

## Transition-state analysis for fracture nucleation in polymers: The Lennard-Jones chain

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We present here a microscopic theory for fracture nucleation in finite chains, which may account for results found in simulations and in some experimental situations. We obtain the characteristic breaking time for an ensemble of one-dimensional Lennard-Jones chains, which is mainly a large prefactor times an Arrhenius rate. We show that the expression scales well and that the activation energy agrees with the analytical results. We show that the delay in the fragmentation is a consequence of the long-range time correlation in the relative motion of two adjacent particles. This correlation is responsible for the origin of a self-organized memory as well as the large elongation necessary for irreversible break to occur. We discuss the possibility of using this simple theory to understand the main characteristic of fragmentation in more complex and realistic systems. [S0163-1829(98)01717-2]

### I. INTRODUCTION

The subject of fractures has been, for a very long time, a field of research in engineering and material science. However, it has only recently attracted the attention of theoretical physics. With the recent development on nonlinear and dissipative dynamics the subject becomes now plausible with a more precise description, going beyond the computational or phenomenological view. The physics and chemistry of fragmentation is a very rich and complex subject, and only for simple systems is an analytical theory of fracture possible. There is a reasonable number of systems such as additives in fluids, and DNA in solutions whose motion in turbulent regime is subject to hydrodynamics scission. In order to understand polymer degradation one must build a theory for the breaking of single chains. This theory of course does not exist, nevertheless, we shall list here some of the main achievements in this direction.<sup>1-12</sup>

There are two fundamental questions that a theory of fracture must answer. First, what is the condition for a given system to be considered stable? Second, how long will it take for an unstable system to break? The problem addressed in Refs. 10-12 is that of developing a theory that provides some basis to answer both questions for anharmonic chains under stress. Real polymers, or any other solids, are indeed three-dimensional objects. However, under stress the main fragmentation occurs along the direction of the bond of two neighbors. Consequently we suggest that the main important motion is in the direction of the stretched chain. This is the most simple model, and may be a stepping stone towards a more general theory, which should include polymers networks, gels, and systems with higher dimensions.

As early as 1920, Griffith<sup>1</sup> discussed the time evolution of continuous macroscopic flows that may be present on solid polymers. However, the first work on chain instability was the famous Peierls instability for an infinity one-dimensional (1D) harmonic chain.<sup>2</sup> The subject of stability for a finite anharmonic chain has been discussed by many different authors (see Refs. 8, 10, 12, and references therein). A model based on equilibrium statistical mechanics was proposed by

Blumberg-Selinger *et al.*<sup>6</sup> They consider the system as an Ising model where a bond breaks or not. Their mean field solution is not appropriate for a one-dimensional system, and as consequence the obtained stability condition is somewhat ill defined. Bueche<sup>4</sup> and Zhurkov<sup>5</sup> have suggested that the solid breaking time must be proportional to a Boltzmann factor. They omitted the dependence on the chain length, and their activation energy needs some corrections. Some improvement in this direction has been made by Crist *et al.*<sup>7</sup> However, their work has no reference to the chain dynamics.

The main shortcoming of those models is the total absence of comparison with experiments and simulations. Since experiments on single chains are quite difficult, one must rely on good computer simulations to model the main aspects of the dynamics of fragmentation. In this way, both computer simulations and analytical results have been obtained for harmonic<sup>8</sup> and anharmonic chains.<sup>9,10</sup> Welland *et al.*<sup>9</sup> performed computer simulations on 1D systems. They used the Lennard-Jones potential and fixed boundary conditions. They evaluated numerically the fracture size probability with the distance to the chain's end. In their work they defined the breaking time as an average of 100 runs. This was an important point, however, we showed later<sup>10</sup> that the distribution of breaking time follows the Poisson law.

To understand the thermodynamics of breaking, extensive simulations were performed<sup>10</sup> to determine the conditions under which an anharmonic stretched chain will break. The dynamic of a rectilinear chain of 100 monomers interacting via the Lennard-Jones potential was followed by solving a set of simultaneous Langevin equations. For such nonlinear systems, the breaking time is strongly dependent on the initial conditions and on the noise sequence. Consequently an ensemble of such chains decays with a Poisson law and one can only obtain the characteristic breaking time. A method to obtain a reliable (characteristic) breaking time was then discussed. It was found that the breaking time was orders of magnitude higher than one would expect from a Kramers-type<sup>13</sup> theory. It was noticed as well that in order for an irreversible break to occur in a stretched chain, a bond must be extended to a length considerably greater than the length

at which the restoring force is maximized. This healing capacity was also observed experimentally in iron whiskers under stress. They contain few defects and remain undamaged in a metastable state before a fracture occurs. This phenomenon was called delayed fracture.<sup>3</sup> Nevertheless our model is restricted to one dimension, and as we do not want to study the phenomena or delayed fracture here, we may claim that this may be a very common phenomenon in physics.

In a previous work<sup>11</sup> we investigated the dynamical renormalization at the onset of a fracture. We discussed a possible mechanism to explain the self-similarity found in fracture patterns. Using this renormalization it was possible to obtain correlations functions for the displacements which for short-range time agree with the (exact) correlations functions for the harmonic chain. Later, we studied<sup>12</sup> the dynamical stability of chains under fracture. We got the limiting conditions that a bond may extend before breaking. The results were in agreement with the simulations. Consequently, for single anharmonic chains the stability conditions are well established.

Our main objective here is to answer the second question, *What is the breaking time of a chain, and how does it depend on the temperature, stress, friction, and number of monomers in the chain?*

The approach that we shall take is to follow the chain dynamics through the breaking process. We make use of both computer simulation and the state of the art reaction rate theory to justify our model for simple chains. We consider an ensemble of  $m$  identical chains, each chain of which has  $N$  particles of mass  $M$ , which at equilibrium are separated from each other by a distance  $a$ . We stretch every bond of the chain by an amount  $S$ , then we connect the chains to a thermal reservoir of temperature  $T$ . The displacement of the  $l$  particle from the equilibrium position is  $\xi_l$ . The chains interacting weakly with each other via a friction force  $-M\gamma_0\dot{\xi}_l$ . Here  $\gamma_0$  is the friction constant and  $\dot{\xi}_l$  is the velocity of the particle at the chain in relation to a static medium. The equation of the motion for the  $l$  particle is then

$$M\ddot{\xi}_l = F(a+S+\xi_l-\xi_{l-1}) - F(a+S+\xi_{l+1}-\xi_l) - M\gamma_0\dot{\xi}_l + f_l(t). \quad (1)$$

Here  $F(x)$  is the force between the first neighbors, which we take from a Lennard-Jones potential,  $f_l(t)$  simulates the thermal bath with intensity  $\sigma\eta$ , with  $\eta$  as a uniform distribution of random numbers in the interval  $-1 \leq \eta \leq 1$ . The value of  $\sigma$  depends on the time increment  $\Delta t$  that one uses to numerically integrate Eq. (1). Our times are given in units of  $\tau_0 = 2\pi/\omega_0$ , ( $\omega_0 = \omega_{S=0}$ ), where  $\omega_S$  is the maximum phonon frequency of the stretched chain. We take the Brownian force as a constant in the time interval  $\Delta t = 0.005\tau_0$  and by the fluctuation dissipation theorem, we get  $\sigma = \sqrt{6M\gamma_0 K_B T / \Delta t}$ .

## II. THE ONE-PARTICLE MODEL

Extensive simulations<sup>10</sup> on single chains have shown that the chain will break in just one bond. This is a very plausible argument when one considers that the possibility of double breaking is not an easy process, in terms of energy. For typical polymers at room temperature, we estimate the double

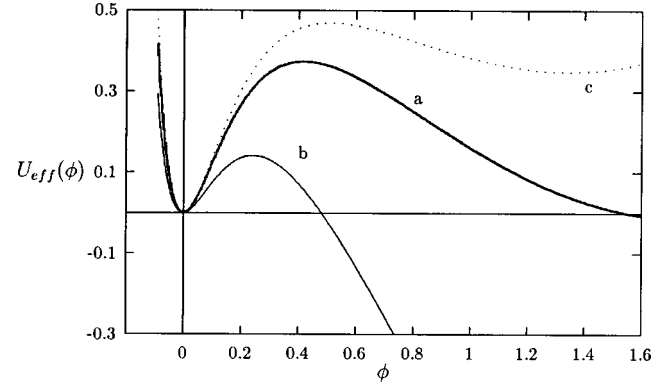


FIG. 1. Effective potential for the break of a bond as a function of the bond elongation. Energies are in units of the binding energy  $\epsilon$ , and distance in units of the lattice space  $a$ . The chain has 100 particles and is submitted to a strain  $S$ . The interaction between the particles is given by the Lennard-Jones potential. (a)  $S=S_0$ ; (b)  $S=0.019$ ; (c)  $S=0.014$ .

breaking probability to be  $\exp(-150)$  smaller than the probability of single breaking. From this point of view, one may say that the average time for a chain to break will be the average time for one of its bonds to break. From that, an effective potential for the breaking of a single bond may be obtained for a chain of fixed length  $L=N(a+S)$ . The chain of  $N$  particles in which a bond is stretched by an extra amount  $\phi$ , while the others  $N-1$  bonds relax, has a potential energy of

$$U_{\text{eff}}(\phi) = U(a+S+\phi) + (N-1)U[a+S-\phi/(N-1)]. \quad (2)$$

This definition of the effective breaking potential may be applied to any pair potential  $U$ . However, in this work we shall restrict our simulations to the 12:6 Lennard-Jones potential with unity binding energy. Equation (2) shows that for any chain of length  $N$  there is a finite strain  $S_0$ , such that the elastic energy accumulated in the chain  $NW$  [ $W=U(a+S_0)-U(a)$ ] should be equal to the necessary energy to break a bond  $NW=1$ . For any  $S>S_0$ , the effective potential has the metastable minimum at  $\phi=0$ , and the absolute minimum has a  $\phi_0$  corresponding to a broken chain. This means that  $U_{\text{eff}}(\phi_0) < U_{\text{eff}}(0)$ . In this situation the global minimum corresponds to a break. Observe that for any realistic pair potential  $U$  must have a maximum strain  $S_{\text{max}}$  as well, beyond which there is no restoring force in the chain. The Lennard-Jones potential has  $S_{\text{max}}=1.109$ . In Fig. 1 we plot the effective potential as a function of the bond elongation  $\phi$ . In Fig. 1(a) we have  $S=S_0$ ; Fig. 1(b)  $S>S_0$ ; Fig. 1(c)  $S<S_0$ . In Fig. 1(b) we notice that the broken chain is the stable situation.

Now that an effective breaking potential has been clearly defined, the main simplification of this theory will be to describe the chain fragmentation process as the evolution of one particle in the effective potential, Eq. (2), from the metastable to the global equilibrium position. The average time for the  $l$ th bond to break will be the average time for a particle to escape from this potential. The equation of motion for a particle in this potential is then

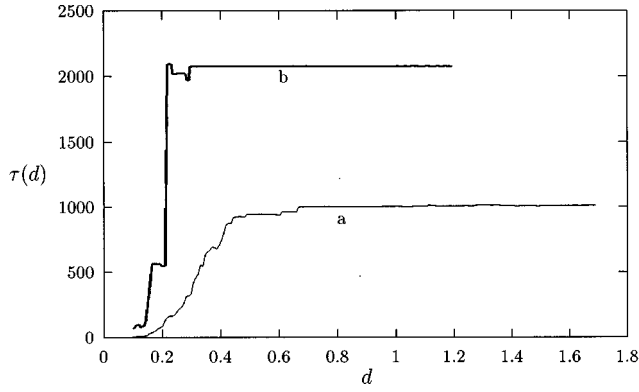


FIG. 2. Characteristic first time passage  $\tau(d)$  for a bond to reach a distance  $d$  as a function of  $d$ . The time is in units of  $2\pi/\omega_0$ , where  $\omega_0$  is the unstretched phonon frequency. We use  $T=0.025$  and  $S=0.035$ . Here through we use  $\gamma=0.25\omega_0$ . (a) A chain with 100 particles. The average is over 800 experiments; (b) a single particle moving in an effective potential with the same conditions as in (a). The average is over 2000 experiments.

$$\mu \ddot{\phi} = F_{\text{eff}}(\phi) - \mu \gamma_0 \dot{\phi} + g(t). \quad (3)$$

Since  $\phi$  is the relative displacement between two real particles, the effective mass  $\mu$  is then  $\mu=M/2$ ,  $F_{\text{eff}}$  is the effective force derived from the potential, Eq. (2), the second term is the friction force, and  $g$  the correspondent noise. The average time for the  $l$ th bond to break will be the average time for this ‘‘particle’’ to escape from the effective potential. From these conditions, it is possible to make an estimation of the escape rate for the transition from a metastable position at  $\phi=0$  to a position outside the barrier where the particle has escaped in an irreversible way.

Now, if we consider that every bond has the same breaking probability, and using reaction rate theory, the average breaking time for the chain can be cast in the form

$$\tau = (\omega_0/\omega_a)(\omega_b/\nu) \tau_0 \exp(\beta E_b)/N. \quad (4)$$

Here  $\omega_b/2\pi$  is the unstable frequency at the top of the barrier and  $\omega_a/2\pi$  is the frequency at the bottom. The factor  $\omega_0/\omega_a$  takes in consideration the change of time units from the particle  $\tau_a=2\pi/\omega_a$  to the chain  $\tau_0$ . The usual Boltzmann factor  $\exp(\beta E_b)$  has  $\beta=1/K_B T$ , and  $E_b$  as the barrier height (see Fig. 1). Equation (4) is the central part of this work. Now we search for an explicit expression for the attempt frequency  $\nu$ . Crist *et al.*<sup>7</sup> presented an estimate for  $\tau$ . However, their results were based on energy considerations, and they omitted the factor  $(\omega_b/\nu)$ . This problem lies at the heart of modern dissipative dynamics, and needs careful analysis.

One systematic approach to the problem of particle evolution over a barrier in a dissipative environment is given by Kramers.<sup>13</sup> He proposed that the main characteristics of a potential with a barrier could be described by two harmonic approximations at the minimum and maximum of the barrier. From that point of view, Eq. (1) can be statistically analyzed to give a characteristic escaping time for the well. Following his ideas, we write

$$\nu = \nu_K = \sqrt{\omega_b^2 + (\gamma_0/2)^2} - \gamma_0/2. \quad (5)$$

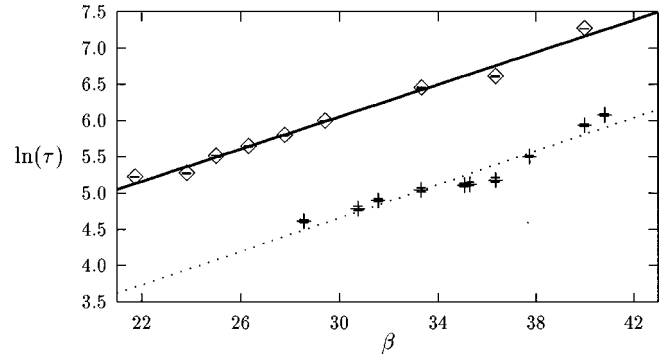


FIG. 3. The logarithm of the breaking time as a function of the inverse of temperature. Here  $S=0.035$ . (a) Upper curve  $N=100$ ; (b)  $N=300$ .

Now we compare the results from Eq. (4) with those of the full simulations for a chain. We integrate Eq. (1) and follow the evolution of a chain until an irreversible break occurs. The characteristic breaking time for a set of 800 chains is shown in Fig. 2. There we plot the first time passage to cross distance  $d$  as a function of  $d$ . In Fig. 2(a), we have an ensemble of 800 chains and in Fig. 2(b) a set of 2000 particles moving in the corresponding effective potential. Here  $S=0.035$ ,  $T=0.025$ , and through this work  $\gamma_0=0.25\omega_0$ . The plateau region is where the irreversible breaking has happened with no more recombinations. The plateau defines the breaking time. We shall notice the higher bond elongation for the chain when compared with the particle.

In Fig. 3 we plot the natural logarithm of the breaking time as a function of the inverse of temperature. Curve (a) is for  $N=100$ , whereas curve (b) is for  $N=200$ . For both chains the results show an Arrhenius rate. Consequently, in analogy with Eq. (4), we suggest for our simulations the attempt frequency  $\nu=\nu_S$  and for the barrier height  $E_b=E_S$ . In Table I we compare the results of simulations with those obtained from our one-particle model. We notice that while the values of  $E_b$  and  $E_S$  are close, the values of  $\nu_S$  are surprisingly, small (large  $\tau$ ) when compared with those of  $\nu_K$ . Notwithstanding the apparent agreement between  $E_b$  and  $E_S$ , we observed that for the set of experiment done  $E_b > E_S$ . This is a puzzle because a careful analysis shows that the effective potential, Eq. (2), has an exact variational principle inside. Consequently, it is not possible by any means for the activation energy  $E_S$  to be smaller than  $E_b$ . Finally, we notice an unexpected large variation on  $\nu_S$  and  $E_S$  with  $N$ .

TABLE I. Parameters for the one-particle effective potential (b), for the Kramers model (K), and for the simulations (s). Here the strain is  $S=0.035$ .

$N$	100	200	300	400
$\omega_b$	3.5970	3.6778	3.7023	3.7142
$\nu_K$	2.0547	2.1242	2.1455	2.1559
$E_b$	0.14135	0.13655	0.13504	0.13429
$\nu_s$	0.00875	0.0191	0.03871	0.0359
$E_s$	0.11	0.09	0.12	0.10

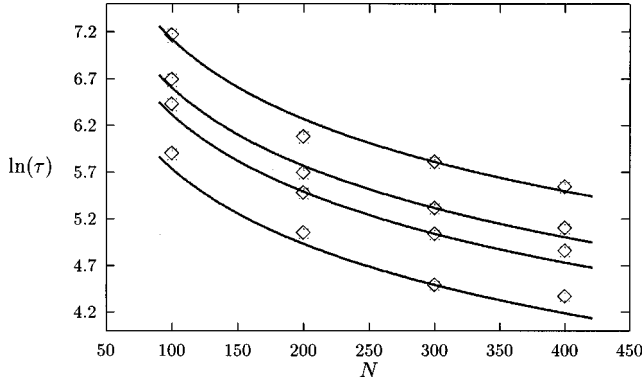


FIG. 4. The logarithm of the breaking time as a function of  $N$ . We use  $S=0.035$ . From top to bottom:  $T=0.025, 0.028, 0.030, 0.035$ . The continuous curves are from the scaling, while the diamonds are from simulations.

Before we discuss those results, we note that Welland *et al.*<sup>9</sup> plotted  $\tau$  as a function of  $T$ . From their results we got  $\ln(\tau)$  as a function of  $\beta$ , which suggested a straight line. However, their four points were not enough to obtain a good activation energy.

### III. THE DARK FACTOR

The above-mentioned results show clearly that something is missing from our one-particle model, and that improvement must be made. First, we observe that the main problem comes from  $\nu_S$ ; its value is too small (large  $\tau$ ). We observe that it does not make any reference to the chain dynamics. Moreover it makes no distinction between a chain with monoatomic basis and that with a diatomic or polyatomic one. Consequently, we may include in  $\nu$  a factor  $D_F$  which will include this missing physics. In this way, Eq. (5) may be rewritten as

$$\nu = \nu_K D_F^{-1}. \quad (6)$$

The factor  $D_F$ , namely, the dark factor,<sup>15</sup> may depend on the temperature, strain, and friction, but does not depend on  $N$ . We notice that both  $\nu$  and  $\nu_K$  have units of frequency, consequently  $D_F$  is dimensionless.

Second, we show that Eq. (4) scales well with  $N$ . For two different  $N$ 's, one may write Eq. (4) as

$$\tau(N) = \tau(N_1) e^{\beta \Delta E_b(N/N_1)}. \quad (7)$$

Here  $\Delta E_b = E_b(N) - E_b(N_1)$  is a small difference due to finite size effects.

In Table I we give values for the parameters of the effective potential as a function of  $N$ . In Fig. 4 we display  $\tau(N)$  as a function of  $N$  for different values of temperatures. We use  $N_1=300$  to scale the other values. The continuous lines are obtained from Eq. (7), whereas the points are obtained from curves similar to those in Fig. 3. As a guide to the eye, we put an error bar of 1%. The four lines from up to down are for the temperatures 0.025, 0.028, 0.030, 0.035. The agreement between the simulations and Eq. (7) is remarkable. As a consequence, we see that the activation energies are really those obtained from the effective potential. For example, for an error  $|\Delta\tau/\tau| \leq 0.01$ , as observed in Fig. 4,

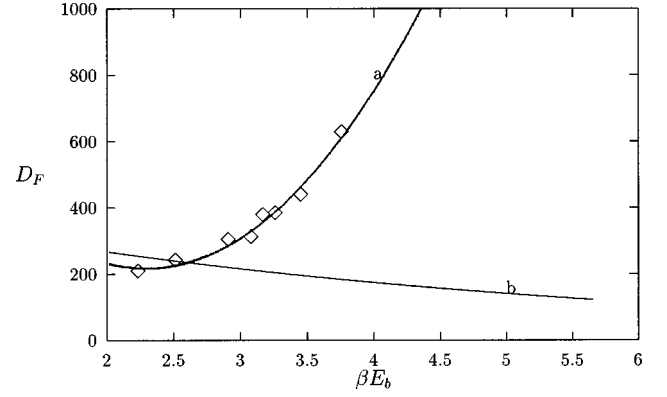


FIG. 5. The dark factor  $D_F$  as a function of  $\beta E_b$ . (a) We fix the temperature and we change the strain  $S$ ; (b) we fix  $S=0.035$ , and we change the temperature.

with  $\beta=40$  we need a precision of  $|\Delta E_b| \leq 3.10^{-5}$ . Indeed the energies are sensitive enough to make the precise correction of 33% when we go from  $N=100$  to  $N=400$  at  $\beta=40$  [ $\exp(\beta \Delta E_b) = 1.33$ ].

This excellent result for the one-particle potential is due to the fact that it has an exact variation principal inside. It is not a mean field potential, but a strongly correlated one. These experiments suggest that the geodesics for the fracture will be trajectories which will minimize the energy following closely the potential, Eq. (2). It is also worthwhile to notice that the  $N^{-1}$  dependence yields

$$\lim_{N \rightarrow \infty} \tau(N) = 0$$

for any value of  $S$  in agreement with the Peirls instability for infinite one-dimensional chains.<sup>2</sup> For an infinite chain the particles has a Gaussian distribution of velocities, some of them with enough energy for an instantaneous breaking.

In Fig. 5 we plot  $D_F$  as a function of  $\beta E_b$  for a chain of 100 particles. In curve (a) we fix the temperature  $T=0.05$ , while in curve (b) we fix the strain  $S=0.035$ . The increase of  $D_F$  with temperature explains the reduction on the apparent barrier  $E_S$  as obtained from Fig. 3. The qualitative aspects of curve (b) may be understood in terms of modern reaction rate theory, where corrections on Kramers rate decrease with  $\beta E_b$ . However, the behavior expressed on curve (a) is opposite to those results presented in Refs. 14 and 17. This rather peculiar behavior shows that  $D_F$  is not a simple function of  $\beta E_b$ . Since energy consideration is not enough to explain the breaking distribution, this suggests a non-Markovian system where the history (memory) of the process is fundamental. That is what we expect by intuition for any process of fragmentation.

The origin of memory must be searched for in the correlations between neighboring particles in the chain. Using Eq. (1) we write down an equation for the difference  $\phi_l = \xi_l - \xi_{l-1}$ , and we reorganize those equations in such a way that at the breaking point  $l=k$ ,  $\phi_k = y$ , and  $\phi_{l \neq k} = y/(N-1) + y_l$ . Here  $y_l$  is a small oscillation and  $\sum y_l = 0$ . Now Eq. (3) may be rewritten as

$$\mu \ddot{y}(t) = F_{\text{eff}}(y) - \mu \int_0^t \Gamma(t-t') \dot{y}(t') dl' + h(t), \quad (8)$$

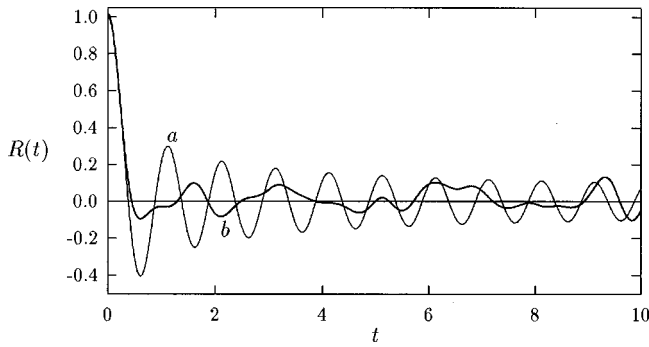


FIG. 6. The time-dependent correlation function  $R(t)$  for the relative displacement. Here time is given in units of  $2\pi/\omega_S$ . (a) The theoretical value for the harmonic chain; (b) the full simulations for the anharmonic chain.

where the new noise

$$h = (f_k - f_{k-1} + g)/2$$

now has a coherent part

$$g = 2F(a+S) - F(a+S+y_{l+1}) - F(a+S+y_{l-1}) \quad (9)$$

given by the motions of the neighboring particles. This coherent motion requires a memory function  $\Gamma(t)$  which according to fluctuation-dissipation theory, reads

$$\langle h(t)h(t') \rangle = \mu k_B T \Gamma(t-t'), \quad (10)$$

here  $\langle \rangle$  means thermal average. Since we know the time evolution of  $h(t)$  we may use the ergodic theorem

$$\langle h(t)h(t') \rangle = \lim_{T \rightarrow \infty} \left( \frac{1}{T} \right) \int_0^T h(t+t'')h(t'+t'') dt''. \quad (11)$$

By use of Eqs. (9)–(11), one may construct the self-organized memory  $\Gamma(t)$ . The important fact is that from a pure chaotic motion the system builds up a memory.

Using a harmonic approximation on Eq. (9), we obtain the approximate analytical result

$$\Gamma(t) = 2\gamma_0 \delta(t) + \frac{\omega_S^2}{2} R(t),$$

where

$$R(t) = \frac{\langle y_l(t)y_l(0) \rangle}{\langle y_l(0)y_l(0) \rangle}.$$

Now, using a similar argument to those used by Florencio and Lee<sup>18</sup> for the classical harmonic chain, we obtain

$$R(t) = J_0(\omega_S t),$$

where  $J_0$  is the zero order Bessel function.

In Fig. 6, we plot  $R(t)$  as a function of  $t$ . Here, time is given in units of  $2\pi/\omega_S$ . Curve (a) is  $J_0(\omega_S t)$  for the harmonic chain. Curve (b) is for the full simulation of the anharmonic chain. The short time behavior for the approximation is quite reasonable.

In the last fifteen years important progress has been made in the understanding of reaction rates for the generalized Langevin equation (GLE). The first improvement is from

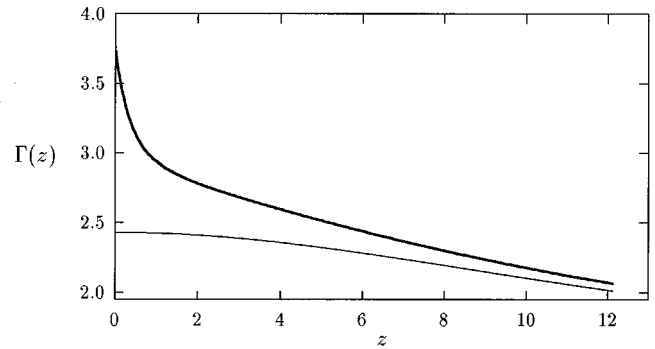


FIG. 7. The Laplace transform of the memory function  $\tilde{\Gamma}(z)$  as a function of  $z$ . Data are the same as in Fig. 6.  $\tilde{\Gamma}(z)$  is in units of  $1/\omega_S$ , while  $z$  is in units of  $\omega_S$ . (a) Upper curve anharmonic modes; (b) the harmonic modes.

Grote-Hynes theory,<sup>16</sup> which basically replaces  $\nu_K$  by a self-consistent  $\nu_{GH}$  which is the maximum value of

$$\nu^2 + \nu \tilde{\Gamma}(\nu) = \omega_b^2. \quad (12)$$

Here  $\tilde{\Gamma}(z)$  is the Laplace transform of  $\Gamma(t)$ .

In Fig. 7 we plot  $\tilde{\Gamma}(z)$  as a function of  $z$ . Here  $\tilde{\Gamma}(z)$  is in units of  $\gamma_0$ , and  $z$  in units of  $\omega_0$ . The upper curve is for full anharmonic modes, while the lower curve is for the harmonic approximation. One can see that for small  $z$  the dynamic memory is larger than the static one and has a very sharp variation. Using  $\tilde{\Gamma}(z)$  in Eq. (12), one obtains  $\nu_K/\nu_{GH} \approx 9$ . Notwithstanding that this result is not capable of accounting for all discrepancies, it clearly points out the right direction.

The next step comes from the observation that both the Kramers and Grote-Hynes results are up bond limits to the reaction rate.<sup>17</sup> The main idea is that the first time passage of a particle through a barrier is not irreversible since fluctuations may bring it back. For low barriers  $\beta E_b < 10$ , the nonlinear modes interact with the coherent noise and that delays the reaction.<sup>17,14</sup> From a systematic review of those theories for a particle, we may write

$$D_F = \nu_K \nu_{GH}^{-1} \lambda, \quad (13)$$

where

$$\lambda = \sqrt{\frac{\beta \mu \omega_b^2}{2\pi}} \times \int \exp \left[ -\beta \left( \frac{\mu \omega_b^2}{2} (\phi - \phi_b)^2 + U_{\text{eff}}^{\text{ah}}(\Omega \phi) \right) \right] d\phi. \quad (14)$$

The superscript ah stands for the anharmonic part of the potential. Here  $\Omega$  is a coupling parameter, which relates the noise with the nonlinear modes.<sup>17</sup> Again, notice that  $\lambda$  is dimensionless. We have computed the values of  $\lambda$  in the region  $20 < \beta < 50$ ; they contribute only with a small factor, so this approach is unable to explain the highest values of  $D_F$ .

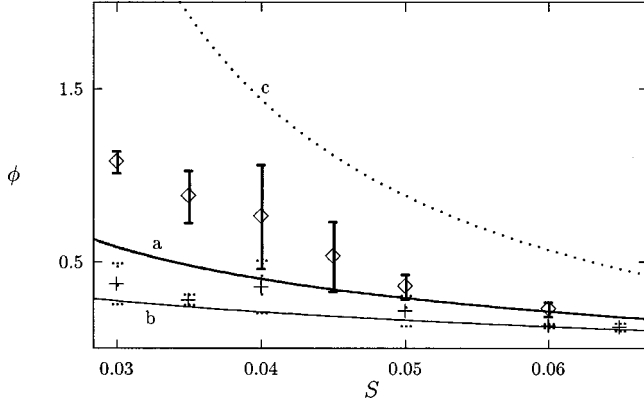


FIG. 8. Theoretical critical bond length and experiments as a function of the strain. (a)  $\phi_m$ ; (b)  $\phi_b$ ; (c)  $\phi_h$ . The experiments are described by diamonds for the chains and by the single error bars for the particles. For the chains we average over 10 ensembles of 800 chains. For the particles we average over 10 ensembles of 2000 independent particles each.

#### IV. BEYOND THE ONE-PARTICLE MODEL

We have exhausted the reaction rate theory for a one-particle model, without being able to give a full description of the problem. Now we shall leave the simplicity of the one-particle reasoning and look in the opposite direction: *What is the main difference between the chain dynamics and the one-particle motion, which was not included in our model?* To answer this question, it is crucial to notice that in a chain the critical elongation  $\phi_c^*$  is larger than that of a single particle  $\phi_p^*$ . We have already investigated this phenomenon, looking at the stability of the modes of the anharmonic chain in the continuous limit.<sup>12</sup> There we found the existence of three important bound lengths for the chains  $\phi_b$ ,  $\phi_m$ , and  $\phi_h$ ; values which necessarily fulfill  $\phi_b < \phi_m < \phi_h$ . Here  $U_{\text{eff}}(\phi_m)=0$  is the minimum critical value and  $\phi_h$  is the maximum value for the bond length obtained from the stability conditions. From this kind of argument one expects  $\phi_m < \phi_c^* < \phi_h$ .

In Fig. 8 the bond elongation is plotted as a function of the strain. There we plot the critical values obtained by the simulations  $\phi_c^*$  and  $\phi_p^*$ , and the theoretical values  $\phi_b$ ,  $\phi_m$ , and  $\phi_h$ . We see that the simulations fall on the expected limits obtained from the stability conditions. From Fig. 8 and Fig. 2 we also see that the system stays in the region  $\phi_m < \phi_c^* < \phi_h$  longer than at equilibrium, consequently, this characterizes a nonequilibrium situation. Indeed, the system is very far from equilibrium, and consequently we expect that the usual ergodic hypothesis, Eq. (11), used in most reaction rate calculations will not be appropriate to describe the problem. However, it is still possible to evaluate Eq. (14) using the fact that the particle will spend the most time around  $\phi_c^*$ . With this *ad hoc* hypothesis one may rewrite  $D_F$  as

$$D_F = \alpha \frac{\nu_K}{\nu_{\text{GH}}} \sqrt{\frac{\beta \mu \omega_b^2}{2\pi}} \exp\left[\frac{\beta K_\phi}{2} (\phi_c^* - \phi_b)^2\right]. \quad (15)$$

Here  $\alpha$  is some parameter that may come from normalization of the nonequilibrium distribution.  $K_\phi$  is the second derivative of the effective potential at  $\phi_c^*$  which is positive.

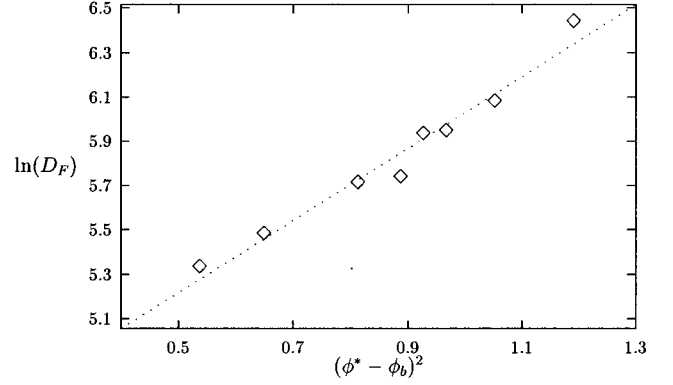


FIG. 9. The logarithm of  $D_F$  as a function of  $(\phi_c^* - \phi_b)^2$ . Here  $T=0.05$ .

In Fig. 9 we plot the logarithm of  $D_F$  as a function of  $(\phi_c^* - \phi_b)^2$  for  $T=0.05$ . The straight line is the minimum square fit and is given by  $\ln(D_F)=4.57+2.66(\phi_c^* - \phi_b)^2$ . We compare with  $\beta K_\phi/2=2.7\pm 0.6$  for  $S=0.035$ . We have not been able to find the parameter  $\alpha$ . However, for  $\alpha=2.3$  the agreement is perfect.

Large values of  $\phi_c^*$  are not only characteristic of the Lennard-Jones potential, indeed they are a consequence of the long-range interaction described by any power-law behavior<sup>12</sup> of the type  $U \propto x^{-\alpha}$ , where  $\alpha$  is a constant. They represent a large class of lattices, since in general one expects that any physical system may have an ionic or dipolar behavior even as a secondary phenomenon.

Now we shall discuss two opposite limits of large and small  $D_F$ . In Fig. 5 we notice that a small  $D_F$  is obtained for large  $S$  and low  $T$ . We performed new simulations with  $S=0.05$  and  $T$  in the range  $0.01 < T < 0.005$ , and we get  $D_F(T \approx 0.006) \sim 20$ . In that limit  $\phi_c^* \rightarrow \phi_b$ , and the systems will not be very far away from equilibrium. Here the break means that it is just crossing the barrier. This is the usual process described in detail by the Grote-Heynes approximation, for which the minimum value predicted is  $D_F \approx 9$ .

Finally, let us consider the extreme limit  $S \rightarrow S_0$ . For a system of particles in such a potential, we expect that after thermal equilibrium is reached half of the particles may be found at both sides of the well. For such a chain as  $S \rightarrow S_0$ , however,  $\phi_c^* \rightarrow \infty$ , and this gives an infinite breaking time, even for a finite barrier  $E_b$  as shown in Fig. 1(a). This is a result that cannot be obtained using one-particle theory.

#### V. CONCLUSIONS

We developed a microscopic theory that gives us simple analytical expressions for the characteristic breaking time of an ensemble of chains in contact with a thermal reservoir. As a starting point we tried to create a one-particle theory. For that we defined an effective potential which turns out to be an exact variational minima for those trajectories that bring the system from a metastable position to a stable one. As a result we notice the existence of a very low attempt frequency compared with that of the chain vibration.

With the definition of corrective factor  $D_F$ , the chain dynamics was introduced in our model. Two points distinguish the chains from the particle. First, the existence of a self-

organized memory  $\Gamma(t)$ . Second, the existence of a long critical length  $\phi_c^*$  necessary for an irreversible break. The first makes our model non-Markovian. Moreover, the second suggests a system far from equilibrium, where time and ensemble averages are not exchangeable. In this way, the reaction rate becomes an exponential function of this critical value which reduces to the one-particle model, in the limit  $\phi_c^* \rightarrow \phi_b$ .

This theory has the main characteristic obtained in computer simulations. As a result the breaking time may be expressed as a product of a typical Arrhenius rate times a non-trivial dark factor. Experiments on single chains with periodic boundary conditions, coupled with a thermal bath, are difficult to do. The closest ideal noninteracting chains are diluted solutions of macromolecules. Odell and Taylor<sup>19</sup> computed the kinetic rate for DNA dissociation in an elongated fluid. They used Eigner's data<sup>20</sup> to estimate the attempt frequency as  $\nu = 6.5 \times 10^7 \text{ s}^{-1}$ . The vibration frequency is well known from IR spectroscopy for the  $P=O$  linkage to be of the order of  $10^{12} \text{ s}^{-1}$ . The difference between theory and experiments suggest a  $D_F$  of the order  $10^4$  to  $10^5$ . These results are shown for  $\beta E_b \geq 4.5$  in Fig. 5, curve (a). They are possible for strains a bit smaller than those we have here, or for a large correlation length. This is a good example of large  $D_F$ . These biological systems are characterized by a small  $E_b$  and a strong resistance to fragmentation. It is not too hard to speculate that its internal structure has important spatial and temporal memory and that nature built DNA in such a

way as to make it mechanically resistant. As expected from this theory even without a precise knowledge of the system we may suggest  $D_F \gg 1$ , and propose a procedure to compute the rate. However, to obtain this for DNA goes beyond the objective of this work.

In conclusion, we developed a theory for chain fragmentation which gives us the result obtained by simulations. The breaking rate is an Arrhenius rate times an attempt frequency. The attempt frequency is described by the Kramers rate divided by a dark factor  $D_F$  which is larger than unity. There are, at least, two important situations where the dark factor  $D_F$  is important. First, all real time simulations are done in the range of small  $\beta E_b$ , since large values of it are not accessible by present day computers. Second, most gels and soft materials fall in this range. This, of course, is the situation of a large class of materials including biological ones, which for low  $E_b$  may break only due to thermal fluctuations at environmental temperatures. For those phenomena,  $D_F$  should be taken in consideration. In particular we predict large values of  $D_F$ , and an underestimated activation energy  $E_b$ .

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<sup>15</sup>We name it the dark factor in analogy with cosmology where most of the matter of the universe is missing; here most of the time is missing.

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