Thermal Degradation of Unstrained Single Polymer Chain: Non-linear Effects at Work

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We examine the thermally-induced fracture of an unstrained polymer chain of discrete segments coupled by an anharmonic potential by means of Molecular Dynamics simulation with a Langevin thermostat. Cases of both under- and over-damped dynamics are investigated, and a comparison with recent studies of bond scission in model polymers with harmonic interactions is performed.

In the present investigation we model the thermal degradation of a linear polymer chain where monomers are coupled by an anharmonic potential by means of Molecular Dynamics simulation with a Langevin thermostat. Cases of both under- and over-damped dynamics are investigated, and a comparison with recent studies of bond scission in model polymers with harmonic interactions is performed.

Our extensive simulations reveal many properties of the scission dynamics in agreement with the notion of random breakdown of independent bonds, e.g., the mean time of chain rupture, $\langle \tau \rangle$, follows an Arrhenian behavior with temperature $T$, and depends on the number of bonds $N$ in the polymer as $\langle \tau \rangle \propto N^{-1}$. In contrast, the rupture rates of the individual bonds along the polymer backbone indicate clearly the presence of self-induced inhomogeneity resulting from the interplay of thermal noise and nonlinearity.

Eventually we examine the fragmentation kinetics during thermolysis. We demonstrate that both the probability distribution function of fragment sizes as well as the mean length of fragments at subsequent times $t$ characterize degradation as predominantly a first order reaction.

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I. INTRODUCTION

The study of degradation and stabilization of polymers is important both from practical and theoretical viewpoints. Disposal of plastic wastes has grown rapidly to a world problem so that increasing environmental concerns have prompted researchers to investigate plastics recycling by degradation as an alternative. On the other hand, degradation of polymers in different environment is a major limiting factor in their application. Thermal degradation (or, thermolysis) plays a decisive role in the design of flame-resistant polyethylene and other plastic materials. It can also be used in conjunction with chromatography to characterize polymeric structure. Recently, with the advent of exploiting biopolymers as functional materials the stability of such materials has become an issue of primary concern.

Most theoretical investigations of polymer degradation have focused on determining the rate of change of average molecular weight. The main assumptions of the theory are that each link in a long chain molecule has equal strength and equal accessibility, that they are broken at random, and that the probability of rupture is proportional to the number of links present. Experimental study of polystyrene, however, have revealed discrepancies with the theory so, for example, the thermal degradation stops completely or slows down markedly when a certain chain length is reached. Thus, all of the afore-mentioned studies investigate exclusively the way in which the distribution of bond rupture probability along the polymer backbone affects the fragmentation kinetics and the distribution of fragment sizes as time elapses. Only few theoretic studies have recently explored how does the single polymer chain’s dynamics itself affect the resulting bond rupture probability. In both studies, however, one has worked with a phantom Gaussian chain (that is, one has used harmonic bond potentials in the simulations) in order to linearize the problem and make it tractable by some analytic approach like the multidimensional Kramers theory, used by Lee and the Wilemski-Fixman approach, employed by Fugmann and Sokolov. In addition, these investigations have carried out in the heavily damped regime of polymer dynamics where acceleration and inertial effects are neglected.

In the present investigation we model the thermal degradation of a linear polymer chain where monomers are connected by more realistic non-linear (anharmonic) forces (Morse and Lennard-Jones) using Langevin molecular dynamics simulation in 3d. By changing the friction coefficient of the particles, $\gamma$, we examine the scission dynamics of the bonds in both the under- and over-damped cases and find significant qualitative differences.

We investigate the average time of bond breakdown $\langle \tau \rangle$, referred to frequently as the Mean First Breakage Time (MFBT) in the literature, regarding its dependence on temperature $T$, on the number of bonds $N$ in the polymer chain, or the friction $\gamma$ for both free chains as well as for tethered chains with the one end fixed at a given position in space. We produce also maps, presenting the temporal evolution of various quantities (strain, potential and kinetic
energy, relative velocity) of each particular segment or bond in an effort to detect indications for collective excitations in the course of thermolysis. Also events of bond recombination (self-healing) are investigated whereby the probability distribution of distances, traveled by the affected monomers and times, elapsed between scission and recombination are obtained. While many properties of the thermal degradation process are in agreement with the notion of randomly breaking bonds, the obtained rate histograms of bond rupture indicate unambiguously that the interplay of noise and non-linear interactions are responsible for a certain kind of self-induced multiple-scale-length inhomogeneity regarding the position of the breaking bonds along the backbone of the chain.

The paper is organized as follows: after this brief introduction, we sketch our model in Section II, and present our main results in Section III. We end this report by a short discussion and some concluding remarks in Section IV.

II. THE MODEL

We consider a 3d coarse-grained model of a polymer chain which consists of N repeatable units (monomers) connected by bonds, whereby each bond of length b is described by a Morse potential,

\[ U_M(r) = D \{ \exp[-2\alpha(r-b)] - 2 \exp[-\alpha(r-b)] \} \tag{1} \]

with a parameter \( \alpha \equiv 1 \). The dissociation energy of such bonds is \( D \), measured in units of \( k_B T \), where \( k_B \) denotes the Boltzmann constant and \( T \) is the temperature. The maximum restoring force of the Morse potential, \( f_{\text{max}}^{M} = -dU_M/dr = \alpha D/2 \), is reached at the inflection point, \( r = b + \alpha^{-1} \ln(2) \). This force \( f_{\text{max}}^{M} \) determines the maximal tensile strength of the chain. Since \( U_M(0) = \exp(2\alpha b) - 2 \exp(\alpha b) \approx 1.95 \), the Morse potential, Eq. (1), is only weakly repulsive and beads could penetrate one another. Therefore, in order to allow properly for the excluded volume interactions between bonded monomers, we take the bond potential as a sum of \( U_M(r) \) and the so called Weeks-Chandler-Anderson (WCA) potential, \( U_{\text{WCA}}(r) \), (i.e., the shifted and truncated repulsive branch of the Lennard-Jones potential);

\[ U_{\text{WCA}}(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} + \frac{1}{4} \right] \Theta(2^{1/6}\sigma - r) \tag{2} \]

with \( \Theta(x) = 0 \) or 1 for \( x < 0 \) or \( x \geq 0 \), and \( \epsilon = 1 \). The non-bonded interactions between monomers are also taken into account by means of the WCA potential, Eq. (2). Thus the interactions in our model correspond to good solvent conditions. Thus, the length scale is set by the parameter \( \sigma = 1 \) whereby the the monomer diameter \( b \approx 2^{1/6}\sigma \).

In our MD simulation we use a Langevin equation, which describes the Brownian motion of a set of interacting particles whereby the action of the solvent is split into slowly evolving viscous force and a rapidly fluctuating stochastic force:

\[ m \vec{v}_i(t) = -\zeta \vec{v}_i(t) + \vec{F}_M^i(t) + \vec{F}_{\text{WCA}}(t) + \vec{R}(t). \tag{3} \]

The random force which represents the incessant collision of the monomers with the solvent molecules satisfy the fluctuation-dissipation theorem \( \langle R_{ij}(t)R_{ij}(t') \rangle = 2\zeta k_B T \delta_{ij}\delta(t-t') \). The friction coefficient \( \zeta \) of the Langevin thermostat, used for equilibration, has been set at 0.25. The integration step is 0.002 time units (t.u.) and time is measured in units of \( \sqrt{m/\sigma^2D} \) where \( m \) denotes the mass of the beads.

We start the simulation with a well equilibrated conformation of the chain as a random coil and examine the thermal scission of the bonds for both a free chain as well as for a chain that is tethered with the end-monomer to a fixed position in space. We measure the elapsed time \( \tau \) until a bond rupture occurs, and average these times over more than \( 2 \times 10^4 \) events so as to determine the mean \( \langle \tau \rangle \) which we also refer to as Mean First Breakage Time (MFBT). In the course of the simulation we also sample the probability distribution of breaking bonds regarding their position in the chain (a rupture probability histogram), the probability distribution of the First Breakage Time, \( \tau \), the kinetic and potential energy of all bonds as well as the local strain along the chain.

Since in the problem of thermal degradation there is no external force acting on the chain ends, a well defined activation barrier for a bond scission is actually missing, in contrast to the case of applied tensile force. Therefore, a definition of an unambiguous criterion for bond breakage is not self-evident. Moreover, depending on the degree of stretching, bonds may break and then recombine again. Therefore, in our numeric experiments we use a sufficiently large expansion of the bond, \( r_h = 5b \), as a threshold to a broken state of the bond. This convention is based on our checks that the probability for recombination of bonds, stretched beyond \( r_h \), is vanishingly small, i.e., below 1%.
III. SIMULATION RESULTS

A. Dependence of the MFBT $\langle \tau \rangle$ on chain length $N$ and temperature $T$

Our consideration of the $\langle \tau \rangle$ vs. $N$ dependence is based on the assumption that bonds in the chain break entirely at random and the scission events happen independent from one another [18]. Consider the survival probability of the $i$-the bond in the chain, $S_i(t)$, (i.e., the probability that after elapsed time $t$ the bond $i$ is still intact). $S_i(t)$ may be written as $S_i(t) = \exp(-\omega_i t)$, where $\omega_i$ is the corresponding scission rate of bond $i$. Then, for presumably random and independent scission events, the survival probability of the total chain reads

$$S(N, t) = \prod_{i=1}^{N} S_i(t) = \exp(-N \bar{\omega} t)$$

(4)

where the average bond scission rate is given by

$$\bar{\omega} = \frac{1}{N} \sum_{i=1}^{N} \omega_i$$

(5)

Thus, the MFBT $\langle \tau \rangle$ of the whole chain can be represented as

$$\langle \tau \rangle = -\int_0^\infty t \frac{\partial}{\partial t} S(N, t) = \frac{1}{N \bar{\omega}}$$

(6)

where we have used the general relationship between the survival probability and the mean first passage time (see, e.g., Sec. 5.2.7 in ref. [20]). It is worth noting that the product of probabilities in Eq. (4) corresponds to the well known mean field approximation in the theory of phase transitions where one neglects the correlations [19].

Our MD simulation results concerning the dependence of MFBT $\langle \tau \rangle$ on chain length $N$ are shown in Fig. 1. Evidently, one observes a power-law decrease, $\langle \tau \rangle \propto N^{-\beta}$, with $\beta \approx 1.0 \pm 0.15$ regardless of temperature.

![Graph showing the dependence of MFBT $\langle \tau \rangle$ on chain length $N$ for different temperatures of the heat bath ($\gamma = 0.25$). Dashed / dotted lines with a slope $\approx -1.0$ represent fitting curves for grafted/free chains.](image)

FIG. 1: Mean first passage time $\langle \tau \rangle$ vs chain length $N$ for different temperatures of the heat bath ($\gamma = 0.25$). Dashed / dotted lines with a slope $\approx -1.0$ represent fitting curves for grafted/free chains.

This finding confirms the basic assumption that bonds break entirely at random and the scission events happen independent from one another. One may readily verify from the semi-log plot, Fig. 1, that this $\langle \tau \rangle$ vs $N$-relationship holds for both free and tethered single chains at all temperatures that have been examined. We should like to note...
here that this $\langle \tau \rangle$ vs $N$ relationship in thermolysis is very different from the case of polymer breakdown under tension. When external force is applied, $\langle \tau \rangle$ becomes nearly independent of chain length $N$ as the tensile strength increases \[21\]. In that case the chain thermal breakage has been treated within the multidimensional Kramers-Langer escape theory. It has been shown \[21\] that the process of bond scission is governed by a single collective unstable mode which peaks at an “endangered” bond and decays exponentially towards both chain’s ends. This explains why in this case the MFBT is scarcely affected by the chain length $N$.

The dependence of the absolute value of the MFBT $\langle \tau \rangle$ on inverse temperature, $1/T$, shown in Fig. 2, appears also in agreement with the general notion of polymer degradation as a thermally activated process. Since, as mentioned in Section II, an unambiguous criterion for scission is to a great extent arbitrary, an appropriate critical separation of the beads that form a stretched bond, $r_h$, has to be chosen such that the probability for recombination of a broken bond is negligible. With $r_h = 5$ we find that less than 1% of such bonds do subsequently recombine.

Fig. 2 demonstrates an expected variation of $\langle \tau \rangle$ with (inverse) temperature, namely an Arrhenian-dependence $\tau \propto \exp(\Delta E_b/k_B T)$. Evidently, the measured “activation barrier” $\Delta E_b$ depends weakly on the threshold for bond rupture $r_h$, and is found to increase somewhat as $r_h$ is varied in a broad interval $3 \leq r_h \leq 10$. Note that a threshold $r_h \approx 3$ corresponds to the position $r_{max}$ of maximal tensile strength of the bond (i.e., the inflection point of the Morse potential $U_M(r)$) so that any value of $r_h \geq 3$ could be considered in principle as appropriate for bond scission. Comparison of the results for different rupture thresholds, Fig. 2, indicates that for $r_h \geq 5.0$ the energy barrier $\Delta E_b$ starts to be independent of $r_h$. This allows us to estimate the activation barrier of thermally-induced scission event to the value of around 0.8$D$ where $D$ is depth of the potential well, Eq. (1).

B. Life time probability distribution

In Fig. 3 we present the probability distribution function $W(\tau)$ of the random scission times $\tau$ for several temperatures $T$ indicated in the legend. Evidently, with decreasing temperature the rupture times $\tau$ rapidly spread over a broad time interval even though the location of the PDF maximum hardly changes. It appears that $W(\tau)$ is well described by a Poisson - distribution function $W(t) \propto t^{n(T)} \exp(-t/\tau(T))$ (as one would expect for uncorrelated random events) with temperature - dependent exponents $n(T)$ and $\tau(T)$. In the inset to Fig. 3 one may verify that both exponents change linearly with $T$. Evidently, the width of $W(\tau)$, which determines the variance of the life time $\tau(T)$, declines with growing temperature of the system.
FIG. 3: First breakage time distributions $W(\tau)$ for a grafted chain with $N = 30$, $\gamma = 0.25$ at different temperatures as indicated. Symbols denote simulation result and full lines stand for the fitting function $W(t) \propto t^n \exp(-t/\tau)$. The temperature dependence of $n$ and $\tau^{-1}$ is shown in the inset.

C. Self-healing bonds

Concluding this first set of results, we consider briefly the “self-healing” of broken bonds during thermal degradation since it helps to determine the appropriate criterion for a given bond to be declared broken. As in our previous work on chain scission in the presence of constant load [21], we studied the process of recombination (self-healing) after a given bond has exceeded the threshold length $r_h$. In thermolysis the effect of self-healing should be even more pronounced due the the absence of external force, which brings the fractions of the polymer chain further apart with time.

In Fig. 4 we show the probability distribution of healed bonds $P_h(t)$ against time $t$ elapsed after the bond length has exceeded the threshold distance $r_h = 5.0$. Evidently, $P_h(t)$ is well approximated by a Gaussian distribution except for the longer times $2 \leq t \leq 6$. Interestingly, the maximum of the Gaussian is centered at a positive value of $t \neq 0$, meaning that recombination begins with some time lag after the bond length has gone beyond $r_h$ due to inertia. A related distribution of the bond extensions $Q_h(h)$ beyond the one that corresponds to the maximal restoring force $f_{\text{max}}$ (that is, beyond the inflection point of the Morse potential) is shown in the inset of Fig. 4. It is seen that the chance for self-healing decreases exponentially fast with the stretching $h$ whereby a deviation from the exponential relationship can be detected only for $Q_h < 10^{-3}$. It becomes thus clear that for the adopted threshold of $r_h = 5.0$ the probability for subsequent recombination of a broken bond is vanishingly small.

Generally, on the ground of the afore-mentioned results it appears that one deals with a thermally activated breakdown of a single macromolecule, manifested by random uncorrelated events of bond scission. These results provide no clue, however, to what extent non-linear effects due to anharmonic interactions may play a role in thermolysis by inducing some degree of collectivity in rupture events.

D. Time-evolution maps of bond scission

We tried to shed more light on the process of chain scission by producing time-evolution maps which display the variation of different physical quantities, characteristic for all individual bonds in a polymer chain, as a function of time. The idea behind this approach is to detect possible collective excitations which might be responsible for bond breakage. It is believed that a localized collective excitation will manifest itself by moving with time along the chain so that a path on the time map would indicate its location.

In Fig. 5 (left) we show the potential energy of successive bonds along the polymer backbone as a function of elapsed time after the start of the simulation. The number of repeatable units is $N = 30$ and the first segment is tethered to
a fixed position during the simulation while the 30-th segments moves freely. The variation of the kinetic energy of individual beads with time is shown in Fig. 5 (right).

A visual inspection of both maps suggests the lack of any coherence between the local values of the kinetic and potential energies! On the potential energy map (which indicates the distribution and time evolution of strain along the polymer backbone) one can clearly detect several events of bond scission. Evidently, several bonds break and recombine in the time interval $10^2 \div 80$ t.u. A real bond rupture, however, takes place in the 6-th bond at $t \approx 100$ t.u. and the chain remains broken until the end of the observation time. Notwithstanding, it is hard to detect a well expressed pattern in the potential energies of the individual bonds that would indicate the existence localized non-linear excitation (a soliton) as a possible precursor to a scission event. It appears that close to the tethered end of the chain, bond 1, the potential energy of the bonds is generally lower than in the other half of the chain. From the map of the kinetic energy, however, it is impossible to detect time and position of the breaking event at all. One merely sees that the fixed end of the chain has almost zero kinetic energy, in contrast to the free end whose kinetic energy remains high. Quiescent segments (dark spots) occur mainly inside the chain. As mentioned before, the map of the bond strain resembles strongly that of the potential energy and is, therefore, not displayed here.

An even more detailed picture of the individual motion of the monomers during thermal destruction is provided by Fig. 6 where in the map we plot the relative velocities of the segments, connected by a particular bond, over a time $85 \leq t \leq 120$. The map shows the first fifteen bonds where a scission takes place. As explained in the scheme in Fig. 4, the vector of the relative velocity $\Delta \vec{v}_i = \vec{v}_{i+1} - \vec{v}_i$ is oriented perpendicular to the bond vector $\Delta \vec{r}_i = \vec{r}_{i+1} - \vec{r}_i$ when such a bond rotates. Parallel (anti-parallel) orientation of $\Delta \vec{v}_i$ with respect to $\Delta \vec{r}_i$ indicates shrinking or stretching of the bond $i$. As is evident from the velocity map, the latter occur seldom and with small relative velocity. Predominantly the bonds are seen to perform rather fast rotations regarding their previous orientation. Again, the breaking bond (whose evolution is shaded yellow in Fig. 6) shows no distinct behavior with regard to the other bonds in the chain. Altogether, no particular pattern of collective excitations can be detected from the velocity map - nothing indicates the imminent failure of endangered bond.

E. Preferential scission of bonds along the backbone

It turns out that considerably more insight into the nature of thermally activated chain rupture may be derived from the probability distribution of scission events along the backbone of the chain.

FIG. 4: Probability distribution $P_h(t)$ of maximal times $t$ (impulses), and $Q_h(h)$ - of maximal bond lengths $h$ (circles, cf. inset) before a recombination / healing event in a chain with $N = 30$, $T = 0.1$, $\gamma = 0.25$ takes place. $P_h(t)$ is fitted by a Gaussian function, centered around a non-zero value, $t = 0.16$, blue (thick) line; and $Q_h(h)$ indicates exponential decay - blue (thin) line.
FIG. 5: Color maps showing the time evolution of the potential energy (left panel), and the kinetic energy (right panel) of successive bonds / beads in a $N = 30$ chain that breaks at time $t \approx 100$ t.u. for $T = 0.1, \gamma = 0.25$. Different colors indicate the value of the energy as indicated in the legend.

In Fig. 7 we show the distribution of the MFBT $\langle \tau_n \rangle$ of the individual bonds $n$ for a chain with $N = 30$ in the under-damped regime $\gamma = 0.25$ where inertial dynamics matter. We compare two cases: an entirely free polymer chain and a tethered chain where one of the end-monomers, $n = 1$, is fixed at a certain position in space. The simulation data is characterized by considerable disarray as compared to cases with applied external tensile force [21] despite the very large statistics (more than $1.5 \times 10^6$ scission events) that was achieved in the computer experiment. For the free chain we find that $\langle \tau_n \rangle$ of the bonds at both chain ends is about 10% shorter, if such a bond is going to break. As we shall see below, however, terminal bonds seldom happen to break. As expected, the distribution of $\langle \tau_n \rangle$ is symmetric with respect to the middle of the chain. In the case of a tethered chain, the bond in the neighborhood of the grafting bead survives longer than those in the middle. The bond at the free end of the chain is the most short lived one.

The non-uniformity in the distribution of scission events along the polymer backbone is well pronounced also in the probability histograms, Fig. 8, where we display the (normalized) probability that a certain bond $n$ along the polymer backbone will break within a time interval. Both grafted and free chains are compared for different chain lengths $N = 30, 60, 100$ and 150. The asymmetry between scission rates for bonds that are respectively closer to the fixed, or the free end of the polymer, is well pronounced. Two salient features of the probability histograms, shown in Fig. 8, appear characteristic:

i) a well expressed modulation of the rupture frequency along the consecutive bond number, which is best visible in the case of a free chain with $N = 30$. There one observes a modulation within an interval that seems to encompass roughly 15 bonds. In longer chains such modulation still persist albeit the periodic pattern gets distorted.

ii) For grafted chains a modulation also exists, however, one observes a build-up of rupture probability in the immediate vicinity of the fixed monomer even though the very first few bonds hardly break. This effect is most pronounced in the longest chain $n = 150$.

While the probability histograms, presented in Fig. 8, unambiguously indicate the existence of persistent differences in the likelihood of bond breaking in regard with the consecutive number of a particular bond along the chain backbone, the origin and the physical background of such inhomogeneity is not self-evident. On the ground of the observed modulation of the scission probability one may speculate that this self-induced inhomogeneity results from the interplay of thermal noise and the nonlinearity of the bond-potential. It is furthermore conceivable that both
control parameters such as the temperature $T$ and the nonlinearity of the interactions, as well as other factors (e.g., the friction $\gamma$, i.e., under / over-damped dynamics) would affect the multi-scale-length inhomogeneity. Presumably this finding presents an example of more general phenomena where different spatio-temporal order induced by the noise in nonlinear systems [22].

Since temperature is a major factor in thermal degradation, we present in Fig. 9 the probability histogram for two different temperatures, $T = 0.07$ and $T = 0.1$. One can see that the rupture histogram visibly changes shape due to temperature. Evidently, a decrease of temperature results in changing the positions of the local maxima which shift closer to each other while the modulation of rupture PDF grows. Also, at lower temperature the histogram becomes less flat and the non-uniformity in the rupture probability increases.

Another interesting point concerns the different impact of under- (over)-damped dynamics on the distribution of breaking events along the polymer backbone. The impact of friction $\gamma$ is displayed in Fig. 10 along with the effect which non-bonded interactions exert on the rupture probability. Indeed, it is evident from Fig. 10 that a change of
FIG. 8: Overview of rupture probability vs consecutive bond number for a chains composed of $N = 20, 40, 60$ and 80 beads ($T = 0.1, \gamma = 0.25$).

FIG. 9: Comparison of rupture histograms for grafted chains degraded at different temperature of the heat bath. $N = 30, \gamma = 0.25$.

the system dynamics from under- to over-damped one by a 40–fold increase in $\gamma$ leads to qualitative changes in bond breakage. The most striking effect of dynamics is the change in the frequency of scissions at both ends of a free chain. When inertial effects are strong, terminal bonds are the least likely to break while in the overdamped regime these become the most vulnerable ones! The well-pronounced dip in between the two maxima for $\gamma = 0.25$ also appears to vanish in the case of strong friction.

One should note that a shape of the probability histograms, as for $\gamma = 0.25$, with the terminal bonds being the most resistant to rupture, has been inferred from the experiments of Sheiko et al. [23] on adsorption-induced thermal degradation of carbon-carbon bonds on mica. The distribution of fragment lengths with time in the course of thermolysis implies a more or less constant scission probability along most of the backbone while at the ends this probability drops significantly [23]. A similar conclusion is suggested by the ultrasonic degradation experiments of Glynn et al. [24] with polystyrene who found that the bonds in the middle of the chain break preferentially to those at the ends. Probably, in the case of under-damped dynamics over-stretched terminal bonds can quickly restore their equilibrium length when friction is low and the restoring force needs only to pull back few segments at the chain end.

In contrast, if chain motion is heavily damped, one might argue that the over-stretched terminal bonds of a free chain need comparatively significantly more time to attain their normal length. During this time they are longer exposed to destructive thermal kicks which makes them more likely to break. This would explain the increased vulnerability of bonds the closer they are to the chains ends in the over-damped dynamic regime.

Another interesting effect underlines the role of the non-bonded neighbors in the rupture kinetics is also shown in Fig. [10] One can readily verify from the respective histogram that the terminal bonds break nearly 30% more often
FIG. 10: Rupture histograms for free chains composed of $N = 30$ particles bonded by Morse potential in the under-damped, $\gamma = 0.25$, and overdamped, $\gamma = 10$, regimes. The presence / absence of non-bonded interactions (indicated, respectively, as “on” and “off”) has also a dramatic effect on bond scission!

as those in the middle of the chain when the non-bonded interactions are switched off. In some sense, one could claim that the non-bonded interactions, when absent, render the chain breakage similar to what one has in the over-damped case.

In order to gain more insight into this behavior we recall that in a good solvent the mean squared end-to-end distance of a polymer chain $R_e^2$ is significantly larger than the radius of gyration, $R_g^2$, that is, $R_e^2 \approx 6R_g^2$. This suggests that the terminal beads ‘live’ predominantly at the outskirts of the polymer coil where the chance for collision with another monomer is reduced. Excluded volume interactions are thus weaker on the average, and, correspondingly, terminal bonds are on the average less stretched, i.e., they are less likely to break.

As far as our Langevin MD simulation deals essentially with anharmonic (Morse and Lennard-Jones) interactions between chain monomers, it appears useful to make a comparison with a reference system, a purely harmonic chain Fig. 11, that has been studied recently [17, 18]. As in [18], the threshold $r_h$ for rupture of such a Gaussian chain is set arbitrary to some extension of the harmonic bond - bonds longer than $r_h$ are then considered broken. It is seen from Fig. 11 that shape of the rupture histogram in the overdamped case, $\gamma = 10$, is similar to that of our Morse chain in the same dynamic regime, and resembles closely the histogram shape in Fig. 10 when non-bonded interactions are switched off. Our simulation result reproduces very well the recent observations of Fugmann and Sokolov [18], cf. Fig. 2 in [18], who modeled the thermally induced breakdown of a Gaussian chain. In the under-damped regime, however, which was not studied before, the Gaussian chain histogram is strongly leveled off, retaining only a very

FIG. 11: Rupture histograms of a 30-particles free harmonic chain for under- ($\gamma = 0.25$) and over-damped cases ($\gamma = 10$). The inset shows mean values of breakage times with respect to consecutive bond number for grafted and free chains. ($T = 1.5$)
weak (symmetric) increase in the rupture probability of the individual bonds as one moves away from the center of the chain and approaches the free ends. Any trace of self-induced inhomogeneity as in the case of non-linear interactions, Fig. [S] is absent. This supports again our assumption that the observed inhomogeneity in the rupture probability distribution among individual bonds occurs as a result from interplay between the thermal noise and the nonlinearity.

A test of this conclusion is suggested by the study of another property - the average strain of the bonds (b) with respect to the consecutive bond number, shown in Fig. [12]. One can see that this quantity resembles the behavior of rupture probability regarding n. The terminal bonds are less stretched than the other ones and therefore break seldom. Moreover, the the effective spring constant $\lambda_n$ of the individual bonds which is given by the variance of the strain, $\langle \Delta b_n^2 \rangle$, shown in the right panel in Fig. [12] behaves similarly. Indeed, the Hamiltonian $H = \frac{1}{2} \sum_{n=1}^{N} \lambda_n \langle \Delta b_n \rangle^2$ of the chain defines a bond length probability distribution function $P \propto \exp\{-H/k_BT\}$. The distribution of individual strain is Gaussian, $P_n(\Delta b_n) \propto \exp\{- (\Delta b_n)^2/k_BT\langle \Delta b_n^2 \rangle\}$ with $\langle \Delta b_n^2 \rangle = k_BT/\lambda_n$. Thus one can see that in an uniform chain there appear regions of effectively “stiffer” bonds (at the ends of the chain), and of “softer” bonds (away from the ends) that are less or more likely to stretch and break, respectively. Remarkably, in a harmonic Gaussian chain, where excluded volume effects are absent, both (b) and $\lambda_n$ are seen to be entirely uniformly distributed, Fig. [12] (lowest panels)! This proves that the observed inhomogeneity is indeed attributed to the nonlinearity of the bond potential.

F. Molecular Weight Distribution during Thermal Degradation

Finally, we examine the course of the degradation kinetics which is manifested by a time-dependent probability distribution function, $P(n, t)$, of the fragments of the initial macromolecule as time elapses after the onset of the process - Fig. [13]. The initial length of our polymer is $N = 100$ and the temperature $T = 0.10$. Averages of $P(n, t)$, obtained over $10^4$ cycles of scission - Fig. [13a] - are shown to evolve in time from a $\delta$-like distribution at $t = 0$ to a rather flat distribution with a rapidly growing second maximum around sizes of $n \approx 2 \div 5$. After a short time of $\approx 250$ t.u., the initial chain has already disintegrated into small clusters whose length is most probably $n \approx 1$. At late times, $t \approx 10^4$ t.u., the distribution $P(n, t)$ attains again a sharply-peaked $\delta$-like shape. We would like to stress that the observed variation of $P(n, t)$ resembles strongly the one, found in recent experiments with bond scission in poly(2-hydroxyethyl methacrylate) chains [28, 25]. If one assumes that the scission kinetics is described by a first-order reaction, then one may derive an analytic expression for the decrease in the average length of the fragments with elapsed time [25] as

$$
\left( \frac{1}{N(t)} - \frac{1}{N_\infty} \right) = \left( \frac{1}{N_0} - \frac{1}{N_\infty} \right) e^{-kt},
$$

where $N_0$ is the initial contour length at $t = 0$ and $N_\infty$ is the mean contour length of polymer chains at infinite time. $k$ is a first-order rate constant. This result, Eq. (7), is compared with our simulation data in Fig. [13b]. In normal coordinates (inset) the course of the theoretical result can hardly be distinguished from from the simulation data. The final fragment size is $N_\infty = 1$. Upon a closer look in semi-log coordinates, however, the exponential decay $\propto \exp(-kt)$ is found to deviate slightly at late times $t > 2 \times 10^4$ t.u. We interpret the observed discrepancy as an indication that
fragment recombination may occasionally take place at late times when the fragments become sufficiently small and mobile. Recombination comprises a second-order (binary) reaction which adds to the dominant first-order reaction of decay and, therefore, contributes to the observed deviations. Nonetheless, it appears that our simulation model faithfully accounts for the degradation kinetics.

IV. CONCLUDING REMARKS

In this work we presented a MD simulation study of the thermal degradation of a single polymer molecule at different conditions, such as temperature, friction, length of the polymer, etc. A major emphasis has been placed on exploring the effect of the nature (linear or not) of the monomer interactions on the scission process.

According to our results, the basic notion of the fragmentation process as a result of random and independent scission of bonds is supported by the observed dependence of the MFBT $\langle \tau \rangle$ on the chain length $N$ as $\langle \tau \rangle \propto 1/N$. In addition, the variation of the life time, $\langle \tau \rangle$, with (inverse) temperature turns out to be an Arrhenian-law, $\langle \tau \rangle \propto \exp(\Delta E_b/k_B T)$ whereby the activation energy is rather close to the potential well depth of the Morse interaction.

A very detailed investigation of the time-evolution maps of bond and segment properties during thermolysis does not indicate any existence of some kind of localized nonlinear excitations (solitons) which would mediate the energy transfer and cause bond breakage.

In contrast, the distribution of the bond rupture probability reveals the existence of a multiple length-scale inhomogeneity which is self-induced presumably as a result of the interplay between thermal noise and the nonlinearity of the bond potential. This inhomogeneity does not exist in the Gaussian chain model where the forces depend linearly on distance between monomers which supports the notion of force anharmonicity (i.e., non-linearity) as an origin of the observed inhomogeneity.

In addition, two major factors have been found to effect the scission kinetics of a single polymer chain - (i) the presence and relative strength of excluded volume (i.e., non-bonded) interactions between monomers, and (ii) the particular kind of chain dynamics (over- or under-damped regimes). Both effects have been demonstrated to discriminate strongly between terminal bonds and bonds away from the chain ends as far as the probability of breakage is concerned.

In this study we examine the fragmentation kinetics during thermal degradation and obtain the time evolution of the fragment size distribution after the onset of the process. We find that the size distribution agrees well with experimental observations. The time variation of the mean fragment size indicates that the scission process can be well described by means of a first-order reaction kinetics with only small deviations due to recombination events.

It is a matter of a future investigation to elucidate fully the nature of this interesting phenomenon.
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Mean Bond Extension

Mean Squared Bond Extension

Fragment size - n

PDF(n)

Consecutive Bond Number

Time