Eur. Phys. J. E **7**, 291–295 (2002)
DOI 10.1140/epje/i200102018

THE EUROPEAN PHYSICAL JOURNAL E
EDP Sciences

Anomalous viscosity exponent in a discretized model for a chain diffusion in one dimension

S.E. Guidoni[1], H.O. Mártin[2], and C.M. Aldao[1,a]

[1] Institute of Materials Science and Technology (INTEMA), Universidad Nacional de Mar del Plata-CONICET, Juan B. Justo 4302, 7600 Mar del Plata, Argentina
[2] Physics Department, School of Exact and Natural Sciences, Universidad Nacional de Mar del Plata, Deán Funes 3350, 7600 Mar del Plata, Argentina

Received 24 September 2001 and Received in final form 28 January 2002

Abstract. We present a one-dimensional Monte Carlo simulation for the diffusion motion of a chain of N beads. We found that the scaling exponent for the viscosity can be smaller or greater than 3. This *anomalous* behavior cannot be attributed to the diffusivity scaling or the length fluctuations but is due to the chain dynamics details during diffusion in which the end beads play the key role. The viscosity exponent 3 and its expected relation with the diffusivity exponent are recovered in the asymptotic regime ($N \to \infty$).

PACS. 66.10.Cb Diffusion and thermal diffusion – 83.10.Kn Reptation and tube theories

1 Introduction

Islands and clusters diffusion mechanisms can be much more complex than those for single-atom diffusion [1]. If only single-jump mechanisms are considered, *i.e.* cluster dynamics results from the sequential motion of individual atoms, and we restrict to one dimension, the cluster reduces 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 worm-like fashion. This mechanism, named reptation in polymer physics, plays a key role in the dynamics of entangled polymer melts, a problem of enduring interest [2].

The fundamental assumption in the dynamics of entangled polymers is that neighboring chains constrain a given chain to diffuse only along a confining tube and then the chain executes a one-dimensional random walk [3,4]. The model, 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 $\beta = 3$. Many experiments give the mentioned scaling for the diffusivity but the viscosity scales as $M^{3.4}$. There have been several explanations for these results, most of them consisting in modifications of the reptation theory [5]. However, the molecular-weight dependence of the viscosity being stronger than the reptation prediction remains controversial.

[a] e-mail: cmaldao@mdp.edu.ar

In this paper we introduce and analyze a model that describes a chain diffusing in one dimension. We avoid a number of complications that can arise in a realistic model [6,7]. We do not focus in reproducing experiments but in presenting a very simple model with a rich behavior. The found dynamics is similar to that described in the original work of de Gennes [3]. However, our model can exhibit a scaling exponent for the viscosity *larger or smaller* than 3. Furthermore, these resulting values cannot be explained through the diffusivity scaling and/or the amplitude of the chain length fluctuations. Here we show that this scaling needs to be considered as the consequence of the chain dynamics during diffusion.

2 Repton model and viscosity

The repton model proposed by Rubinstein consists of N random walkers (reptons) in one dimension [8]. 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 must be preserved. The model contains a parameter, z, that reflects the dimension of the problem. z is the number of possible gates for an end repton to move. Then, there are $z-1$ possible gates to enter into an empty cell and only one gate to move into an already occupied one. Accordingly, the probability of a move in the middle of the chain in any direction is $1/z$ and at the end of the chain the probability of a move that lengthens the configuration is $(z-1)/z$.

The relaxation process can be studied by following the rates at which a cluster of reptons vacates initially occupied sites. Let $x_{\rm R}(t)$ be the leftmost propagation of the right end of the cluster at time t and, similarly, let $x_{\rm L}(t)$ be the rightmost propagation of the left end of the cluster. The zero-shear-rate viscosity is calculated by integrating the stress [9] which is proportional to the number of these sites, *i.e.*

$$\eta_0 = \frac{1}{\langle L\rangle}\int_0^\infty \langle x_{\rm R}(t) - x_{\rm L}(t) + 1\rangle {\rm d}t, \qquad (1)$$

where $\langle L\rangle$ is the length average and the integral is evaluated only for positive values of the integrand.

Interestingly, Rubinstein found that the viscosity scales with the cluster size with exponents greater than 3, that should be seen as effective exponents. The exact value depends on the parameter z; for the case $z = 6$, which can be understood to correspond to a three-dimensional cubic lattice, β takes a value of 3.36 predicting what is observed in experiments. It has been proposed that the basic difference between de Gennes solution of reptation and the repton model is that in de Gennes solution fluctuations are preaveraged (see, for example, Refs. [2,10] and [11]). Indeed, de Gennes reptation is a random walk of a fixed-length object. However, it is possible for one end to move independently of the other and thus the length of the chain can vary. This is the case in the repton model in which the length of the cluster can fluctuate by stretching and contracting. It was found that fluctuations affect the viscosity as a factor $[1-k/M^{1/2}]^3$ with k being a constant [10]. This is not a power law with an exponent of 3.4 but it could approximate the viscosity over the range of molecular weights used in experiments [12,13]. This explanation fails for our model because we found that resulting values for the viscosity exponent can be *larger but also smaller* than 3. Also, we found that the expected relation $\beta = \alpha + 2$ in one dimension is not always valid.

3 The model

Let us consider a chain consisting of N particles or beads that can hop to nearest site only if this site is empty. Hops are accomplished by picking a particle at random and attempting to move it. Particles can hop to right or left, but no more than a site can be empty between two particles. If allowed by these rules, the probability for a successful hopping is the same for all the particles except for those at the ends. A particle not being at one of the ends, a middle particle, can be in any of the four configurations (a), (b), (c), or (d) shown in Figure 1. If it is in configurations (a) or (b), it is unable to move. If the particle is in configurations (c) or (d) it can move to the right or the left, respectively. After being randomly selected the probability of hopping is taken to be $p_{\rm c}$.

In Figure 1 the possible hoppings for an end particle are also shown. In configuration (e) the end particle, if selected, can only jump to the right and the resulting configuration is that of (f). This jump probability is named

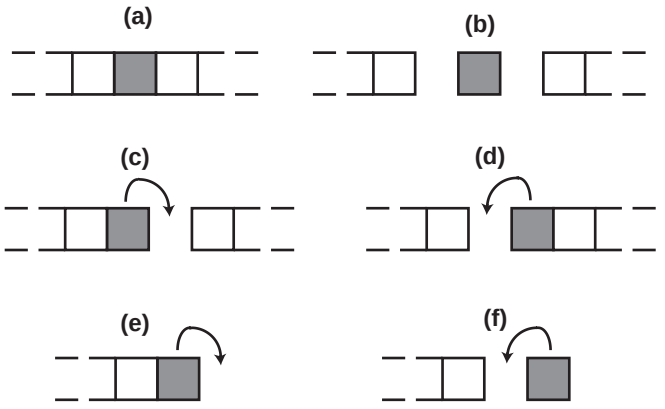

Fig. 1. Configurations for middle ((a), (b), (c), (d)) and end ((e), (f)) particles and their possible hops.

$p_{\rm a}$. In configuration (f) the end particle can only jump to the left and, if selected, the attempted jump succeeds with probability $p_{\rm b}$. Hence, $p_{\rm a}$, $p_{\rm b}$, and $p_{\rm c}$ are the free parameters in our model ($0 \leqslant p_{\rm a}, p_{\rm b}, p_{\rm c} \leqslant 1$).

Thus, the computer model is based on the random walk in a one-dimensional lattice of N particles conforming a chain. At time t one particle of the chain is randomly selected. Once selected, the probability to jump 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. Although at first glance the rules of our model look different than those of the repton model, there is a direct correspondence between both models regarding diffusion. However, since in the repton 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 end of chains.

An empty site in the chain will be named 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 moving away from the chain or towards the chain, respectively. An end particle jumping attempt that creates a hole is successful with probability $p_{\rm a}(1 - P_{\rm h})$, where $P_{\rm h}$ is the hole probability. Similarly, an end particle jumping attempt that annihilates a hole succeeds with probability $p_{\rm b}P_{\rm h}$. In equilibrium we expect the same probability for creation and annihilation. Then, $P_{\rm h}$ can be expressed as

$$P_{\rm h} = \frac{p_{\rm a}}{p_{\rm a} + p_{\rm b}} \quad . \qquad (2)$$

Note that $P_{\rm h}$ is independent of $p_{\rm c}$. The average number of holes in a chain is $P_{\rm h}(N-1)$ since there are $(N-1)$ positions available for holes. Then the average length of chain $\langle L\rangle$ and its fluctuation amplitude are given by

$$\langle L\rangle = N + P_{\rm h}(N-1), \qquad (3)$$

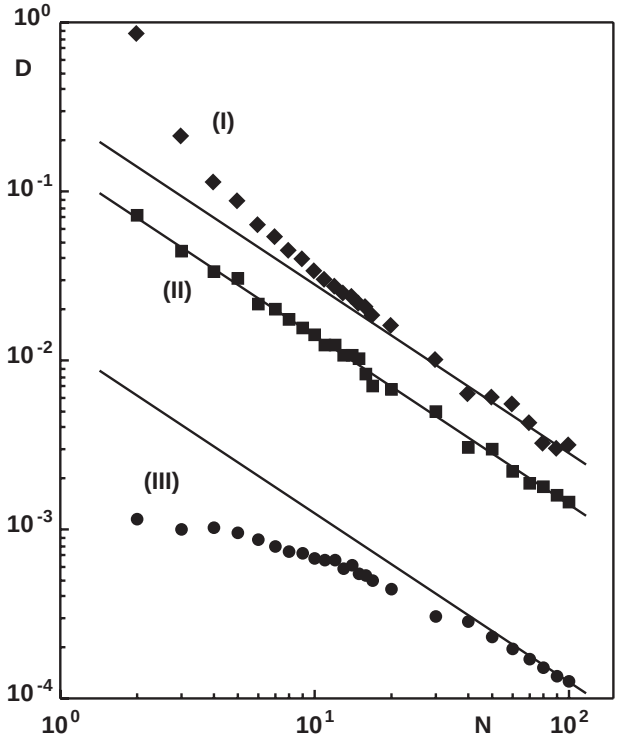

Fig. 2. Diffusion coefficient of the center of mass for chains consisting of N beads. The parameters of the model (p_a, p_b, p_c) are (1, 1/5, 1/5) for case I, (5/6, 1/6, 1) for case II, and (5/36, 1/36, 1) for case III. Straight lines correspond to the asymptotic behavior with slope -1. For the sake of clarity, diffusivity values for case I were multiplied by 10 and those for case III by 0.1.

$$\left\langle (L - \langle L \rangle)^2 \right\rangle = (N-1) P_\mathrm{h} (1 - P_\mathrm{h}) \,. \tag{4}$$

Monte Carlo simulations verify these results.

4 Results and discussions

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

$$D = \frac{\left\langle [X_\mathrm{m}(t) - X_\mathrm{m}(0)]^2 \right\rangle}{2t} \quad , \tag{5}$$

where X_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. Note that case I corresponds to the repton model for $z = 6$ but cases II and III have no correspondence in the repton model. Parameters have been chosen to have always the same average number of holes ($P_\mathrm{h} = 5/6$) and then the same average length and length fluctuation (see Eqs. (3) and (4)). In the asymptotic regime D presents always a slope $1/N$. This is the expected diffusivity dependence for a one-dimensional model corresponding to the curvilinear diffusivity of a chain in three dimensions (*i.e.* α=1). The exponent α 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 Tab. 1).

All the particles conforming the chain have the same chance to be chosen to perform a hop but, in general, they do not have the same chance to hop. On average, the probability that, once chosen, an end particle performs a jump to the right or to the left is

$$J_\mathrm{e} = (1 - P_\mathrm{h}) p_\mathrm{a} = P_\mathrm{h} p_\mathrm{b} \,, \tag{6}$$

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

$$J_\mathrm{m} = (1 - P_\mathrm{h}) P_\mathrm{h} p_\mathrm{c} \,. \tag{7}$$

Using equation (2), the ratio between expressions of equations (6) and (7) can be written as

$$\frac{J_\mathrm{e}}{J_\mathrm{m}} = \frac{p_\mathrm{a} + p_\mathrm{b}}{p_\mathrm{c}} \,. \tag{8}$$

If $p_\mathrm{a} + p_\mathrm{b} = p_\mathrm{c}$, the probability to jump 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 we are dealing with an *uncorrelated* diffusion. This is satisfied in case II but not in cases I and III for which hops become *correlated*. We are not dealing with a model in which the past move is directly taken into account in the following step but diffusion becomes correlated as a consequence of the established rules through the resulting configurations. Indeed, if the $p_\mathrm{a} + p_\mathrm{b} = p_\mathrm{c}$ condition is satisfied, in all possible configurations the next hop has the same probability to be to the right or to the left. (Note that for case II α is close to 1 for large and small values of N). Conversely, if $p_\mathrm{a} + p_\mathrm{b} \neq p_\mathrm{c}$, in many configurations the probability to hop in one direction can be different than in the other one.

In Figure 3 the numerically calculated values of η_0 through equation (1) are presented (see Tab. 1). The found slopes in the double-logarithmic scale converge to 3 as N increases for the three cases studied. However, case I presents a larger slope at low N as found in reference [6]. Values of η_0 for a fourth case (IV) corresponding to p_a=1/5, p_b=1 and p_c=1/5 are also shown.

The diffusivity for case IV is exactly the same than 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 equations (2), (6), and (7). The probabilities that, once chosen, an end particle and a middle particle make a jump to the right or to the left are $p_\mathrm{a} p_\mathrm{b}/(p_\mathrm{a} + p_\mathrm{b})$ and $p_\mathrm{a} p_\mathrm{b} p_\mathrm{c}/(p_\mathrm{a} + p_\mathrm{b})^2$, respectively. Consequently, the jumping probability of any particle for cases I and IV is the same and hence diffusivities have the same value, a result which is confirmed in the simulations. Also, the amplitude of the fluctuations are the

Table 1. Exponents α and β for different values of the free parameters p_a, p_b, and p_c obtained using our model. $\beta = 2 + \alpha$ is the expected relation between diffusivity and viscosity exponents. Relative errors are around 5% for α and 1% for β.

					$4 \leqslant N \leqslant 20$			$20 \leqslant N \leqslant 100$		
Case	p_a	p_b	p_c	P_h	α	β	$2+\alpha$	α	β	$2+\alpha$
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
IV	1/5	1	1/5	1/6	1.22	3.05	3.22	1.05	3.05	3.05

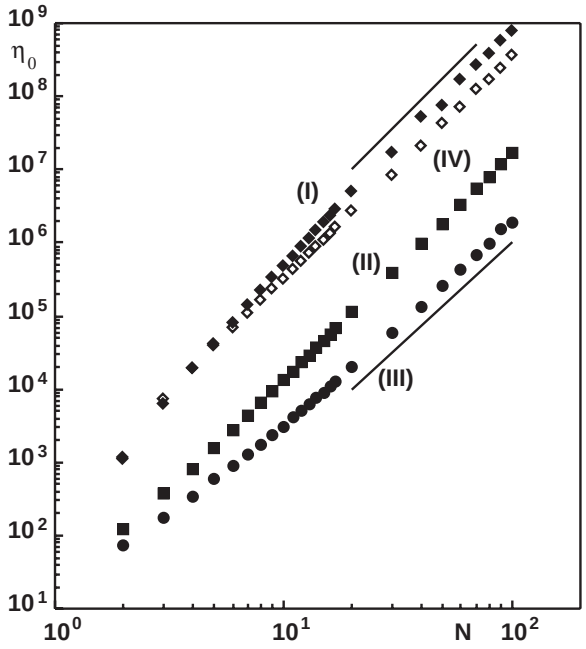

Fig. 3. The viscosity as a function of the number of beads N for the three cases of Figure 2 and that for case IV for which the parameters of the model (p_a, p_b, p_c) are (0.2, 1, 0.2). For the sake of clarity, viscosity values for case I and IV were multiplied by 100 and those for case II by 10. The straight lines have the slopes of the cases I and III for $20 \leqslant N \leqslant 100$ and were drawn as a guide to the eye.

same than in case I (see Eq. 4) but the number of holes is now very different (see Eq. 2). Interestingly, chains with the same diffusivity and fluctuations amplitude present different viscosities. Furthermore, β can be larger (case I) or smaller (case IV) than expected from the diffusivity exponent. Indeed, the diffusivity exponent is 1.22 for $4 \leqslant N \leqslant 20$ and viscosity exponents are 3.46 and 3.05 for cases I and IV, respectively. These results show that β also depends on P_h.

The viscosity in our model for case I reproduces the values obtained through the repton model if we subtract $(N-1)$ from the length in our chains [6] (exponent α is not affected by this chain contraction). Note that with similar rules different results are obtained indicating that the exact value of η_0 depends on the details of the model. Since diffusivity is related to the *long-term evolution* of the center of mass of the chain, it is insensitive to the change of some parameters. On the other hand, since the viscosity is related to the *transient process* by which the chain abandons its original position, it should not surprise us to find that the viscosity is very sensitive to the details of the model as well as the definition adopted to determine it.

A simplified model of reptation in which internal beads instantaneously attain the equilibrium distribution has been proposed and analyzed by Leegwater [14]. This is equivalent to our model for the limit case in which $p_c \gg p_a, p_b$. In Leegwater's model only the two end particles are relevant for diffusion and then the curvilinear diffusion coefficient D_c becomes independent of the chain length. Assuming a Gaussian random walk configuration of a chain, the three-dimensional coefficient is $D_{3D} \approx D_c/N \approx 1/N$, result which is approximately found in the simulations.

The results found by Leegwater can be derived and expressed in terms of the parameters of our model. With equations (2) and (6), the probability that, once chosen, an end particle performs a jump can be written as

$$J_e = \frac{p_a p_b}{p_a + p_b}. \tag{9}$$

Since internal beads instantaneously reach the equilibrium distribution, every time an end particle jumps the center of mass of the chain moves 1/2 of the distance l between adjacent sites of the lattice. Considering l=1, the diffusivity of the center of mass is

$$D = \frac{p_a p_b}{2(p_a + p_b)}, \tag{10}$$

which is independent of the chain length.

5 Conclusions

We have presented a computer model that simulates the diffusion of a chain of particles in one dimension. The introduced model presents chain length dependencies for the viscosity exponent that can be larger or smaller than 3. This nonuniversal behavior appears in the range of N that corresponds to the molecular weights tested in experiments. The physical origin of the scaling discrepancy between α and β was shown not to be due to the amplitude of the chain length fluctuations but a consequence of the chain dynamics details in diffusing. The resulting behavior points to the relevance of the chain movements due to the dynamics of end beads and its relation with the dynamics of internal beads. We also found that, eventually in all the studied cases, universality is recovered for large enough values of N and β converges to the expected value of 3.

This work was partially supported by the National Council for Scientific and Technical Research (CONICET) of Argentina. One of us (CMA) would like to thank Michael Rubinstein for enlightening e-mail discussions.

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