Polymer fragmentation in extensional flow

Armando M. Maroja,[1,2,*] Fernando A. Oliveira,[2,†] Michał Cieśla,[3] and Lech Longa[2,3,‡]

[1]*Curso de Física, Universidade Católica de Brasília. 72170-100, Taguatinga DF, Brazil*
[2]*International Center of Condensed Matter Physics and Instituto de Física, Universidade de Brasília. CP 04667, 70919-970 Brasília DF, Brazil*
[3]*Jagellonian University, Institute of Physics, Department of Statistical Physics, Reymonta 4, Kraków, Poland*

In this paper we present an analysis of fragmentation of dilute polymer solutions in extensional flow. The transition rate is investigated both from theoretical and computational approaches, where the existence of a Gaussian distribution for the breaking bonds has been controversial. We give as well an explanation for the low fragmentation frequency found in DNA experiments.

Since the original studies of de Gennes [1] and Hinch [2] the investigations of dilute polymer solutions in extensional flow has received a lot of attention [3,4]. The main objective of the present paper is to show that some of the phenomena, such as experimentally observed Gaussian distribution of scission products [4], can be obtained by use of a simple model. Another important point is the very small value of the transition-state rate obtained experimentally. This value is 10^{-5} times smaller than the computed one using a transition-state theory [5]. We believe that understanding those observations in a more simple frame may help us to get deeper insight into fragmentation processes of complex polymeric structures at the microscopic level.

As early as in 1939 Kuhn [6] proposed a model for polymers in which beads were connected by elastics forces. Recently, Blumberg-Selinger *et al.* [7] have considered a model where a bond was allowed to break or not. They showed that this system could be mapped on into an Ising-like model with mean-field limit describing the stretching and failure of a two-dimensional solid. In the absence of experiments (only in the last few years precise experiments have been performed [8]), computer simulations have become a useful tool for modeling fragmentation. Welland *et al.* [9] addressed the question of where a chain with fixed ends is likely to break. Doer and Taylor [10] studied the breaking of harmonic chains and some of us worked out a theory of fragmentation of anharmonic chains under periodic boundary conditions and homogeneous strain [11,12,14,15].

At first sight, the fragmentation of polymers in an extensional flow sounds as an immediate generalization of the previous results. Nothing could be more misleading. Indeed, experiments on stretching of single chains in a uniform flow, held at one end by optical tweezers, show that the subject remains controversial despite its long history [8,16,17].

In order to gain an insight into the process of polymer fragmentation we shall perform Langevin dynamics simulations of a chain with N beads of mass M in a uniform flow. The simulation model attempts to incorporate just enough details to observe fragmentation without impeding the efficiency of the simulation. As a result, we ignore the internal dynamics of the beads and treat them as particles of mass M. The geometric center of the chain is put at the center of the four roll mill [16,18], where the fluid velocity vanishes. We focus our analysis on the particle l of the chain and assume that the fluid velocity V_l grows linearly as we move off the center: $V_l = (1 - 2l/N)V_F$. Here $|V_F|$ is the maximal fluid velocity as experienced by the chain. For large V_F the chain may break instantaneously, while for small V_F it may not break at all.

The equations of motion are integrated according to the methodology of Langevin dynamics. More specifically, the classical motion of a particle, say l, is taken to be the Langevin equation, which consists of inertial terms, force field, frictional drag, and noise, respectively,

$$M\frac{d^2 u_l}{dt^2} = F(a + u_l - u_{l-1}) - F(a + u_{l+1} - u_l) - \gamma M(\dot{u}_l - V_l) + f_l(t). \tag{1}$$

Here u_l is the displacement from the equilibrium position and $F(x)$ is the force between the nearest neighbors, which we obtain from a 12:6 Lennard-Jones potential $U_{LJ}(x)$. Additionally, a is the lattice parameter, such that $F(a)=0$, and $\epsilon = -U_{LJ}(a)$ is the binding energy. The friction between the particle and the fluid is given by $-\gamma M(\dot{u}_l - V_l)$, where γ is the friction constant. We take γ as being size and position independent. In order to save computer time and simplify the theory further we keep the motion parallel to the direction of the fluid velocity and suppress the transversal vibrations. We believe this will not affect the main results, which should hold for an isotropic fluid subject to a uniform velocity field.

For the actual computation reduced quantities are used, where the units have been renormalized to a mass M of 1, an equilibrium bond length a of 1, and a Lennard-Jones ϵ of 1. It follows that the reduced distance is equal to r/a, the reduced temperature is $k_B T/\epsilon$, the reduced energy is E/ϵ, and the reduced time is t/τ_0, where $\tau_0 = 2\pi/\omega_0$ with ω_0 being the maximal phonon frequency of the chain without stress.

*Email address: armando@ucb.br
†Email address: fao@iccmp.br
‡Email address: uflonga@kinga.cyf-kr.edu.pl

Langevin dynamics, Eq. (1), simulates the effect of individual solvent molecules through a fast-changing force $f_l(t)$ of intensity $\sigma \eta_l$, where η_l are the random numbers. Here we take η_l uniformly distributed on the interval $-1 \leqslant \eta_l \leqslant 1$. The value of σ depends on the time increment Δt that one uses to numerically integrate Eq. (1). Assuming that the Brownian force is constant in the interval Δt (in practice $\Delta t = 0.005 \tau_0$) and taking regard of the fluctuation-dissipation theorem we get $\sigma = \sqrt{6M\gamma k_B T/\Delta t}$. Clearly, the nonconservative forces simulate the thermal bath [11].

Before performing extensive simulations on polymer fragmentation we first construct simpler, effective theory, which is a generalization to inhomogeneous strain of the one-particle model presented in the papers [11,14,15]. We start by noting that the energy necessary to pull the monomer k apart a distance ϕ from its equilibrium position is given by

$$U_{eff}(k,\phi) = \sum_{j \neq k} \left[U_{LJ}(a+S_j) + S_j R_j \right] + U_{LJ}(a+S_k+\phi)$$
$$+ (S_k + \phi)R_k, \tag{2}$$

where S_j is the "strain" at the position j due to the friction with the fluid. The strain and the resulting force R_j are defined by the condition

$$R_j = F(a+S_j) = -\gamma M \sum_{l=I_e}^{j} V_l, \tag{3}$$

where $I_e = (1,N)$ stands for the ends of the chain where the counting starts, and j is within the half segment, i.e., $|j-I_e| \leqslant N/2$. Equations (2) and (3) define an effective potential for the breaking process. Note from Eq. (3) that the strongest force acts on the middle of the chain.

In Fig. 1 we plot the potential $U_{eff}(k,\phi)$ as a function of separation ϕ for $N=100$ and for two different monomers: $k=50$ (curve a) and $k=30$ (curve b). The first case corresponds to the monomer being positioned in the middle of chain while the second one is for the monomer located off center. The fluid velocity is $V_F=0.02$ and we use a moderate damping $\gamma = 0.25\omega_o$. As clearly seen from Fig. 1 the breaking process is more frequent in the middle of the chain than in any other place, and this frequency should decrease with increasing distance from the center. This observation is consistent with the value of the energy barrier $E(x)$, as a function of the distance x ($x \ll Na/2$) to the middle of the chain. It reads

$$E(x) = E_b + 4\alpha \left(\frac{x}{N}\right)^2 + \cdots, \tag{4}$$

where, for properly chosen V_F, e.g., $E_b(N,V_F) = E_b(NV_F)$ (see Table I) the parameter α could be made independent of N.

Now that an effective potential for a polymer in an extensional flow has been identified, we can study the fragmentation process as a generalized thermal activation over a bar-
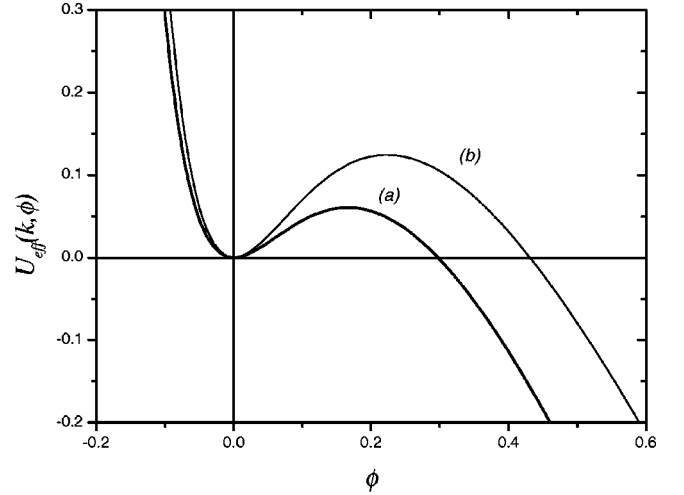

FIG. 1. Effective potential for breaking of a bond at site k as a function of the bond elongation ϕ. The intrachain interaction is given by a 12:6 Lennard-Jones potential and the interaction with the fluid by a viscous force proportional to the relative velocity. Energies are in units of binding energy, distance in units of lattice constant a, time is in units of $\tau_0 = 2\pi/\omega_0$, where ω_0 is the maximum phonon frequency. The chain has 100 particles and the fluid speed at the chain's end is $V_F = 0.02$. We take the friction constant as $\gamma = 0.25\omega_0$. (a) $k=50$ and (b) $k=30$.

rier. Before we start to compute the breaking rates for the polymers, let us discuss briefly the main ideas of the reaction rate theory.

Consider a set of independent particles in a metastable situation, for example, at the position $x=0$ of the potential well of Fig. 1. The particles are in a thermal bath at the temperature T, smaller than the activation barrier E_b, i.e., $E_b \gg k_B T$. The probability p of the particle make a jump over the barrier in a time interval Δt is

$$p = \frac{\Delta t}{\tau}, \tag{5}$$

where τ is the first time passage or the characteristic time. For $\Delta t \ll \tau$ the crossing probability is small and those rare events are well described by a Poisson law. Consequently the number of particles in the well $n(t)$ decays as $n(t) = n(0)\exp(-t/\tau)$. From this follows a practical way to obtain the characteristic time τ and the crossing rate $K = \tau^{-1}$: we just have to count the number of particles in the well.

TABLE I. Main parameters for the effective breaking theory. We use the effective potential to obtain the activation energy E_b and the attempt frequency $\bar{\nu}_K$. Here $\gamma = 0.25\omega_o$; the subscript S refers to the results obtained from simulations.

N	V_F^{-1}	E_b	E_S	$\bar{\nu}_K$	ν_S	α	α_S
100	50	0.0606	0.0246	4.507	0.0153	0.22	0.31
200	100	0.0606	0.0179	8.938	0.005 23	0.32	0.32
300	150	0.0606	0.0193	13.37	0.003 10	0.31	0.32

The attempt to obtain reliable values for K is the main subject of the centennial effort, known as reaction-rate theory [19–22] which, as we shall see, is not always successful. In order to explain the temperature dependence of a chemistry reaction Arrhenius [19] proposed that the reaction rate K would be the product of the jumping probability $\exp(-\beta E_b)$ ($\beta = 1/k_B T$) times the attempt frequency ν, i.e., the frequency that the particle will try to jump. The Arrhenius law reads

$$K = \nu \exp(-\beta E_b). \tag{6}$$

As a first approximation Arrhenius suggested that ν would be approximately the vibration frequency of the well ν_a, $\nu \approx \nu_a = \omega_a/2\pi$.

A half-century after Arrhenius, Kramers [20] returned to a rigorous analysis of the problem. First, he did a "harmonization" of the potential as

$$U(x) = \begin{cases} E_b - \dfrac{1}{2}\omega_b^2(x-x_b)^2, & \text{for } x \approx x_b \\ \dfrac{1}{2}m\omega_a^2 x^2, & \text{for } x \approx 0. \end{cases} \tag{7}$$

Here x_b and $\omega_b/2\pi$ are, respectively, the coordinate and the unstable frequency at the barrier. Then he solved a Fokker-Planck equation and rediscovered the Arrhenius law. Moreover, he found the attempt frequency ν as

$$\nu \cong \nu_K = \frac{\omega_a}{\omega_b}\left(\sqrt{\omega_b^2 + \frac{\gamma^2}{4}} - \frac{\gamma}{2}\right), \tag{8}$$

which, for most of the cases, is of the same order as the Arrhenius result. Kramers main contribution was to put the Arrhenius law in a more fundamental framework, and to call attention for two new points. First, it is very important to understand what happens near the top of the barrier, i.e., the unstable motion. Second, the presence of friction γ must be taken in consideration (for a review, see Ref. [21]). Since then it was found that a large number of phenomena in physics and chemistry follows this simple description, Eq. (6), given that the energy barrier satisfy $E_b > k_B T$.

Let us now turn back to our problem of polymer fragmentation. From a simple analysis we expect that the total breaking rate K will be the sum of all local Kramers rates

$$K = K_K = \sum_{i=-N/2}^{N/2} K_i, \tag{9}$$

where K_i is the breaking rate at the site i. In this way the parameters of Eq. (8) do depend on the position along the chain, and so does ν_K. In order to evaluate Eq. (9), let us consider its continuous limit, and $\omega_a = \omega_a(x)$ and $\omega_b = \omega_b(x)$. The probability $P(x)\,dx$ of breaking between x and $x+dx$ should follow the Boltzmann distribution

$$P(x) = C \exp[-\beta E(x)], \tag{10}$$

with C being the normalization constant and $E(x)$ given by Eq. (4). We define the breaking rate as the total rate to cross all the local barriers of the breaking potential, Eq. (2). That is, we generalize Kramers ideas for a set of local wells to get

$$\tau^{-1} = \tau_K^{-1} = N\bar{\nu}_K \exp(-\beta E_b), \tag{11}$$

where τ is the characteristic time for an irreversible breaking and

$$\bar{\nu}_K = \int \nu_K(x) P(x) dx,$$

is the average of all the Kramers frequencies for the local wells.

Unfortunately, Eq. (11) is not able to account for all the complexity of the breaking phenomena even in chains submitted to uniform strain [11–15]. Consequently, some few improvements need to be done. Since the Arrhenius factor $\exp(-\beta E_b)$ is in agreement with computer simulations [15], we propose that only the attempt frequency must be modified. In this way we rewrite Eq. (11) as

$$\tau = f_c \tau_K. \tag{12}$$

We have introduced the dimensionless factor f_c to take care of possible collective dynamical effects and, as we shall see, it has the "complexity" of the process. We shall call it the *complexity factor*. One should bear in mind that for chains submitted to a homogeneous "strain" and under periodic boundary conditions, f_c would be size independent. Moreover, if Kramers theory could be easily applied to our situation, f_c would be a number of order of unity. We shall return to f_c, after we present the result of our simulations.

Finally, we use Eq. (10) to compute the "mean-square displacement" of breaking bonds, i.e., the variance of location where the bonds breaks, as

$$\sigma_x^2 = \langle x^2 \rangle = \frac{N^2}{8\alpha} k_B T. \tag{13}$$

Now we perform Langevin dynamics simulations by numerically integrating Eq. (1) for an ensemble of chains subject to different sequences of random forces. The thermodynamic parameters used are the same as those of the effective model. We ask for the time needed for one of the bonds of the chain to exceed a distance d, i.e., $\phi = u_l - u_{l-1} > d$. The number of survival chains $n(t)$, i.e., those whose distance did not exceed d, as function of time, is a Poisson distribution with a characteristic time $\tau(d)$. We follow the evolution of $\tau(d)$ as function of d until we reach the distance d^*, where $\tau(d^*)$ does not change anymore. This characterizes an *irreversible evolution over the barrier, or an irreversible breaking*, with characteristic breaking time $\tau = \tau(d^*)$.

In Fig. 2 we plot the logarithm of the breaking time as a function of the inverse of temperature. The parameters are the same as in Fig. 1. Every experiment involves an ensemble of 2000 chains. We see that the figure displays an Arrhenius law similar to that of Eq. (11). However, the fit predicts an activation energy $E_s = 0.0246 \pm 0.005$, while the
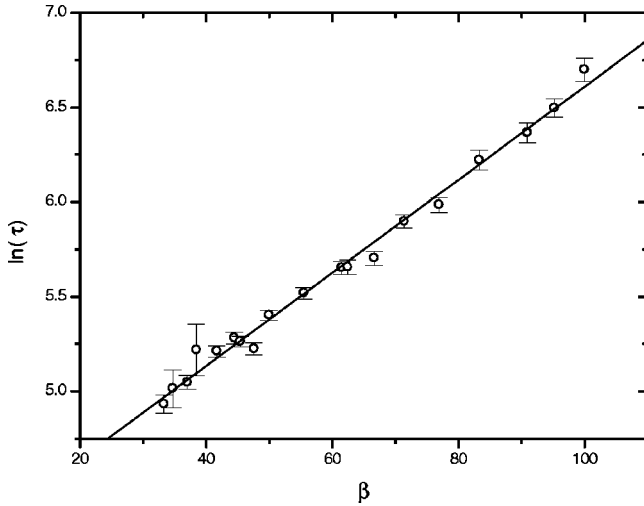
FIG. 2. Logarithm of breaking time as function of the inverse of temperature. We use the same parameters as in Fig. 1. The graph displays an Arrhenius rate with activation energy $E_s = 0.025$.

calculation, given in Table I, yields $E_b = 0.0606$. The attempt frequency ν_S is found to be several orders of magnitude smaller than the Kramers frequency $\bar{\nu}_K$. Moreover the activation energy cannot be smaller than $E_b < E(x)$, Eq. (4), since $E(x)$ is itself the minimum possible energy for breaking at position x. Consequently, we shall assume that the energy is taken directly from the effective potential for breaking, Eq. (2), which explains the origin of the factor f_c introduced in an *ad hoc* way in Eq. (11).

In Table I we collect values of parameters α, E_b, and $\bar{\nu}_K$ as functions of N and V_F. The theoretical values are those computed from Eqs. (4)–(13). We choose N and V_F in such a way that the chains will have the same energies E_b and, consequently, similar α. The values obtained from simulations have the subscript S.
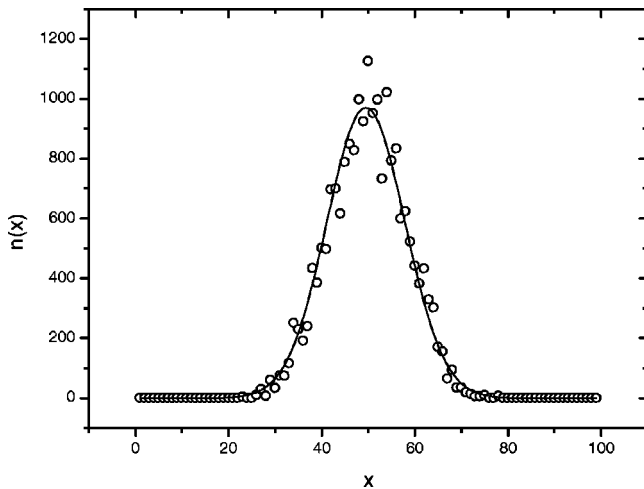
In Fig. 3 we show the distribution of breaking bonds as

FIG. 3. Distribution of breaking bonds as function of the position. Parameters are as in Fig. 1 and temperature $T = 0.018$. In the experiments 20 000 chains were broken. The full line is the Gaussian fit to the data.
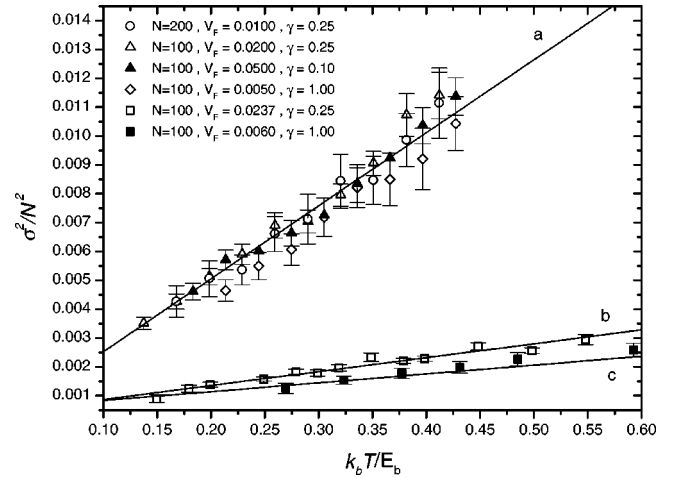

FIG. 4. Dispersion of breaking bonds as function of temperature. In order to display several temperature ranges on single graph we scale the temperature by E_b. In (a) the theoretical values are $\alpha = 0.32$ and $E_b = 0.0606$; the simulations give $\alpha_S = 0.32 \pm 0.01$. In (b) the theoretical values are $\alpha = 0.205$ and $E_b = 0.0100$; the simulations give $\alpha_S = 0.21 \pm 0.04$. In (c) the theoretical values are $\alpha = 0.189$ and $E_b = 0.00742$; the simulations give $\alpha_S = 0.20 \pm 0.01$.

function of position for $T = 0.018$. The remaining chain parameters are the same as in Fig. 1. In the experiment 20 000 chains were broken. The full curve is a Gaussian distribution fitted to the data, which suggests that the dispersion is indeed in agreement with Eq. (13). At this point it is perhaps worthwhile to comment on the effect of transverse fluctuations. We expect that they do not, within our model, affect the distribution of breaking bonds. However, they do affect, by a factor of the order of 2, the complexity factor. Since f_c is already unknown by a factor which is at least of the order of 10^4, we will not be concerned here with a full theory to explain f_c.

In Fig. 4 we collect a set of data for σ_x^2/N^2 versus temperature. We scale the temperature by E_b in such a way that different ranges of temperature can be visualized on the same graph. We use as well a large variation of the damping, i.e., $0.1\omega_o \lesssim \gamma \lesssim 1.0\omega_o$. In curve a the empty circles represent data for $\gamma = 0.25\omega_o$, $V_F = 0.01$, and for $N = 200$. The remaining data of this figure correspond to $N = 100$. Here, the empty triangles are parametrized by $\gamma = 0.25\omega_o$ and $V_F = 0.02$, and the full triangles are for $\gamma = 0.10\omega_o$ and $V_F = 0.05$. The diamonds represent simulations with $\gamma = 1.0\omega_o$ and $V_F = 0.02$.

The data combine together as an evidence for Eq. (13). Its validity is further supported by the simulations for $N = 300$ and $V_F = 0.00666$ (the corresponding data are not shown in the figure). Additionally, the parameter α displays the correct temperature dependence and the universal (size independent) behavior. Interestingly, remarkable agreement is obtained between $\alpha_S = 0.32 \pm 0.01$ from the minimum square fit and $\alpha = 0.32 \pm 0.01$ from the effective potential [$\alpha = 0.31$, 0.32, and 0.33; see Table I].

Similar agreement is displayed by curves b and c of Fig. 4. For curve b, where $\gamma = 0.25\omega_o$ and $V_F = 0.0237$, the theoretical values are $\alpha = 0.205$ and $E_b = 0.0100$. The simulations give $\alpha_S = 0.21 \pm 0.04$. For curve c with $\gamma = 1.0\omega_o$, V_F

$=0.006$ we have $\alpha=0.189$ and $E_b=0.00742$, while the simulations predict $\alpha_s=0.20\pm0.01$. Finally, we shall notice that for $T\to0$, i.e., $\sigma_x\ll1$, the Gaussian distribution approaches a Dirac delta function centered at the middle of chain. This explains some of experiments [5,23], where molecules are fractured in half.

Why such perfect agreement for α and such discrepant behavior for E_b? As we have mentioned before this collective effect is in the complexity factor f_c. This factor has the chain dynamics, and as well, complex phenomena such as kink nucleation [12]. Indeed we have proved that the typical distance d^* to an irreversible crossing is larger to a chain than to a particle in the effective potential Eq. (2). This of course contributes to decrease the fragmentation rate. The chain dynamics creates new phenomena that need to be incorporated in the reaction-rate theory. Those phenomena get complex as we increase the system dimensions [13].

A factor similar to f_c was obtained for chains submitted to homogeneous strain S subject to periodic boundary conditions [15]; there $f_c=f_c(T,S)$ is size independent. That is, for given temperature and strain, the ratio $\tau(N_1)/\tau(N_2)=N_2\exp[\beta(E_1-E_2)]/N_1$ is independent of f_c and, hence, it can be computed. The results show that $\tau(N)$ scales with N [15], and that the effective potential provides very accurate values for activation energies E_b. The large value of f_c and its dependence on T could be explained by the existence of collective modes, which induce an extra coherent noise in the system. This itself yields time-dependent friction and modifications to the Langevin equation [14,15,22].

In our case the fact that α is precisely the same strongly suggests that the potential, Eq. (2), and its barrier, Eq. (4), should be correct. We used as well other inverse power-law potentials and found that the results are nearly the same, low attempt frequency, an underestimated barrier, and a Gaussian distribution of breaking bonds. Thus, deviation from Gaussian distribution found in some experiments [8] must be due to an inhomogeneous flow, rather than the chain dynamics. As values of α can be measured and computed in polymers, it would be interesting to carry out experiments measuring both the activation energy and the bond dispersion for a single chain as function of temperature.

In conclusion we developed a microscopic theory that gives a simple analytical result for the dispersion of breaking bonds of a chain in an extensional flow. It shows as well that the difference between the computed activation energy and those found from the simulations may be explained by the complexity factor f_C, which is responsible for the collective effects, such as memory [14] and nucleation of kinks [12,24]. As supported by our simulations f_C can assume values of the order 10^4 to 10^6. This explains the result reported by Odell [4], where difference between experiment and theory for the attempt frequency is of the same order. This discrepancy is a decreasing function of $\mu=E_b/k_BT$, when we fix E_b and change the temperature, and an increasing function of μ when we fix the temperature and change E_b. Clearly, this proves that f_C is not only a function of μ, as one would expect from statistical arguments.

Fracture is a complex nonlinear phenomenon, surprisingly complex even in one dimension. At the present state of the art, only for homogeneous chains it is possible to obtain an approximate expression for f_C. A full theory for more realistic systems is still lacking.

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