

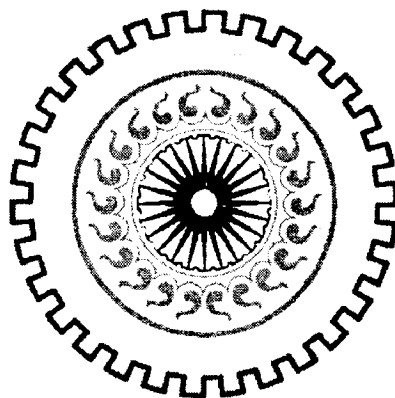
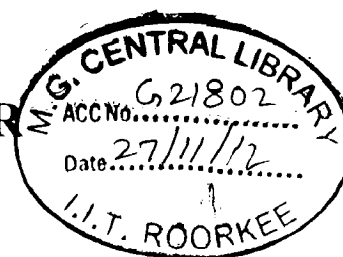
# RUPTURE DYNAMICS IN POLYMERS WITH INTERCONNECTING BONDS

A DISSERTATION

*Submitted in partial fulfillment of the  
requirements for the award of the degree  
of*

**MASTER OF TECHNOLOGY  
in  
ADVANCED CHEMICAL ANALYSIS**

By  
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JUNE, 2012**

# CERTIFICATE

I hereby certified that the work entitled “**RUPTURE DYNAMICS IN POLYMERS WITH INTERCONNECTING BONDS**” has been carried out by **Mr. Subodh Kumar**, Department of chemistry, IIT Roorkee, under the guidance of my supervision during August 2011 to June 2012.

To the best of my knowledge the same has not been submitted elsewhere for award of any degree.

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## CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in this dissertation entitled **“RUPTURE DYNAMICS IN POLYMERS WITH INTERCONNECTING BONDS”** in partial fulfillment of the requirement for the award of the degree of **MASTER OF TECHNOLOGY** submitted in the department of chemistry, IIT Roorkee is an authentic record of my own work carried out during the period from August 2011 to June 2012 under the supervision and guidance of Assistant Professor **Dr. Pallavi Debnath**.

The matter in this project work has not been submitted for the award any other degree.

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**SUBODH KUMAR**

# ABSTRACT

In this dissertation work, we study the rupture dynamics of interconnecting bonds between two flexible polymers under the action of external force. The modified geometry that resembles most type of adhesion clusters coupled to cytoskeleton that have to function under mechanical load; is taken as our model system so that the problem remains one dimensional and tractable. Extensive stochastic simulations of the model system are performed. The model system exhibits rich rupture dynamics which is essentially sequential. A mean field analytical formulation of the dynamics of the model system is also carried out. But the inherent coupling between the bond and transducer dynamics restrains an exact treatment. An alternate route to solve the coupled mean field equations has been suggested.

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# 1. INTRODUCTION AND LITERATURE REVIEW

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Rupture dynamics in model systems has been thoroughly investigated to understand microscopic origin of various physical phenomena involving relative motion of surfaces, which arise mainly due to transduction or propagation of applied external load through the systems investigated. Wide range of phenomena including frictional forces due to relative motion of shearing surfaces [1-8], earthquake models for fault dynamics [2, 3], bio-composites having hierarchical structures exhibiting relative motion at each level of hierarchy[4-7], adhesive bonds between biological receptors and ligands [8]. Specifically we classify the huge literature pertaining to the present work as follows:

## 1.1 Rupture Dynamics and Friction

We discuss here mainly the frictional forces arising due to relative motion of shearing surfaces [9-12]. One of the important areas of investigations that has been somewhat overlooked is that of strongly irreversible tribological processes, which include cold welding, material mixing, and tribochemical and triboelectrical effects. But only a few experimental investigations [13–15] and molecular dynamics simulations [16–19] have been performed to study these strongly irreversible phenomena at a microscopic scale. Experimental studies of dynamics of cold welds [13] and adhesive boundary lubrication [14] have suggested that macroscopic friction might originate from the formation and rupture of microscopic bonds (junctions) that form between surfaces in close vicinity.

Theoretically, Schallamach, in 1963 attributed rubber friction to molecular bonds between rubber and the track, both formation and breaking of bonds being thermally activated rate process [20]. Theory on this basis agreed semi-quantitatively with the experimental results by Grosch [21]. This pioneering work by Schallamach stimulated numerous studies by theorists with different variations of the toy rupture models to understand the microscopic origin of the underlying mechanism. Notable among them, is the more recent work by Filippov and coworkers [1], where they propose a microscopic model that establishes a relationship between the dynamics of formation and rupture of individual bonds and macroscopic frictional phenomena. They suggest mechanisms of sliding and stick-slip motions that have been observed in tribological experiments with adhesive boundary lubricated surfaces [14] and cold welding [13]. Here they go beyond the elastic response of the embedded system to include strongly nonlinear rupture effects that contribute essentially to energy dissipation. Their model includes two rigid plates connected by bonds (junctions) that spontaneously break and then reform upon a contact. The model system we study in this thesis is very similar to that of Filippov et. al. with the generalization that the transducer (plate) is flexible and modeled as a bead spring polymer, which is discussed in Chapter 2.

Closely related models exist using the pioneering Burridge Knopoff spring-and-box model and its successor as in Ref [3] of earthquake dynamics, which consists of a one dimensional array of blocks coupled by horizontal springs (very similar to a bead spring polymer) sliding on a frictional surface. This particular one dimensional set up is connected by other set of springs (similar to interconnecting bonds) to a parallel rigid driving bar moving horizontally at a constant velocity. Using these models for understanding block substrate friction at the microscopic level; calculations were done by Perrson et. al., [22, 23] but the



detailed microscopy, its relationship to the macroscopic plate motion, and, in particular, the conclusions are all different.

## 1.2 Hierarchical systems

Biomaterials like wood and bone are hierarchical composite structures of minerals and proteins [4-7]. Wood has a complex hierarchical structure, where the constituent tube shaped wood-cells are embedded in the matrix of hemicelluloses and lignin. These wood-cells contain semi-crystalline cellulose microfibrils wound in the form of a Z-helix around the lumen. In a typical experiment by Keckes et al. [5] tensile tests were performed both on individual wood cells and on wood foils to study distinct deformation mechanisms inside the cell wall and those mediated by cell-cell interactions. Mechanical properties of both the individual cells and the intact tissue are found to be quite similar, they reveal a “stick-slip” mechanism during tensile loading. The authors explained their results using a phenomenological model of the irreversible deformation process, where a soft elastic matrix transmits shear stresses between cellulose fibrils. When the critical shear stress is exceeded, the matrix deforms easily and as the stress is released the bonds reform at a new position, similar to a “Velcro” fastener.

Similar to wood also bone possesses a hierarchical structure. Bone is a nanocomposite of hydroxyapatite crystals and an organic matrix that contains mainly collagen (a protein). Thompson et al. attempted to explore the molecular basis of bones toughness experimentally [7] using atomic force microscopy. They stretched single collagen fibers supported on glass cover slips as well as on bone and performed bone indentation tests. They reported that bone contains polymers with “sacrificial bonds” that both protect the polymer backbone and dissipate energy. They found that the time required for these bonds to reform after stretching correlates with the bone recovery time in the indentation tests. This led them to suggest that these sacrificial bonds

may be partially responsible for the toughness of the bone. Bonelike biocomposites can be modeled by a tension-shear chain model, where the mineral platelets that carry tensile load are embedded in a protein matrix that transfers loads between the platelets via shear [24]. This is again a phenomenological model and a microscopic understanding of the mechanism involved in these systems under shear still remains a challenge.

On the theoretical side, there are models in the literature where macroscopic friction is modeled by the rupture of microscopic bonds that form between rigid planar surfaces in close vicinity [1]. The macroscopic frictional properties are related to microscopic formation and rupture of bonds. These bonds between the plates can spontaneously break and reform upon a contact. The bond rupture is treated as an activated process, where the activation energy is lowered by the external force, while the bond formation depends on the contact time. The idea to interpret friction as a thermally activated process goes back to work on the friction of rubber by Schallamach [20]. The simulation results of Ref. [1] show three different regimes of motion characterized by different rates of rupture and formation relative to the driving velocity. Low and high velocity regimes correspond to sliding regimes, characterized by thermal bond dissociation and no bond formation processes, respectively, while the intermediate regime corresponds to stick-slip behavior, where processes of spontaneous and shear-induced bond dissociation compete.

### **1.3 Adhesion Phenomena**

Another closely related subject is the theoretical description of the stochastic dynamics of cooperative molecular bonds under load, which plays an important role for force spectroscopy of ligand-receptor bonds [25, 26], cell adhesion [27], and the cooperative transport by molecular

motors [28]. The first two subjects, namely ligand-receptor bonds and cell adhesion are more relevant to the work in this thesis.

Adhesion of biological cells is based on clusters containing a large number of adhesion receptors which mediate contact to specific ligands either carried by other cells or attached to the extra cellular matrix. Adhesion clusters are two-dimensional assemblies of transmembrane adhesion proteins which are held in the plasma membrane of the cell by hydrophobic interaction. On the cytoplasmic side (the inside of the cell) the receptors can be linked to the cytoskeleton. In many cases, an assembly of different accessory proteins ('cytoplasmic plaque') strengthens and regulates these links. A binding pocket on the extracellular side allows specific interaction with appropriate ligands. In general, the function of cell adhesion is twofold. The physical contact enables cells to resist and transmit mechanical forces and to maintain the integrity of tissues and the whole organism. Moreover, cells use adhesion sites like fingers which allow them to feel their environment and collect information about physical properties, such as the presence of binding sites and the presence of other cells, elasticity of substrates and strength of forces acting on the cells. In general, many processes such as embryonic development, cell migration or the immune response depend crucially on the specific adhesion of cells.

Advancements in single molecule force spectroscopy has made it possible to measure the binding strength of a pair of receptor-ligand molecules using vesicles [29], atomic force apparatus [30-32], or optical tweezers [33] as transducers. Specifically over the last years, the AFM has become a standard tool to investigate adhesion strength of specific receptor-ligand bonds, both for single molecules and for multiple bonds in the context of single cells [34-36]. Thus, the essential constituents mediating biological adhesion have become accessible to quantitative physical experiments [37]. This experimental progress has lead to theoretical studies

of the rupture of such pairs under loading. Thermal activation being a main contributing factor, Kramers-like descriptions of the rupture process with time-dependent potentials show that the rupture strength of such bonds depends on the loading rate [38–40]. Such behavior has been found experimentally indeed [41, 42].

Adhesive contact and the rupture thereof often involve not just one but several molecular pairs of the same or different species [43], like clusters of adhesion molecules in cell-matrix adhesions. The role of force at adhesion clusters is also of interest to biological community, since it has been shown that force at cell-matrix adhesions correlate with contact size and intracellular signaling [44]. Hence in order to make contact with situations of biological interest, the quantitative effort has to be extended to clusters of adhesion bonds. For instance, micropipette techniques have been used to study cluster dissociation under a linear ramp of force [45], in good agreement with a theoretical analysis by Seifert [25, 26]. However, physiological loading of adhesion clusters is usually more or less constant on the time scale of cluster lifetime. The stability of adhesion clusters under constant force has been first modeled by Bell [43], but his treatment was based on a simplifying deterministic equation for the mean number of bonds.

## **1.4 Theoretical Models**

The problems discussed so far in this thesis are all complex many body problems with rupture occurring in real three dimensions. This complexity makes the systems analytically and computationally intractable without any further approximation. To draw meaningful insights into the basic mechanisms like scaling behavior of physical quantities even at the microscopic level may not need such structural complexity and that is what statistical mechanics is all about.

The common feature in friction between shearing surfaces, mechanical behavior of the hierarchical systems and cell adhesion discussed so far is rupture or failure mechanism, specifically caused by relative motion between two surfaces under the action of applied external load. To model these systems and extract important physical behavior one normally uses one dimensional rupture models [1, 25-27]. The model systems generally considered in these problems consist of two parallel transducers with interconnecting bonds which can both rupture and bind stochastically. Dynamics including either of the bonds or the transducer in short dynamics of the system depending on the model specification are studied under the action of load. The quantities of interest for friction phenomena are time series of spring force, which exhibit the characteristic stick-slip phenomena [1]; force-extension profiles characteristic of the hierarchical systems, includes mechanical response similar to metal [47], and dynamics of loading and rupture probabilities for adhesion clusters [25-27, 48]. If the transducer is flexible as it is in the thesis, one generally models the transducer as a flexible or semiflexible polymer depending on the dynamical properties one is interested on. This opens up another very closely related field of investigation and that is polymer degradation, polymer scission under the influence of tensile stress [49]. Recent models on adhesion employs formulation tailor made to describe specific real biological environments, though insightful but are very problem specific and hence have very limited scope [50].

## **1.5 Aim of the project**

The main purpose of the project is to explore the rupture dynamics of the parallel bonds between two flexible transducers under the action of a fixed load. It will be interesting to see how the load is shared among the interconnecting bonds. This analysis is very generic, and is applicable to any

of the cases mentioned above, results of which will give more insights into the essential constituents mediating the underlying microscopic mechanism.

Earlier unspecific theoretical models [25-27], with direct relevance to the proposed project address generic features of the adhesion clusters. For example of generic property Ref. [25] addresses the following question: How does the time and force necessary to break an adhesive contact under dynamic loading depend on the number of bonds initially present? Within a simple model they studied the rupture of multiple bonds of same type under dynamical loading, where the load is distributed almost uniformly among several bonds such that these bonds act in parallel. The resulting simple type of cooperativity leads to different scaling regimes for the rupture time and rupture force. In their model the transducer is Hookean. An extension will be to consider realistic cases where the transducer is an elastic membrane. Also in their model the receptor is confined to a substrate, while the ligand is connected by a polymer.

In Ref. 26, authors incorporate further two generalizations of explicitly including rebinding events for bonds, and self-consistent calculation of rates using full potential gives a better agreement with experiments on adhesive strength of living cells. Ref. [27] addresses another general feature of the adhesion cluster. It presents new formulas for cluster lifetimes as a function of cluster size, rebinding rate and force. Their model too consists of a cluster with constant number of *parallel* bonds, of which the closed bonds share the constant force equally. They include rebinding as well, and do a detailed theoretical analysis of the stochastic dynamics of the bonds. In all of the above [25-27] the force is transmitted or transduced to the bonds by a rigid transducer and hence the load is distributed equally among all the bonds and moreover in Ref. [27] the transducers are fixed.

In the present thesis we propose a generalization by allowing the transducer to be a flexible polymer chain (bead spring model), where the load is not distributed equally among the closed bonds but instead the loading is determined by interplay between the polymer elasticity, and the strength of the interconnecting bonds. This we believe will capture the more realistic picture of the adhesion clusters.

## 2. THEORETICAL APPROACH

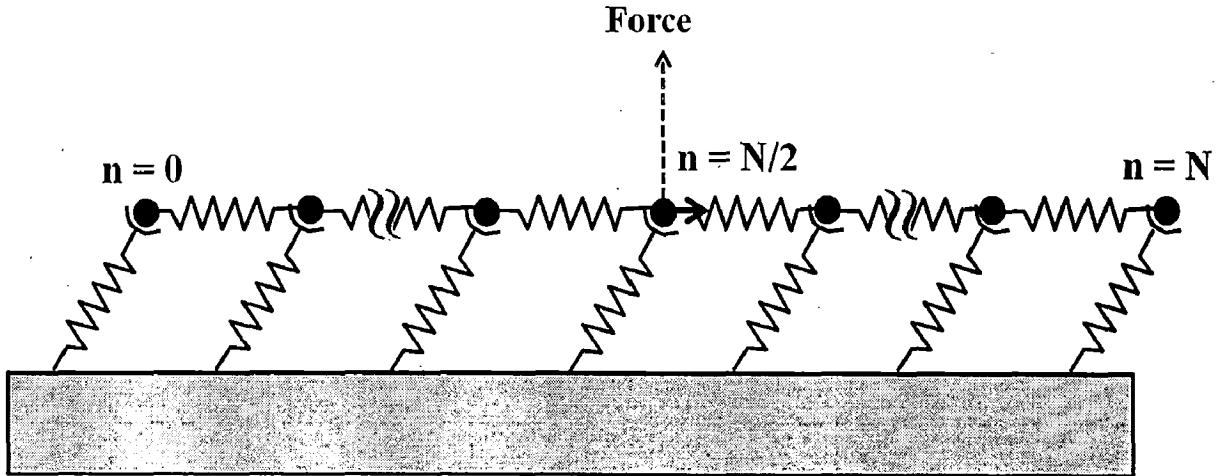
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As we reasoned earlier, our theoretical approach is very generic and is applicable to any of the phenomena discussed in the previous chapter. Since all of the phenomena have a very distinct underlying rupture mechanism, single polymer rupture model turns out to be very generic theoretical tool to understand microscopic origin of the characteristic mechanical response of the systems involving essentially relative motion between two entities. Within the generic formulation, we adopt a model geometry that resembles most type of adhesion clusters coupled to cytoskeleton that have to function under mechanical load.

### 2.1 Model system

We consider a flexible transducer, which is built from an elastic material., to be very specific a straight one-dimensional polymer which is oriented parallel to a rigid planar substrate and connected by  $N$  molecular bonds to this substrate. The distance  $d$  between the polymer and substrate is small and will be neglected in the following. The polymer is oriented in the  $x$ -direction. The planar substrate is rigid and fixed, and we apply a force in a direction perpendicular to the transducer (polymer), which is therefore transducing force onto the bonds and called the “transducer”. Our model then resembles an adhesion cluster [25], but also makes the problem two-dimensional. For tractability reasons we confine our problem to one-dimension, by taking the direction of applied at  $n = N/2$  to be parallel to the orientation of the polymer, as shown by the solid arrow in Fig 1. Hence under the applied force, the rod starts sliding in  $x$ -direction, i.e., parallel to its orientation. The onset of a sliding motion requires the rupture of all  $N$  molecular bonds with the substrate, which is a stochastic process.





Schematic representation of the model system used. Dashed arrow represents the direction of force as applied in models for adhesion clusters. Solid arrow represents the direction of force in our model. Squiggles denotes the section of polymer (beads and springs) not shown.

The polymer is modeled as a collection of beads connected by elastic springs of stiffness  $k_T$  and equilibrium length  $a$  (bead spring polymer [51]). For an elastic transducer the spatial arrangement of bonds will matter because a certain tension profile will be induced in the transducer upon shearing, which depends on the spatial arrangement of the bonds. We make the simplest choice and consider equidistant bonds. We choose the discretization of the elastic material such that at each bead one bond is attached and the length  $a$  is also the bond distance. Then we denote the displacements of beads out of their equilibrium positions  $x_{n,0}$  by  $x_n(t)$  with  $n = 0, \dots, N - 1$  using the same index  $n$  as for the bonds. The external force  $F_T$  will act onto the middle bead  $n = N/2$  with the largest  $x$ -coordinate. The equilibrium position of the last bead  $n = 0$  is  $x_{0,0}(0) = 0$  such that the equilibrium positions are  $x_{n,0} = na$ .

We consider  $N$  identical flexible bonds with a stiffness  $k_b$ , connecting the transducer to the substrate and can undergo stochastic rupture events. These bonds can also rebind but we will

start with the simplest case of pure rupture without rebinding. The state of each bond  $n = 0, \dots, N - 1$  is characterized by a discrete variable  $q_n$ , that can take only two values 0 and 1 representing an open and closed bond respectively [1]. We assume that initially all the bonds are closed, i.e. at  $t = 0$ . As time progresses, transducer slides along the direction of applied force  $F_T$ , a force  $f_n = k_b x_n$  develops on each intact bond, in a direction opposite to that of  $F_T$ . No force develops on a ruptured bond. Hence the overdamped equations of motion for each bead, which interacts with both neighbors and one bond can be written [51]. The force onto bead  $n$  from the right neighbor in positive  $x$ -direction is  $k_T (x_{n-1} - x_n)$ , the force from the left neighbor in negative  $x$ -direction is  $-k_T (x_n - x_{n+1})$ . This leads to  $n$  equations of motion for each bead (monomer)

$$\gamma \partial_t x_n = k_T (x_{n+1} - 2x_n + x_{n-1}) - q_n k_b x_n + \delta_{n, N/2} F_T + \zeta_n(t) \quad (2.1)$$

where we use the same friction constant  $\gamma$  for each bead and a thermal noise with  $\langle \zeta_n \rangle = 0$  following white noise statistics as  $\langle \zeta_n(t) \zeta_m(t') \rangle = 2k_B T \gamma \delta_{nm} \delta(t - t')$ . The force from the bond  $n$  is given by  $-f_n = -k_b x_n$ . Only the bead  $n = N/2$  couples to the external force  $F_T$ , which leads to the  $\delta$ -term. The boundary conditions to eq. 1 needs to be specified. At the the end  $n = 0$ , the first term on the rhs of (2.1) becomes  $-k_T (x_0 - x_1)$  (from the left neighbor only). We can use the same equation (2.1) also for bead  $n = 0$  if we introduce a bead  $x_{-1}$  with  $x_{-1} - x_0 = 0$ . Such a boundary condition is equivalent to a free (relaxed) end. Likewise, we have to impose some boundary condition at the end  $n = N - 1$  which can be either fixed with  $x_{N-1} = 0$  or free (relaxed), which can be implemented by introducing a bead  $n = N$  with  $x_{N-1} - x_N = 0$ . To look at a delamination process the latter free boundary condition seems more physical.

Bond rupture is modeled as thermally activated escape over a transition state barrier (Kramers theory) [43]. This gives rise to a  $n$ -dependent bond dissociation rate (i.e., the transition probability per time from state  $q = 1$  to state  $q = 0$ ).

$$k_{-,n} = k_0 e^{f_n/f_b} = k_0 e^{k_b x_n/f_b} \quad (2.2)$$

where  $k_0$  is the bond dissociation rate in the absence of force and  $f_b = k_B T/x_b$  is a force scale of the bond set by the distance  $x_b$  from the bound state to the transition state and the thermal energy  $k_B T$ . We start with the simplest case of pure rupture without rebinding, such that  $k_+ = 0$ . The equation of motion as in Eq. (2.1) together with the rate for bond dissociation as given by Eq. (2.2) completely define the stochastic model and can be simulated numerically, the results of which are discussed more succinctly in the next chapter.

In the limit of a rigid transducer with large  $k_T$  all displacements become equal,  $x \equiv x_n$ , one arrives at the single equation of motion for rigid transducer (by indentifying the friction coefficient of a rigid transducer made from  $N$  beads is  $N$  times as large as for a single bead and similarly the noise as the sum over the noise exerted on each constituent beads), very similar to the rupture dynamics of multiple bonds as described in Refs. [25, 27] as all intact bonds are sharing the force. The difference is the dynamics of the transducer, which represents a second stochastic process. The transducer dynamics enters the rupture dynamics via the bond force  $f_n = k_b x_n$  in the bell equation [Eq. (2)], and the rupture dynamics feed back into the transducer dynamics via the interconnecting bond force term  $-q_n f_n$  as in Eq. (1). This generates a certain time delay between rupture and subsequent loading of the remaining bonds.

## 2.2 Mean field approach

The equation of motions (Eq. 1) and rupture dynamics (Eq. 2) are functions of both distribution of bead positions and bond variables represented as  $\{x_n\}$  and  $\{q_n\}$  respectively. The  $\{q_n\}$  distribution ( $p(\{q_n\}, t)$ ) is governed by master equation [52] as

$$\partial_t p(\{q_n\}, t) = \sum_n (\mathbb{E}_n - 1) r_n p + \sum_n (\mathbb{E}_n^{-1} - 1) g_n p \quad (2.3)$$

where  $\mathbb{E}_n$  is the step operator specific for each bead index  $n$ , and defined as  $\mathbb{E}f(n)=f(n+1)$ ,  $\mathbb{E}^{-1}f(n)=f(n-1)$ .  $r_n \equiv r(q_n)$  is the transition rate (transition probability per unit time) of the variable  $q_n$  rupture rate as given by Eq. 2.2. For the case of no rebinding the transition rates are given as

$$\begin{aligned} r_n &= r(q_n) = w_{q_n \rightarrow q_n - 1} = q_n k_0 e^{k_b x_n / f_b} \\ g_n &= g(q_n) = w_{q_n \rightarrow q_n + 1} = 0 \end{aligned} \quad (2.4)$$

In order to incorporate the stochastic dynamics of the transducer, i.e.  $x_n$ , we have to consider the joint probability  $P(\{q_n\}, \{x_n\}, t)$  of finding  $\{q_n\}$  distribution of the bonds and  $\{x_n\}$  distribution of the bead positions at time  $t$ . The evolution of this joint probability is given by the Fokker-Planck equation as

$$\begin{aligned} \partial_t P(\{q_n\}, \{x_n\}, t) &= \sum_n (\mathbb{E}_n - 1) r_n p + \sum_n (\mathbb{E}_n^{-1} - 1) g_n p \\ &\quad - \sum_n [\partial_{x_n} \{ \partial_t x_n p \} - D \partial_{x_n}^2 p] \\ &= \sum_n (\mathbb{E}_n - 1) q_n k_0 e^{k_b x_n / f_b} p - \sum_n [\partial_{x_n} \{ \partial_t x_n p \} - D \partial_{x_n}^2 p] \end{aligned} \quad (2.5)$$

where  $D = k_B T / \gamma$  is the diffusion constant. In the absence of thermal noise  $D=0$ . Substituting the equation of motion as in Eq. 2.1 in Eq. 2.5, we have the complete Fokker Planck equation, solution of which represent the full solution of stochastic dynamics.

In the mean field approach, instead of solving the full problem one obtains deterministic differential equations for the mean values as

$$\begin{aligned} \langle x_n \rangle (t) &= \int d\{x_n\} x_n P(\{q_n\}, \{x_n\}, t) \\ \langle q_n \rangle (t) &= \int d\{q_n\} q_n P(\{q_n\}, \{x_n\}, t) \end{aligned} \quad (2.6)$$

Hence the mean field equations for the stochastic dynamics in our model system are given as

$$\gamma \partial_t \langle x_n \rangle = k_T (\langle x_{n+1} \rangle - 2 \langle x_n \rangle + \langle x_{n-1} \rangle) - k_b \langle q_n x_n \rangle + \delta_{n,N/2} F_T \quad (2.7)$$

$$\partial_t \langle q_n \rangle = -k_0 \langle q_n e^{k_b x_n / f_b} \rangle \quad (2.8)$$

In the mean-field approach we neglect all correlations of the variables on the right hand sides of Eqs. 2.7 and 2.8 and write them as

$$\begin{aligned} \gamma \partial_t \langle x_n \rangle &= k_T (\langle x_{n+1} \rangle - 2 \langle x_n \rangle + \langle x_{n-1} \rangle) - k_b \langle q_n \rangle \langle x_n \rangle + \delta_{n,N/2} F_T \\ &= k_T \partial_n^2 \langle x_n \rangle - k_b \langle q_n \rangle \langle x_n \rangle + \delta(n - N/2) F_T \end{aligned} \quad (2.9)$$

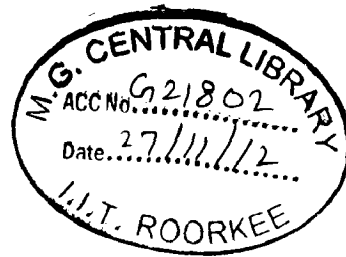
$$\partial_t \langle q_n \rangle = \langle r_n \rangle = -k_0 \langle q_n \rangle e^{k_b \langle x_n \rangle / f_b} \quad (2.10)$$

by applying a continuum approximation in the equation for  $\langle x_n \rangle$ . The free end boundary conditions in the continuum limit becomes

$$\partial_n \langle x_n \rangle |_{n=0} = 0 \text{ and } \partial_n \langle x_n \rangle |_{n=N} = 0 \quad (2.11)$$

Eqs. 2.9 and 2.10 form two coupled partial differential equations with Neumann boundary conditions for  $\langle x_n \rangle$  as in Eq. 2.11. The coupled partial differential equations do not allow an exact solution. To gain meaningful insights is hence a challenge.

One way to proceed would be to look at appropriate stationary solutions and do a stability analysis. This will pave the way to a moving boundary solution [53] of the problem as is indicated by the full stochastic simulation results.



### 3. RESULTS AND DISCUSSION

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Equations 2.1 and 2.2 are simulated using the method of Filippov et. al [1]. All the calculations were done on a 64-bit Dell workstation in the institute computer center. Bell equation as in Eq. 2.2 was implemented exactly as detailed in Ref [1] for modeling the off rate. We use a random number generator for modeling the stochastic rupture event.

The results from full scale stochastic simulation are shown in Figures [1-11]. Fig 1 and 2 shows that the mean complete rupture time is an increasing function of polymer size  $N$ , which is the hallmark of a sequential (rupture) mechanism. We find that the results are more sensitive to few parameters like friction coefficient  $\gamma$ , polymer size  $N$ , applied force  $F_T$ .  $F_T$  decreases the mean rupture time of all the bonds, while larger friction coefficient of the surroundings increases the rupture time as shown in Figure 1. We obtain the characteristic stick-slip phenomena of shearing surfaces as shown in Figs (3-5). More distinct stick slip phenomena are obtained for high friction (from both variables) coefficient values as can be seen in Figs. 3. Figs. 4 shows stick-slip phenomena for different values of  $k_b$ , the strength of interconnecting bonds, where the trace for each  $k_b$  are off by some phase, the fact of which needs to be further investigated. Fig . 5 shows stick-slip phenomena for different values of loading force  $F_T$ . Stick-slip phenomena is more pronounced for large values of  $F_T$  and this may be due to the fact that force free rupture is more pronounced at low loading force, which needs to be verified. Continuous  $\langle x_n \rangle$  trails are obtained in Figs 6 and 7. Similar trails for  $\langle q_n \rangle$  are obtained in Figures 8 and 9. Average number of intact bonds is plotted as a function of time during simulation in Figs. 10 and 11. Approximate solutions of the mean field equations may reproduce these continuous profiles for bead position and bond variables and may give further insights into the underlying mechanism.

## 4. CONCLUSION

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The results from full scale stochastic simulation show a sequential rupture mechanism. This again consolidates the suggested stability analysis of the mean field approach, which argues that the dynamics shifts from one stationary steady state solution to another as time progresses until complete rupture is attained. The stick-slip phenomena obtained is another interesting result at the level of theory applied and needs to further investigated.

We indeed see rich dynamics of the system that gives insights into the loading mechanism and the ensuing rupture mechanism. The correlation of the parameters among themselves is clearly exhibited in the results.

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## Figures

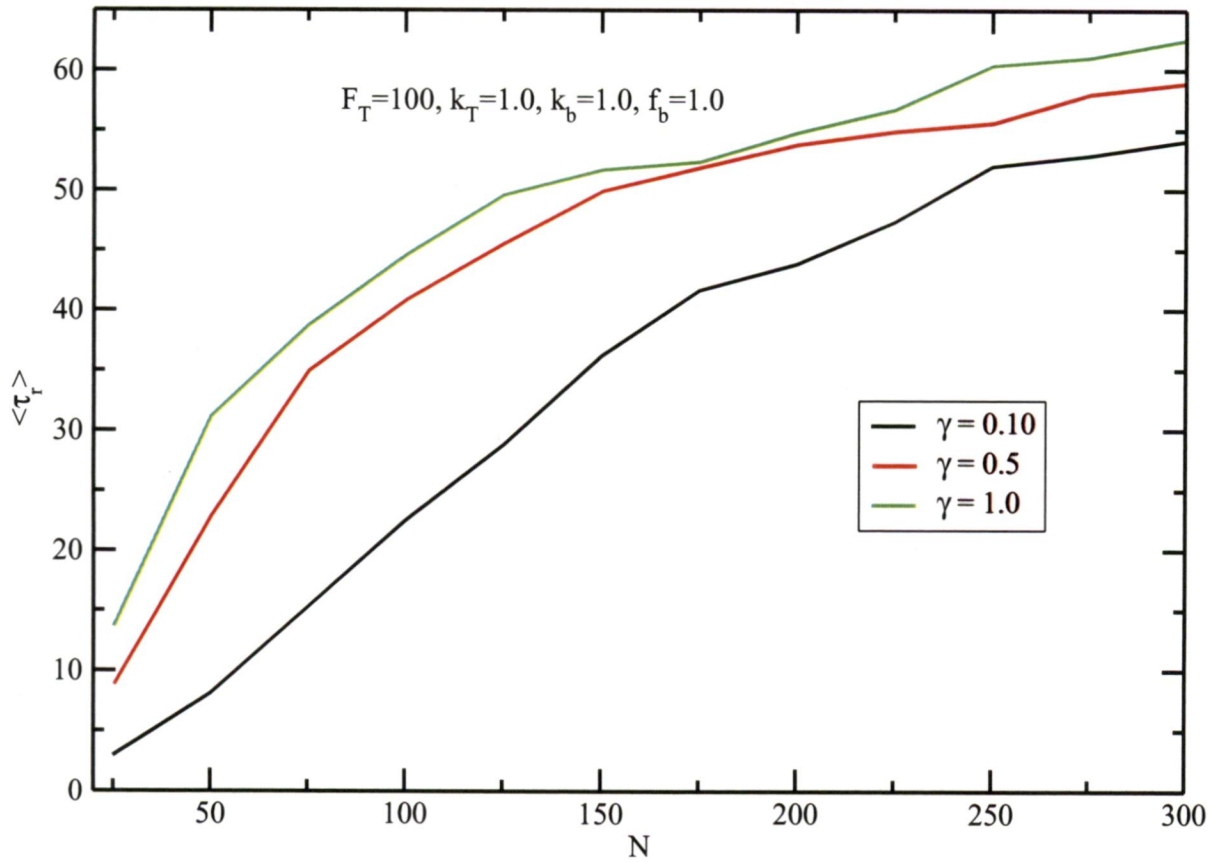


Figure 1: Complete mean rupture time  $\langle \tau_r \rangle$  vs polymer size (number of monomers/beads)  $N$  at different values of friction coefficient  $\gamma$ . The other fixed parameters are as shown in the inset. Complete rupture time was averaged over 100 runs.

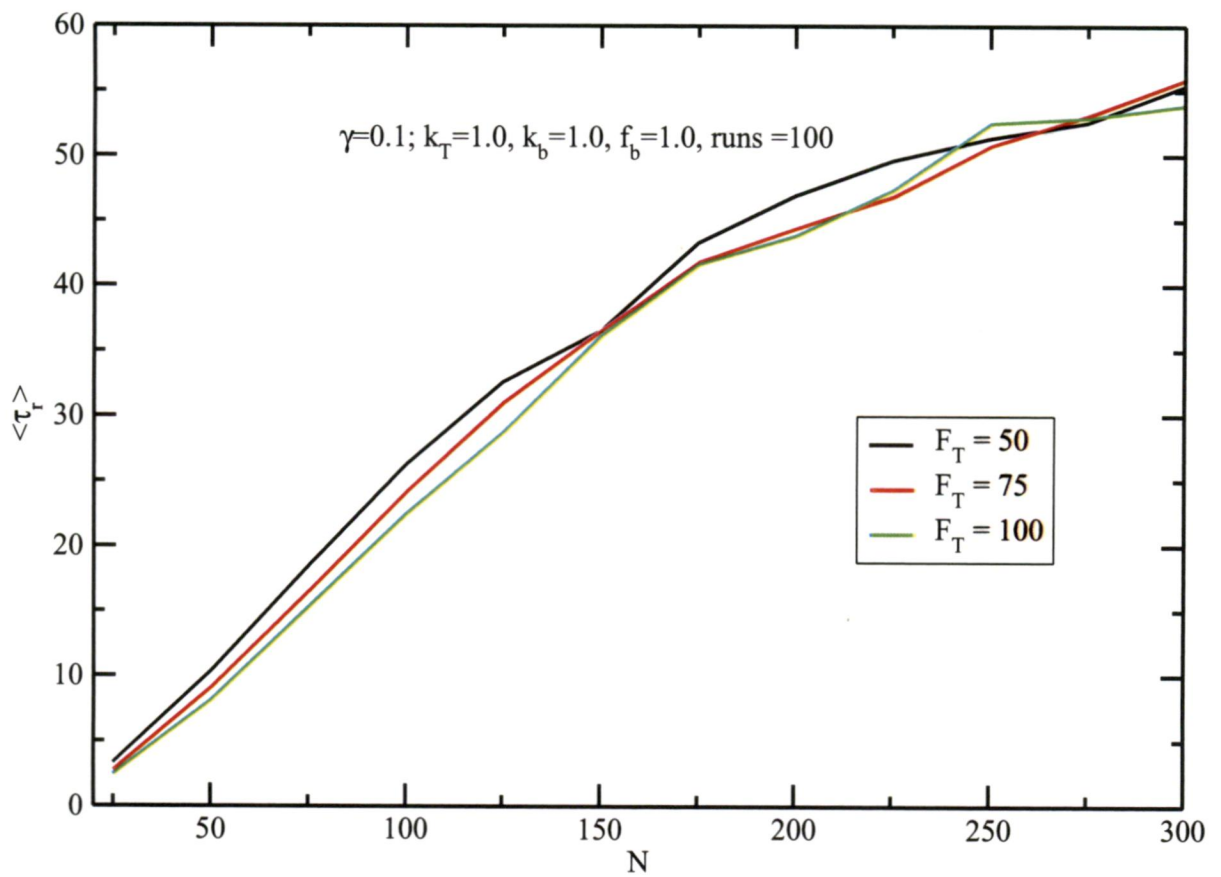


Figure 2: Complete mean rupture time  $\langle \tau_r \rangle$  vs polymer size (number of monomers/beads)  $N$  at different values of  $F_T$ . The other fixed parameters are as shown in the inset. Complete rupture time is averaged over 100 runs.

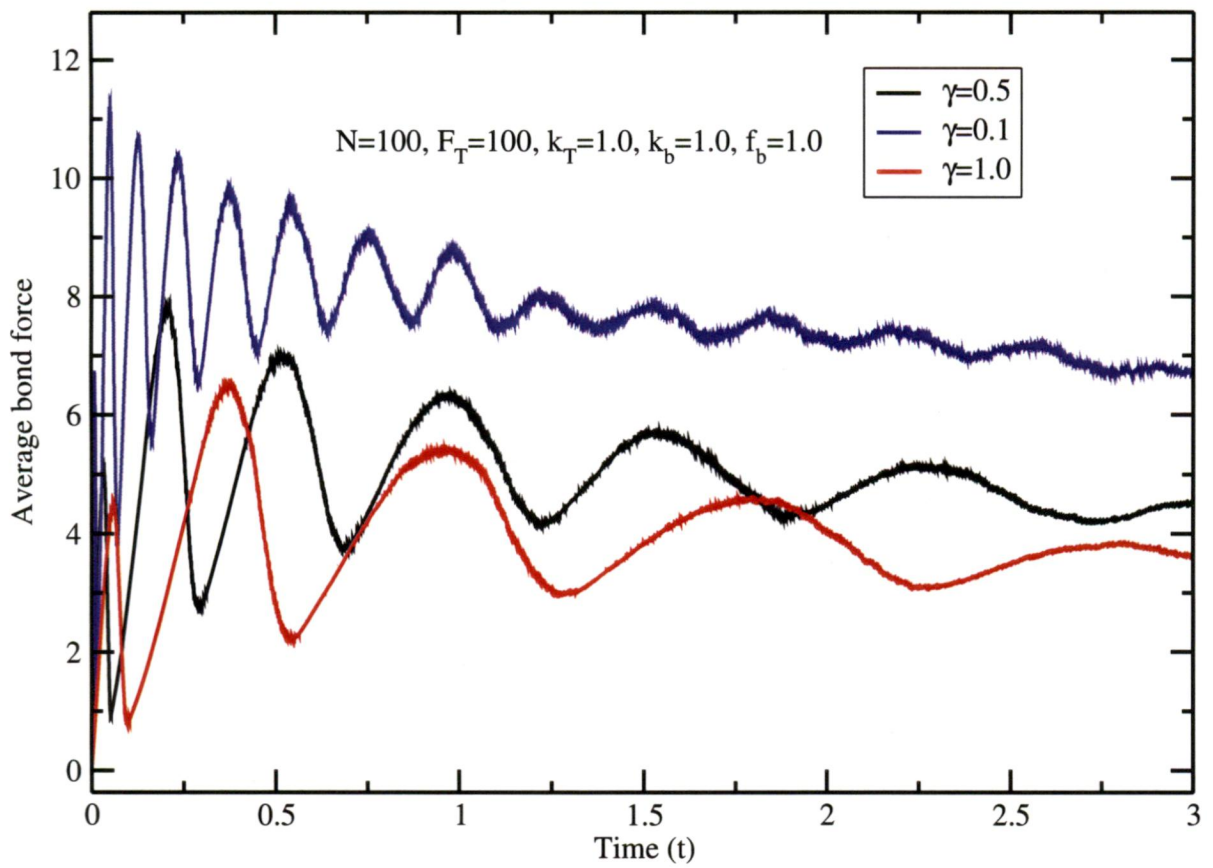


Figure 3: Average bond force vs time  $t$  at different values of friction coefficient  $\gamma$  for polymer size  $N = 100$ . The other fixed parameters are as shown in the inset. Total bond force of all the intact bonds is averaged over 1000 runs.

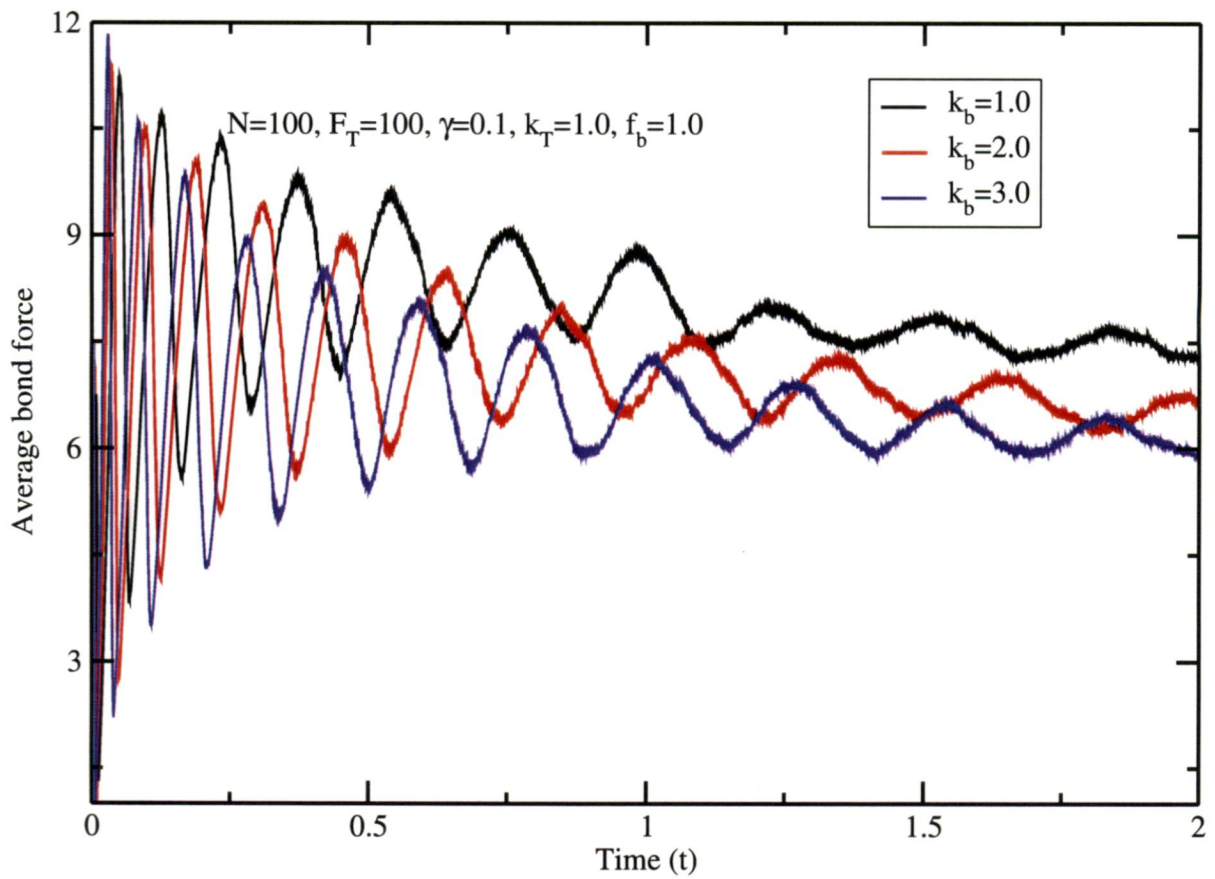


Figure 4: Average bond force vs time  $t$  at different values of strength of interconnecting bonds  $k_b$  for polymer size  $N = 100$ . The other fixed parameters are as shown in the inset. Total bond force of all the intact bonds is averaged over 1000 runs.

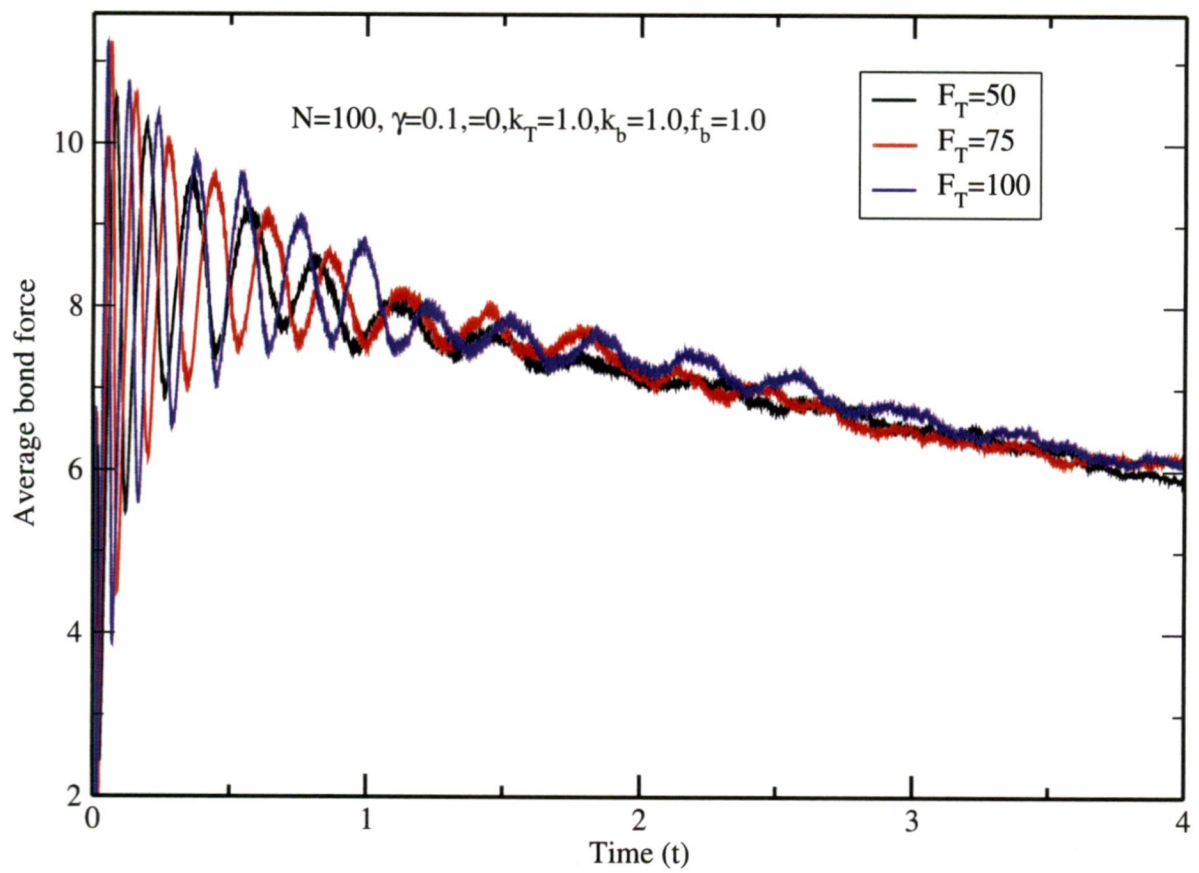


Figure 5: Average bond force vs time  $t$  at different values of loading force  $F_T$  for polymer size  $N = 100$ . The other fixed parameters are as shown in the inset. Total bond force of all the intact bonds is averaged over 1000 runs.



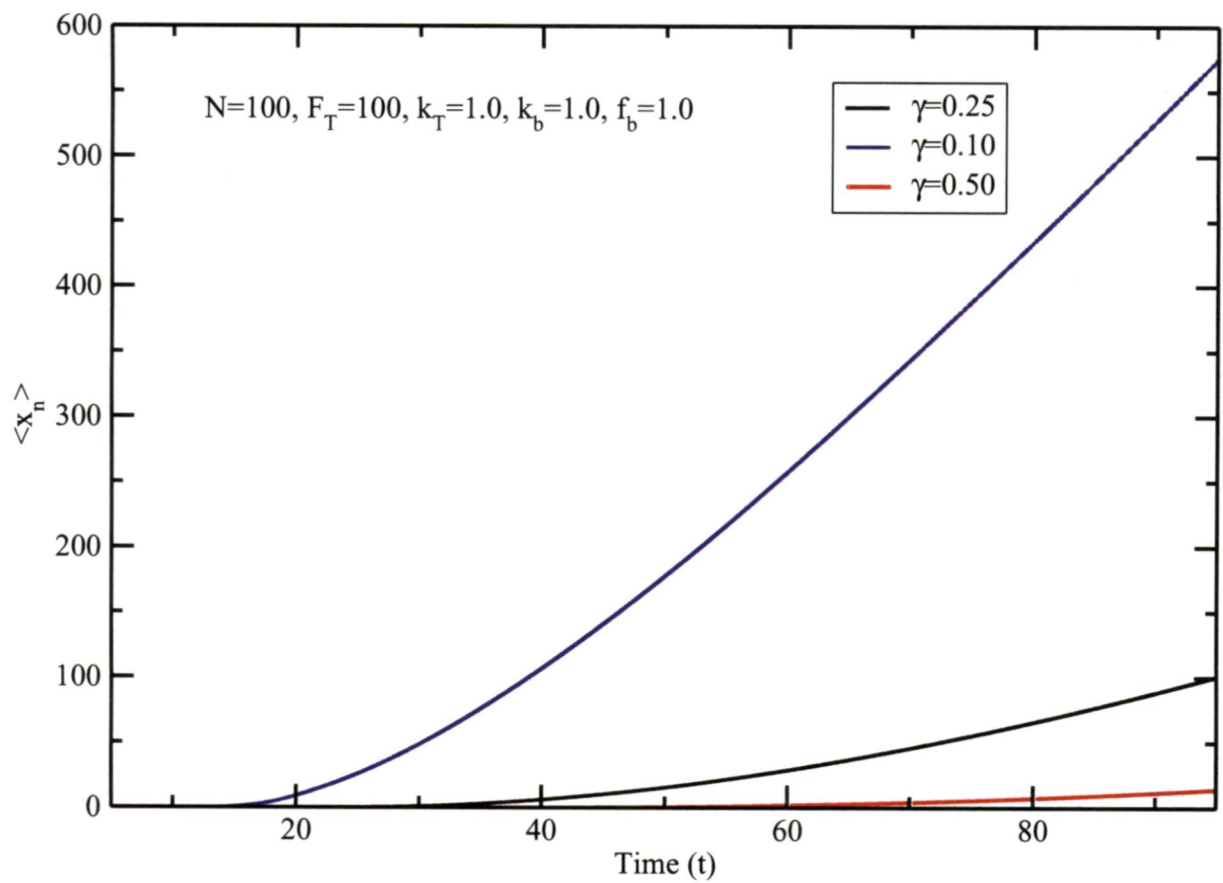


Figure 6: Average position of the 10th bead vs time  $t$  at different values of friction coefficient  $\gamma$  for polymer size  $N = 100$ . The other fixed parameters are as shown in the inset.  $x_n$  is averaged over 100 runs. The parameters are chosen such that maximum sequential rupture is observed

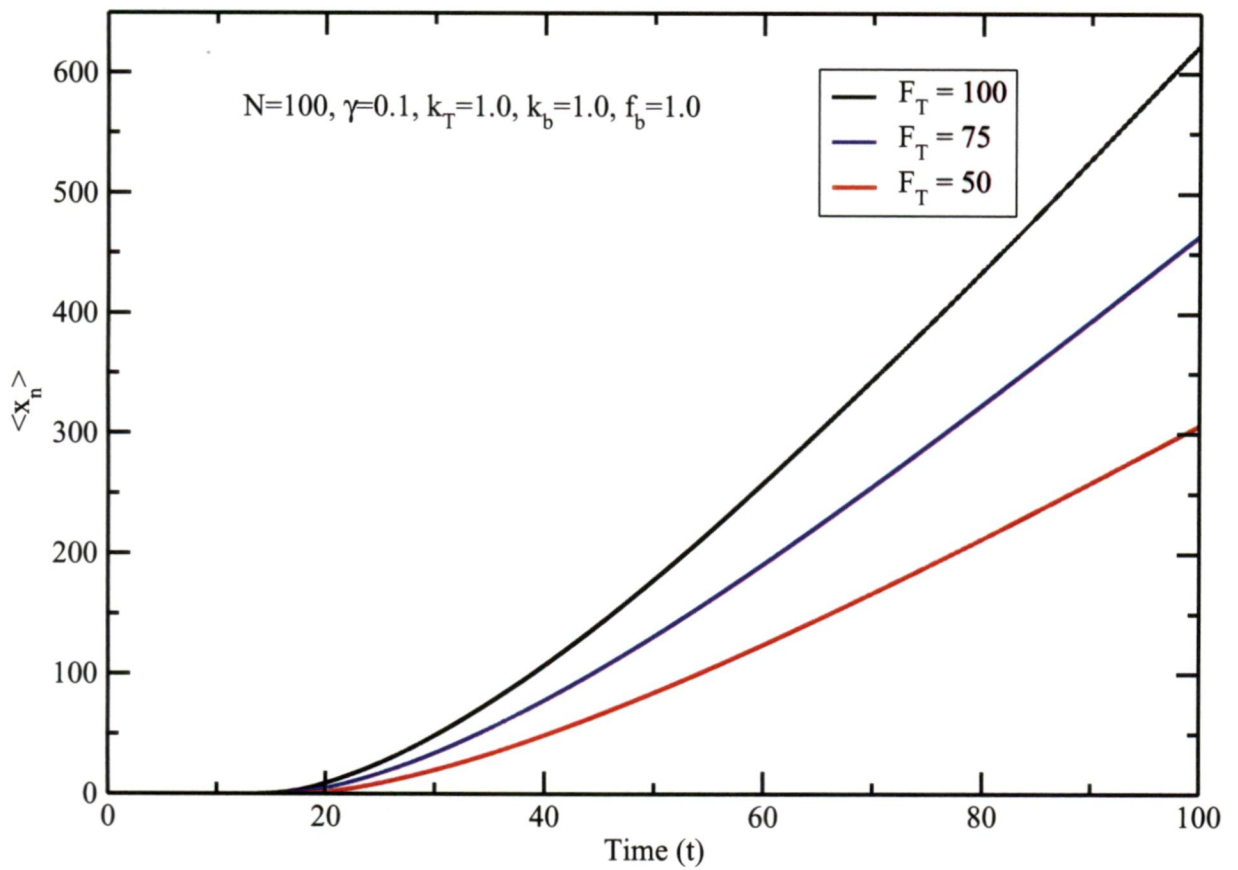


Figure 7: Average position of the 10th bead vs time  $t$  at different values of applied force  $F_T$  for polymer size  $N = 100$ . The other fixed parameters are as shown in the inset.  $x_n$  is averaged over 100 runs. The parameters are chosen such that maximum sequential rupture is observed

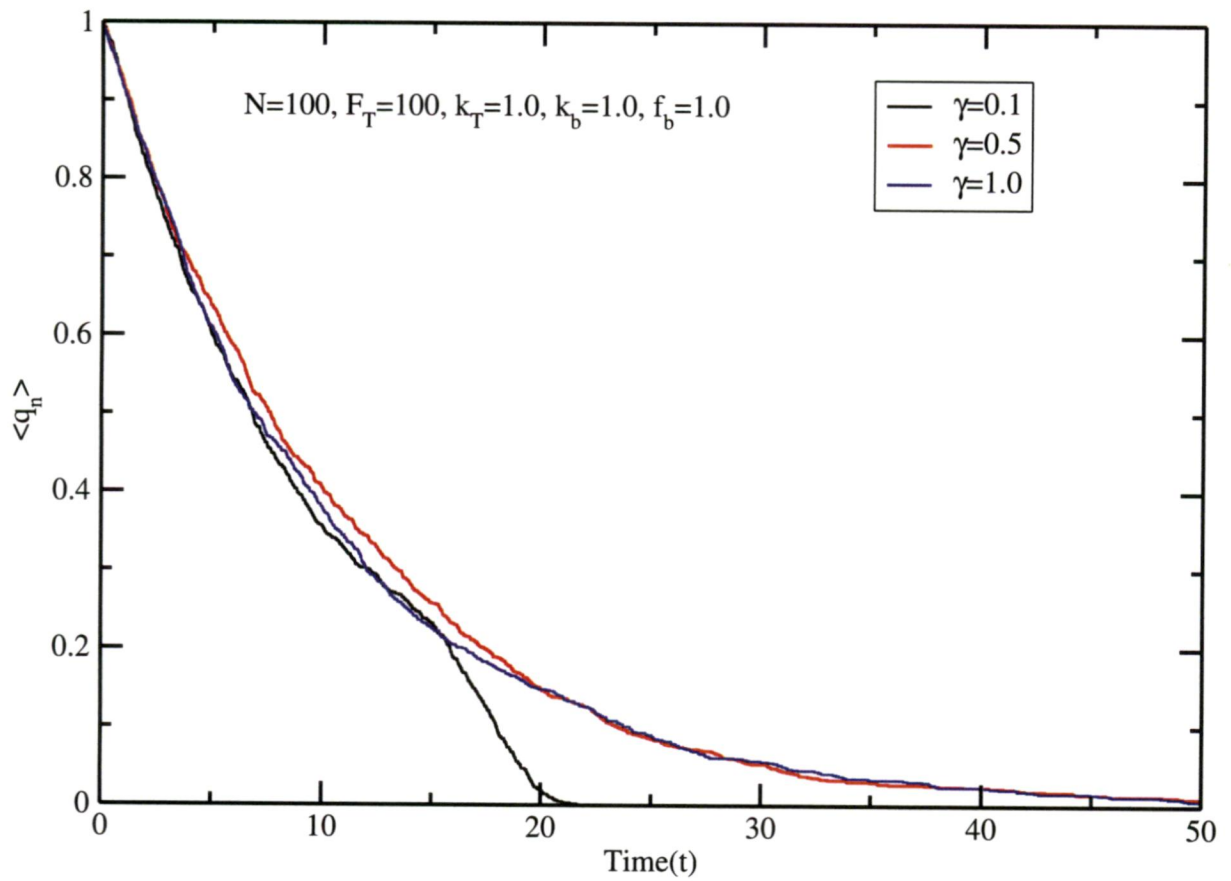


Figure 8: Average bond variable of the 10th bead vs time  $t$  at different values of friction coefficient  $\gamma$  for polymer size  $N = 100$ . The other fixed parameters are as shown in the inset.  $q_n$  is averaged over 1000 runs. The parameters are chosen such that maximum sequential rupture is observed

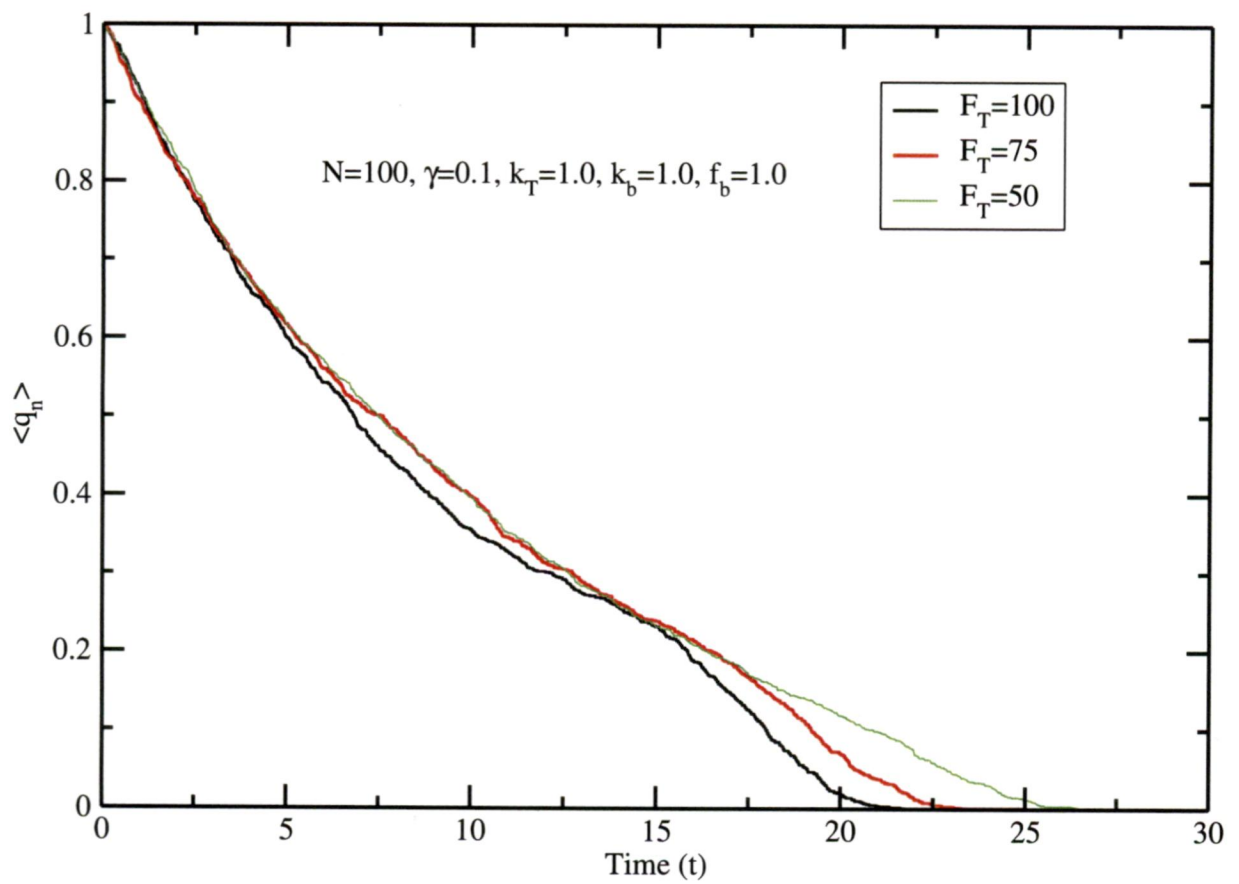


Figure 9: Average bond variable of the 10th bead vs time  $t$  at different values of applied force  $F_T$  for polymer size  $N = 100$ . The other fixed parameters are as shown in the inset.  $q_n$  is averaged over 1000 runs. The parameters are chosen such that maximum sequential rupture is observed

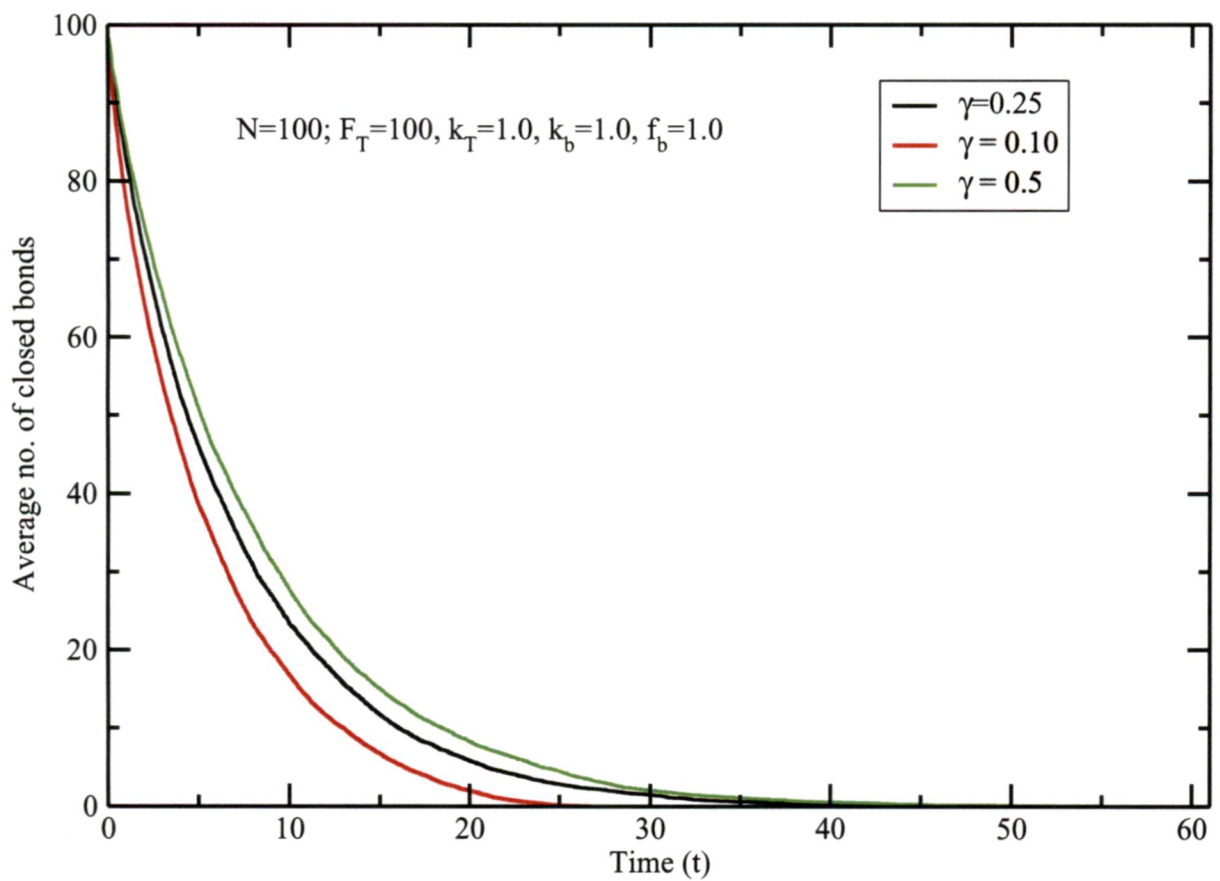


Figure 10: Total average number of closed bonds vs time  $t$  at different values of friction coefficient  $\gamma$  for polymer size  $N = 100$ . The other fixed parameters are as shown in the inset. This quantity is averaged over 100 runs. The parameters are chosen such that maximum sequential rupture is observed

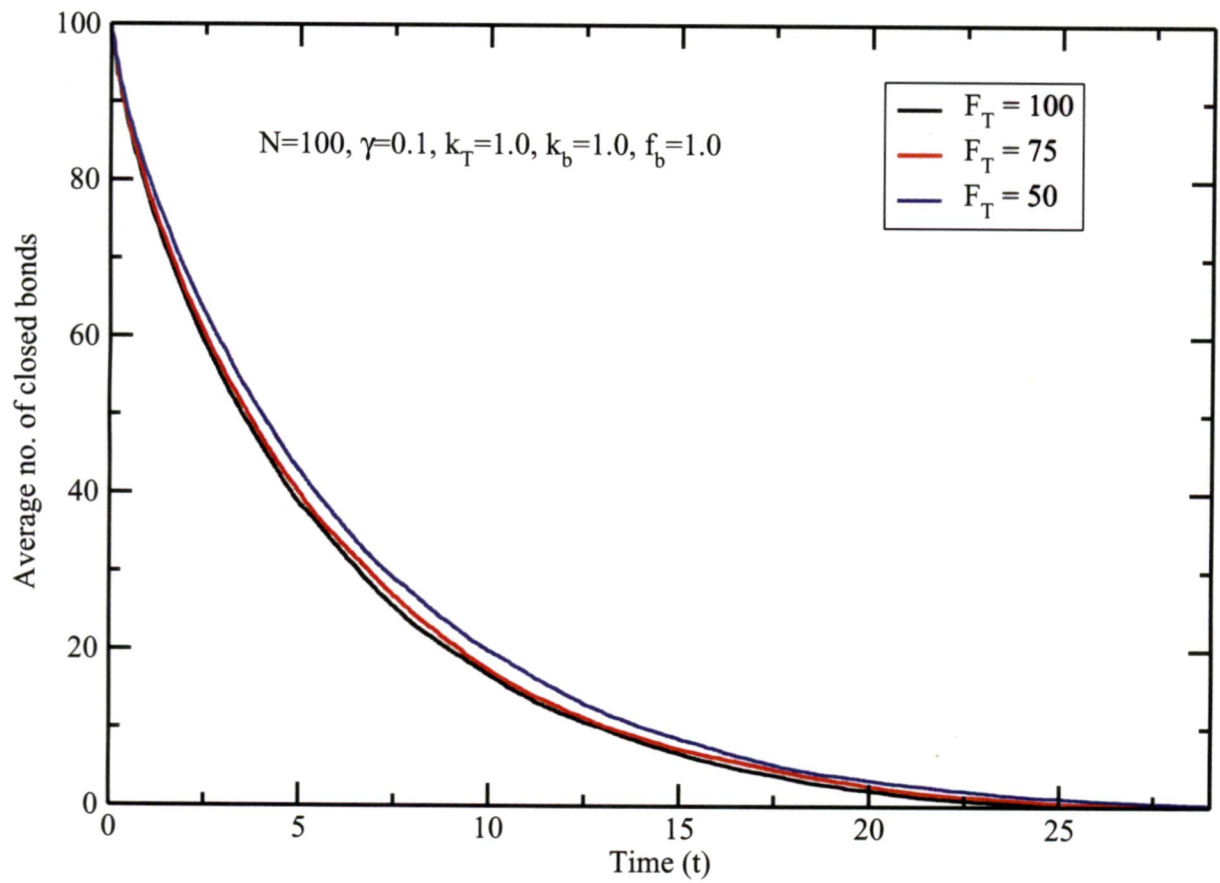


Figure 11: Total average number of closed bonds vs time  $t$  at different values of applied force  $F_T$  for polymer size  $N = 100$ . The other fixed parameters are as shown in the inset. This quantity is averaged over 100 runs. The parameters are chosen such that maximum sequential rupture is observed