Chapter 6

Beyond Transition State Theory:
Rate of Separation of the Broken Ends

6.1 Introduction

In the third chapter we have seen that the rates calculated using quantum transition state theory do not agree with the simulation results of Oliveira and Taylor [46]. We incorporated damping into the system in the previous chapter by introducing the idea that each unit of the polymer is connected to a large number of harmonic oscillators. Though we found that the rate is decreased, the agreement with the simulations is still poor.

In this chapter we look more closely at the actual dynamics taking place during the breaking process. 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 $\frac{\Omega}{4\pi \sqrt{|p_0|}}$ (see the Eq. (3.66)). The time of crossing the barrier is $t_{\text{cross}} = 1/\left(\frac{\Omega}{4\pi \sqrt{|p_0|}}\right)$. However, even if crossing (i.e. the bond is broken) has occurred, 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.

### 6.2 Connection with Brownian Particle

The classical Hamiltonian describing the motion is:

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

(6.1)

In the above, $\alpha$ is the slope of the potential energy curve, in the region where the potential
is linear in distance of separation (i.e. linear in $(b + \xi_n - \xi_{n-1})$). 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 $(n, n+1, n+2, \ldots)$ as $(0, 1, 2\ldots)$, and
taking the chain to be very long ($N \to \infty$), we can write the Hamiltonian as

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

(6.2)

The problem now is to calculate the time that it takes $\xi_0$ to exceed the value $\xi_c$ 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
The Hamiltonian is

\[ H_{\text{broken}} = \frac{1}{2} \rho \int_0^\infty dx \xi_t(x,t)^2 + \frac{1}{2} T \int_0^\infty dx \xi_x(x,t)^2 - \alpha \xi(0,t). \]  

(6.3)

In the above, subscripts \( t \) and \( x \) indicate partial differentiation with respect to these variables, \( \rho \) is the density of the chain per unit length (\( = m/b_+ \), \( b_+ \) being the length of a stretched bond, at its equilibrium position) and \( T = mb_+\omega^2_+ \) is the tension in the chain.

The speed of sound in the chain is given by \( c = \sqrt{T/\rho} \). 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 the Eq. (6.3) 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 forced wave equation

\[ \rho \xi_{tt}(x,t) = T \xi_{xx}(x,t) + \alpha \delta(x). \]  

(6.4)

To solve the above equation, we use transform techniques. We first define the Fourier cosine transform of \( \xi(x,t) \) by

\[ \tilde{\xi}(w,t) = \int_0^\infty dx \xi(x,t) \cos(wx). \]  

(6.5)

We take the Fourier cosine transform of equation (6.4) to get

\[ \rho \tilde{\xi}_{tt}(w,t) + T w^2 \tilde{\xi}(w,t) = \alpha - T \xi_x(0,t). \]  

(6.6)

Once the chain is broken, the end of the chain is not under strain and hence we put \( \left( \frac{\partial \xi(x,t)}{\partial x} \right)_{x=0} = 0 \). Now we introduce the Laplace transform of \( \tilde{\xi}(w,t) \) by

\[ \Xi(w,s) = \int_0^\infty dt \tilde{\xi}(w,t)e^{-st}. \]  

(6.7)
This obeys the equation

\[
\left( \rho s^2 + Tw^2 \right) \Xi(w, s) = \frac{\alpha}{s} + \rho \xi_t(w, 0) + \rho s \xi(w, 0),
\]

where

\[
\xi_t(w, 0) = \int_0^\infty dx \xi(x, 0) \cos(wx).
\]

Solving for \(\Xi(w, s)\)

\[
\Xi(w, s) = \frac{1}{\left(\rho s^2 + Tw^2\right)} \left( \frac{\alpha}{s} + \rho \xi_t(w, 0) + s \rho \xi(w, 0) \right).
\]

Taking the inverse transforms leads to

\[
\xi(x, t) = \mathcal{L}^{-1} \left[ \frac{2}{\pi} \int_0^\infty dw \cos(wx) \frac{1}{\left(\rho s^2 + Tw^2\right)} \left( \frac{\alpha}{s} + \rho \xi_t(w, 0) + s \rho \xi(w, 0) \right) \right]
\]

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

\[
\xi(0, t) = \frac{\alpha}{\sqrt{T \rho}} t + \zeta(t)
\]

with

\[
\zeta(t) = \zeta_1(t) + \zeta_2(t).
\]

Here

\[
\zeta_1(t) = \frac{2}{\pi} \int_0^\infty dw \xi(w, 0) \mathcal{L}^{-1} \frac{\rho s}{\left(\rho s^2 + Tw^2\right)}
\]

\[
= \frac{2}{\pi} \int_0^\infty dw \xi(w, 0) \cos(\omega t).
\]

Thus

\[
\zeta_1(t) = \xi(x, 0)_{x=ct}
\]

(6.13)
Chapter 6. Beyond Transition State Theory: Rate of Separation of the Broken Ends

97

and

\[ \zeta(t) = \frac{2}{\pi} \int_0^\infty dw \xi_t(w, 0) \mathcal{L}^{-1} \left( \frac{\rho}{\rho s^2 + T w^2} \right) = \frac{2}{\pi} \int_0^\infty dw \xi_t(w, 0) \frac{\sin(c w t)}{c w}. \tag{6.14} \]

The equation (6.11) shows that the broken end of the chain undergoes translational motion with a uniform velocity equal to \( -\frac{\sigma}{\sqrt{T_p}} \). In addition, it undergoes diffusive motion, due to thermal fluctuations which is represented by the term \( \zeta(t) \). In the appendix, we calculate the correlation function for this and show that

\[ \langle \zeta(t) \zeta(t_1) \rangle = \frac{2k_B T}{\rho c} \min(t, t_1). \tag{6.15} \]

The above correlation function is just that for Brownian motion, with a diffusion coefficient \( D = \frac{k_B T}{\rho c} \). 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 \( D \).

6.3 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 started at \( \xi = 0 \) and is drifting in the positive direction with a velocity \( v \) towards the point \( \xi_c (>0) \) and it is also undergoing 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 \( \xi \) at the time \( t \), given that it was at \( \xi = 0 \) at the time \( t = 0 \). \( P(\xi, t) \) obeys the diffusion equation

\[ P_t(\xi, t) = D P_{\xi \xi}(\xi, t) - v P_\xi(\xi, t). \tag{6.16} \]
Chapter 6. Beyond Transition State Theory: Rate of Separation of the Broken Ends

This has to be solved subject to the condition that \( P(\xi_0, 0) = 0 \). Then, one has to calculate the survival probability

\[
P_{\text{surv}}(t) = \int_{-\infty}^{\xi} d\xi P(\xi, t)
\]

(6.17)

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

\[
\langle t \rangle = \int_0^\infty dt P_{\text{surv}}(t).
\]

(6.18)

To solve the equation (6.16) we use Laplace transform techniques. We first define \( \overline{P}(\xi, s) = \int_0^\infty dt P(\xi, t) e^{-st} \). It obeys the differential equation

\[
s\overline{P}(\xi, s) - D \overline{P}_{xx}(\xi, s) + v \overline{P}_\xi(\xi, s) = \delta(\xi).
\]

(6.19)

This equation is to be solved, subject to the condition that \( \overline{P}(\xi_0, s) = 0 \). We give the details of the solution in the appendix. The solution is found to be

\[
\overline{P}(\xi, s) = \frac{e^{\frac{v(\xi-\xi_0)\sqrt{s^2+4Ds}}{2D}} - e^{\frac{v(\xi-\xi_0)\sqrt{s^2+4Ds}}{-2D}}}{\sqrt{s^2+4Ds}}.
\]

(6.20)

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

\[
\overline{P}(s) = \int_{-\infty}^{+\infty} d\xi \overline{P}(\xi, s) = \frac{1}{s} \left[ 1 - e^{\frac{v\xi_0 - \xi_0\sqrt{s^2+4Ds}}{2D}} \right].
\]

(6.21)

The average survival time is then

\[
\langle t \rangle = \int_0^\infty P(t) dt
\]

\[
= \lim_{s \to 0} \int_0^\infty e^{-st} P(t) dt = \lim_{s \to 0} \overline{P}(s) = \xi_0 / v.
\]

In the last step we have used the L’Hospital’s rule. Interestingly, this is just the time that one would have estimated neglecting the diffusive motion of the chain end [165]. Now,
Chapter 6. Beyond Transition State Theory: Rate of Separation of the Broken Ends

Taking $\xi_e = d_e/2$ and using $v = \frac{a}{\sqrt{f}}$, we find the average passage time of the two ends, over the distance $d_e$ to be

$$\langle t \rangle = d_e \rho c / (2\alpha). \quad (6.22)$$

Now one has the problem of choosing the value of $d_e$. The simplest estimate that one can make is that the ends should be separated by a distance equal to the stable bond length. Let $b_e$ 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. 6.1). We take the potential between $b_e$ and $b_-$ to be linear, neglecting the curved portion near the top of the barrier. Let $l = b_e - b_-$. Then, the slope $\alpha$ of the potential is given by $\alpha = \Delta E / l$, which leads to the crossing time as: $\langle t \rangle = l d_e \rho c / (2\Delta E)$. Using this expression, we have estimated the time of crossing the distance $d_e$ for the Lennard Jones model. This is compared with the time of crossing the barrier ($= 1$/prefactor of the rate in the classical equation) in Fig.6.2. The results 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.6.3. On comparing the results with those of the simulation, we find that the agreement is still poor. The modification in the rate is small and is still about 100 times the result of the simulation! What could be the reason for this?

6.4 First Passage with Friction

While our calculations till now have considered the vibrational motion of the atoms of the chain in isolation, Oliveira and Taylor has an external friction and fluctuating force in their simulations (see their Eq. 3) [46]. So perhaps it is not surprising that our results are not in agreement with the simulation. We now make the same kind of analysis for the chain in presence of friction. Due to the presence of friction, the problem can no longer be described by a Hamiltonian. But we write the continuum version of their equations of
Figure 6.1: 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.
Figure 6.2: The figure compares the time required for crossing the barrier ($t_{\text{cross}}$) and the time required for the broken ends to separate to the critical distance. The distance is in units of $a_{\text{LJ}}$ and time in units of $\tau_0$. 
motion, which is:

$$\rho \xi_{tt} (x, t) + \rho \gamma \xi_t (x, t) = T \xi_{xx} (x, t) + \alpha \delta (x) + f(x, t),$$ \hspace{1cm} (6.23)

\(\gamma\) is the friction coefficient, and \(f(x, t)\) is the fluctuating force, having the mean zero and correlation

$$\langle f(x_1, t_1) f(x_2, t_2) \rangle = 2 \rho \gamma k_B T \delta (x_1 - x_2) \delta (t_1 - t_2).$$ \hspace{1cm} (6.24)

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

$$\xi (x, t) = \mathcal{L}^{-1} \left[ \frac{2}{\pi} \int_0^\infty dw \cos (wx) \frac{1}{(\rho s^2 + \rho \gamma s + Tw^2)} \left( \frac{\alpha}{s} + \rho \xi_t (w, 0) + s \rho \xi (w, 0) + \Phi (w, s) \right) \right].$$ \hspace{1cm} (6.25)

In the above,

$$\Phi (w, s) = \int_0^\infty dt \int_0^\infty dx \cos (wx) f(x, t) e^{-st}.$$ \hspace{1cm} (6.26)

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

$$\xi (0, t) = \mathcal{L}^{-1} \left[ \frac{2}{\pi} \int_0^\infty dw \cos (wx) \frac{1}{(\rho s^2 + \rho \gamma s + Tw^2)} \left( \frac{\alpha}{s} + \rho \xi_t (w, 0) + s \rho \xi (w, 0) - \rho \gamma \xi_t (w, 0) + \Phi (w, s) \right) \right].$$ \hspace{1cm} (6.27)

In the above, all terms other than the first term on the right hand side are random, arising from thermal fluctuations. So on calculating the averages of both the sides, we get

$$\langle \xi (0, t) \rangle = \mathcal{L}^{-1} \left[ \frac{2}{\pi} \int_0^\infty dw \frac{\alpha}{s (\rho s^2 + \rho \gamma s + Tw^2)} \right] = \mathcal{L}^{-1} \left[ \frac{\alpha}{\rho c s \sqrt{s^2 + \gamma s}} \right] = \frac{\alpha}{\rho c} t e^{-\gamma t/2} \left( I_0 (\gamma t/2) + I_1 (\gamma t/2) \right).$$ \hspace{1cm} (6.28)

In the above, \(I_n (\gamma t/2)\) denotes modified Bessel function of order \(n\) [166]. As 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 travelling a distance $d_2$ 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 analogue of the diffusion equation (6.16) 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 equation (6.16), 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 $d_e$ in the presence of friction. In the small force regime the calculated time is two-three orders greater than the time taken for crossing the barrier. Applying this correction we have calculated the lifetimes for a polymer under LJ potential. In Fig. 6.3 we compare the values of the logarithms of lifetimes for the three cases- (1) without considering the motion of the broken ends (2) considering the motion of the broken ends but without friction and (3) with friction. Our calculations which takes account of friction differs only one order of magnitude from the simulations of Oliveira and Taylor [46].

6.5 Conclusion

In this chapter, we analysed the motion of the broken ends after the breaking has occurred. The two ends have to be separated by a minimum distance, within which it is possible for the two broken ends to come back and heal the bond. We calculated the time required for the two broken ends to separate from one another by this critical distance. In the absence of friction, for the range of parameters considered in the simulation, this time is of the same order of magnitude as that is required for crossing the barrier. However, in the presence of friction, the calculated time is two to three orders of magnitude greater than the time taken for crossing the barrier, thus making our results in agreement with the simulations within an order of magnitude.
Figure 6.3: Plot of logarithm of the lifetime against the strain for the Lennard Jones potential for the three cases: transition state theory (solid curve), motion of broken ends without friction (dotted curve) and with friction (dashed curve). Energy is given in units of $\epsilon$, distance in units of $a_{LJ}$, temperature $T$ in units of $\epsilon/k_B$ and time in units of $\tau_0$. Here $T = 0.05$ and $\gamma = 0.25 \omega_0$. The figure shows that the damped motion of the broken ends can increase the lifetime by two orders of magnitude.
Chapter 7

Summary and Conclusions

In this chapter we summarise the entire work that had been done in this thesis.

7.1 Expression for the Rate Using QTST

We considered a single polymer molecule which is imagined to be a chain of $N$ units of mass $m$ joined together by bonds obeying the Morse potential. It has one end fixed and a force $F$ is acting on the other end. We use multidimensional quantum transition state theory (QTST) to derive expressions for the rate of breaking of the polymer. The force modifies the potential of each bond so that for any nonzero value for the force $F$, the potential has two extrema, one being a minimum and the other a maximum. If a bond gets a certain activation energy, it can go over the barrier resulting in the breaking of the bond and consequently of the polymer. The activation energy can be easily calculated as the difference in the potential of the two extrema. As the simplest approach, we consider the vibrational motion of just one bond that may break and neglect coupling to the rest of the system. If coupling is included, the partition function will involve $N$ frequency factors. But we need to consider only the ratio of the partition functions at the two extrema. The unstable frequency in the transition state and the ratio of the square of the frequencies of the equilibrium and transition states can be found using partition technique. The rate expression is derived also for the special case in which there is a foreign atom.
along the main chain of the polymer. The calculations are repeated for a polymer whose units interact by Lennard–Jones potential. On comparing our results with the simulation results of Oliveira and Taylor, we see that our results are larger by orders of magnitude.

7.2 Polymer Molecule in the Presence of a Bath of Harmonic Oscillators

Oliveira and Taylor [46] have included friction in their starting equation for the simulations and so and we consider our system to be present in a bath of harmonic oscillators which can interact linearly with every unit. To be in agreement with Oliveira and Taylor [46] we take the friction to be Ohmic and also neglect quantum effects. We do the normal mode analysis for this and obtain an expression for the rate. But although the rate is found to be decreased, the decrease is only of one order of magnitude, and still the final result is not in agreement with the simulations.

7.3 Rate of Separation of the Broken Ends

To understand this discrepancy, we go beyond TST. We assume that even if the crossing over the barrier has occurred, it is not necessary that the reaction should occur. After the crossing, the two ends have to separate by a minimum distance, within which it is possible for the two broken ends to come back and heal the bond. We calculate the time required for the two broken ends to separate from one another through this critical distance. For this we assume that after the breaking, the potential energy decrease is linearly dependent on the separation of the two ends. Using a continuum approximation we write the equation of motion for the system in the form of a forced wave equation. The solution of the wave equation shows that the broken end of the chain undergoes translational motion with a uniform velocity. In addition, it undergoes diffusive motion due to thermal fluctuations. Calculation of correlation function shows that the motion of the end of the chain is similar to that of a Brownian particle. We calculate the average
time that such a particle spends within the critical distance before going out for the first
time from this region. This is compared with the time of crossing the barrier. The results
show that in the small force regime, the first passage rate is considerably lower than that
of the crossing rate and hence the rate determining step. The actual frequency may be
obtained by adding the two times and then taking the inverse. On comparing the results
with those of the simulations, we find that the agreement is still poor.

7.4 Separation in the Presence of Friction

We attribute this discrepancy to the fact that as the broken ends are moving, they suffer
damping due to the friction of the surrounding medium. We analyse the motion of the
broken ends in presence of friction by solving the continuum version of the equations used
by Oliveira and Taylor. We obtain an expression for the mean position of the broken
end as a function of time from which we can calculate the time needed for the end to
travel the critical distance. It is seen that in the small force regime the calculated time
is two-three orders greater than the time taken for crossing the barrier thus making our
results in agreement with the simulations within an order of magnitude.

7.5 Conclusions

The main findings of our work are summarised below.

1. The life time of the bond is somewhat sensitive to the potential that is used in the
calculations – using Lennard-Jones or the Morse potential lead to rather different
answers.

2. For a given potential, 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 more than by one order of magnitude.
3. For the breaking of polyethylene, quantum effects are important only for temperatures below 150 K.

4. The lifetime strongly depends on the strain and as the strain varies over a narrow range, the lifetime varies rapidly from $10^5$ seconds to $10^{-5}$ seconds.

5. If we change one unit of the polymer by a foreign atom, say by one sulphur atom, in the main chain itself, by a weaker bond, the rate is found to increase by orders of magnitude.

6. Introducing friction into Multidimensional transition state theory can decrease the rate but by only one order of magnitude.

7. 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.