

Theory of polymer breaking under tension

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We consider the breaking of a polymer molecule which is fixed at one end and is acted upon by a force at the other. The polymer is assumed to be a linear chain joined together by bonds which satisfy the Morse potential. The applied force is found to modify the Morse potential so that the minimum becomes metastable. Breaking is just the decay of this metastable bond, by causing it to go over the barrier. Increasing the force causes the potential to become more and more distorted and eventually leads to the disappearance of the barrier. The limiting force at which the barrier disappears is $D_e a/2, D_e$ with a the parameters characterizing the Morse potential. The rate of breaking is first calculated using multidimensional quantum transition state theory. We use the harmonic approximation to account for vibrations of all the units. It includes tunneling contributions to the rate, but is valid only above a certain critical temperature. It is possible to get an analytical expression for the rate of breaking. We have calculated the rate of breaking for a model, which mimics polyethylene. First we calculate the rate of breaking of a single bond, without worrying about the other bonds. Inclusion of other bonds under the harmonic approximation is found to lower this rate by at the most one order of magnitude. Quantum effects are found to increase the rate of breaking and are significant only at temperatures less than 150 K. At 300 K, the calculations predict a bond in polyethylene to have a lifetime of only seconds at a force which is only half the limiting force. Calculations were also done using the Lennard-Jones potential. The results for Lennard-Jones and Morse potentials were rather different, due to the different long-range behaviors of the two potentials. A calculation including friction was carried out, at the classical level, by assuming that each atom of the chain is coupled to its own collection of harmonic oscillators. Comparison of the results with the simulations of Oliveira and Taylor [J. Chem. Phys. **101**, 10 118 (1994)] showed the rate to be two to three orders of magnitude higher. As a possible explanation of discrepancy, we consider the translational motion of the ends of the broken chains. Using a continuum approximation for the chain, we find that in the absence of friction, the rate of the process can be limited by the rate at which the two broken ends separate from one another and the lowering of the rate is at the most a factor of 2, for the parameters used in the simulation (for polyethylene). In the presence of friction, we find that the rate can be lowered by one to two orders of magnitude, making our results to be in reasonable agreement with the simulations.

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I. INTRODUCTION

We consider the breaking of a polymer subjected to a force at one of its ends, a problem that has attracted quite a bit of attention in the recent past. Doerr and Taylor¹ have analyzed a harmonic-oscillator model for the breaking. They assume the breaking to occur if the bond length of any particular bond exceeds a critical distance x_c and obtain an expression for the rate, by an analysis similar to that of Slater's theory of unimolecular reactions.² The rate has the expected Arrhenius form, the activation energy equal to the energy required to stretch the length of a bond to x_c . At the simplest level, the coupling to other bonds is not important. They also find corrections to the rate due to the fact that the rate of breaking is calculated in the absence of actual breaking, and find that collective vibrational motion is important. To verify this, Oliveira and Taylor³ performed an interesting molecular dynamics simulation of the breaking process and found the collective motion of the atoms of the chain to be important. Such simulations have the disadvantage of being rather time consuming and somewhat difficult to use to arrive at general conclusions. Many a time, the events do not happen on a time scale that is accessible to such simulations. Thus Oliveira and Taylor³ were not able to do direct simulation of polyethylene at room temperature, but had to extrapolate

from the data at higher temperatures. Further, such simulations are constrained in that one is able to use only classical mechanics. From Doerr and Taylor¹ and Oliveira and Taylor,³ it is found that vibrations of neighboring bonds play an important role in determining the rate of breaking—they may force the atoms to come back and heal the bond. Nordholm *et al.*⁴ studied the dynamics of a one-dimensional monatomic chain under tensile stress using molecular dynamics. They too found that chain healing in the simulated motion causes a significant deviation from the rates calculated using Rice, Ramsperger, Kassel, and Marcus (RRKM) theory.

In the following, we use multidimensional quantum transition state theory (QTST) to derive expressions for the rate of breaking of a long polymer molecule subject to a force. The analysis is straightforward and allows one to draw conclusions with a minimum amount of labor. It is to be noted that the multidimensional version of transition state theory that we use is very powerful and is capable of reproducing results that are obtained from the Fokker-Planck equation.⁵ The multidimensional QTST works in terms of normal modes, appropriate for motion in the vicinity of the saddle point. Hence, within the limits of the harmonic approximation, it automatically accounts for these effects. We report results for both classical and quantum versions of the transition state theory (TST). To compare with the simulations, we

extend our calculations to include friction and do a classical multidimensional TST calculation. On comparing the results with those of Oliveira and Taylor,³ we find the TST results to be larger by orders of magnitude. To understand this discrepancy, we go beyond TST and consider the dynamics of separation of the two broken ends, after the polymer has been broken. Using a continuum approximation, we find the rate at which the two ends separate.⁶ Doerr and Taylor¹ and Oliveira and Taylor³ made use of the Lennard-Jones (LJ) potential to represent the potential energy of a bond as a function of its length. In the following, we make use of the Morse potential as well as the LJ potential for the calculations. A somewhat similar investigation already exists in the literature.⁷ However, these authors did not calculate the rate and their investigation was much less detailed. A related investigation is that of Oliveira⁸ who used a one-particle model and transition state theory for the dissociation.

We now give an outline of the paper. In Sec. II, we give a very brief description of the multidimensional version of the transition state theory that we use. The version that we use is quite powerful and is valid provided the temperature is greater than a critical temperature. This is followed in Sec. III by a discussion of the model that we study. Section IV gives the simplest model that one could adopt, viz., the rate of breaking calculated assuming that the dynamics of only one bond is important. Section V gives the details of the normal-mode analysis that we perform for the initial and transition states. These are used to derive an expression for the rate in Sec. VI A. The results are presented for the case where there is no friction acting on the atoms of the chain. As the simulations are performed in the presence of friction, we present results also for this case, without giving detailed derivations, as they are similar to the case with friction. It is found that the results are not in agreement with the simulations. In Sec. VII A, we outline our procedure for going beyond the transition state theory, by taking into account the breaking process and the possibility of the healing of the broken bonds. We keep our discussions on this at a classical level, because (i) the simulations have been done at the classical level, (ii) quantum effects are not important unless the temperature is very low, and (iii) quantum effects have been analyzed in an interesting paper by Levitov *et al.*⁹ who developed the ideas of Dyakonov.¹⁰

II. MULTIDIMENSIONAL TRANSITION STATE THEORY—A BRIEF OVERVIEW

QTST provides a simple approach to the calculation of the rate of a reaction. We make use of a multidimensional version that has been applied successfully to calculate the rate in a variety of problems.^{5,11,12} It works under the harmonic approximation for all the vibrations and the reaction coordinate, and has the advantage of having *tunneling contributions included in the rate*. Small amplitude motion in the vicinity of the saddle point will have one unstable direction, and the angular frequency associated with it shall be denoted as Ω . The QTST expression for the rate is¹³

$$R = \frac{\Omega}{4\pi \sin(\beta\hbar\Omega/2)} \frac{Q^\ddagger}{Q} e^{-\beta E_a}, \quad (1)$$

where E_a is the activation energy of the reaction and $\beta = 1/(k_B T)$. Q^\ddagger denotes the partition function for the transition state, with only the stable modes included. Q is the partition function for the initial state. $\Omega/4\pi \sin(\beta\hbar\Omega/2)$ arises from the unstable mode. This expression includes tunneling too and is valid only if the temperature T is greater than $T_c = \hbar\Omega/(2k_B\pi)$ [see Eq. (3.7) of Nikitin¹³]. Under the harmonic approximation for all the modes, the rate is

$$R = \frac{\Omega}{2\pi \sin\left(\frac{\beta\hbar\Omega}{2}\right)} \frac{\prod_j \sinh\left(\frac{\beta\hbar\omega_j}{2}\right)}{\prod_j^\ddagger \sinh\left(\frac{\beta\hbar\omega_j^\ddagger}{2}\right)} e^{-\beta E_a}, \quad (2)$$

where ω_j is the frequency of the j th mode for the initial state and ω_j^\ddagger is the corresponding frequency for the transition state. In the above equation, the product for the transition state does not include the unstable mode and this is indicated by the superscript \ddagger on the product. In the limit $\beta\hbar\omega_j/2 \ll 1$ one gets the classical result

$$R_{class} = \frac{1}{2\pi} \frac{\prod_j \omega_j}{\prod_j^\ddagger \omega_j^\ddagger} e^{-\beta E_a}. \quad (3)$$

III. THE MODEL

We consider a polymer molecule having one end fixed and a force acting on the other end, as shown in Fig. 1. van der Vegte *et al.*¹⁴ have used a magnetic levitation force microscope to study the breaking at the point of attachment of such a system (as this bond was the weakest). Our analysis, however, is for breaking in the bulk of the chain and not at the end. We imagine the polymer to be a chain of units of mass m joined together by bonds obeying the Morse potential. Thus, denoting the position of the n th atom as u_n and taking the number of bonds to be N , we can write the potential energy of the system to be

$$V_{total} = \sum_{n=1}^N V_M(u_n - u_{n-1} - b) - F u_N. \quad (4)$$

We take u_0 to be equal to zero. In the above, the Morse potential V_M is defined by $V_M(y) = D_e(1 - e^{-ay})^2$. D_e and a are parameters characterizing the Morse potential. The force acting on the last atom is F and it causes the term $F u_N$. From the variables u_n , it is convenient to change over to a new set of variables $y_n = u_n - u_{n-1} - b$, with the distortion of the n th bond from its equilibrium length b . Then we can write

$$V_{total} = \sum_{n=1}^N V(y_n) - N b F \quad (5)$$

with the modified potential for each bond, $V(y)$, defined by

$$V(y) = D_e(1 - e^{-ay})^2 - Fy. \quad (6)$$

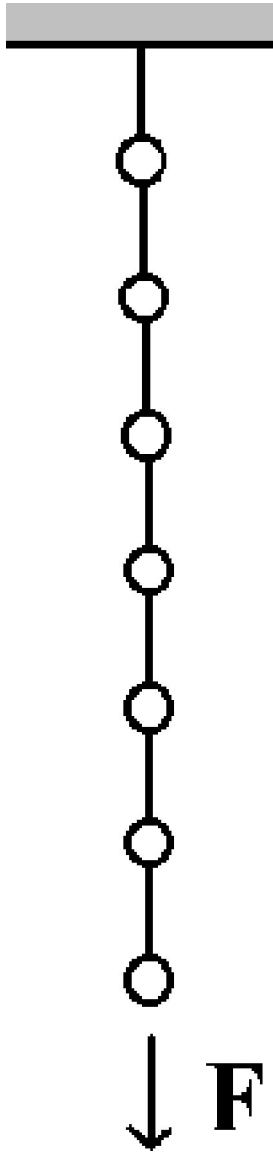


FIG. 1. The model investigated in the paper consists of N units each of mass m , joined together by bonds obeying the Morse (Lennard-Jones) potential. It is fixed at one end and is acted upon by a force F at the other end.

The last term in Eq. (6) is of no consequence and shall be neglected. Thus we see that the effect of an externally applied force at one end is just to change the potential of each bond from the Morse potential to this new modified Morse potential. To understand the form of this potential, we give plots of its functional form for different values of the dimensionless force $F_1 = 2F/(D_e a)$ in Fig. 2. The figure shows that for any nonzero value for the force F_1 , the potential has two extrema, one being a minimum and the other a maximum. The values of y for the two are $y_{\pm} = 1/a \ln[2/1 \pm \sqrt{1-F_1}]$. Note that the above definition implies $y_+ < y_-$. For any $0 < F_1 < 1$, each bond is metastable (see Fig. 2). It can go over the barrier if it gets a certain activation energy, resulting in the breaking of the bond and consequently of the polymer. The activation energy for this process is

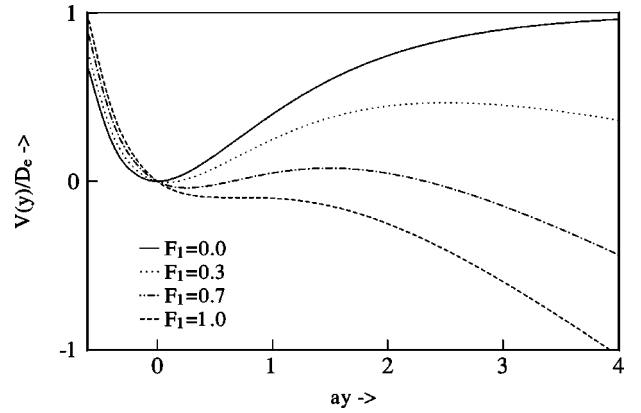


FIG. 2. Shapes of the modified Morse potential plotted against ay , for different values of $F_1 = 2F/(D_e a)$.

$$E_a = V(y_-) - V(y_+) = D_e \left[\sqrt{1-F_1} + \frac{F_1}{2} \ln \left[\frac{1-\sqrt{1-F_1}}{1+\sqrt{1-F_1}} \right] \right]. \quad (7)$$

As one increases F_1 the values of y_+ and y_- get closer. Also, there is lowering of the barrier for dissociation. For $F_1 = 1$, $y_+ = y_-$ and activation energy is zero. This limiting force is $F = D_e a/2$.

IV. THE SINGLE BOND BREAKING RATE

The simplest approach to the calculation of the rate would be the following: We consider the vibrational motion of just one bond that may break and neglect coupling to the rest of the system. This kind of approach, but with coupling to the rest included as friction, was considered by Oliveira.³ We do not include the coupling to the rest of the system in this section. As the motion involves stretching of the bond between two units, each unit having a mass m , the reduced mass for the vibrational motion is $m/2$. The potential energy for vibration in the neighborhood of the minimum of the potential is $\frac{1}{2} V''(y_+) (y - y_+)^2$ where $V''(y_+) = D_e a^2 (\sqrt{1-F_1} + 1 - F_1)$. So the frequency of vibration of the diatomic molecule is $\omega_s = a \sqrt{2D_e/m} (\sqrt{1-F_1} + 1 - F_1)^{1/2}$. In a similar manner, the frequency of the unstable mode is $\Omega_s = a \sqrt{2D_e/m} (\sqrt{1-F_1} - 1 + F_1)^{1/2}$. Using these frequencies and the version of QTST in Sec. II, we get the rate to be

$$R_s = \frac{\Omega_s \sinh\left(\frac{\hbar \beta \omega_s}{2}\right)}{2 \pi \sin\left(\frac{\hbar \beta \Omega_s}{2}\right)} e^{-\beta E_a}. \quad (8)$$

V. THE NORMAL-MODE ANALYSIS

A. The eigenvalue problem

We now proceed to make a multidimensional calculation of the rate. This requires a normal-mode analysis of vibrations of the chain around the equilibrium position as well as

around the saddle point. In the following, we calculate this for the transition state. The calculations are similar and simpler for vibrations around the equilibrium position. The equilibrium state has a V_{total} minimum and this is obtained by having all $y_i = y_+$. There are N saddle points where V_{total} is an extremum, corresponding to the breaking of each of the N bonds. At a given saddle point, one of the bonds is stretched (the one that breaks); the bond length is y_- which corresponds to the maximum of the potential $V(y)$. All the other bonds have an equilibrium bond length equal to y_+ , which is the minimum of the potential $V(y)$. On crossing each saddle point, breaking would occur. There are other extrema too, but they all occur at higher activation energies. To analyze the motion around a saddle point, we denote the displacement of the j^{th} atom from its equilibrium position by ξ_j and take the bond between the atom numbers n and $n+1$ to be the one that will break. Then, for small amplitude vibrations around the saddle point, we have the Hamiltonian

$$H = \sum_j \frac{p_j^2}{2m} + \frac{1}{2} \times \left(\sum_{j=1 \neq n+1}^N m \omega_+^2 (\xi_j - \xi_{j-1})^2 - m \omega_-^2 (\xi_{n+1} - \xi_n)^2 \right). \quad (9)$$

The quantities ω_+ and ω_- are defined by the equation $m \omega_{\pm}^2 = \pm V''(y_{\pm})$ and are given by

$$\omega_{\pm}^2 = \frac{D_e a^2}{m} (\sqrt{1 - F_1} \pm (1 - F_1)). \quad (10)$$

The angular frequencies of the normal modes are the eigenvalues of the matrix

$$\mathcal{D}_N^{\ddagger} = \omega_+^2 \begin{bmatrix} \mathbf{D}_{n-1} & -U^t & & & \\ -U & 1 - \gamma & \gamma & & \\ & \gamma & 1 - \gamma & -W & \\ & & -W^t & \mathbf{D}_{N-n-1} & \end{bmatrix}, \quad (11)$$

where $U = [00 \dots 1]$, $W = [10 \dots 0]$, and $\gamma = \omega_-^2 / \omega_+^2$. The matrix \mathbf{D}_{n-1} is $(n-1) \times (n-1)$ given by

$$\mathbf{D}_{n-1} = \begin{bmatrix} 2 & -1 & & & \\ -1 & 2 & -1 & & \\ & -1 & 2 & -1 & \\ & & -1 & 2 & -1 \\ & & & \dots & \dots \end{bmatrix}. \quad (12)$$

The matrix \mathcal{D}_N^{\ddagger} would have one unstable mode, which corresponds to the crossing of the barrier and is the reaction coordinate. We shall in the following assume that the polymer is fairly long and that it is a bond in the bulk that is broken, as this simplifies our analysis. One can analyze other cases also, but the analysis is tedious. Further, we do not expect the rates to be very different even if it is not a bond in the bulk that is broken. The above implies that n and $N-n$

are taken to be large numbers. We have to calculate the frequency of the unstable mode and the ratios of the partition functions in Eq. (2). These quantities are very conveniently found using the partitioning technique and Green's matrix.

B. The Green's matrix

Green's matrix is

$$\mathbf{G}^{0,n}(\bar{\omega}^2) = [\bar{\omega}^2 - \mathbf{D}_n]^{-1}. \quad (13)$$

We denote the first diagonal element of Green's matrix $G_{11}^{0,n}(\bar{\omega}^2)$. Partitioning Green's matrix as in the following equation,

$$G^{0,n}(\bar{\omega}^2) = \begin{bmatrix} \bar{\omega}^2 - 2 & W \\ W^t & \bar{\omega}^2 - \mathbf{D}_{n-1} \end{bmatrix}, \quad (14)$$

and using the formulas of Appendix A leads to the first diagonal element of Green's matrix to be $G_{11}^{0,n}(\bar{\omega}^2) = (\bar{\omega}^2 - 2 - G_{11}^{0,n-1}(\bar{\omega}^2))^{-1}$. In the limit where n is very large ($n \rightarrow \infty$), the first diagonal element of Green's matrix has to be independent of n . That is, $G_{11}^{0,n}(\bar{\omega}^2) \approx G_{11}^{0,n-1}(\bar{\omega}^2)$. We shall then omit the superscripts n and $n-1$, and we get the result

$$G_{11}^0(\bar{\omega}^2) = (\bar{\omega}^2 - 2 - G_{11}^0(\bar{\omega}^2))^{-1}. \quad (15)$$

This equation may be solved to get the matrix element $G_{11}^0(\bar{\omega}^2)$. Using the condition that $G_{11}^0(\bar{\omega}^2) \rightarrow 0$ as $\bar{\omega}^2 \rightarrow \pm \infty$ leads to

$$\begin{aligned} G_{11}^0(\bar{\omega}^2) &= \frac{1}{2} (\bar{\omega}^2 - 2 + \sqrt{\bar{\omega}^4 - 4\bar{\omega}^2}) \quad \text{if } \bar{\omega}^2 < 0 \\ &= \frac{1}{2} (\bar{\omega}^2 - 2 + i\sqrt{4\bar{\omega}^2 - \bar{\omega}^4}) \quad \text{if } 0 < \bar{\omega}^2 < 4 \\ &= \frac{1}{2} (\bar{\omega}^2 - 2 - \sqrt{\bar{\omega}^4 - 4\bar{\omega}^2}) \quad \text{if } \bar{\omega}^2 > 4. \end{aligned} \quad (16)$$

In determining the matrix element for $0 < \bar{\omega}^2 < 4$, we have assumed $\bar{\omega}^2$ to have a small negative imaginary part.

C. The frequency of the unstable mode

The frequencies of the modes are determined by the determinantal equation $|\omega^2 - \mathcal{D}_N^{\ddagger}| = 0$. Denoting $\bar{\omega}^2 = \omega^2 / \omega_+^2$, this equation may be written as $|\bar{\omega}^2 - \mathbf{D}_N^{\ddagger}| = 0$, with $\mathbf{D}_N^{\ddagger} = \mathcal{D}_N^{\ddagger} / \omega_+^2$. Using the partitioning technique, we get

$$\begin{aligned}
|\bar{\omega}^2 - \mathbf{D}_N^\dagger| &= |\bar{\omega}^2 - \mathbf{D}_{n-1}| |\bar{\omega}^2 - \mathbf{D}_{N-n-1}| \\
&\times \det \begin{bmatrix} \bar{\omega}^2 - 1 + \gamma - G_{11}^{0,n-1}(\bar{\omega}^2) & \\ & -\gamma \end{bmatrix} \\
&\times \begin{bmatrix} & -\gamma \\ \bar{\omega}^2 - 1 + \gamma - G_{11}^{0,N-n-1}(\bar{\omega}^2) & \end{bmatrix} = 0. \quad (17)
\end{aligned}$$

The unstable mode can be found by putting $\bar{\omega}^2 = -\bar{\Omega}^2$, with $\bar{\omega}$ real, replacing the matrix elements of Green's matrix in the above equation with $G_{11}^0(-\bar{\Omega}^2)$, and using Eq. (16) for

$G_{11}^0(\bar{\omega}^2)$. This gives $\bar{\Omega} = 2\gamma/\sqrt{1+2\gamma}$, which leads to

$$\Omega = \omega_+ \bar{\Omega} = \frac{2\omega_-^2}{\sqrt{\omega_+^2 + 2\omega_-^2}}. \quad (18)$$

VI. TRANSITION STATE THEORY

A. The rate

We now proceed to the calculation of the rate of breaking using Eq. (2). Under the harmonic approximation, the rate given by this equation can be calculated exactly. Using infinite product expansions for $\sin(x)$ and $\sinh(x)$, we can write the rate given by Eq. (2) as

$$R = \frac{\Omega}{2\pi} e^{-\beta E_a} \frac{\prod_j \left[\frac{\beta \hbar \omega_j}{2} \prod_{l=1}^{\infty} \left\{ 1 + \left(\frac{\beta \hbar \omega_j}{2l\pi} \right)^2 \right\} \right]}{\left(\frac{\beta \hbar \Omega}{2} \right) \prod_{l=1}^{\infty} \left\{ 1 - \left(\frac{\beta \hbar \Omega}{2l\pi} \right)^2 \right\} \prod_k^\dagger \left[\frac{\beta \hbar \omega_k^\dagger}{2} \prod_{l=1}^{\infty} \left\{ 1 + \left(\frac{\beta \hbar \omega_k^\dagger}{2l\pi} \right)^2 \right\} \right]}. \quad (19)$$

Putting $z = \beta \hbar \omega_+ / (2\pi)$, and defining p_l by

$$p_l = \frac{\prod_j (l^2 + (z\omega_j/\omega_+)^2)}{\prod_j (l^2 + (z\omega_j^\dagger/\omega_+)^2)}, \quad (20)$$

we get

$$R = \frac{\Omega}{2\pi} \left(\sqrt{|p_0|} \prod_{l=0}^{\infty} p_l \right) e^{-\beta E_a}. \quad (21)$$

We can write the classical expression for the rate (letting $\hbar \rightarrow 0$) as

$$R_{class} = \frac{\Omega}{2\pi} \sqrt{|p_0|} e^{-\beta E_a}, \quad (22)$$

where p_0 is found in Appendix B [see Eq. (B6)]. This gives

$$R_{class} = \frac{1}{2\pi} \frac{2\omega_+ \omega_-}{\sqrt{\omega_+^2 + 2\omega_-^2}} e^{-\beta E_a}. \quad (23)$$

The fully quantum-mechanical rate may be written as

$$R = \kappa R_{class}, \quad (24)$$

where

$$\kappa = \frac{\sqrt{2\gamma-1} \sin h(z\sqrt{3}\pi)}{\sqrt{3} \sin(z\sqrt{2\gamma-1}\pi)} \kappa_1. \quad (25)$$

(see Appendix B for the definition of κ_1). We refer to κ as the quantum correction factor. Having obtained the rate, one can also calculate the lifetime of a bond as $\tau = (1/R)$. We can

now use the above expressions to calculate the rate of the dissociation of a bond of a polyethylene molecule that is subject to stress. For the calculations, following Oliveira and Taylor,³ we take the value of D_e to be 360 kJ/mole and m as the mass of the CH_2 unit. For the Morse potential, the force constant for small amplitude vibrations near the minimum is $2D_e a^2$. Following Oliveira and Taylor,³ we take this to be 280 N/m, and use this to fix the value of the Morse parameter a . We give in Fig. 3 a plot of the logarithm of the lifetime of the bond against the applied force for several temperatures. The limiting force at which the barrier disappears is found to be 4.574 nN. Increasing the temperature by 50 K, keeping the force fixed, would typically increase the rate by two orders of magnitude. The lifetimes calculated using the single bond breaking formula in Eq. (8) are compared with the results of multidimensional transition state theory in Fig. 4

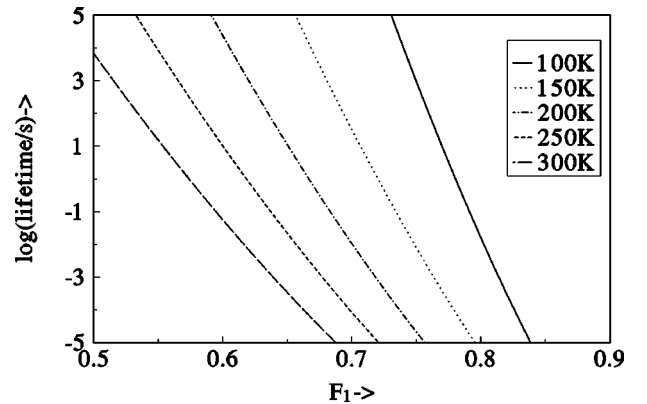


FIG. 3. Plot of logarithm of (lifetime/s) against the applied force, for polyethylene at different temperatures, using the Morse potential and transition state theory. Note that $F_1 = F/(D_e a/2)$ and for polyethylene, the limiting force is $D_e a/2 = 4.574 \times 10^{-9}$ N.

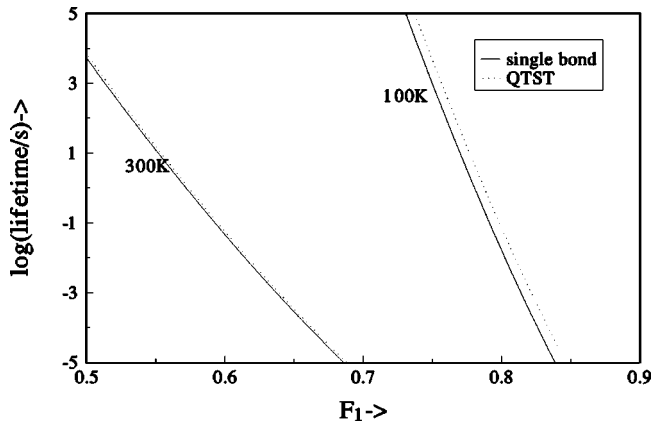


FIG. 4. The figure compares the lifetimes calculated using Eq. (8) and the result of multidimensional transition state theory. It shows that at high temperatures, a rough estimate of the rate can be obtained by a simple approximation that considers the dynamics of only the bond that breaks.

for the two temperatures 100 K and 300 K. It is seen that the many-body effects lower the results by approximately a factor of 2. The expression for the rate is valid only if $T > T_c = \hbar\Omega/(2\pi k_B)$ [see the Eq. (3.36) of Nikitin¹³]. Putting in the values for polyethylene, we find $T_c \approx 50$ K. Thus the formula works at any temperature greater than this, and for all values of the force. If the temperature drops below this, Eq. (25) would break down. In this region, the formula has a divergence due to the vanishing of the sine function in the denominator. Figure 5 compares the result for the Morse potential and the LJ potential (with the parameters ϵ and a_{LJ} chosen so as to reproduce the dissociation energy and force constant of the bond, see Appendix C). The LJ potential leads to a smaller limiting force, equal to 4.101 nN. The lifetime is also smaller, typically by a few orders of magnitude. This means that if one fits the potential using the experimental values of the force constant and dissociation energy to determine the parameters, then Morse and LJ

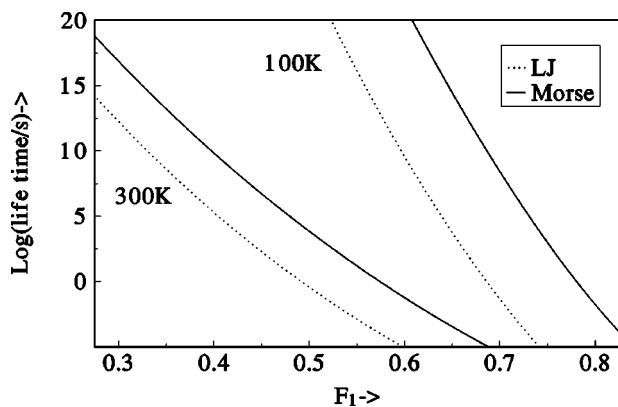


FIG. 5. Plot of logarithm of the lifetime/s against the applied force, for polyethylene at 100 K and 300 K, using Morse and Lennard-Jones potentials (see Appendix C). The limiting forces are different for the two potentials. For polyethylene, the limiting force is 4.574×10^{-9} N if one used the Morse potential while it is 4.101×10^{-9} N with the LJ potential.

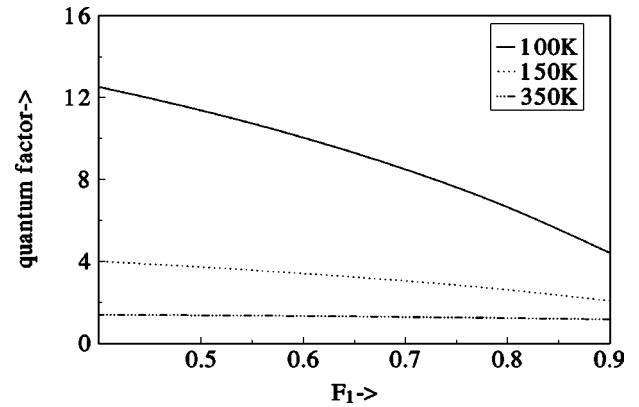


FIG. 6. Plot of the quantum correction factor for the rate as a function of the force, for different temperatures. Calculations were done using the Morse potential.

potentials lead to rather different estimates of the rate of breaking. The reason for this is that the LJ potential vanishes rather slowly in comparison with the Morse potential, which does so exponentially. Consequently, the LJ potential leads to rather longer bond lengths for the breaking bond, making the activation energies very different for the two potentials. Figure 6 gives a plot of the quantum correction factor for the rate for a range of temperatures. At very low temperature (< 50 K for polyethylene), one expects the rate to be dominated by quantum tunnelling, and to become independent of the temperature. One has to use the approach of Levitov *et al.*⁹ in this regime. In the region investigated by us, quantum transition state theory always leads to higher rates than classical transition state theory. The correction, however, is important only if the temperature is less than 150 K. A general conclusion from the calculations is that for polyethylene at normal temperatures, if the force is somewhat greater than half the limiting force, then the bond would break in a matter of seconds. On examining Fig. 3 it is seen that the variation of the lifetime is exponential and that in a somewhat small range of forces, the lifetime varies rapidly from 10^5 s to 10^{-5} s. This high sensitivity is a result of the shift of the length of the breaking bond at the saddle point, which varies rapidly as one changes the applied force. In comparison, the equilibrium bond length varies slowly with the force. This leads to a rather large change in the activation energy, resulting in the sharp variation of the lifetime with force. It has to be remembered that these results are for the lifetime of one bond. The polymer has a large number (N) of such bonds. All these bonds, except the ones near the two ends, would have the same rate of breaking and therefore the rate of polymer breaking would be equal to N times the rate calculated from Eq. (24).

B. Classical TST in presence of friction

As the simulations of Oliveira and Taylor³ included friction, we now include the effect of friction on the dynamics of barrier crossing. For this, we follow the procedure,¹⁵ used for the study of barrier crossing and other dynamical problems in the presence of friction. As in the simulations, the noise acting on each atom is assumed to be independent of one

another, and we imagine that each unit of the polymer is coupled linearly with a set of harmonic oscillators (each unit has its own set of oscillators). Thus for the transition state, instead of the Hamiltonian in Eq. (9), we need to consider

$$\begin{aligned}
H = & \sum_j \frac{p_j^2}{2m} + \frac{1}{2} \sum_{j=1 \neq n}^N m \omega_+^2 (\xi_j - \xi_{j-1})^2 \\
& - \frac{1}{2} m \omega_-^2 (\xi_{n+1} - \xi_n)^2 + \sum_{i=1}^N \sum_{j=1}^N \frac{p_{j\alpha}^2}{2m_{j\alpha}} \\
& + \frac{1}{2} \sum_{\alpha=1}^N \sum_{j=1}^N m_{j\alpha} \omega_{j\alpha}^2 \left(x_{j\alpha} - \frac{c_{j\alpha}}{m_{j\alpha} \omega_{j\alpha}^2} \xi_j \right)^2. \quad (26)
\end{aligned}$$

In the above, $j\alpha$ denotes a harmonic oscillator having a position $x_{j\alpha}$ and momentum $p_{j\alpha}$, coupled to the j th normal mode of the polymer. It has a frequency $\omega_{j\alpha}$ and mass $m_{j\alpha}$. $c_{j\alpha}$ determines the coupling of the oscillator $j\alpha$ to the j th mode. The above Hamiltonian can be analyzed just as earlier. In order to have ohmic friction, it is enough to take $J_j(\omega) = \pi/2 \sum_{\alpha=1}^N (c_{j\alpha}^2/m_{j\alpha} \omega_{j\alpha}) \delta(\omega - \omega_{j\alpha}) = m \gamma \omega$. Now, using the partitioning technique, one can eliminate all the oscillators from the problem and this leads to a matrix identical to the one in Eq. (11), except that the j th diagonal element is now given by $\omega^2 - 2\omega_+^2 - \sum_{\alpha=1}^N (c_{j\alpha}^2/mm_{j\alpha}) ([1/\omega_{j\alpha}^2] + [1/\omega^2 - \omega_{j\alpha}^2])$. Proceeding as before, we find the unstable mode to have the frequency Ω

$$R_{class}^{frict} = \frac{\omega_+ (\sqrt{2\omega_-^2 + \omega_+^2} \sqrt{16\omega_-^4 + 2\gamma^2\omega_-^2 + \gamma^2\omega_+^2} - \gamma(2\omega_-^2 + \omega_+^2))}{4\pi\omega_-(2\omega_-^2 + \omega_+^2)} e^{-\beta E_a}.$$

Figure 7 shows a plot of a logarithm of the lifetime for one bond calculated with the above theories, as a function of the amount strain (s), and compares them with the results of Taylor and Oliveira.³ The results are reported in terms of units in which the length of the LJ bond (in the absence of external force) is taken as the unit of length the depth of the LJ potential as the unit of energy, and the time for one oscillation (under the harmonic approximation) of CH_2 in this potential as the unit of time. The unit of time is $2\pi\sqrt{ma^2/72\epsilon} = 5.72477 \times 10^{-14}$ sec. Their simulations correspond to a temperature of 2167 K, which is a very high temperature, so high that the polymer would degrade immediately at this temperature, as is obvious from the lifetime that they find, which is of the order of nanoseconds. On comparing results of such calculations with the simulation, we find that the results of simple multidimensional transition state theory are roughly 500 times too small. With friction included, this difference reduces from 500 to roughly 250 and these results are not in agreement with the simulations. We now analyze the reason for this. Our analysis is at a classical level. It is tough to do this for the quantum problem (of importance at very low temperatures) on which there exists an interesting paper by Levitov *et al.*⁹

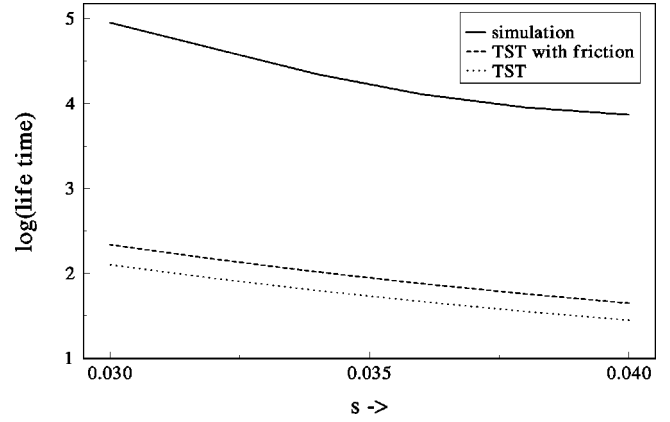


FIG. 7. Plot of logarithm of the lifetime against the strain for the Lennard-Jones potential for transition state theory without friction (dotted line), transition state theory with friction (dashed line), and simulations of Oliveira and Taylor (Ref. 3) (full line). The results are reported in terms of units in which the length of the LJ bond (in the absence of external force) is taken as the unit of length, the depth of the LJ potential as the unit of energy, and the time for one oscillation (under the harmonic approximation) of CH_2 in this potential as the unit of time. The unit of time is $2\pi\sqrt{ma^2/72\epsilon} = 5.72477 \times 10^{-14}$ sec.

$= \sqrt{2\omega_-^2 + \omega_+^2} \sqrt{16\omega_-^4 + 2\gamma^2\omega_-^2 + \gamma^2\omega_+^2} - \gamma(2\omega_-^2 + \omega_+^2) / 2(2\omega_-^2 + \omega_+^2)$. Further, we find that $p_0 = -\omega_+^2/\omega_-^2$, so that the rate in the presence of friction is

VII. BEYOND TRANSITION STATE THEORY

A. Rate of separation of the broken ends

The breaking of the polymer requires activation energy to be possessed by a bond to dissociate, the probability of this being $e^{-\beta E_a}$. If thermal fluctuations give the bond the energy E_a , then it can dissociate, with a frequency $\Omega/(2\pi)\sqrt{|p_0|}$ [see Eq. (22)]. The time of crossing the barrier is $t_{cross} = 1/(\Omega/(2\pi)\sqrt{|p_0|})$. However, even if crossing has occurred (i.e., the bond is broken), it is not necessary that the reaction should occur. Once the crossing has occurred, the two ends have to separate by a minimum distance, within which it is possible for the broken ends to come back and heal the bond. We now calculate the time required for the two broken ends to separate by this minimum distance. The two broken ends separate from one another by translational motion. The potential energy of the system decreases as a function of the separation of the two ends and since the bond is already broken, this decrease is mostly due to the externally applied force. This is obviously linearly dependent on the separation. Denoting the minimum distance as d_c , we find the average time required to move apart by this distance. The classical Hamiltonian describing the motion is

$$H = \frac{1}{2} \sum_{j=1}^N m \xi_j^2 + \frac{1}{2} \sum_{j=1}^N m \omega_+^2 (\xi_j - \xi_{j-1})^2 - \alpha (\xi_{n+1} - \xi_n). \quad (27)$$

In the above, α is the slope of the potential-energy curve, in the region where the potential is linear in distance of separation [i.e., linear in $(b + \xi_{n+1} - \xi_n)$]. On looking at the equations of motion, one realizes that they separate into two uncoupled parts, one for each broken part. It is enough to analyze only one of them, as the behavior of the other is identical (provided both the chains are long). So we consider the part of the Hamiltonian corresponding to $j \geq n$. Renumbering the atoms $(n+1, n+2, \dots)$ as $(0, 1, 2, \dots)$, and taking the chain to be very long ($N \rightarrow \infty$), we can write the Hamiltonian as

$$H_{broken} = \frac{1}{2} \sum_{j=0}^{\infty} m \xi_j^2 + \frac{1}{2} \sum_{j=1}^{\infty} m \omega_+^2 (\xi_j - \xi_{j-1})^2 - \alpha \xi_0. \quad (28)$$

The problem now is to calculate the time that it takes ξ_0 to exceed the value ξ_c given that its initial value was zero, and that the chain is at a temperature T . Obviously, as both the ends are executing translational motion, the distance that each one has to cover would be $\xi_c = d_c/2$. The time should be determined mainly by the long-wavelength modes of the chain. To describe these modes, one can use a continuum approximation to the above Hamiltonian. The continuum version has the advantage that one can obtain analytical results. The Hamiltonian is $H_{broken} = \frac{1}{2} \rho \int_0^{\infty} dx \xi_t(x, t)^2 + \frac{1}{2} \mathcal{T} \int_0^{\infty} dx \xi_x(x, t)^2 - \alpha \xi(0, t)$. ρ is the density of the chain per unit length ($= m/b_+$, b_+ being the length of a stretched bond, at its equilibrium position) and $\mathcal{T} = mb_+ \omega_+^2$ is the tension in the chain. The speed of sound in the chain is given by $c = \sqrt{\mathcal{T}/\rho}$. We imagine that $\xi(0, t) = 0$ until $t = 0$, with the rest of the chain at thermal equilibrium, appropriate to a temperature T . Up to this time, the last term in H_{broken} is not present in the Hamiltonian. At $t = 0$, the chain is broken, and the last term is now present, and it represents the fact that the chain can lower its potential energy by moving its end. Writing the equation of motion for the string gives the forced wave equation

$$\rho \xi_{tt}(x, t) = \mathcal{T} \xi_{xx}(x, t) + \alpha \delta(x). \quad (29)$$

To solve the above equation, we use transform techniques. We first define the Fourier cosine transform of $\xi(x, t)$ by $\bar{\xi}(w, t) = \int_0^{\infty} dx \xi(x, t) \cos(wx)$. The Fourier cosine transform of Eq. (29) gives

$$\rho \bar{\xi}_{tt}(w, t) + \mathcal{T} w^2 \bar{\xi}(w, t) = \alpha - \mathcal{T} \bar{\xi}_x(0, t). \quad (30)$$

Once the chain is broken, the end of the chain is not under strain and hence we put $(\partial \xi(x, t)/\partial x)_{x=0} = 0$. Now we introduce the Laplace transform of $\bar{\xi}(w, t)$ by $\bar{\Xi}(w, s) = \int_0^{\infty} dt \bar{\xi}(w, t) e^{-st}$. This obeys the equation

$$(\rho s^2 + \mathcal{T} w^2) \bar{\Xi}(w, s) = \frac{\alpha}{s} + \rho \bar{\xi}_t(w, 0) + \rho s \bar{\xi}(w, 0), \quad (31)$$

where $\bar{\xi}_t(w, 0) = \int_0^{\infty} dx \xi_t(x, 0) \cos(wx)$. Solving for $\bar{\Xi}(w, s)$ and taking the inverse transforms leads to

$$\xi(x, t) = \mathcal{L}^{-1} \left[\frac{2}{\pi} \int_0^{\infty} dw \cos(wx) \frac{1}{(\rho s^2 + \mathcal{T} w^2)} \times \left(\frac{\alpha}{s} + \rho \bar{\xi}_t(w, 0) + s \rho \bar{\xi}(w, 0) \right) \right], \quad (32)$$

where \mathcal{L}^{-1} stands for the Laplace inverse. As we are interested only in the motion of the end of the chain, we put $x = 0$ in the above to get

$$\xi(0, t) = \frac{\alpha}{\sqrt{\mathcal{T}\rho}} t + \zeta(t) \quad (33)$$

with

$$\zeta(t) = \zeta_1(t) + \zeta_2(t). \quad (34)$$

Here

$$\begin{aligned} \zeta_1(t) &= \frac{2}{\pi} \int_0^{\infty} dw \bar{\xi}(w, 0) \mathcal{L}^{-1} \frac{\rho s}{(\rho s^2 + \mathcal{T} w^2)} \\ &= \frac{2}{\pi} \int_0^{\infty} dw \bar{\xi}(w, 0) \cos(c\omega t) = \xi(x, 0)_{x=ct} \end{aligned} \quad (35)$$

and

$$\begin{aligned} \zeta_2(t) &= \frac{2}{\pi} \int_0^{\infty} dw \bar{\xi}_t(w, 0) \mathcal{L}^{-1} \frac{\rho}{(\rho s^2 + \mathcal{T} w^2)} \\ &= \frac{2}{\pi} \int_0^{\infty} dw \bar{\xi}_t(w, 0) \frac{\sin(c\omega t)}{c\omega}. \end{aligned} \quad (36)$$

Equation (33) shows that the broken end of the chain undergoes translational motion with a uniform velocity $v = \alpha/\sqrt{\mathcal{T}\rho}$. In addition, it undergoes diffusive motion, due to thermal fluctuations which is represented by the term $\zeta(t)$. In Appendix D, we calculate the correlation function for this and show that

$$\langle \zeta(t) \zeta(t_1) \rangle = \frac{2k_B T}{\rho c} \min(t, t_1). \quad (37)$$

The above correlation function is just that for Brownian motion, with a diffusion coefficient $D = k_B T/\rho c$. Thus the motion of the end of the chain is the same as that of a Brownian particle of mass unity, drifting with a velocity v in the positive direction, having the diffusion coefficient D .

B. The first passage time

In our problem we need the average time that such a Brownian particle spends in a region with $\xi < \xi_c$ before going out for the first time from this region. It is given that it

starts at $\xi=0$, drifts in the positive direction with a velocity v towards the point $\xi_c(>0)$, and it also undergoes diffusive motion. This is essentially a first passage problem and may be solved by finding the probability density $P(\xi,t)$ for the particle to be at ξ at the time t , given that it was at $\xi=0$ at the time $t=0$. $P(\xi,t)$ obeys the diffusion equation

$$P_t(\xi,t) = DP_{\xi\xi}(\xi,t) - vP_{\xi}(\xi,t). \quad (38)$$

This has to be solved subject to the condition that $P(\xi_c,t) = 0$. Then, one has to calculate the survival probability

$$P_{surv}(t) = \int_{-\infty}^{\xi_c} d\xi P(\xi,t) \quad (39)$$

from which the average time that it spends in the region may be obtained as

$$\langle t \rangle = \int_0^{\infty} dt P_{surv}(t). \quad (40)$$

To solve Eq. (38) we use Laplace transform techniques. We first define $\bar{P}(\xi,s) = \int_0^{\infty} dt P(\xi,t) e^{-st}$. It obeys the differential equation

$$s\bar{P}(\xi,s) - D\bar{P}_{\xi\xi}(\xi,s) + v\bar{P}_{\xi}(\xi,s) = \delta(\xi). \quad (41)$$

This equation is to be solved, subject to the condition that $\bar{P}(\xi_c,s) = 0$. The solution is found to be

$$\bar{P}(\xi,s) = \frac{\exp\left[\frac{v\xi - |\xi|\sqrt{v^2 + 4Ds}}{2D}\right]}{\sqrt{v^2 + 4Ds}} - \frac{\exp\left[\frac{v\xi - (\xi_c + |\xi - \xi_c|)\sqrt{v^2 + 4Ds}}{2D}\right]}{\sqrt{v^2 + 4Ds}}. \quad (42)$$

From this, we obtain the Laplace transform of the survival probability

$$\begin{aligned} \bar{P}(s) &= \int_{-\infty}^{+\infty} d\xi \bar{P}(\xi,s) \\ &= \frac{1}{s} \left[1 - \exp\left(\frac{v\xi_c - \xi_c\sqrt{v^2 + 4Ds}}{2D}\right) \right]. \end{aligned} \quad (43)$$

The average survival time is then $\langle t \rangle = \lim_{s \rightarrow 0} \bar{P}(s) = \xi_c/v$. Interestingly, this is just the time that one would have estimated neglecting the diffusive motion of the chain end. Now, taking $\xi_c = d_c/2$ and using $v = \alpha/\sqrt{T\rho}$, we find the average passage time of the two ends, over the distance d_c , to be

$$\langle t \rangle = d_c \rho c / (2\alpha). \quad (44)$$

This result may look surprising at first, because the time $\langle t \rangle$ is proportional to c , the speed of sound in the chain. Thus the greater the speed of sound c (the greater the tension in the chain), the greater the time required for the ends to separate. This is due to the following: Any disturbance in the chain

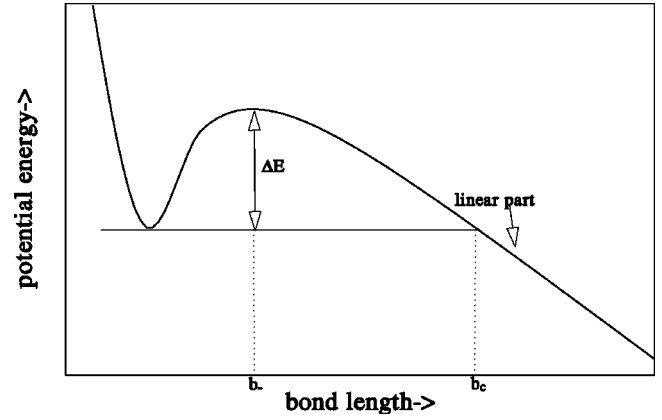


FIG. 8. The figure shows that beyond the transition state potential energy is approximately a linear function of bond length. At b_c the potential energy of the bond is equal to its equilibrium value.

propagates at the speed of sound c . So, when the end is broken, it starts moving and in a time t , the segments within a length ct from the end start moving. If c is larger, then the mass of the portion that is set in motion is correspondingly larger and hence the distance that the broken end travels is smaller.

Now one has the problem of choosing the value of d_c . The simplest estimate that one can make is that the ends should be separated by a distance equal to the stable bond length. Let b_c represents the position corresponding to the bond length such that energy of the final state is equal to the energy of the initial state (see Fig. 8). We take the potential between b_- and b_c to be linear, neglecting the curved portion near the top of the barrier. Let $l = b_c - b_-$. Then, the slope α of the potential is given by $\alpha = \Delta E/l$, which leads to the crossing time as $\langle t \rangle = ld_c \rho c / (2\Delta E)$. Using this expression, we have estimated the time of crossing the distance d_c for the Lennard-Jones model. The calculations show that in the small force regime, the first passage rate is considerably lower than that of the crossing rate and hence is the rate determining step. The actual crossing frequency may be obtained by adding the two times and then taking its inverse. The logarithm of the lifetime so obtained is plotted in Fig. 9 (the dotted curve). Again, on comparison with simulations, we find that the lifetime in the simulations is about 250 times larger, demonstrating that friction plays an important role.

C. First passage with friction

We now calculate the analysis for the motion of the chain in the presence of friction. In the presence of friction, the problem can no longer be described by a simple Hamiltonian as in the previous section. But we can write the continuum version of their equations of motion, which is

$$\rho \xi_{tt}(x,t) + \rho \gamma \xi_t(x,t) = \mathcal{T} \xi_{xx}(x,t) + \alpha \delta(x) + f(x,t), \quad (45)$$

where γ is the friction coefficient, and $f(x,t)$ is the fluctuating force, having the mean zero and the correlation

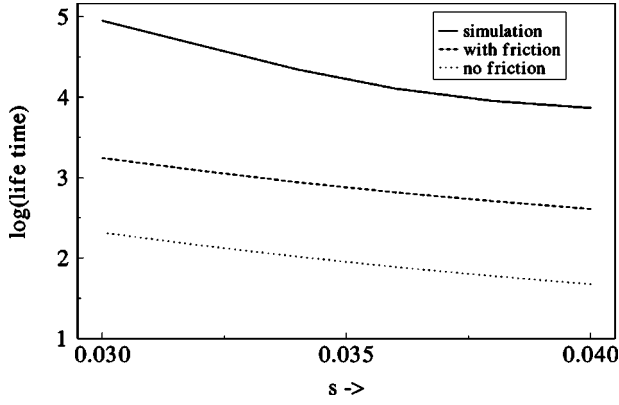


FIG. 9. The figure shows comparison of lifetimes against the strain s , calculated with (a) the rate calculated taking into account healing (dotted line), (b) healing in the presence of friction (dashed line), and (c) simulations (full line). Results are in dimensionless units.

$$\langle f(x_1, t_1) f(x_2, t_2) \rangle = 2\rho\gamma k_B T \delta(x_1 - x_2) \delta(t_1 - t_2). \quad (46)$$

This stochastic wave equation can be analyzed just as was done earlier. Following the same procedure, we get

$$\xi(x, t) = \mathcal{L}^{-1} \left[\frac{2}{\pi} \int_0^\infty dw \cos(wx) \frac{1}{(\rho s^2 + \rho\gamma s + \mathcal{T}w^2)} \times \left(\frac{\alpha}{s} + \rho \bar{\xi}_i(w, 0) + s\rho \bar{\xi}(w, 0) + \Phi(w, s) \right) \right].$$

In the above,

$$\Phi(w, s) = \int_0^\infty dt \int_0^\infty dx \cos(wx) f(x, t) e^{-st}. \quad (47)$$

As in the previous case, we are interested only in the position of the end of the chain, which is

$$\xi(0, t) = \mathcal{L}^{-1} \left[\frac{2}{\pi} \int_0^\infty dw \frac{1}{(\rho s^2 + \rho\gamma s + \mathcal{T}w^2)} \times \left(\frac{\alpha}{s} + \rho \bar{\xi}_i(w, 0) + s\rho \bar{\xi}(w, 0) - \rho\gamma \bar{\xi}_i(w, 0) + \Phi(w, s) \right) \right].$$

All terms other than the first term on the right-hand side are random, arising from thermal fluctuations. So on calculating the average of both the sides, we get

$$\begin{aligned} \langle \xi(0, t) \rangle &= \mathcal{L}^{-1} \left[\frac{2}{\pi} \int_0^\infty dw \frac{\alpha}{s(\rho s^2 + \rho\gamma s + \mathcal{T}w^2)} \right] \\ &= \mathcal{L}^{-1} \left[\frac{\alpha}{\rho c s \sqrt{s^2 + \gamma s}} \right] \\ &= \frac{\alpha}{\rho c} t e^{-\gamma t/2} [I_0(\gamma t/2) + I_1(\gamma t/2)]. \end{aligned} \quad (48)$$

In the above, $I_n(\gamma t/2)$ denotes a modified Bessel function of order n .¹⁶ As was done earlier, the average survival time is given by solving the equation $\langle \xi(0, t) \rangle = d_c/2$ for the time t to find the time for traveling a distance $d_c/2$ by one end of the chain. This is the survival probability of the chain. This result is only an approximation. Strictly speaking, we should write down an analog of the diffusion Eq. (38) for this problem and solve it to find the survival time. As the random terms in this equation are more complex than the ones in the Eq. (38), we have not done this. In the earlier problem we saw that the random terms had no effect on the average survival probability. So we neglect their influence in this problem too.

Using this, we have estimated the time of crossing the distance d_c in the presence of friction, as was done earlier. In Fig. 9 we compare the results (dashed line) with simulations. We find that the lifetime from the simulations is approximately within about 30 times the calculated rate (the two agree within roughly an order of magnitude).

VIII. CONCLUSIONS

We have derived formulas and methods for the calculation of the rate of polymer breaking and applied it to the breaking of polyethylene. This includes multidimensional TST results at classical and quantum levels. Our version of the QTST is valid only if $T > T_c$ (~ 50 K for polyethylene). In our calculations, we fitted the potential with Morse and Lennard-Jones potentials using the bond breaking energy and force constants. We found that the lifetime of the bond is very sensitive to the potential that is used in the calculations—using Lennard-Jones or Morse potentials lead to rather different answers, this being due to different behaviors of the two at longer distances. In the absence of friction, a rough estimate of the rate can be obtained by a simple approximation that considers the dynamics of only the bond that breaks and neglects the coupling to neighboring bonds. Dynamics of neighboring bonds would decrease the rate, but usually not by more than one order of magnitude. For the breaking of polyethylene, quantum effects are important only for temperatures below 150 K. For polyethylene the lifetime strongly depends on the force and as the force varies over a narrow range, the lifetime varies rapidly from 10^5 s to 10^{-5} s. This extreme sensitivity of the rate on the force is due to rapid change of the location of the transition state (saddle point) on the externally applied force. In the presence of friction, the rate determining step for the process in most cases is the separation of the broken ends from one another.

This is particularly true, if there is friction on the two ends from the surroundings. If this is included, then there is fair agreement of the theory with the simulations.

ACKNOWLEDGMENTS

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$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{bmatrix}^{-1} = \begin{bmatrix} (\mathbf{A} - \mathbf{B}\mathbf{D}^{-1}\mathbf{C})^{-1} & -\mathbf{A}(\mathbf{A} - \mathbf{B}\mathbf{D}^{-1}\mathbf{C})^{-1}\mathbf{B}\mathbf{D}^{-1} \\ -\mathbf{D} - (-\mathbf{C}\mathbf{A}^{-1}\mathbf{B})^{-1}\mathbf{C}\mathbf{A}^{-1} & (\mathbf{D} - \mathbf{C}\mathbf{A}^{-1}\mathbf{B})^{-1} \end{bmatrix}. \quad (\text{A2})$$

APPENDIX B: EXPRESSION FOR THE RATE

From the definition of p_l in Eq. (20),

$$p_l = \frac{|l^2 + z^2 \mathbf{D}_N|}{|l^2 + z^2 \mathbf{D}_N^*|}. \quad (\text{B1})$$

Using the same partitioning as in Eq. (11) for both numerator and denominator gives

$$p_l = \frac{\begin{vmatrix} l^2 + 2z^2 - z^4 X_{n-1} & -z^2 \\ -z^2 & l^2 + 2z^2 - z^4 X_{N-n-1} \end{vmatrix}}{\begin{vmatrix} l^2 + (1-\gamma)z^2 - z^4 X_{n-1} & \gamma z^2 \\ \gamma z^2 & l^2 + (1-\gamma)z^2 - z^4 X_{N-n-1} \end{vmatrix}}. \quad (\text{B2})$$

Again we use the same partitioning as in Eq. (11) for both numerator and denominator. In the above, X_{n-1} is the last diagonal element of $[l^2 + z^2 \mathbf{D}_{n-1}]^{-1}$. In the case where n and $N-n-1$ are both large, this would be independent of n and we will denote it by X . It is easily found from the relation $X = (l^2 + 2z^2 - z^4 X)^{-1}$ that

$$X = \frac{1}{2z^4} (l^2 + 2z^2 - \sqrt{(l^2 + 2z^2)^2 - 4z^4}). \quad (\text{B3})$$

Using this in Eq. (B2), we get

$$p_l = \frac{R[l, -1]}{R[l, \gamma]} \quad (\text{B4})$$

with

$$R[l, \gamma] = [l^2 + \sqrt{(l^2 + 2z^2)^2 - 4z^4} - 2\gamma z^2]^2 - 4\gamma^2 z^4. \quad (\text{B5})$$

We can now find the value of p_0 by taking $l \rightarrow 0$ as a limit and this gives

$$p_0 = -1/\gamma = -\omega_+^2/\omega_-^2. \quad (\text{B6})$$

In the limit $l \rightarrow \infty$, $p_l \rightarrow q_l$, where

APPENDIX A: PARTITIONING FORMULA

The matrix identities that we use in the text are given below. For any square matrix of the form $\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{bmatrix}$, with \mathbf{A} and \mathbf{D} square matrices, one has

$$\det \begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{C} & \mathbf{D} \end{bmatrix} = \det \mathbf{A} \det[\mathbf{D} - \mathbf{C}\mathbf{A}^{-1}\mathbf{B}] \quad (\text{A1})$$

and

$$q_l = S[l, -1]/S[l, \gamma], \quad (\text{B7})$$

with $S[l, \gamma] = [2l^2 + 2z^2(1-\gamma)]^2 - 4\gamma^2 z^4$. The infinite product $\prod_{l=1}^{\infty} p_l$ can be rewritten as below:

$$\prod_{l=1}^{\infty} p_l = \prod_{l=1}^{\infty} \frac{R[l, -1]}{R[l, \gamma]} = \left(\prod_{l=1}^{\infty} q_l \right) \kappa_1 \quad (\text{B8})$$

with $q_l = S[l, -1]/S[m, \gamma]$.

$$\begin{aligned} \kappa_1 &= \prod_{m=1}^{\infty} \frac{R[m, -1]/S[m, -1]}{R[m, \gamma]/S[m, \gamma]} \\ &= \prod_{m=1}^{\infty} \frac{\left\{ 1 + \frac{(R[m, -1] - S[m, -1])}{S[m, -1]} \right\}}{\left\{ 1 + \frac{(R[m, \gamma] - S[m, \gamma])}{S[m, \gamma]} \right\}}. \end{aligned} \quad (\text{B9})$$

The infinite product $\prod_{l=1}^{\infty} q_l$ can be analytically evaluated, in terms of the gamma function Γ (see Refs. 16 and 17 for details) to be

$$\prod_{l=1}^{\infty} q_l = \frac{\sqrt{2\gamma-1} \sin h(z\sqrt{3}\pi)}{\sqrt{3} \sin(z\sqrt{2\gamma-1}\pi)}. \quad (\text{B10})$$

The product κ_1 can be evaluated numerically and is found to be rapidly convergent.

APPENDIX C: CALCULATIONS FOR THE LENNARD-JONES POTENTIAL

The modified potential $V(y)$, if one assumed a Lennard-Jones potential for the interaction between two successive atoms, separated by a distance y , is given by

$$V(y) = \varepsilon \left[\left(\frac{a_{LJ}}{y} \right)^{12} - 2 \left(\frac{a_{LJ}}{y} \right)^6 \right] - Fy. \quad (\text{C1})$$

Just as in the case of the Morse potential, if $F > 0$, then $V(y)$ also has a minimum (y_+) and a maximum (y_-) for real $y > 0$. These values of y are equal to $a_{LJ}x$ where x satisfies the equation

$$f_1 x^{13} + 1 - x^6 = 0 \quad (\text{C2})$$

with

$$f_1 = \frac{F a_{LJ}}{12\epsilon}. \quad (\text{C3})$$

Numerical investigation shows that the two roots coalesce at $f_1 = 0.224\,158\,408\,1$. Hence the potential would cease to have a minimum if the force at the end of the polymer exceeds $F_c = 12\epsilon(0.224\,158\,408\,1)/a_{LJ}$.

APPENDIX D: THE CORRELATION FUNCTIONS

From Eq. (35) in the text, $\zeta_1(t) = \xi(x, 0)_{x=ct}$. Therefore, to evaluate the correlation function of ζ_1 we need that of $\xi(x, 0)$. To find this, we consider the chain to be semi-infinite, with the end of the chain held fixed, and the Hamiltonian to be

$$H_{fixed} = \frac{1}{2}\rho \int_0^\infty dx \xi_t(x, t)^2 + \frac{1}{2}\mathcal{T} \int_0^\infty dx \xi_x(x, t)^2. \quad (\text{D1})$$

Before the breaking, the chain is at equilibrium at a temperature T . At the time of breaking ($t=0$), the positions $\xi(x, 0)$ and velocities $\xi_t(x, 0)$ have the generating functional¹⁸

$$\begin{aligned} G[j(x), k(x)] &= N \int D\xi(x, 0) D\xi_t(x, 0) \exp(-H_{fixed}) \\ &\times \exp\left[\left(\int_0^\infty dx \xi_t(x, 0) j(x) + \int_0^\infty dx \xi_x(x, 0) k(x)\right)\right], \end{aligned} \quad (\text{D2})$$

where N is such that $G[j(x), k(x)] = 1$. The functional can be easily evaluated and one obtains

$$G[j(x), k(x)]$$

$$= \exp\left[\frac{k_B T}{2} \left(\frac{1}{\rho} \int_0^\infty dx j(x)^2 + \frac{1}{\mathcal{T}} \int_0^\infty dx k(x)^2\right)\right]. \quad (\text{D3})$$

Using this, one obtains

$$\langle \xi_t(x_1, 0), \xi_t(x_2, 0) \rangle = \frac{k_B T \delta(x_2 - x_1)}{\rho} \quad (\text{D4})$$

and

$$\langle \xi_x(x_1, 0), \xi_x(x_2, 0) \rangle = \frac{k_B T \delta(x_2 - x_1)}{\mathcal{T}}. \quad (\text{D5})$$

From this, we evaluate $\langle \xi(x_1, 0), \xi(x_2, 0) \rangle$. As $\xi(0, 0) = 0$, we can write

$$\xi(x, 0) = \int_0^x dx' \xi_{x'}(x', 0).$$

Hence

$$\begin{aligned} \langle \xi(x_1, 0), \xi(x_2, 0) \rangle &= \int_0^{x_1} dx' \int_0^{x_2} dx'' \langle \xi_{x'}(x', 0), \xi_{x''}(x'', 0) \rangle \\ &= \frac{k_B T}{\mathcal{T}} \min(x_1, x_2). \end{aligned} \quad (\text{D6})$$

Using this, we find

$$\langle \zeta_1(t_1) \zeta_1(t_2) \rangle = \frac{k_B T}{\rho c} \min(t_1, t_2). \quad (\text{D7})$$

Similarly, one can show

$$\langle \zeta_2(t_1) \zeta_2(t_2) \rangle = \frac{k_B T}{\rho c} \min(t_1, t_2) \quad (\text{D8})$$

and

$$\langle \zeta_2(t_1) \zeta_1(t_2) \rangle = 0 \quad (\text{D9})$$

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