig. 3). A long chain shows a preference for configuration 2. (For the sake of analysis simplicity, let us consider that  $p_a \gg p_b$ .) As soon as a jump occurs, say that the chain adopts configuration 3, the value of  $\mu$  reduces to  $\approx 0.8$  and if the chain eventually reaches configuration 6,  $\mu$  keeps this value. On the other hand, a short chain has a preference for configuration 1. (For the sake of analysis simplicity, let us consider that  $p_b \gg p_a$ .) If a jump occurs and configuration 3 is adopted,  $\mu$  is not affected and when the chain eventually adopts configuration 5,  $\mu$  takes a value  $\approx 0.67$ . This explains why  $\mu$  reduces faster for long chains than for short chains at short times. This strongly affects the integral of  $\mu$  and then the viscosity. In what follows we will discuss when the expected relation between  $\alpha$  and  $\beta$  holds.

In Fig. 10 we present  $\mu(t)$  when  $p_a + p_b \neq p_c$ . Results can be rationalized considering extreme cases as follows. (See Fig. 9 and Fig. 3 during the analysis.)

*Short (a):*  $p_a + p_b \ll p_c$  and  $p_a \ll p_b$ . Most of the time the chain is in configuration 1 and then  $\langle L \rangle \approx 3$ . When it evolves to configuration 3,  $\mu$  does not change but, since  $p_a + p_b \ll p_c$ , very likely the chain reaches configuration 5. Every reduction of  $\mu$  is of  $\frac{1}{3}$ .

*Long (a):*  $p_a + p_b \ll p_c$  and  $p_a \gg p_b$ . Most of the time the chain is in configuration 2 and then  $\langle L \rangle \approx 5$ . As soon as it evolves to configurations 3,  $\mu$  reduces to  $\approx 0.8$ . Once in configuration 3 the chain can very likely reach configuration 6. When that happens  $\mu$  maintains the value 0.8. This explains why in the beginning  $\mu$  for the long chain can drop as fast as the short one of the case of short *a*. Eventually,  $\mu$  for the

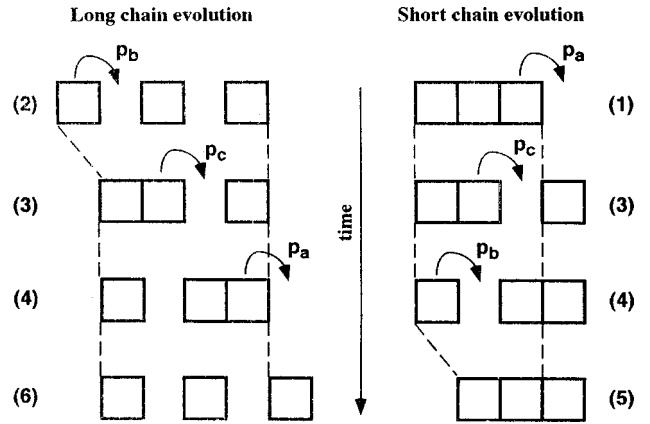


FIG. 9. Evolution for short and long chains. Note that after a jump to the right, chains with configurations 1 and 2 adopt configurations 3; see Fig. 3. This implies a reduction in the number of occupied sites for the chain having initially configuration 2, but for the chain initially with configuration 1  $\mu$  is not altered. When chains eventually evolve to adopt another most probable configuration,  $\mu$  reduces more for a short chain. Dashed lines show how initially occupied sites are vacated.

long chain must decay slower as seen in Fig. 10. The fact that central beads have rapid jumps does not directly contribute to the chain vacating initially occupied sites; the movement of end beads are needed. In cases (a) of Fig. 10 then, the reduction of  $\mu$  with time is dictated by chain diffusion and then viscosity exponents are expected to be directly related to those of diffusion (see case III in Table I).

*Short (b):*  $p_a + p_b \gg p_c$  and  $p_a \ll p_b$ . Most of the time the chain is in configuration 1 and then  $\langle L \rangle \approx 3$ . Since  $p_b$  is large compared to  $p_c$ , the chain stretches to the right and to the left many times before eventually reaching configuration 4. While this happens,  $\mu$  is not affected. That is, the chain will be in configurations of cell 1 for a long time before passing to configurations of a neighbor cell when  $\mu$  reduces to 0.67.

*Long (b):*  $p_a + p_b \gg p_c$  and  $p_a \gg p_b$ . Most of the time the chain is in configuration 2 and then  $\langle L \rangle \approx 5$ . The chain starts in configuration 2 and very rapidly contracts at the right and left, reducing  $\mu$  to  $\approx 0.6$ . This effect is clearly reflected in Fig. 10(b). The rapid initial reduction of  $\mu$  is large enough so that the viscosity of the long chain is smaller than that of the short case (see Fig. 7,  $N=3$ ), a result which is counterintuitive within the framework of the original reptation model (note that the two chains have the same diffusion coefficient). In short, a chain spends a lot of time in cell 1 before adopting a configuration of cell 2. During this time  $\mu$  reduces for a long chain while it is not affected for a short chain.

The above analysis shows that for  $p_a + p_b \gg p_c$  an anomalous relation between diffusion and viscosity can be found. Short chains show larger viscosities while long chains show smaller viscosities than that which would emerge from the original reptation theory. Since this effect reduces with  $N$ , the resulting discrepancy eventually disappears. As a result, the viscosity exponent can be larger or smaller than expected.

To check for the influence of length fluctuations, we took chains of constant length equal to  $\langle L \rangle$  and made their center of mass move as dictated by the center of mass of the chains



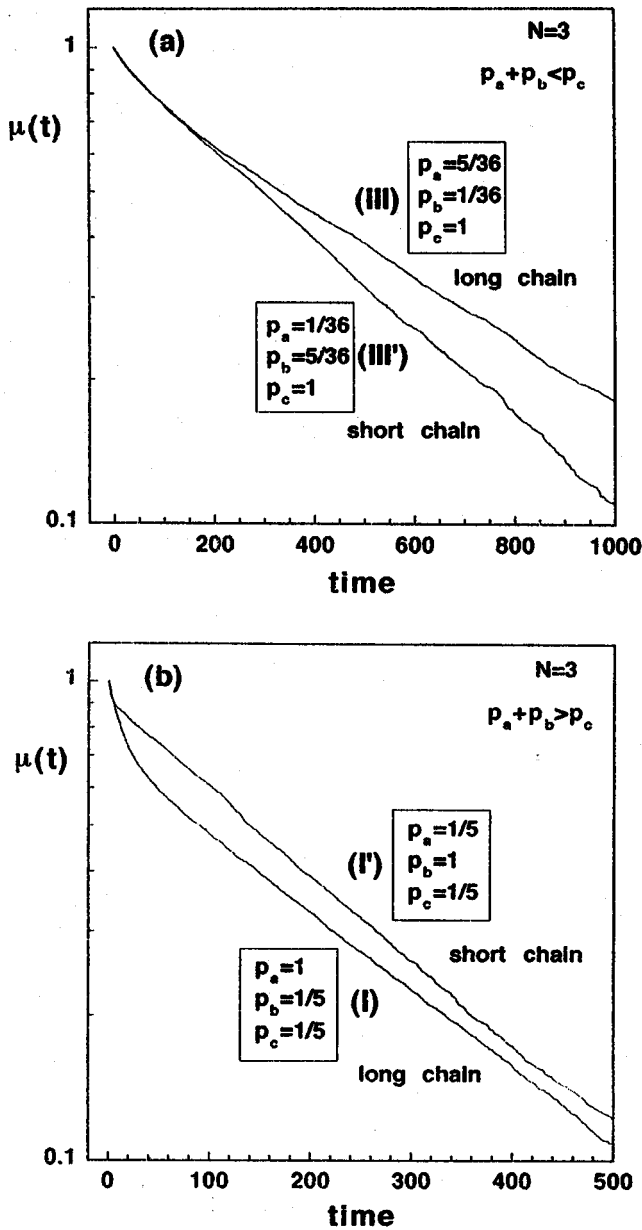


FIG. 10. Function  $\mu(t)$ , see Eq. (30), for long and short chains, cases III and III' (a), and cases I and I' (b). Note that for cases I and I', even though diffusivity is the same, the resulting value of viscosity is larger for the short chain. Values of  $\mu$  are the average of 1000 trials.

that follow our model dynamics during their diffusion. The resulting viscosities as a function of  $N$  for cases I and I' are shown in Fig. 11. We present results for a range of light chains with  $N$  from 3 to 20 where the influence of fluctuations is more significant [see Eq. (9) and Ref. [12]]. Since fluctuations imply an extending and compressing chain while diffusing, an acceleration of the stress relaxation is expected. Results for case I show this trend. However, case I' shows that for small values of  $N$  viscosity is smaller for the chains with rigid length.

This surprising result can be explained with the help of Fig. 3. Since  $p_a < p_b$ , most of the time the chain is in con-

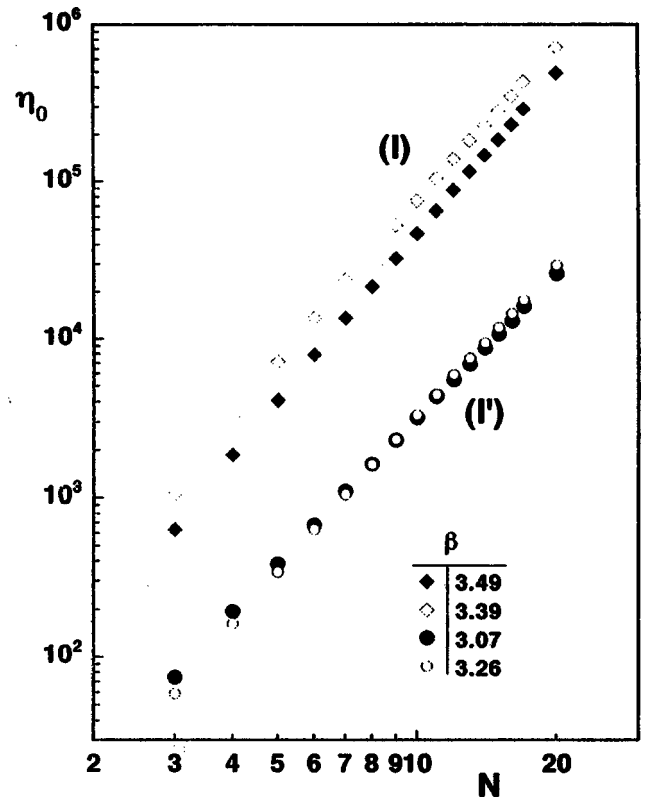


FIG. 11. Full symbols represent the viscosity for chains that follow the rules of our model. Open symbols represent the viscosity for chains of constant length ( $L$ ), for which their centers of mass move as dictated by the center of mass of chains that follow our model dynamics during diffusion. Note that as a consequence of fluctuations the viscosity exponent can be larger or smaller depending on the adopted parameters of the model.

figuration 1 and then  $\langle L \rangle \approx 3$ . When the chain evolves to configuration 3 or 0,  $\mu$  is not affected despite its center-of-mass movements. Meanwhile,  $\mu$  reduces for a rigid chain whose center of mass moves. Eventually for large  $N$ 's the effect of fluctuations vanishes and then the curves overlap. Thus, as a consequence of these details in chain dynamics,  $\beta$  for the rigid chains can be larger or smaller than that for the chain with fluctuating length. Indeed, in case I length fluctuations cause  $\beta$  to increase from 3.39 to 3.49, while in case I' fluctuations cause  $\beta$  to decrease from 3.26 to 3.07.

## V. CONCLUSIONS

We have analyzed in detail a computer model that simulates the diffusion of a chain of beads in one dimension. We found that the chain movements due to the dynamics of end beads and its relation to the dynamics of internal beads play the key role. If the chain has the same probability of hopping to the right or left in all possible configurations ( $p_a + p_b = p_c$ ), its center of mass executes an ordinary random walk and diffusivity and viscosity exponents behave as expected in the reptation model as originally introduced ( $\alpha=1, \beta=2+\alpha=3$ ). When beads do not have the same probability of hopping to the right or left ( $p_a + p_b \neq p_c$ ), bead hops are found to be correlated and diffusivity and viscosity expo-

nents present unexpected values. Thus, the viscosity exponent can be larger or smaller than 3 and fluctuations in the chain length can increase or reduce its value. Eventually in all the studied cases, universality is recovered for large enough values of  $N$ ,  $\alpha$  converges to 1 and  $\beta$  to 3. Since diffusivity is related to the long-term evolution of the center of mass of the chain, it is insensitive to some details of the chain movements. Conversely, viscosity is related to the transient process by which the chain abandons its original posi-

tion. It should not surprise us to find that it depends on some details of the model.

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