DYNAMICS OF A GAUSSIAN CHAIN IN THE GAS PHASE AND IN A CONFINED GEOMETRY

By

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I dedicate this to my parents.
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This dissertation involves a study of the dynamics of a Gaussian chain in different environments.

In the first part, the dynamics of polymers in the gas phase are studied at the theta temperature. Since the mean free path in a gas is large, the collisions of the gas particles with the monomers are ballistic. This ballistic nature of collision can be combined with the probability distribution of a Gaussian chain to determine the correlation of random forces, and this correlation can be exploited to evaluate the friction constant $\zeta_p$.

The second part considers the internal friction of a Gaussian chain placed in a vacuum. The dynamics of a single chain can be described by the Langevin equation, where the random force terms arise from the random collisions of monomers with each other. To find the moment of these random forces, a Gaussian distribution of chain conformation is used. We show that this same mechanism of internal friction is also applicable in solutions.

In the third part, the dynamics of polymer melts near a corrugated boundary are examined. Since the volume interaction is screened in melts, polymers can be treated as Gaussian chains. When a polymer melt flows near a smooth surface, there may exist a nonzero slip velocity. The velocity field for a perturbed boundary is derived using a slip boundary condition. As a chain moves near this boundary, it experiences an oscillatory
shear and the frequency of the strain rate depends on the slip velocity. The dissipation rates for different slip velocities are evaluated.
CHAPTER 1
INTRODUCTION TO POLYMERS IN GASES

Recent ionization techniques such as MALDI (Matrix Assisted Laser Desorption/Ionization) [1–3] or electrospray ionization [4] have made it possible to have large polymers in gases or in a vacuum. Although much is known about how polymers behave in solutions or in melts, there is little information about polymers in gases. Gas phase studies of polymers are very interesting from a statistical physics point of view, and these studies may also contribute valuable knowledge to the biological and materials sciences.

The discovery of MALDI was very remarkable. Polymers are macromolecules and it is very difficult to remove them from solution without fragmenting. However, if polymers can be transferred to the gas phase, mass spectrometry can be used to characterize polymeric materials quickly and accurately. Therefore, researchers have sought a soft ionization technique for many years. MALDI is basically a soft ionization technique, in which a ultraviolet absorbing matrix is used. The polymer is dissolved in a solvent, and then the matrix is added. This matrix is usually a compound like trans-cinnamic acid or 2,5-dihydroxybenzoic acid, which contains an aromatic ring. The choice of matrix depends on the polymer being investigated. The purpose of the matrix is to absorb the ultraviolet light. The mixture is placed on the tip of a sample holder in a air-tight chamber, which is then evacuated. The solvent evaporates and the polymers are dispersed in the matrix. When irradiated by a laser pulse, the energy is absorbed by the matrix molecules which are vaporized, carrying intact polymers with them into the gas phase.

Studies of polymers in the gas phase have importance both in biology and in materials science. Many fundamental properties of biomolecules can be determined in a gas phase structure. To do its task, a biomolecule must have the correct three dimensional conformation. Solvent plays a very important role in determining the conformation and, gas phase studies are helpful in the study of solvent effects. For
example, it is possible to observe hydration effects by adding water molecules one at a time [5]. Gas phase experiments are also used to investigate the mechanism of peptide folding [6] and to determine the relative strengths of intramolecular electrostatic interactions and solute-solvent intermolecular interactions. Protein misfolding problems [7] or comparison to theoretical predictions of DNA structure can be studied in the gas phase. Gas phase studies are important for synthetic polymers as well. X-ray crystallography or NMR provide information about polymer conformations, but synthetic polymers usually have distribution of sizes and these methods will give average conformational data. For information on individual polymer molecules and also for examining some subtle structural features, gas phase studies are much more effective.

In most of the gas phase experiments, the drift time of the ionized polymer is measured. This ion mobility measurement gives collision cross-sections and information about conformations are extracted from this [8]. But for large macromolecules their internal dynamics should be considered, and this has been neglected in previous works. Also the dynamics of macromolecules in gases may be useful to observe subtle features of many reaction mechanisms that are not possible in solutions.

Chapter 1 discusses some statistical properties of polymer chains, in particular the conformations of polymers in gases, explicitly showing the conditions on which the calculations of gas phase dynamics are based. Since gas phase dynamics have not been considered previously, we will examine all terms carefully.

1.1 Statistical distribution of the end-to-end vector of an ideal chain

This section considers some statistical properties of a flexible polymer chain [9]. Let us consider a conformation of an ideal chain as shown in Figure 1-1.

We will deal with the quantity $P(X_1, X_2, ..., X_N)$, which gives the probability of the particular conformation $X_1, X_2, ..., X_{m-1}, X_m, ..., X_N$. For an ideal chain, the position of any bead $m$ depends only on the position of the previous bead $m - 1$. If $g(X_{m-1}, X_m)$ is the probability of finding the bead $m$ at $X_m$ when the bead $m - 1$ is at $X_{m-1}$, then $g$ must
Figure 1-1. Conformation of an ideal polymer chain. Here $\mathbf{X}_m$ is the position vector of bead $m$. For an ideal chain, position of any bead depends only on the position of the previous bead.

satisfy the normalization condition:

$$\int g(\mathbf{x}_{m-1}, \mathbf{x}_m) d^3x_m = 1, \quad (1-1)$$

and the probability takes the form:

$$P(\mathbf{X}_1, \mathbf{X}_2, ..., \mathbf{X}_N) = g(\mathbf{X}_1, \mathbf{X}_2) ... g(\mathbf{X}_{m-1}, \mathbf{X}_m) ... g(\mathbf{X}_{N-1}, \mathbf{X}_N). \quad (1-2)$$

For a freely jointed chain, the value of $g$ depends only on the distance between the points:

$$g(\mathbf{X}_{m-1}, \mathbf{X}_m) = g(|\mathbf{X}_{m-1} - \mathbf{X}_m|). \quad (1-3)$$

If $b$ is the Kuhn segment length, then

$$g(\mathbf{X}_{m-1}, \mathbf{X}_m) = \frac{1}{4\pi b^2} \delta(|\mathbf{X}_{m-1} - \mathbf{X}_m| - b). \quad (1-4)$$
As we know now the distribution of $g$, the probability distribution of the end-to-end vector $R$ for $N$ segments is given by

$$P_N(R) = \int P(X_1, X_2, \ldots, X_N = X_1 + R) d^3 X_2 \ldots d^3 X_{N-1} \quad (1-5)$$

$$= \int \delta \left( \sum_{i=1}^{N-1} y_i - R \right) \prod_{i=1}^{N-1} g(y_i) d^3 y_1 \ldots d^3 y_{N-1}, \quad (1-6)$$

where $y_i = X_{i+1} - X_i$.

The integral representation of the delta function:

$$\delta(y) = (2\pi)^{-3} \int \exp(-i \mathbf{k} \cdot \mathbf{y}) d^3 k. \quad (1-7)$$

Therefore, the distribution of the end-to-end vector is

$$P_N(R) = (2\pi)^{-3} \int \exp(-i \mathbf{k} \cdot R) \tilde{P}_N(k) d^3 k, \quad (1-8)$$

where $\tilde{P}_N(k) = g_k^N$ and $g_k = \int g(y) \exp(i \mathbf{k} \cdot \mathbf{y}) d^3 y$.

Considering Equation 1–1, it is clear that $g_k$ is one for $k = 0$ and drops to zero as $|k|$ grows. Therefore, the function $g_k^N$ has a very narrow peak if $N >> 1$. If the value of $g_k$ is substituted into Equation 1–8, a Gaussian distribution is obtained as the leading order term, with higher order terms giving corrections to this Gaussian distribution:

$$P_N(R) = \left( \frac{2\pi Nb^2}{3} \right)^{-\frac{3}{2}} \exp \left( -\frac{3R^2}{2Nb^2} \right) \left[ 1 - \frac{3}{20N} \left( 5 - \frac{10R^2}{Nb^2} + \frac{3R^4}{N^2b^4} \right) + \ldots \right]. \quad (1-9)$$

Corrections are calculated for the freely joined chain $g_k = \frac{\sin(kb)}{kb^3}$. If $R^2 \sim Nb^2$, the corrections are of the order of $\frac{1}{N}$ and can be neglected for $N >> 1$. If $R^2 >> Nb^2$, the corrections can be significant. In all subsequent calculations, we will use the Gaussian distribution:

$$P_N(R) = \left( \frac{2\pi Nb^2}{3} \right)^{-\frac{3}{2}} \exp \left( -\frac{3R^2}{2Nb^2} \right). \quad (1-10)$$

This work examines dynamics for chains near the theta temperature, i.e., $R^2 \sim Nb^2$, and it is also assumed the chains are very large, i.e., $N >> 1$. Both these conditions
ensure that the distribution of the ideal chain can be treated as Gaussian. Therefore, it is important to consider some properties of a Gaussian chain, as described in the following section.

### 1.2 Free energy of a Gaussian chain

The distribution of the end-to-end vector \( P_N(R) \), which is related to free energy [11], is known. \( P_N(R) \) can be defined as the ratio of number of conformations with end-to-end vector \( R \) to the total number of conformations with all possible end-to-end vectors:

\[
P_N(R) = \frac{W_N(R)}{\int W_N(R)d^3R}, \quad (1-11)
\]

where \( W_N(R) \) is the number of conformations of a chain with \( N \) monomers if the end-to-end vector is \( R \). This quantity is related to entropy by the Boltzmann constant \( k_B \):

\[
S = k_B \ln W_N(R). \quad (1-12)
\]

Therefore, from Equation 1–11

\[
\ln P_N(R) = \ln W_N(R) - \ln \int W_N(R)d^3R. \quad (1-13)
\]

Using Equation 1–12 we get

\[
S = -\frac{3k_B R^2}{2Nb^2} + H(N, b), \quad (1-14)
\]

where \( H \) is a function of \( N \) and \( b \) only, and is independent of \( R \).

The free energy of the chain at temperature \( T \) is

\[
F = U - TS. \quad (1-15)
\]

Since for an ideal chain there is no interaction between monomers, \( U = 0 \),

\[
F = -TS = - \frac{3k_B T}{2Nb^2} R^2 - TH. \quad (1-16)
\]
Therefore, for $R = 0$, $F$ is minimum, and the number of conformations would be maximum. As $R$ increases, the number of conformations decreases and the free energy increases. This dependence of $F$ on $R$ implies an entropic elasticity. To stretch a chain a distance $R$, we need to apply a force

$$f = \frac{\partial F}{\partial R} = \frac{3k_B T}{Nb^2} R. \tag{1–17}$$

This relation is similar to Hooke’s law, with spring constant equals to $\frac{3k_B T}{Nb^2}$. Thus, the spring constant increases as $T$ increases. Elasticity here is entropic in nature. At higher temperatures, the spring becomes more stiff. But Equation 1–17 is valid only for the Gaussian approximation, i.e., for $R << Nb$. If $R$ is comparable to $Nb$ (the maximum extension of the chain), nonlinearity is observed.

The previous derivation considers the conformations of an ideal chain. In reality, polymers are not ideal, and we need to consider thoroughly at what conditions this ideal chain approximation is valid.

1.3 Considerations for a real chain

For an ideal chain, there is no interaction between two monomers that are distant along the chain but placed near to each other in space. For a real chain, such monomers do interact by Van der Waals forces, as shown in Figure 1-2. There are also interactions between monomers and solvent particles if the polymer is in solution. Usually the van der Waals potential that we found in the literature shows the effective potential for the presence of solvent molecules. Later in this section we will see how these potentials are changed when polymers are in the gas phase or in a vacuum. First, the effect of volume interactions will be discussed.

To derive the thermodynamic quantities of a system of interacting monomers, we will consider a model of disconnected links. In this model, monomers act merely as a system of beads with the interaction potential $u(r)$. The distribution for any configuration
Figure 1-2. Van der Waals potential between monomers. In solution, solvent mediated interaction gives this potential. In gases, the number of gas particles is very small within the pervaded volume of a polymer. So the potential results from direct interaction between monomers.

\[ \Gamma \text{ is} \]

\[ P(\Gamma) = \exp \left( -\frac{E(\Gamma)}{k_B T} \right) \prod g_j, \tag{1-18} \]

where \( g_j \) are the bonds, and \( E(\Gamma) \) is the interaction for the Gaussian model, i.e., \( E(\Gamma) = \sum u(\mathbf{x}_i - \mathbf{x}_j) \).

For a Gaussian coil the density is very low (Equation 1–10). In low density systems, thermodynamic functions can be expanded into a power series of monomer number density \( n \). The free energy can be written in terms of virial coefficients:

\[ F = F_{\text{ideal}} + F_{\text{int}}, \tag{1-19} \]

\[ F_{\text{int}} = N k_B T (nB + n^2 C + \ldots), \tag{1-20} \]

where \( B \) and \( C \) are the virial coefficients. The contribution from binary collisions is hidden in \( B \). Similarly, \( C \) relates to triple collisions. At lower concentrations, the higher order collision terms become negligible. If we consider very large chain, i.e., \( N \gg 1 \),
the binary collision term $B$ should be sufficient to determine the free energy in most cases.

Two things can happen if there are volume interactions. Since the volume interactions have both attractive and repulsive parts, a chain can either swell or compress. The physics of volume interactions was first considered theoretically by P. J. Flory [10]. The effect of volume interaction can be quantified by a term $\alpha$ which is the ratio of the mean square of end-to-end vector of a real chain to an ideal chain:

$$\alpha^2 = \frac{R^2}{R_0^2}. \quad (1-21)$$

For $\alpha > 1$, the coil is swollen and for $\alpha < 1$, the coil is compressed. The free energy of a real chain would be a function of this quantity $\alpha$:

$$F(\alpha) = F_{el}(\alpha) + F_{int}(\alpha), \quad (1-22)$$

in which $F_{el}$ is the free energy related to entropy and $F_{int}$ is related to the volume interaction.

Use of a Gaussian distribution to determine the entropy change gives [9]

$$\frac{F_{el}}{k_B T} \sim \frac{R^2}{N b^2} \sim \alpha^2 \quad \text{for} \quad \alpha > 1, \quad (1-23)$$

$$\frac{F_{el}}{k_B T} \sim \frac{N b^2}{R^2} \sim \alpha^{-2} \quad \text{for} \quad \alpha < 1. \quad (1-24)$$

Combination of these two equations gives

$$\frac{F_{el}}{k_B T} \sim \alpha^2 + \frac{1}{\alpha^2}. \quad (1-25)$$

If we consider the coil to be a cloud of links distributed uniformly within the volume $\sim R^3$, Equation 1–20 gives

$$\frac{F_{int}}{k_B T} \sim R^3 B \left( \frac{N}{R^3} \right)^2 + R^3 C \left( \frac{N}{R^3} \right)^3 + ... \sim \left( \frac{BN^{1/2}}{b^3} \right) \alpha^{-3} + \left( \frac{C}{b^6} \right) \alpha^{-6} + ... \quad (1-26)$$
The minimum of the total free energy will give the equilibrium value of $\alpha$:

$$\alpha^5 - \alpha = \left(\frac{BN^{\frac{1}{2}}}{b^3}\right) + \left(\frac{C}{b^5}\right) \alpha^{-3}. \tag{1–27}$$

Thus, $\alpha$ can be very large if $B > 0$ and $N \gg 1$, and for $\alpha \gg 1$, we can neglect the second term on both the left and right sides of Equation 1–27 to give

$$\alpha \sim \left(\frac{BN^{\frac{1}{2}}}{b^3}\right)^{\frac{5}{4}}. \tag{1–28}$$

Thus, $R \propto N^{\frac{5}{3}}$, and since $N^{\frac{5}{3}} \gg N^{\frac{1}{2}}$ for $N \gg 1$, the real chain would be much larger than the ideal chain. For a repulsive volume interaction, i.e., for $B > 0$, there would be significant swelling.

In the opposite limit $\alpha \ll 1$, which can be realized for $B < 0$ and $N \gg 1$. For this case, left side of Equation 1–27 can be neglected to give

$$\alpha \sim \left(-\frac{BN^{\frac{1}{2}}b^3}{C}\right)^{-\frac{1}{3}}. \tag{1–29}$$

Thus, the radius of the chain $R \propto N^{\frac{1}{3}}$, and since $N^{\frac{1}{3}} \ll N^{\frac{1}{2}}$ for $N \gg 1$, the size of the chain would be greatly reduced. Any attractive interaction, i.e., $B < 0$, would cause the chain to collapse.

The size of the real chain would be equal to the size of an ideal chain when $\alpha = 1$. From Equation 1–27, this is true when

$$B \sim -\left(\frac{C}{b^3}\right) N^{-\frac{1}{2}}. \tag{1–30}$$

$N^{-\frac{1}{2}} \ll 1$ for a long chain $N \gg 1$. Thus a real chain behaves as an ideal chain when $B$ goes to zero.

We will next consider details of the two body interaction between monomers. The probability of finding two monomers at a distance $r$ is proportional to the Boltzmann factor $\exp \left( -\frac{U(r)}{k_B T} \right)$. Since two monomers cannot occupy the same space, the probability
of finding two monomers at short distances is zero. In the Lennard-Jones potential, there is a negative energy region, and the probability of finding two monomers in this region is large. One way to provide a pictorial view of the two body interaction is to consider the Mayer f-function \[ 11 \], defined as

\[
 f(r) = \exp \left( -\frac{U(r)}{k_B T} \right) - 1. \tag{1-31}
\]

This corresponds to the difference between the Boltzmann factors for two monomers at a distance \( r \) and monomers at an infinite distance from each other. For small distances, the energy \( U(r) \) is large due to hard core repulsion, and the Mayer f-function is negative. For the attractive region, the Mayer f-function is positive as shown in Figure 1-3.

\[ f \]

\[ r \]

Figure 1-3. Mayer f-function. It shows the relative strength between the attractive and repulsive parts of the Lennard-Jones potential for a given temperature.

The second virial coefficient \( B \), also known as the excluded volume, is defined as

\[
 B = -\int f(r) d^3r = \int \left[ 1 - \exp \left( -\frac{U(r)}{k_B T} \right) \right] d^3r. \tag{1-32}
\]

For short distances, the Mayer f-function gives a positive contribution to the integration for the excluded volume, while for the attractive region, the contribution is negative. \( B \) is zero only when the positive contribution from the hard-core repulsion is canceled by the negative contribution from the attractive part.
If the temperature is varied, the contributions coming from different distances change, resulting in the dependence of excluded volume on temperature. For hard core repulsion $U(r) \gg k_B T$, and the Mayer f-function is given by

$$f(r) = \exp\left(-\frac{U(r)}{k_B T}\right) - 1 \approx -1 \text{ for } r < b.$$  \hspace{1cm} (1–33)

In the attractive region, the interaction energy is smaller than the thermal energy, and the exponential can be expanded to give

$$f(r) = \exp\left(-\frac{U(r)}{k_B T}\right) - 1 \approx -\frac{U(r)}{k_B T} \text{ for } r > b.$$  \hspace{1cm} (1–34)

The excluded volume is given by

$$B = -4\pi \int_0^\infty f(r)r^2\,dr \hspace{1cm} (1–35)$$
$$= 4\pi \int_0^b r^2\,dr + \frac{4\pi}{k_B T} \int_b^\infty U(r)r^2\,dr \hspace{1cm} (1–36)$$
$$= \frac{4\pi}{3} b^3 \left(1 - \frac{\theta}{T}\right), \hspace{1cm} (1–37)$$

where

$$\theta = -3\left(\frac{1}{k_B b^2}\right) \int_b^\infty U(r)r^2\,dr.$$  \hspace{1cm} (1–38)

For $r > b$, $U(r) < 0$, and $\theta$ is always positive. For $T < \theta$, $B$ is negative, and for $T > \theta$, $B$ is positive. At $T = \theta$, $B$ is zero, and a real chain behaves like an ideal chain. Equation 1–37 says that at higher temperature, the free energy increases if monomers are cramped in a smaller space. So the system tries to minimize the energy gain. In solution, when monomers cramp in a smaller space, there is entropy cost due to two effects. First, monomers do not have sufficient space to move around; and second, they are not able to mix with the solvent particles. In gases, number of gas particles within the pervaded volume is very small. So, the entropy effect due to solvent-monomer mixture would not be present, resulting in a higher theta temperature in gases.
CHAPTER 2
DYNAMICS OF A FLEXIBLE POLYMER CHAIN IN THE GAS PHASE

2.1 Dynamics of a Brownian particle

The dynamics of a polymer chain can be described by the Brownian motion of the connected beads. First, the Brownian motion of a single particle in solution will be considered without any interaction, and then we will subject it to a harmonic potential. After considering all the relevant issues of Brownian motion for a single particle, the dynamics of individual chains will be discussed.

Brownian motion refers to the motion of colloidal particles in solution. Solvent particles make random collisions with the colloidal particle causing it to make irregular movements. The motion of this particle can be described as a random walk problem. We have already seen that the root mean square end-to-end vector of a polymer chain is proportional to the number of monomers $N$. Similarly, the root mean square distance traveled by the colloidal particle would be proportional to the number of collisions. Since the number of collisions is proportional to time $t$, it is obvious that $\langle r^2 \rangle \propto t$. If we consider Brownian motion in one dimension then

$$\frac{\langle x^2 \rangle}{t} = \text{constant.} \quad (2-1)$$

To learn more about the nature of this constant [12], let us consider a tube of cross sectional area $A$, and let $c(x, t)$ is the number of particles in a volume element centered about $x$ at time $t$, and $W(x)$ be the probability that a particle will go from $x$ to the origin in a time interval $t$. The number of particles in the volume element centered around the origin at time $t$ would be

$$c(0, t) = \int_{-\infty}^{\infty} c(x, 0)W(x)dx. \quad (2-2)$$
Since we are considering the movements in small time interval, $c(0, t)$ can be expressed by Taylor expansion:

$$c(0, t) = c(0, 0) + \left( \frac{\partial c}{\partial t} \right)_x t + \frac{1}{2} \left( \frac{\partial^2 c}{\partial t^2} \right)_x t^2 + \ldots.$$  \hspace{1cm} (2–3)

For a small time interval, $W(x)$ would be very small for large $x$. Expanding $c(x, 0)$ in terms of $x$ gives

$$c(x, 0) = c(0, 0) + \left( \frac{\partial c}{\partial x} \right)_t x + \frac{1}{2} \left( \frac{\partial^2 c}{\partial x^2} \right)_t x^2 + \ldots.$$ \hspace{1cm} (2–4)

Since $W(x)$ satisfies the normalization condition $\int_{-\infty}^{\infty} W(x) \, dx = 1$,

$$\int_{-\infty}^{\infty} c(0, 0) W(x) \, dx = c(0, 0), \hspace{1cm} (2–5)$$

$$\int \left( \frac{\partial c}{\partial x} \right)_t x W(x) \, dx = 0, \hspace{1cm} (2–6)$$

$$\int \left( \frac{\partial^2 c}{\partial x^2} \right)_t x^2 W(x) \, dx = \left( \frac{\partial^2 c}{\partial x^2} \right)_t \langle x^2 \rangle. \hspace{1cm} (2–7)$$

Combining Equations 2–2, 2–3 and 2–4 gives

$$\frac{\partial c}{\partial t} = \frac{1}{2} \langle x^2 \rangle \left( \frac{\partial^2 c}{\partial x^2} \right). \hspace{1cm} (2–8)$$

Compare this result with Fick’s law $\langle j(x) \rangle = -D \left( \frac{\partial c}{\partial x} \right)$, we see that the constant in Equation 2–1 is equal to the diffusion constant.

The diffusion constant can be evaluated using the fluctuation dissipation theorem [13]. Since much of this dissertation is related to fluctuation dissipation theorem, it is important to discuss how the value of diffusion constant $D$ is obtained.

Diffusion is phenomenologically described by Fick’s law:

$$j(x) = -D \left( \frac{\partial c}{\partial x} \right), \hspace{1cm} (2–9)$$
where $j(x)$ is the flux at point $x$. If there is any external force, this law has to be modified. For external force $F$, the colloidal particle will move with a constant speed $v$

$$v = \frac{F}{\zeta},$$

(2–10)

where $\zeta$ is the friction constant. This velocity will give additional flux so that the total flux is

$$j(x) = -D \left( \frac{\partial c}{\partial x} \right) + \frac{c}{\zeta} F.$$  

(2–11)

If $F = -\frac{\partial U}{\partial x}$, then

$$j = -D \left( \frac{\partial c}{\partial x} \right) - \frac{c}{\zeta} \frac{\partial U}{\partial x}.$$  

(2–12)

At equilibrium $c$ can be obtained by the Boltzmann distribution:

$$c_{eq} \propto \exp \left( -\frac{U(x)}{k_B T} \right).$$

(2–13)

and also at equilibrium the total flux would be zero:

$$j = 0$$

(2–14)

$$= -D \frac{\partial c_{eq}}{\partial x} - \frac{1}{\zeta} c_{eq} \frac{\partial U}{\partial x} = 0$$

(2–15)

$$= \exp \left( -\frac{U}{k_B T} \right) \left( \frac{\partial U}{\partial x} \right) \left( \frac{D}{k_B T} - \frac{1}{\zeta} \right) = 0.$$  

(2–16)

Thus, $D = \frac{k_B T}{\zeta}$, which is the Einstein relation relating fluctuation of a system to its dissipation [14]. This is description of diffusion in coordinate space.

We can also look into the diffusion problem in momentum space. The motion of a Brownian particle can be written as [13]

$$\zeta \frac{dx}{dt} = -\frac{\partial U}{\partial x} + f(t),$$

(2–17)

in which the influence of the surrounding medium has been separated into two parts: $\zeta \frac{dx}{dt}$ is the systematic part, which corresponds to dynamical friction and $f(t)$ is the fluctuating part. The friction term can be obtained using Stokes’ law. If the radius of the
colloidal particle is $a$ and viscosity of the surrounding liquid is $\eta$, then $\zeta = 6\pi\eta a$. On the other hand, the fluctuating part $f(t)$ satisfies two conditions [15]: $f(t)$ is independent of velocity and it varies very rapidly compared to $u$. If in a time interval $\Delta t$ the change in velocity is negligible, $f(t)$ will go through so many fluctuations by this time interval that there would not be any correlation between $f(t)$ and $f(t + \Delta t)$.

Since $f(t)$ is a random variable, it is necessary to know what distribution is followed by these variables. Let us consider Brownian motion of a free particle ($U = 0$). The Langevin equation is

$$\zeta \frac{dx}{dt} = f(t). \quad (2-18)$$

If the particle is at the origin at $t = 0$, the position of the particle at time $t$ is

$$x(t) = \frac{1}{\zeta} \int_0^t f(t') dt'. \quad (2-19)$$

This can be related to the diffusion problem in coordinate space. We know that when a particle diffuses in solution then $\langle x(t) \rangle = 0$ and $\langle x^2(t) \rangle = 2Dt$. The distribution of $f(t)$ can be determined by satisfying these conditions.

According to Equation 2–19,

$$\langle x(t) \rangle = \frac{1}{\zeta} \int_0^t \langle f(t') \rangle dt' = 0. \quad (2–20)$$

So

$$\langle f(t) \rangle = 0, \quad (2–21)$$

and

$$\langle x^2(t) \rangle = \frac{1}{\zeta^2} \left\langle \int_0^t f(t') dt' \int_0^t f(t'') dt'' \right\rangle. \quad (2–22)$$
The above equation requires a double integral over $t$. As $\langle x^2(t) \rangle \propto t$, the time correlation must be proportional to the delta function, i.e., $\delta(t)$:

$$
\langle x^2(t) \rangle = \frac{1}{\zeta^2} \int_0^t \int_0^t dt' dt'' \langle f(t') f(t'') \rangle \\
= \frac{1}{\zeta^2} A \int_0^t \int_0^t \delta(t' - t'') dt' dt'' \\
= \frac{A}{\zeta^2}t. 
$$

(2–23)

(2–24)

(2–25)

Combining this with $\langle x^2(t) \rangle = 2Dt$ gives $A = 2\zeta k_B T$. Finally,

$$
\langle f(t) f(t') \rangle = 2\zeta k_B T \delta(t - t'). 
$$

(2–26)

This equation gives the mean square rate at which momentum is being transferred to the particle [16].

Considering now Brownian motion in a harmonic potential $U = \frac{1}{2} kx^2$, the Langevin equation for such potential is

$$
\frac{dx}{dt} = -kx + f(t), 
$$

(2–27)

which is a stochastic differential equation. Initially we will solve for $x(t)$ as a function of $f(t)$. Then the average of any variable $A(x(t))$ is obtained from the given distribution of $f(t)$. Solution of Equation 2–27 gives

$$
x(t) = \frac{1}{\zeta} \int_{-\infty}^t dt' \exp \left( -\frac{(t - t')}{\tau} \right) f(t'),
$$

(2–28)

where $\tau = \frac{\zeta}{k}$. The autocorrelation of $x$ is given by

$$
\langle x(t)x(0) \rangle = \frac{1}{\zeta^2} \int_{-\infty}^t dt' \int_{-\infty}^0 dt'' \exp \left( -\frac{(t - t' - t'')}{\tau} \right) \langle f(t') f(t'') \rangle

\begin{align*}
&= \frac{1}{\zeta^2} \int_{-\infty}^t dt' \int_{-\infty}^0 dt'' \left[ 2\zeta k_B T \delta(t' - t'') \right] \exp \left( -\frac{(t - t' - t'')}{\tau} \right) \\
&= \frac{2k_B T}{\zeta} \int_{-\infty}^0 \exp \left( -\frac{(t - 2t'')}{\tau} \right) dt'' \\
&= \frac{k_B T}{k} \exp \left( -\frac{t}{\tau} \right).
\end{align*}

(2–29)

(2–30)

(2–31)

(2–32)
Equation 2–32 shows that the autocorrelation of $x$ decays exponentially with time with relaxation time equal to $\frac{\zeta}{k}$. For a more stiff chain, relaxation is faster. If the solution is more viscous, it will oppose the equilibration process of the spring.

2.2 Dynamics of a single chain in solution

The dynamics of a single Brownian particle subjected to harmonic potential was discussed above. The dynamics of the polymer is described by the Brownian motion of beads that are connected along the chain as shown in Figure 2-1.

![Figure 2-1. Mechanical model of a polymer chain. Dynamics of polymer chain is described by the Brownian motion of the beads connected by a spring.](image)

If the length between bead satisfies a Gaussian distribution (Section 1.1), then

$$g(x, x') = \left(\frac{2\pi b^2}{3}\right)^{-\frac{3}{2}} \exp\left(-\frac{3(x-x')^2}{2b^2}\right), \quad (2–33)$$

where

$$\langle(x-x')^2\rangle = b^2. \quad (2–34)$$

Thus, the probability of a certain conformation $\{r_n\}$ is

$$P\{r_n\} = \prod_{n=1}^{N} \left(\frac{3}{2\pi b^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3(r_n)^2}{2b^2}\right) \quad (2–35)$$

$$= \left(\frac{3}{2\pi b^2}\right)^{\frac{3}{2}} \exp\left[-\sum_{n=2}^{N} \frac{3(R_n - R_{n-1})^2}{2b^2}\right]. \quad (2–36)$$

This Gaussian chain can be represented by a mechanical model in which the beads are considered to be connected by a harmonic spring whose potential energy is given by

$$U(\{R_n\}) = \frac{3k_BT}{2b^2} \sum_{n=2}^{N} (R_n - R_{n-1})^2. \quad (2–37)$$
A Boltzmann distribution with this potential will give the same distribution as in Equation 2–36.

We can describe the equation of motion of the beads by the Langevin equation

$$\frac{\partial \mathbf{R}_n}{\partial t} = \sum_m \mathbf{H}_{nm} \cdot \left( -\frac{\partial U}{\partial \mathbf{R}_m} + \mathbf{f}_m(t) \right),$$

(2–38)

where \( \mathbf{H}_{nm} \) is the mobility matrix.

First, the Rouse model of polymer dynamics will be discussed [13]. In the Rouse model, there is no hydrodynamic interaction, and the mobility matrix contains only the diagonal term:

$$\mathbf{H}_{nm} = \frac{\mathbf{I}}{\zeta} \delta_{nm}. \quad (2–39)$$

The interaction potential of the Gaussian chain is given by

$$U = \frac{k}{2} \sum_{n=2}^{N} (\mathbf{R}_n - \mathbf{R}_{n-1})^2,$$

(2–40)

where the spring constant is \( k = \frac{3k_B T}{\ell^2} \). Therefore, in Rouse model the equation of motion is

$$\zeta \frac{d\mathbf{R}_n}{dt} = -k(2\mathbf{R}_n - \mathbf{R}_{n+1} - \mathbf{R}_{n-1}) + \mathbf{f}_n,$$

(2–41)

where the random force \( \mathbf{f}_n \) follows the following distribution:

$$\langle \mathbf{f}_n \rangle = 0,$$

(2–42)

$$\langle f_{n\alpha}(t) f_{n'\beta}(t') \rangle = 2\zeta k_B T \delta_{nm} \delta_{\alpha\beta} \delta(t - t').$$

(2–43)

In the continuous limit Equation 2–41 can be written as

$$\zeta \frac{\partial \mathbf{R}_n}{\partial t} = k \frac{\partial^2 \mathbf{R}_n}{\partial n^2} + \mathbf{f}_n.$$

(2–44)

Equation 2–41 does not include the beads at the end. For the end beads:

$$\zeta \frac{d\mathbf{R}_1}{dt} = -k(\mathbf{R}_1 - \mathbf{R}_2) + \mathbf{f}_1.$$  

(2–45)
\[ \zeta \frac{d\mathbf{R}_N}{dt} = -k(\mathbf{R}_N - \mathbf{R}_{N-1}) + \mathbf{f}_N. \]  \hspace{1cm} (2–46)

The end beads can be included in Equation 2–44 if the hypothetical beads are defined as \( \mathbf{R}_0 = \mathbf{R}_1 \) and \( \mathbf{R}_{N+1} = \mathbf{R}_N \). This gives the following boundary condition in the continuous limit:

\[ \frac{\partial \mathbf{R}_n}{\partial n} \bigg|_{n=0} = 0, \]  \hspace{1cm} (2–47)

\[ \frac{\partial \mathbf{R}_n}{\partial n} \bigg|_{n=N} = 0. \]  \hspace{1cm} (2–48)

To solve Equation 2–44, which is a coupled differential equation, consider normal mode \( \mathbf{X}_p \) which is defined as

\[ \mathbf{X}_p = \frac{1}{N} \int_0^N dn \cos \left( \frac{p\pi n}{N} \right) \mathbf{R}_n(t) \text{ where } p = 0, 1, 2, \ldots . \]  \hspace{1cm} (2–49)

With these normal modes Equation 2–44 becomes

\[ \zeta_p \frac{d\mathbf{X}_p}{dt} = -k_p \mathbf{X}_p + \mathbf{f}_p. \]  \hspace{1cm} (2–50)

where \( \mathbf{f}_p \) is

\[ \mathbf{f}_p = 2 \int dn \cos \left( \frac{p\pi n}{N} \right) \mathbf{f}_n(t). \]  \hspace{1cm} (2–51)

The constants before the integrals in Equations 2–49 and 2–51 can be chosen arbitrarily as long as they give the exact value of \( \frac{\zeta_p}{k_p} \). Here we have chosen Doi’s convention \[13\].

The mean square of \( \mathbf{f}_p \) would give \( \zeta_p \) in Equation 2–50, and the Gaussian distribution of the chain will give \( k_p \). \( \zeta_p \) is related to the the correlation of the random forces \( \mathbf{f}_p \) according to
\[
\langle f_{p\alpha}(t) f_{q\beta}(0) \rangle = 4 \int_0^N \int_0^N d\eta d\mu \cos \left( \frac{p\pi \eta}{N} \right) \cos \left( \frac{q\pi \mu}{N} \right) \langle f_{\alpha\alpha}(t) f_{\beta\beta}(0) \rangle
\]

(2–52)

\[
= 4 \int_0^N \int_0^N d\eta d\mu \cos \left( \frac{p\pi \eta}{N} \right) \cos \left( \frac{q\pi \mu}{N} \right) \left[ 2\zeta_0 T \delta_{\alpha\beta} \delta_{np} \delta(t) \right]
\]

(2–53)

\[
= 4 \int_0^N \int_0^N d\eta \cos \left( \frac{p\pi \eta}{N} \right) \cos \left( \frac{q\pi \mu}{N} \right) \left[ 2\zeta_0 T \delta_{\alpha\beta} \delta(t) \right]
\]

(2–54)

\[
= 4N\zeta_0 T \delta_{\alpha\beta} \delta_{pq} \delta(t).
\]

(2–55)

So \( \langle f_{p\alpha}(t) f_{q\beta}(0) \rangle = 2\zeta_0 k_B T \delta_{\alpha\beta} \delta_{pq} \delta(t) \) gives \( \zeta_0 = 2N\zeta \).

When the polymer is in solution, there is no correlation between the random forces acting on different monomers, due to the very small mean free path. The large mean free path in gases implies a certain degree of correlation between these random forces.

Another term in Equation 2–50 is \( k_0 \), the spring constant for the Fourier mode \( \mathbf{X}_p \), which depends only on the average conformations of the chain. The spring constant \( k_0 \) can be evaluated for the equilibrium distribution of \( \mathbf{X}_p \):

\[
\frac{1}{2} k_0 \langle \mathbf{X}_p^2 \rangle_{eq} = \frac{3}{2} k_B T,
\]

(2–56)

which comes from the equipartition theorem. Equation 2–49 gives

\[
\mathbf{X}_p = -\frac{1}{p\pi} \int_0^N d\eta \sin \left( \frac{p\pi \eta}{N} \right) \frac{\partial \mathbf{R}_n}{\partial \eta},
\]

(2–57)

and \( \langle \mathbf{X}_p^2 \rangle \) at equilibrium would be

\[
\langle \mathbf{X}_p^2 \rangle_{eq} = \frac{1}{p^2 \pi^2} \int d\eta \int d\mu \sin \left( \frac{p\pi \eta}{N} \right) \sin \left( \frac{p\pi \mu}{N} \right) \langle \frac{\partial \mathbf{R}_n}{\partial \eta} \cdot \frac{\partial \mathbf{R}_m}{\partial \mu} \rangle_{eq}.
\]

(2–58)

We can write

\[
\frac{\partial \mathbf{R}_n}{\partial \eta} \cdot \frac{\partial \mathbf{R}_m}{\partial \mu} = -\frac{1}{2} \frac{\partial^2}{\partial \eta \partial \mu} (\mathbf{R}_n - \mathbf{R}_m)^2.
\]

(2–59)

Thus,

\[
\langle \mathbf{X}_p^2 \rangle_{eq} = -\frac{1}{2p^2 \pi^2} \int d\eta \int d\mu \sin \left( \frac{p\pi \eta}{N} \right) \sin \left( \frac{p\pi \mu}{N} \right) \frac{\partial^2}{\partial \eta \partial \mu} \langle (\mathbf{R}_n - \mathbf{R}_m)^2 \rangle_{eq}.
\]

(2–60)
The Gaussian distribution comes into play in the term \( \langle (R_n - R_m)^2 \rangle_{eq} \). We are considering Gaussian chain for which \( \langle (R_n - R_m)^2 \rangle_{eq} \approx b^2 |n - m| \). Using this value in Equation 2–60 we get \( \langle X_p^2 \rangle_{eq} \), which leads to

\[
k_p = \frac{6\pi^2 k_B T}{2Nb^2} p^2 \text{ for } p = 0, 1, 2, \ldots.
\] (2–61)

The solution of Equation 2–50 is given by

\[
\langle X_{\rho\alpha}(t)X_{q\beta}(0) \rangle = \delta_{pq}\delta_{\alpha\beta}\frac{k_B T}{k_p} \exp \left(-\frac{t}{\tau_p}\right),
\] (2–62)

where \( \tau_p = \frac{\zeta_p}{k_p} = \frac{\zeta N^2 b^2}{3\pi^2 k_B T p^2} \).

Equation 2–63 shows that in the Rouse model the relaxation time \( \tau_{pr} \propto N^2 \).

Because the Rouse model neglects the hydrodynamic interaction, the prediction is not consistent with experimental results. The Hydrodynamic interaction was taken into account in Zimm model \[13\], which defines the mobility matrix as

\[
H_{nn} = \frac{I}{\zeta},
\] (2–64)

\[
H_{nm} = \frac{1}{8\pi\eta|\mathbf{r}_{nm}|} [\mathbf{r}_{nm}\mathbf{r}_{nm} + \mathbf{I}] \text{ for } n \neq m.
\] (2–65)

Here, the \( H_{nm} \) (Oseen tensor) includes hydrodynamic interaction in the equation of motion. If the force on a monomer \( m \) is known, Oseen tensor will give the velocity at the position of monomer \( n \). Solution of Langevin equation in Zimm model gives \( \tau_{pr} \propto N^2 \), where \( \tau_{pr} \) is the relaxation time for mode \( p \). Thus the hydrodynamic interaction increases the rate of relaxation.

### 2.3 Friction constant \( \zeta \) in a gas

When we consider the motion of an object whose size is much larger than the mean free path of a fluid particle, we use hydrodynamic equations. For example, from Navier-Stokes equation we know that the friction constant of a sphere with radius \( a \) is \( \zeta = 6\pi\eta a \), where \( \eta \) is the viscosity of the fluid. But the mean free path in gas would be
much larger than the typical Kuhn radius of a monomer. Thus hydrodynamics can not be used to evaluate the friction constant and the concept of viscosity breaks down here. The kinetic theory of gases must be used to determine the friction constant.

In Uhlenbeck’s paper on Brownian motion [17], the derivation of the friction constant in a gas considered the rotational Brownian motion of a small mirror, and this dissertation makes use of the same method. Since the friction constant depends on the geometry, a sphere of radius \( r \) will be assumed. The exact friction constant for a sphere of radius \( r \) is

\[
\zeta = \frac{4\pi mn\bar{v}b^2}{3} \tag{2–68}
\]

where \( m \), \( n \) and \( \bar{v} \) are respectively mass, density and mean velocity of the gas particles. This differs from the equation derived here because the area is assumed to be \( \pi r^2 \) and ignores the curvature of the sphere. Only a rough calculation provided to show the physics involved.

Consider a sphere which moves to the right in the direction of \( x \) with velocity \( u \). The number of gas particles which strike this from the left per unit time is given by

\[
N_L = (\pi b^2) \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} n \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty (v_x - u) \exp \left(-\frac{mv^2}{2k_B T}\right) dv_x dv_y dv_z, \tag{2–66}
\]

where \( n \) = number density of gas particles. Here the sphere is considered as a disk with area \( \pi b^2 \).

The total momentum imparted from the left per unit time is given by

\[
P_L = (\pi b^2)(nm) \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty (v_x - u)^2 \exp \left(-\frac{mv^2}{2k_B T}\right) dv_x dv_y dv_z \tag{2–67}
\]

\[
= (\pi b^2)(nm) \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \int_{-\infty}^\infty \exp \left(-\frac{mv_x^2}{2k_B T}\right) dv_x \int_{-\infty}^\infty \exp \left(-\frac{mv_y^2}{2k_B T}\right) dv_y \int_0^\infty (v_x - u)^2 \exp \left(-\frac{mv_x^2}{2k_B T}\right) dv_x \tag{2–68}
\]

\[
= (\pi b^2)(nm) \left( \frac{m}{2\pi k_B T} \right)^{\frac{3}{2}} \left( \frac{2\pi k_B T}{m} \right) \int_0^\infty (v_x^2 - 2v_x u) \exp \left(-\frac{mv_x^2}{2k_B T}\right) dv_x + O(u^2). \tag{2–69}
\]
Similarly, the total momentum imparted per unit time from the right is given by

\[ P_R = (\pi b^2)(nm) \left( \frac{m}{2 \pi k_B T} \right)^{\frac{3}{2}} \left( \frac{2 \pi k_B T}{m} \right) \int_{-\infty}^{0} \left( v_x^2 + 2v_x u \right) \exp \left( -\frac{mv_x^2}{2k_B T} \right) dv_x + O(u^2). \]  

(2–70)

Thus, the total momentum imparted per unit time is

\[ P = P_L + P_R = (\pi b^2)(nm) \left( \frac{m}{2 \pi k_B T} \right)^{\frac{3}{2}} \left( \frac{2 \pi k_B T}{m} \right) (-4u) \int_{0}^{\infty} v_x \exp \left( -\frac{mv_x^2}{2k_B T} \right) dv_x. \]  

(2–71)

If we write the friction force as \( F = -\zeta u \), then the friction constant is

\[ \zeta \propto mn\bar{v}^2, \]  

(2–72)

where \( \bar{v} \) is the mean velocity of gas particles.

Equation 2–72 is an interesting result. In the hydrodynamic limit, the viscosity of an ideal gas does not depend on density, and therefore, \( \zeta \) would be also independent of density. In our case, \( \zeta \) is a function of density and by varying the density we can easily change the relaxation times. Also here \( \zeta \) is proportional to \( b^2 \), unlike the Stokes’ case where \( \zeta \propto b \).

Recently properties of polymers in vacuum have been considered [19–22]. In this work the dynamics of polymers in gases are investigated as shown in the following section.

### 2.4 Calculation of the relaxation time \( \tau_p \) in the gas phase

For gas phase dynamics, the first thing to consider is the correct equation of motion. Equation 2–44, the Langevin equation for the Rouse model, is true in hydrodynamic limit. Although the mean free path is very large in a gas, we can still consider the same Equation 2–44, but the correlation of the random forces would be different.

Since the mean free path, \( \lambda \), is large, after hitting a monomer \( n \), a gas particle can strike other monomers without making collisions with other gas particles. So
the collisions the gas particles make with the monomers are ballistic, as shown in Figure 2-2.

![Figure 2-2. Gas particles (brown) making ballistic collisions with the monomers (black). Since the mean free path in a gas is large, there is hardly any chance that two gas particles will meet within the pervaded volume of a polymer.](image)

The ballistic nature of collisions implies that random forces on different monomers are correlated, and this correlation depends on the conformations of the polymer.

The conformations of a polymer in the gas phase was discussed in Section 1.3. Considering dynamics at \( \theta \) temperature, we know that the polymer behaves ideally at this temperature and its conformation is described by a Gaussian distribution. A particular conformation gives the relative position between monomers in 3D space. So the impact of ballistic collisions would heavily depend on polymer conformation.

We can think of a gas particle which, after making a collision with some monomer, recoils along some direction, say the X direction. What is the probability that it will meet other monomers before returning to ambient gas? Because an ideal chain follows the distribution of a 3D random walk, some properties of this random walker need to be considered to find this probability.

Let \( P_{1D}(N, x) \) be the probability distribution in one dimension:

\[
P_{1D}(N, x) = \frac{1}{\sqrt{2\pi x^2}} \exp \left( -\frac{x^2}{2(x^2)} \right).
\]  

(2–73)
The probability distribution along the y coordinate, i.e., $P_{1D}(N, y)$ would be independent of the value previously assigned to $x$ if $N$ is large and $x$ is much smaller than the full extension of the chain, i.e., $N \gg 1$ and $x \ll Nb$ [10]. Similarly, $P_{1D}(N, z)$ is independent of $x$ and $y$ when $N \gg 1$ and $x \ll Nb$, $y \ll Nb$. So for small extensions of a long chain, $P_{1D}(N, x)$ depends only on $x$, $P_{1D}(N, y)$ only on $y$, and $P_{1D}(N, y)$ only on $z$. We can write the 3D probability distribution function as the product of three one-dimensional distributions:

$$P_{3D}(N, R) dR_x dR_y dR_z = P_{1D}(N, R_x) dR_x P_{1D}(N, R_y) dR_y P_{1D}(N, R_z) dR_z. \quad (2-74)$$

If the gas particle is moving along the $X$ direction, we need to consider the random walk of the polymer in the $YZ$ plane. If we know the probability that a random walker moving in the $YZ$ plane will return to the origin, this would give the probability of meeting other monomers as the gas particle moves along the $X$ direction. From Pólya's theorem, we know that a random walk in 2D is recurrent, and the number of times that the random walker comes back to the origin diverges logarithmically. So the probability to meet other monomers while moving along the $X$ direction approaches unity with increasing monomer number. Since the distribution of a 3D random walker is homogeneous in space, this would be true for all gas particles regardless of their recoil direction. The distribution will not be homogeneous for monomers located on the edges, but that number is small and we will assume an isotropic distribution for all monomers.

Turning back to the particle that was moving along the $X$ direction, if it just made a collision with monomer $n$, what is the probability that it will hit monomer $n'$, escaping all other monomers in between? This would correspond to the probability of returning to the origin for the first time in the $YZ$ plane after taking $|n - n'|$ steps. Therefore, we need to know the first-passage time for 2D random walk. The probability to return to the origin
for the first time in 2D is [23]

\[ P_{nn'} = \frac{1}{4\pi} \left( \frac{R}{b} \right)^2 \frac{1}{|n - n'|(|n - n'|)^2}, \]  

(2–75)

where \( R \) is the monomer radius and \( b \) is the bond length and Equation 2–75 holds when \( n \) and \( n' \) are not very close and we will assume it to be true for \( n - n' > 1 \). Thus, the random forces on \( n \) and \( n' \) will be correlated with this probability. We want to solve the Langevin equation for the following normal modes:

\[ \mathbf{X}_p = \frac{1}{N} \sum \cos \left( \frac{p \pi n}{N} \right) \mathbf{R}_n, \]
\[ \mathbf{f}_p = 2 \sum \cos \left( \frac{p \pi n}{N} \right) \mathbf{f}_n, \]  

(2–76)

where \( \mathbf{R}_n \) is the position vector of monomer \( n \) and \( \mathbf{f}_n \) is the random force on monomer \( n \).

The correlation between random forces of mode \( p \) and \( q \) is given by

\[ \langle \mathbf{f}_p(t) \cdot \mathbf{f}_q(0) \rangle = 4 \left( \sum \cos \left( \frac{p \pi n}{N} \right) \mathbf{f}_n(t) \cdot \sum \cos \left( \frac{q \pi n'}{N} \right) \mathbf{f}_{n'}(t) \right). \]  

(2–77)

The entire collision process can be divided into two parts. A gas particle may return directly to the surroundings after colliding with a monomer, or it may go from one monomer to other with probability \( P_{nn'} \). Now we will consider the polymer as monomers distributed within a sphere as in Figure 2-3, and then the first process (i.e., when gas particles go back directly to the environment) can be treated as external interaction for the sphere. Here momentum is transferred to or from the sphere by external forces, and so the correlation of random forces would give the delta term \( \langle \mathbf{f}_n \cdot \mathbf{f}_{n'} \rangle \propto \delta_{nn'} \).

In the second process, the gas particles make successive collisions within the sphere. These involve momentum transfer from monomer to monomer only and no external forces are involved. So we will assume \( \mathbf{f}_n = -\mathbf{f}_{n'} \) to ensure momentum conservation. As \( \mathbf{f}_p = 2 \sum \cos(\frac{p \pi n}{N}) \mathbf{f}_n \), there would be a term \( \cos(\frac{p \pi n}{N}) - \cos(\frac{p \pi n'}{N}) \) in the summation for \( \mathbf{f}_p \). This is very important result, which will be exploited in the rest of Chapter 2. It simply puts some restrictions on the correlation of the normal modes, i.e., the normal mode of the friction constant would be different from the normal mode of the
friction constant obtained from uncorrelated random forces. Now we can write Equation 2–77 as

\[ \langle \mathbf{f}_p(t) \cdot \mathbf{f}_q(0) \rangle = 4 \int \int d\mathbf{n}\, d\mathbf{n}' \cos \left( \frac{p \pi \mathbf{n}}{N} \right) \cos \left( \frac{q \pi \mathbf{n}'}{N} \right) \langle \mathbf{f}_p(t) \cdot \mathbf{f}_q(0) \rangle \]

\[ - 4 \int \int d\mathbf{n}\, d\mathbf{n}' \mathbb{P}_{nn'} \left[ \cos \left( \frac{p \pi \mathbf{n}}{N} \right) - \cos \left( \frac{p \pi \mathbf{n}'}{N} \right) \right] \langle \mathbf{f}_p(t) \cdot \mathbf{f}_q(0) \rangle . \]  

(2–78)

Considering the summation involving \( \mathbb{P}_{nn'} \),

\[ l(p, q) = \sum_{n, n'} P_{nn'} \left[ \cos \left( \frac{p \pi \mathbf{n}}{N} \right) - \cos \left( \frac{p \pi \mathbf{n}'}{N} \right) \right] \left[ \cos \left( \frac{q \pi \mathbf{n}}{N} \right) - \cos \left( \frac{q \pi \mathbf{n}'}{N} \right) \right] \]

\[ = \frac{1}{\pi} \left( \frac{R}{b} \right)^2 \sum_{n, n'} \left[ \frac{\sin \left( p'(n - n') \right) \sin \left( q'(n - n') \right)}{|n - n'| (\ln |n - n'|)^2} \right] \left[ \sin \left( p'(n + n') \right) \sin \left( q'(n + n') \right) \right]. \]

(2–79)

(2–80)

where we have used the notation \( p' = \frac{p \pi}{2N} \) and \( q' = \frac{q \pi}{2N} \).
For \( p = q \):

\[
l(p) = \frac{1}{\pi} \left( \frac{R}{b} \right)^2 \sum_{n, n' \geq n' + 1} \sin^2 \left( \frac{p'(n - n')}{\ln|n - n'|} \right) \sin^2 \left( \frac{p'(n + n')}{\ln|n - n'|} \right).
\]  (2–81)

![Transformation of coordinates](image)

Figure 2-4. Transformation of coordinates. Integration must be performed over a rectangular area. When the coordinates are changed, the shape of the area changes.

To perform the summation we will make a change in coordinates:

\[
u = n - n',
\]  (2–82)

\[
v = n + n'.
\]  (2–83)

If \( n \) were varied along the axis \( n' = 0 \), \( v \) would be equal to \( u \) (Figure 2-4). Similarly, varying \( n' \) along the axis \( n = N \) would give \( v = 2N - u \). With the new coordinates Equation 2–81 becomes

\[
l(p) = \frac{1}{\pi} \left( \frac{R}{b} \right)^2 \left[ \int_2^N du \frac{\sin^2 p'u}{u(\ln u)^2} \int_{v_1}^{2N-u} dv \sin^2 p'v + \int_{-N}^{-u} du \frac{\sin^2 p'u}{|u|(\ln|u|)^2} \int_{-u}^{2N+u} dv \sin^2 p'v \right].
\]  (2–84)

First we will integrate over \( v \) for a constant \( u \) (Appendix A):

\[
l(p) = \frac{1}{\pi} \left( \frac{R}{b} \right)^2 \left[ 2N \int_2^N du \frac{\sin^2 p'u}{u(\ln u)^2} - 2 \int_2^N du \frac{\sin^2 p'u}{|u|(\ln u)^2} \right] + \frac{1}{\pi} \left( \frac{R}{b} \right)^2 \left[ \frac{1}{2p'} \int_2^N du \frac{\sin 2p'u}{u(\ln u)^2} - \frac{1}{4p'} \int_2^N du \frac{\sin 4p'u}{u(\ln u)^2} \right].
\]  (2–85)
We will consider the limiting cases for both very large and very small $\rho$. For large $\rho$, the sine function will oscillate very rapidly. Since the last two terms on the right side of Equation 2–85 are proportional to $\sin \rho$, they will contribute little. Also, the $\frac{1}{\rho}$ term in front of the integrals further decreases the contribution of the last two terms, which can be neglected.

For small $\rho$, $\sin \rho' u \approx \rho' u$, and the leading contribution from the last two terms on the right side of Equation 2–85 would be proportional to $(\rho' u)^3$, so that we can neglect those terms in this limit as well. Therefore, for both limits, we need to retain only the first two terms in Equation 2–85. Thus,

$$l(\rho) \approx \frac{1}{\pi} \left( \frac{R}{b} \right)^2 \left[ 2N \int_2^N du \frac{\sin^2 \rho' u}{u (\ln u)^2} - 2 \int_2^N du \frac{\sin^2 \rho' u}{(\ln u)^2} \right]. \quad (2–86)$$

Combining Equations (2–78) and (2–86) gives

$$\langle \mathbf{f}_p(t) \cdot \mathbf{f}_p(0) \rangle = 4 \left( 2 \zeta k_B T \delta(t) \right) \int \int dnd' \cos \left( \frac{p\pi n}{N} \right) \cos \left( \frac{p\pi n'}{N} \right) \delta_{nn'}$$

$$- 4 \left( 2 \zeta k_B T \delta(t) \right) \frac{1}{\pi} \left( \frac{R}{b} \right)^2 \left[ 2N \int_2^N du \frac{\sin^2 \rho' u}{u (\ln u)^2} - 2 \int_2^N du \frac{\sin^2 \rho' u}{(\ln u)^2} \right]. \quad (2–87)$$

The correlation of random forces would be proportional to the friction constant of mode $p$, i.e., $\langle \mathbf{f}_p(t) \cdot \mathbf{f}_p(0) \rangle = 2\zeta_p k_B T \delta(t)$. Combining this with Equation 2–87 gives

$$\zeta_p = 2N \zeta - \frac{8\zeta}{\pi} \left( \frac{R}{b} \right)^2 \left[ N \int_2^N du \frac{\sin^2 \rho' u}{u (\ln u)^2} - \int_2^N du \frac{\sin^2 \rho' u}{(\ln u)^2} \right]. \quad (2–88)$$

We will write $\zeta_p$ as

$$\zeta_p = 2\zeta \left[ N - \Delta N \right], \quad (2–89)$$

where

$$\Delta N = \frac{4}{\pi} \left( \frac{R}{b} \right)^2 \left[ N \sum_{2}^{N} \frac{\sin^2 \rho' u}{u (\ln u)^2} - \sum_{2}^{N} \frac{\sin^2 \rho' u}{(\ln u)^2} \right]. \quad (2–90)$$
The relaxation time for mode \( p \) is \( \tau_p = \frac{\zeta}{k_p} \), where \( k_p = \frac{6\pi^2 k_b T}{N B_p} p^2 \) (Section 2.2). This is the spring constant for a Gaussian chain. From Equation 2–89 we will have

\[
\frac{1}{\tau_p} = \frac{k_p}{2 \zeta (N - \Delta N)}
\]

\[
= \frac{1}{\frac{2 \zeta N}{k_p} (1 - \frac{\Delta N}{N})}.
\]

Here \( \frac{2 \zeta N}{k_p} \) is the Rouse relaxation time: \( \tau_{pr} = \frac{2 \zeta N}{k_p} \) (Section 2.2). Thus,

\[
\frac{1}{\tau_p} = \frac{1}{\tau_{pr} (1 - \frac{\Delta N}{N})}
\]

\[
= \frac{1}{\tau_{pr}} + \frac{(\frac{\Delta N}{N}) (\frac{1}{\tau_{pr}})}{1 - \frac{\Delta N}{N}}
\]

\[
= \frac{1}{\tau_{pr}} + \frac{1}{\tau_{pr} (\frac{N}{\Delta N} - 1)}
\]

\[
= \frac{1}{\tau_{pr}} + \frac{1}{\tau_{pm}},
\]

where \( \tau_{pm} = \tau_{pr} \left( \frac{N}{\Delta N} - 1 \right) \). Here sub-script \( m \) is used to indicate that this relaxation arises from multiple collisions of a single gas particle with different monomers.

![Graph](image)

Figure 2-5. Ratio of \( \tau_{pm} \) to \( \tau_{pr} \) as a function of \( N \). The relaxation process can be divided into two parts. \( \tau_{pr} \) is similar to the Rouse time. \( \tau_{pm} \) comes from the multicollision process.
Now we will investigate the properties of $\tau_{pm}$ for small $\rho$. For small $\rho$:

\[
\Delta N = \frac{4}{\pi} \left( \frac{R}{b} \right)^2 \left[ N \sum_{2}^{\frac{1}{2}N} \frac{(p'u)^2}{u(\ln u)^2} - \frac{1}{N} \sum_{2}^{\frac{1}{2}N} \frac{(p'u)^2}{(\ln u)^2} \right],
\]

(2–97)

\[
= \frac{\pi \rho^2}{N} \left( \frac{R}{b} \right)^2 \left[ \sum_{2}^{\frac{1}{2}N} \frac{u}{(\ln u)^2} - \frac{1}{N} \sum_{2}^{\frac{1}{2}N} \frac{u^2}{(\ln u)^2} \right].
\]

(2–98)

Before examining a plot by $\frac{\tau_{pm}}{\tau_p}$ vs $N$, we can make some rough approximations of the behavior to this ratio from Equation 2–98. First consider the sum $\sum_{2}^{\frac{1}{2}N} \frac{u}{(\ln u)^2}$. Here $\ln u$ saturates quickly and we have an integration over $u$ with upper limit $N$. Similarly in the second sum, we have an integration over $u^2$ with the same upper limit but there is also a factor $\frac{1}{N}$ in front of the sum. From these we can predict that $\Delta N$ would be one or two orders of magnitude smaller than $N$ (Figure 2-5).

This can be considered as a multi relaxation process. We know that the dynamics of polymers in solution also involves different relaxation times, such as translational and rotational/internal relaxations. In dilute solutions, dynamic light scattering experiments can resolve translational and internal modes. First the intensity autocorrelation can be measured for different scattering vectors, followed by an inverse Laplace transform to separate these two modes [24]. Similarly, dynamic light scattering measurements can be used in gases to determine $\tau_{pm}$.

So far we have considered chains at the theta temperature. Above this temperature (Section 1.3), the polymer size would be larger and the polymer would be more porous to the gas particles. Below the theta temperature, the monomer density will increase and the impact of multicollision processes would be larger. And also below the theta temperature, the collisions between the monomers would be more frequent, because of the higher monomer density. The collisions between the monomers contribute to internal dissipation which will be considered in Chapter 3.

In summary, we have considered the dynamics of a flexible chain at the theta temperature in the gas phase. For this condition, the random force terms in Langevin
equation are correlated, as described by the statistical property of a Gaussian chain. 

The relaxation time can be divided into two parts: $\tau_{px}$ and $\tau_{pm}$. Here $\tau_{px}$ is similar to the Rouse relaxation time, but with the important difference that $\zeta$ here is the gas friction constant which is much smaller than the friction constant in solution. The $\tau_{pm}$ is comparable to $\tau_{px}$, although it is larger than $\tau_{pr}$ and does not have an exact power law dependence on $N$ as is true in the Rouse case. Measurement of the dynamic structure factor can reveal these relaxation times.
CHAPTER 3
FIRST-PRINCIPLES CALCULATIONS OF THE INTERNAL FRICTION OF A GAUSSIAN CHAIN

3.1 Introduction to internal friction

The term internal friction in Polymer Physics refers to a dissipative mechanism that does not involve solvent. This has been a long standing area of research and there are various theories to explain this mechanism [25–29]. Since the friction constant is much smaller in gases, internal friction will have a significant impact on the dynamics of polymers in the gas phase. Chapter 3 will explain the shortcomings of previous theories of internal friction and will propose new theory and will show all relevant calculations.

There are two different origins of internal friction: one due to interactions of monomers distant along the chain, and the second due to changes in bond angles. P. G. de Gennes considered internal friction of the first kind, and his ideas of internal friction [29] are described briefly here.

\begin{equation}
\zeta_s \dot{r}_n + \zeta_b \sum \Lambda(r_n - r_m)(\dot{r}_n - \dot{r}_m) = F_n,
\end{equation}

where $\Lambda(r_n - r_m)$ is the probability of contact of two monomers, $\zeta_s$ is the friction due to the solvent, and $\zeta_b$ can be tentatively related to the viscosity of the monomeric liquid. For
a good solvent, $\Lambda(r_n - r_m) = k|n - m|^{-1.97} \cong k|n - m|^{-2}$. If we take the normal mode $r_n \sim \cos(\frac{\pi n}{N})$, then Equation 3–1 gives a renormalized friction $\zeta_p = \zeta_s(1 + \varphi_p)$, where $\varphi_p = k\pi^2 \frac{\varphi}{\zeta_s}(\frac{p}{N})$. For a theta solvent, $\Lambda(r_n - r_m) \cong k|n - m|^{-2}$, $\varphi_p \propto (\frac{p}{N})^{\frac{1}{2}}$. Relaxation time is $\frac{\zeta_s}{\zeta_p}$. Thus, a plot of the relaxation time versus viscosity can be extrapolated to zero viscosity to give the internal friction term.

In summary, P. G. de Gennes made the assumption that friction on monomer $n$ by monomer $m$ is proportional to their relative velocity and the total friction on monomer $n$ can be obtained by summing over all other monomers. Friction on a single object, such as a sphere immersed in liquid definitely depends on its speed. But a polymer is a connected object, and when monomer $m$ moves, it drags other monomers with it. So summing over all relative velocities can not give the total friction force on a single monomer. In essence, this is a phenomenological theory, and it also can not assign a value to the proportionality constant $\zeta_b$.

The second type of internal friction is known as Kelvin damping. If the bond angle changes, there is an energy cost and this gives rise to internal friction (Figure 3–2). Recently, the internal friction term of a polymer in a vacuum was studied by computer simulation [30]. The friction term considered in this paper is similar to Kelvin friction term, which is proportional to $\frac{\partial}{\partial t} \left( \frac{\varphi P_n}{\partial m^n} \right)$, and shows how the bond angle changes with time. The results of Deutsch et al. are described here.

When Kelvin damping is included, the equation of motion is

$$\rho \frac{\partial^2 R_n}{\partial t^2} = \left( k + C \frac{\partial}{\partial t} \right) \frac{\partial^2 R_n}{\partial m^n} + f_n,$$

where $\rho$ is the mass of a monomer unit. In normal modes Equation 3–2 becomes

$$\rho \frac{\partial^2 X_p}{\partial t^2} = -\left( \frac{\rho N}{\pi} \right)^2 \left( k + C \frac{\partial}{\partial t} \right) X_p + f_p.$$

If noise term $f_p$ is neglected, this is the equation for a damped harmonic oscillator.

The prefactor $C$ depends on the potential due to bond angles. A potential between the
nearest neighbors of monomers can be written as

\[ U_{\text{val}} = \frac{U_b}{4} \left( |r_{i+1} - r_{i-1}|^2 - r_0^2 \right) \tag{3-4} \]

in which \( r_0 \) can be chosen to give the optimum value of the bond angle, depending on the chemical structure of the polymer.

Figure 3-3. Time correlation function for the normal modes. Here blue is for \( p = 1 \), green for \( p = 2 \) and red for \( p = 3 \). Figure taken from J. M. Deutsch, Phys. Rev. E 81, 061804 (2010). Copyright (2010) by the American Physical Society (http://link.aps.org/doi/10.1103/PhysRevE.81.061804).
Figure 3.3 shows autocorrelation function for $U_b = 10$. It shows that the motion is underdamped for long wavelength modes even for a strong potential. In summary, this paper shows Kelvin damping in vacuum. But a polymer is an one dimensional object placed in a 3D setting. Monomers distant along the chain may come close in space and make random collisions, and for an ideal chain, the number of monomers involved in such random collisions can be quite large [10]. We will see that normal mode of the friction term due to random collisions between monomers is proportional to $\frac{1}{\sqrt{N}}$, whereas Kelvin friction term is proportional to $\frac{1}{N^2}$ (Equation 3-3). Although the prefactor is different in these two cases, the $\frac{1}{\sqrt{N}}$ term in Kelvin friction ensures that it is much smaller.

These shortcomings of previous theories necessitate first-principles calculations of internal friction. With modern ionization techniques, it will be possible to place polymers in a vacuum and measure the internal friction directly. Direct measurement will also help to check the validity of the extrapolation scheme used for polymers in solution thus far. At first we will calculate internal friction for polymers in isolation, and at the end we will show that this mechanism is applicable in solutions as well.

### 3.2 Microscopical derivation of internal friction constant $\zeta_p$

The origin of the internal friction in this model is the random collisions of monomers with each other. If we place a polymer chain in vacuum, we can write the following equation of motion:

$$\zeta \frac{\partial R_n}{\partial t} = k \frac{\partial^2 R_n}{\partial t^2} + f_n. \quad (3-5)$$

Here $k$ is the spring constant, similar to the term used in Equation 2-44, and $f_n$ is the random force on monomer $n$ due to its collisions with other monomers as shown in Figure 3-4.

We have seen in Section 2.1 (Equation 2-26) how the friction constant $\zeta$ is related to the mean square momentum transfer by random collisions. In Equation 3-5, $\zeta$ is related to the mean square momentum transfer to a monomer by random collisions,
Figure 3-4. Monomers distant along the chain undergo random collisions. Random forces on a pair of monomers can be treated as equal and opposite. Here \( f_5 = -f_6 \) and \( f_6 = -f_{14} \).

and only other monomers are involved in these random collisions. The value of \( \zeta \) will be determined and subsequently used to solve Equation 3–5 in terms of normal modes.

We will assume that at temperature \( T \), monomers will follow Maxwell's momentum distribution. To determine the internal friction for a Gaussian chain, the Gaussian distribution for conformations will be used to find the number of monomers at a given distance. First let us find the mean square momentum transfer in these collisions.

We will consider the monomers as hard spheres, and assume that the collisions they make are elastic. If two monomers collide, the angle of deflection \( \chi \) in the center of mass reference frame is given by

\[
\chi(b_{im}, g) = \pi - 2b_{im} \int_{r_m}^{\infty} \frac{d\tau}{\sqrt{1 - \frac{\varphi(r)}{2\mu g^2} - \frac{b_{im}^2}{\tau^2}}}, \tag{3–6}
\]

where \( b_{im} \) is the impact parameter, \( \varphi(r) \) is the interaction potential, \( \mu \) is the reduced mass, and \( g \) is the initial relative speed.

If \( R \) is the radius of a hard sphere, \( r_m \) will be \( 2R \) for an impact parameter less than \( 2R \) and \( \varphi(r) = 0 \) within the range of integration. Therefore \( \chi(b_{im}) = \pi - 2b_{im} \int_{2R}^{\infty} \frac{d\tau}{\sqrt{1 - \frac{\varphi(r)}{2\mu g^2} - \frac{b_{im}^2}{\tau^2}}} = \pi - 2 \sin^{-1} \left( \frac{b_{im}}{2R} \right) \). Setting \( \nu \) be the speed of one sphere in the laboratory reference frame and, with the other sphere at rest in this frame. If \( \psi \) is the deflection angle for the sphere which is moving with velocity \( \nu \) in the laboratory reference frame and \( \xi \) is
the deflection angle for the sphere at rest, then \( \psi + \xi = \frac{\pi}{2} \). Also for equal masses, \( \psi = \frac{\pi}{2} \). This gives \( \xi = \sin^{-1}\left(\frac{b_{im}}{2R}\right) \). After the collision, the sphere which was at rest acquires speed \( \nu' \) in the laboratory frame, and from momentum conservation we will find

\[
\nu' = \frac{\nu}{\left(\sin \xi \cot (\psi + \cos \xi)\right)} = \nu \sqrt{1 - \left(\frac{b_{im}}{2R}\right)^2}.
\]

Thus, when a sphere with momentum \( p \) collides with a sphere at rest, the momentum transfer for the impact parameter \( b_{im} \) is \( p \sqrt{1 - \left(\frac{b_{im}}{2R}\right)^2} \).

Now we want to know the mean square momentum transfer \( \langle p'^2 \rangle \). Monomers can collide with any impact parameter and can have any velocity. Therefore, we will average over all impact parameters and incoming momentums:

\[
\langle p'^2 \rangle = \frac{\int \int p^2 (1 - \left(\frac{b_{im}}{2R}\right)^2) f(p) db_{im} dp}{\int db_{im} \int f(p) dp} = 2 mk_B T.
\]

(3–7)

(3–8)

It is now necessary to evaluate the number of collisions a given monomer will have per unit time. If \( P(2R) \) is the monomer number density at a distance \( 2R \) from the center of a given monomer, the average number of collisions this monomer will make per unit time is \( \langle \frac{dP}{dt} \rangle = 4 \pi (2R)^2 \bar{v}_\perp P(2R) \). Here we will use \( \bar{v}_\perp = \frac{\int_0^\infty dv \nu \exp\left(-\frac{mv^2}{2k_B T}\right)}{\int_0^\infty \exp\left(-\frac{mv^2}{2k_B T}\right)} \), and the distribution of conformations for an ideal chain for \( P(2R) \) (Section 1.1). As with the end-to-end radius, the distance between any two points of an ideal chain follows a Gaussian distribution. Thus, for an ideal chain, Equation 1–10 is true for any two points \( m - m' = n \). So

\[
P(2R) = \sum_{n=1}^{N} \left(\frac{3}{2\pi nb^2}\right)^{\frac{3}{2}} \exp\left(-\frac{3(2R)^2}{2nb^2}\right)
\]

\[
= \left(\frac{3}{2\pi b^2}\right)^{\frac{3}{2}} \sum_{p=0}^{\infty} (-1)^p \left(\frac{6R^2}{b^2}\right)^p \left(\frac{1}{p!}\right) \sum_{n=1}^{N} \frac{1}{n^{p+\frac{3}{2}}}.
\]

(3–9)

(3–10)
For $N \to \infty$, 

$$P(2R) = \left(\frac{3}{2\pi b^2}\right)^\frac{3}{2} \sum_{\rho=0}^{\infty} (-1)^\rho \frac{1}{\rho + \frac{1}{2}} \left(6\left(\frac{R}{b}\right)^2\right)^\rho$$  \hspace{1cm} (3–11)$$

$$\approx \left(\frac{3}{2\pi \pi}\right)^\frac{3}{2} \frac{1}{b^3} + \frac{1}{b^3} O \left(\frac{R^2}{b^2}\right) .$$  \hspace{1cm} (3–12)$$

Thus, the mean square momentum transfer per second is

$$\langle \rho^2 \rangle \langle d\Gamma / dt \rangle = \frac{(3\frac{3}{2})(4)}{\pi} (k_B T)^{\frac{3}{2}} \sqrt{m} \left(\frac{R^2}{b^3}\right) .$$  \hspace{1cm} (3–13)$$

Since $\langle f(t) f(0) \rangle = 2\zeta k_B T \delta(t)$, above equation gives $\zeta = \left(\frac{(2)(3\frac{3}{2})}{\pi}\right) \left(\frac{R^2}{b^2}\right) (m k_B T)^{\frac{1}{2}}$.

To solve Equation 3–5, the normal components of random forces are given by

$$f_p = \frac{1}{\sqrt{N}} \int dn \cos \left(\frac{p \pi n}{N}\right) f_n .$$  \hspace{1cm} (3–14)$$

If monomers $n$ and $n'$ collide, random forces on these two monomers will be equal and opposite. Since all the random force terms on the right side of Equation 3–14 come as pairs, the presence of any term (for example $f_1$) immediately implies that there is another term equal to $-f_1$. This is a very important fact, and determines what values of $f_p$ are allowed. We want to find relaxation $\tau_p$ which is proportional to $\zeta_p / k_p$. Here $k_p$ is the property of the Gaussian chain (Section 1.1) and does not change unless the temperature changes. But the term $\zeta_p$ will be different if the random forces come as pairs. This imposes restrictions on the dissipative mechanism and these are central to the remaining derivations.

We have to consider all the possible collisions with probability $P_{nn'}$, i.e., probability that monomer $n'$ will collide with $n$. We will assume that two monomers will collide only when they are at the same point and we know this probability from the properties of Gaussian chain (Section 1.1). Since $f_n = -f_{n'}$, one term in the summation for $f_p$ will be proportional to $\left(\cos \left(\frac{p \pi n}{N}\right) - \cos \left(\frac{p \pi n'}{N}\right)\right)$. So the time correlation of $f_p$ and $f_q$ will be
\[ \langle \mathbf{f}_p(t) \cdot \mathbf{f}_q(0) \rangle = \frac{1}{N} \int \int dndn' P_{nn'} \left[ \cos \left( \frac{p \pi n}{N} \right) - \cos \left( \frac{p \pi n'}{N} \right) \right] \left[ \cos \left( \frac{q \pi n}{N} \right) - \cos \left( \frac{q \pi n'}{N} \right) \right] \langle \mathbf{f}_n(t) \cdot \mathbf{f}_n(0) \rangle. \]  
\hspace{1cm} (3-15)

Here \( \langle \mathbf{f}_n(t) \cdot \mathbf{f}_n(0) \rangle \) is related to the mean square momentum transfer, i.e., \( \langle \mathbf{f}_n(t) \cdot \mathbf{f}_n(0) \rangle = \langle p^2 \rangle \frac{d}{dt} \delta(t) \), and \( P_{nn'} \) is the probability of two monomers \( n \) and \( n' \) being at the same point. Thus,

\[ \langle \mathbf{f}_p(t) \cdot \mathbf{f}_q(0) \rangle = \frac{4}{N} \langle p^2 \rangle \langle \frac{d}{dt} \rangle \delta(t) \int \int dndn' \left[ \sin \left( \frac{p \pi (n-n')}{2N} \right) \sin \left( \frac{q \pi (n-n')}{2N} \right) \right] \left[ \sin \left( \frac{p \pi (n+n')}{2N} \right) \sin \left( \frac{q \pi (n+n')}{2N} \right) \right]. \]  
\hspace{1cm} (3-16)

Consider the summation

\[ l(p, q) = \sum_{n,n',n \neq n'} \left[ \sin \left( \frac{p'(n-n')}{2N} \right) \sin \left( \frac{q'(n-n')}{2N} \right) \right] \left[ \sin \left( p'(n+n') \right) \sin \left( q'(n+n') \right) \right]. \]  
\hspace{1cm} (3-17)

where we have used the notation \( p' = \frac{p}{2N} \) and \( q' = \frac{q}{2N} \). To perform the summation we will make a change in coordinates (Section 2.4):

\[ u = n - n', \]  
\hspace{1cm} (3-18)

\[ v = n + n'. \]  
\hspace{1cm} (3-19)

This will give:

\[ l(p, q) = \sum_{u=1}^{N} \sin \left( p'u \right) \sin \left( q'u \right) \frac{2^{N-u}}{|u|^{\frac{3}{2}}} \sum_{v=u}^{2N-u} \sin \left( p'v \right) \sin \left( q'v \right) \]  
\hspace{1cm} \sum_{u=-N}^{-1} \sin \left( p'u \right) \sin \left( q'u \right) \frac{2^{N+u}}{|u|^{\frac{3}{2}}} \sum_{v=-u}^{2N+u} \sin \left( p'v \right) \sin \left( q'v \right). \]  
\hspace{1cm} (3-20)
For diagonal element \( p = q \):

\[
I(p) = \int_1^N du \frac{\sin^2 p' u}{u^2} \int_u^{2N-u} dv \sin^2 p' v + \int_{-N}^{-1} du \frac{\sin^2 p' u}{|u|^2} \int_u^{2N+u} dv \sin^2 p' v. \tag{3-21}
\]

Integration over \( v \) (Appendix B) gives

\[
I(p) = 2N \int_1^N du \frac{\sin^2 p' u}{u^3} - 2 \int_1^N du \frac{\sin^2 p' u}{u^3} + \frac{1}{2p'} \int_1^N du \frac{\sin 2p' u}{u^3} - \frac{1}{4p'} \int_1^N du \frac{\sin 4p' u}{u^3}. \tag{3-22}
\]

We are interested in the modes for which \( p' \to 0 \). For the trigonometric series the following identity \([32]\) is used:

\[
\sum_{n=1}^{\infty} \frac{\sin nx}{n^\beta} \approx x^{\beta-1} \Gamma(1 - \beta) \cos \frac{1}{2} \pi \beta, \quad \text{for } x \to 0^+, 0 < \beta < 2. \tag{3-23}
\]

\[
\frac{1}{2p'} \sum_1^N du \frac{\sin 2p' u}{u^3} \approx \frac{1}{2p'} (2p')^{\frac{1}{2}} \Gamma\left(-\frac{1}{2}\right) \cos \frac{3\pi}{4}
\]

\[
= \frac{1}{\sqrt{2}} \frac{\sqrt{N}}{\sqrt{p}}. \tag{3-24}
\]

\[
\frac{1}{4p'} \sum_1^N du \frac{\sin 4p' u}{u^3} = \frac{\sqrt{N}}{\sqrt{p}}. \tag{3-25}
\]

\[
2N \sum_{u=1}^\infty \frac{\sin^2 p' u}{u^3} \approx 2N \sum_{u=1}^{\frac{3}{2}} \frac{(p' u)^2}{u^3}
\]

\[
\approx \frac{4\sqrt{\pi}}{3\sqrt{2}} \frac{\sqrt{N}}{\sqrt{p}}. \tag{3-26}
\]
\[ 2 \sum_{u=1}^{N} \frac{\sin^2 p'u}{u^2} = \sum_{u=1}^{N} \frac{1 - \cos 2p'u}{u^2} \]  \hspace{1cm} (3–29)

\[ = \sum_{u=1}^{N} \frac{1}{u^2} - \sum_{u=1}^{N} \frac{\cos 2p'u}{u^2} \]  \hspace{1cm} (3–30)

\[ \approx 2(\sqrt{N} - 1) - \frac{1}{\sqrt{2}} \frac{\sqrt{N}}{\sqrt{p'}}. \]  \hspace{1cm} (3–31)

Using Equations 3–25, 3–26, 3–28 and 3–31 in Equation 3–22, \( l(p) \) is given by

\[ l(p) = \sqrt{N} \left[ 1.67 \sqrt{p} + 1.12 \frac{1}{\sqrt{p'}} - 2 \right], \]  \hspace{1cm} (3–32)

which leads to the following result for \( \zeta_p \):

\[ \zeta_p = 0.42 (mk_B T)^{\frac{1}{2}} \left( \frac{R^2}{b^3} \right) \left[ \frac{1.67 \sqrt{p} + 1.12 \frac{1}{\sqrt{p'}} - 2)}{\sqrt{N}} \right]. \]  \hspace{1cm} (3–33)

This derivation is true for \( p' \to 0 \). For a finite chain the \( \frac{1}{\sqrt{p'}} \) term can not be neglected compared to \( \sqrt{p} \). For very large chain, \( p' \to 0 \) for large \( p \). Thus, \( \frac{1}{\sqrt{p'}} \ll \sqrt{p} \). In that case, \( \zeta_p \) would be similar to de Gennes term, which is proportional to \( \sqrt{\frac{p}{N}} \). But from an experimental point of view, only very small \( p' \)'s are important, because relaxation times for large \( p \) are very fast and hardly measured experimentally. Also, it is necessary to consider the nondiagonal terms. The relaxation time can be determined by measuring the dynamic structure factor from scattering experiments. This structure factor will depend on nondiagonal elements as well.

The above derivation provides a first-principles calculation of internal friction for a Gaussian chain. If the temperature is changed, the term \( P_{nn'} \) will be different and a different expression for \( \zeta_p \) will be obtained. Equation 3–33 also shows the exact proportionality constant which is \( 0.42 (mk_B T)^{\frac{1}{2}} \left( \frac{R^2}{b^3} \right) \). All the chemistry of different polymers are hidden in the term \( \left( \frac{R^2}{b^3} \right) \).
Now we will consider the nondiagonal term. Equation 3–20 gives (Appendix C)

\[
I(p, q) = \frac{1}{4(p' - q')} \left[ (-1)^{p-q} + 1 \right] \int_1^N \frac{du}{u^2} \left[ \sin 2p'u - \sin 2q'u - \sin 2(p' - q')u \right] + \frac{1}{4(p' + q')} \left[ (-1)^{p+q} + 1 \right] \int_1^N \frac{du}{u^2} \left[ \sin 2p'u + \sin 2q'u - \sin 2(p' + q')u \right].
\]

(3–34)

Considering \(I(p, q)\) for small \(p\) and \(q\), use of the identity of Equation 3–23 gives

\[
I(p, q) = \frac{\sqrt{N}}{\sqrt{2}} \left[ \frac{2p^3 - 2q^3 - (\sqrt{p + q})(p - q) - (\sqrt{p - q})(p + q)}{p^2 - q^2} \right].
\]

(3–35)

The term \(\sqrt{N}\) in the above equation is not unexpected. Compare the diagonal term \(I(p)\) (Equation 3–22) with the non diagonal term \(I(p, q)\) (Equation 3–34). Since \(I(p)\) is proportional to \(\sin^2 p'u\) and \(I(p, q)\) depends on \(\sin p'u\) and \(\sin q'u\), we may expect at first that \(I(p, q)\) would be much smaller than \(I(p)\). But since \(p\) and \(q\) are small, the terms \(\sin 2p'u\) and \(\sin 2q'u\) do not undergo many oscillations, so that \(I(p, q)\) does not drop very rapidly with \(N\).

![Figure 3-5](image)

Figure 3-5. Nondiagonal term \(I(p, q)\) as a function of \(q\) (case I). Here the value of \(I(p, q)\) for \(N = 500\) is magnified 1.5 times its rescaled value. For \(N = 1000\), it is 1.7 times its rescaled value.
Figure 3-6. Nondiagonal term $I(p, q)$ as a function of $q$ (case II). Here the value of $I(p, q)$ for $N = 500$ is magnified 1.3 times its rescaled value. For $N = 1000$, it is 1.5 times its rescaled value.

Figure 3-7. Rescaled $I(p, q)$ for three different $N$. The ratio of $\frac{I(p)}{I(p,q)}$ does not change for different $N$. Since both $p$ and $q$ are small, there are very few oscillations (Equation 3–34) and this causes the nonvanishing value of $I(p, q)$. 
Figures 3-5, 3-6, 3-7 and 3-8 show Matlab plots of \( I(p, q) \) versus \( q \). Figure 3-7 is the rescaled \( I(p, q) \), using the ratio of the diagonal terms that allow every chain to start from the same point for \( p = q = 1 \). \( I(p, q) \) for different values of \( N \) overlap when rescaled. Figures 3-5 and 3-6 show how the \( I(p, q) \) approach each other. Figures 3-5 and 3-6 also show that the ratio \( \frac{I(p)}{I(p, q)} \) changes little as \( N \) increases. As stated above, since \( p \) and \( q \) are small, there are few oscillations, so that \( N \) does not play a significant role here. Figure 3-8 is an expanded view of Figure 3-7. For \( N = 100 \) the diagonal term is about 50, and the value of the first nondiagonal term is about 3.5. The nondiagonal terms are comparable to one only for \( q \lesssim 10 \). Thus, nondiagonal terms are small compared to the diagonal term but are not negligible for small \( q \).

For uncorrelated random forces the correlation matrix is always diagonal. But correlation among the random forces generates some nondiagonal terms, which will be used to calculate the correlation between two different modes \( \mathbf{X}_p \) and \( \mathbf{X}_q \).
Considering the following equation (Section 2.1),

\[
\zeta \frac{dx}{dt} = -kx + f(t), \quad (3-36)
\]

the solution is given by

\[
x(t) = \frac{1}{\zeta} \int_{-\infty}^{t} dt' \exp \left( -\frac{(t - t')}{\tau} \right) f(t'). \quad (3-37)
\]

Thus, the time correlation between two modes \(X_p\) and \(X_q\) is given by

\[
\langle X_p(t) \cdot X_q(0) \rangle = \frac{1}{\zeta_p \zeta_q} \int_{-\infty}^{t} dt_1 \int_{-\infty}^{0} dt_2 \exp \left[ -\frac{(t - t_1)}{\tau_p} \right] \exp \left[ -\frac{(0 - t_2)}{\tau_q} \right] \langle f_p(t_1) \cdot f_q(t_2) \rangle. \quad (3-38)
\]

When there is no correlation, \(\langle f_p(t_1) \cdot f_q(t_2) \rangle = 2\zeta_p k_B T \delta_{pq} \delta(t_1 - t_2)\), and

\[
\langle X_p(t) \cdot X_q(0) \rangle = \frac{1}{\zeta_p \zeta_q} \int_{-\infty}^{t} dt_1 \int_{-\infty}^{0} dt_2 \left[ 2\zeta_p k_B T \delta(t_1 - t_2) \right] \exp \left[ -\frac{(t - t_1)}{\tau_p} \right] \exp \left[ -\frac{(0 - t_2)}{\tau_q} \right]. \quad (3-39)
\]

Thus,

\[
\langle X_p(t) \cdot X_q(0) \rangle = \delta_{pq} \frac{k_B T}{k_p} \exp \left( -\frac{t}{\tau_p} \right). \quad (3-40)
\]

In our case \(\langle f_p(t_1) \cdot f_q(t_2) \rangle = 2\zeta_k B T l(p, q) \delta(t_1 - t_2)\), where \(l\) is a function of \(p\) and \(q\) and not \(\delta_{pq}\). Since \(\tau_p\) and \(\tau_q\) can not be equal, nonvanishing terms come due to this \(l\):

\[
\langle X_p(t) \cdot X_q(0) \rangle = \frac{1}{\zeta_p \zeta_q} \int_{-\infty}^{t} dt_1 \int_{-\infty}^{0} dt_2 \exp \left[ -\frac{(t - t_1)}{\tau_p} \right] \exp \left[ -\frac{(0 - t_2)}{\tau_q} \right] [2\zeta_k B T l(p, q) \delta(t_1 - t_2)]
\]

\[
= \frac{l(p, q) [2\zeta_k B T]}{\zeta_p \zeta_q} \int_{-\infty}^{0} dt_2 \exp \left[ -\frac{(t - t_2)}{\tau_p} \right] \exp \left[ -\frac{(0 - t_2)}{\tau_q} \right], \quad (3-41)
\]

\[
= \frac{l(p, q) [2\zeta_k B T]}{\zeta_p \zeta_q} \exp \left( -\frac{t}{\tau_p} \right) \int_{-\infty}^{0} dt_2 \exp \left[ t_2 \left( \frac{1}{\tau_p} + \frac{1}{\tau_q} \right) \right], \quad (3-42)
\]

\[
= \frac{l(p, q) [2\zeta_k B T]}{\zeta_p \zeta_q} \left[ \frac{1}{\left( \frac{1}{\tau_p} + \frac{1}{\tau_q} \right)} \right] \exp \left( -\frac{t}{\tau_p} \right), \quad (3-43)
\]

\[
= \frac{l(p, q) [2\zeta_k B T]}{\zeta_q k_p + \zeta_p k_q} \exp \left( -\frac{t}{\tau_p} \right). \quad (3-44)
\]
Equation 3–45 shows that there exists correlation between different modes. For gas phase dynamics, there are also correlated random forces (Section 2.4) and thus, will have non vanishing correlation between different modes.

The term \( \langle X_p(t) \cdot X_q(0) \rangle \) can be evaluated by measuring the dynamic structure factor, which depends on \( \langle X_p(t) \cdot X_q(0) \rangle \). In fact all the theories of relaxation have discussed so far can be verified experimentally by measuring the dynamic structure factor. The following discussion of this important factor will show at what point nonvanishing correlation between different modes comes into play.

The dynamic structure factor is defined as

\[
g(k, t) = \frac{1}{N} \sum_{n,m} \left\langle \exp \left( i \left[ k \cdot (R_n(t) - R_m(0)) \right] \right) \right\rangle,
\]

and can be evaluated by measuring the time correlation of the scattered intensity. There are two regimes. If the scattering wavelength is large, i.e., \( kR_g \ll 1 \), the measurement probes only the translational motion of the entire chain. If the wavelength is small, i.e., \( kR_g \gg 1 \), the internal motion of the chain is probed. The term inside the bracket in Equation 3–46 can be written as

\[
\left\langle \exp \left( i \left[ k \cdot (R_n(t) - R_m(0)) \right] \right) \right\rangle = \exp \left( -\frac{k^2}{6} \varphi_{mn}(t) \right),
\]

where \( \varphi_{mn}(t) = \left\langle (R_n(t) - R_m(0))^2 \right\rangle \). Since \( R_n = 2 \sum X_p \cos \left( \frac{p\pi n}{N} \right) \),

\[
\varphi_{mn}(t) = \left\langle \left[ 2 \sum X_p(t) \cos \left( \frac{p\pi n}{N} \right) - 2 \sum X_q(0) \cos \left( \frac{q\pi m}{N} \right) \right]^2 \right\rangle \quad (3–48)
\]

\[
= 4 \sum_{p=1} \cos^2 \left( \frac{p\pi n}{N} \right) \left\langle X_p^2(t) \right\rangle + \cos^2 \left( \frac{p\pi m}{N} \right) \left\langle X_q^2(0) \right\rangle - 2 \sum \sum \cos \left( \frac{p\pi n}{N} \right) \cos \left( \frac{q\pi m}{N} \right) \left\langle X_p(t) \cdot X_q(0) \right\rangle \quad (3–49)
\]

The third term on the right side of Equation 3–49 contains the nondiagonal element. We have already seen that when the difference between \( p \) and \( q \) is large, nondiagonal terms are negligible and the non zero contribution arises only from the neighbors. Since we
are summing over all \( p \) and \( q \), these contributions from the neighbors add to give the
total structure factor. The exact calculation of the structure factor is quite involved, but
Equation 3–49 at least shows how nondiagonal elements would contribute in \( g(k, t) \).

3.3 Internal friction in solution

The discussion above has considered internal friction in vacuum. Now we want to
see the applicability of this theory of internal friction in solution.

When a polymer is in solution, this mechanism for internal friction is still applicable.
In the equation of motion, a random force term must be included to account for the
collisions with other monomers. When two monomers collide in vacuum, the noncolliding
monomers do not know about the event unless they are nearest or next nearest
neighbors. But in solution when two monomers will collide, the information of the
collision is carried to other monomers by hydrodynamic interactions. We need to
know what velocity field would be created for a pair of equal and opposite forces, as
determined by the behavior of the Oseen tensor.

The equation of motion is

\[
\frac{\partial R_n}{\partial t} = \sum_m H_{nm} \cdot \left( -\frac{\partial U}{\partial R_m} + f_m(t) \right),
\]

(3–50)

where \( H_{nm} \) is the Oseen tensor (Equation 2–65). Consider the part \( \sum H_{nm} \cdot f_m(t) \), i.e.,
the velocity field created by the random force:

\[
v_n = \sum H_{nm} \cdot f_m(t),
\]

(3–51)
in which

\[
H_{nm} \cdot f_m = \frac{1}{8\pi\eta|\mathbf{r}_{nm}|} \left[ \mathbf{\hat{r}}_{nm} \mathbf{\hat{r}}_{nm} + \mathbf{I} \right] \cdot f_m
\]

(3–52)

\[
= \frac{1}{8\pi\eta|\mathbf{r}_{nm}|} \left[ \frac{\mathbf{r}_{nm} \cdot \mathbf{f}_m}{|\mathbf{r}_{nm}|^2} + \mathbf{f}_m \right].
\]

(3–53)
If the force on monomer $m$ is along the $x$ direction, i.e., $f_m = f_x \hat{i}$, then [33]

$$v_n = \sum_{8\pi |r_{nm}|} \frac{1}{8\pi \eta |r_{nm}|} \left[ \frac{X_{nm} \hat{i} + Y_{nm} \hat{j} + Z_{nm} \hat{k}}{r_{nm}^2} \right] X_{nm} f_x + f_x \hat{i}. \quad (3–54)$$

So that

$$(H_{nm} \cdot f_m)_x = \frac{f_x}{8\pi \eta} \left( \frac{1}{r_{nm}^3} + \frac{X_{nm}^2}{r_{nm}^3} \right). \quad (3–55)$$

$$(H_{nm} \cdot f_m)_y = \frac{f_x}{8\pi \eta} \frac{X_{nm} Y_{nm}}{r_{nm}^3}. \quad (3–56)$$

$$(H_{nm} \cdot f_m)_z = \frac{f_x}{8\pi \eta} \frac{X_{nm} Z_{nm}}{r_{nm}^3}. \quad (3–57)$$

This force arises from the head-on collision of $m$ with monomer $m'$ as shown in Figure 3-9. We want to determine the velocity field at the position of the monomer $n$ located at $r_{nm} = Y_{nm} \hat{y}$. Figure 3-9 shows that

$$r_{nm'} = \sqrt{(2R)^2 + r_{nm}^2}, \quad X_{nm'} = -2R. \quad (3–58)$$
So the $x$ component of velocity at position $r_n$ is

$$(v_n)_x = \frac{f_x}{8\pi\eta} \left[ \left( \frac{1}{r_{nm}} + \frac{X_{nm}^2}{r_{nm}^3} \right) - \left( \frac{1}{r_{nm'}} + \frac{X_{nm'}^2}{r_{nm'}^3} \right) \right].$$  \hfill (3–59)

Here we are assuming that only $m$ and $m'$ are colliding and only these two monomers will contribute to the sum in Equation 3–51. From Figure 3-9, $X_{nm} = 0$. So

$$(v_n)_x = \frac{f_x}{8\pi\eta} \left[ \frac{1}{r_{nm}} - \frac{1}{r_{nm}} \frac{1}{\sqrt{r_{nm}^2 + (2R)^2}} - \frac{(2R)^2}{\left(\sqrt{r_{nm}^2 + (2R)^2}\right)^3} \right]$$ \hfill (3–60)

$$= \frac{f_x}{8\pi\eta} \left[ \frac{1}{r_{nm}} - \frac{1}{r_{nm}} \frac{1}{\left(1 + \frac{(2R)^2}{r_{nm}^2}\right)^{\frac{3}{2}}} - \frac{(2R)^2}{r_{nm}^3 \left(1 + \frac{(2R)^2}{r_{nm}^2}\right)^{\frac{3}{2}}} \right]$$ \hfill (3–61)

$$= \frac{f_x}{8\pi\eta} \left[ \frac{1}{r_{nm}} - \frac{1}{r_{nm}} \left(1 - \frac{1}{2} \frac{(2R)^2}{r_{nm}^2} + \ldots\right) - \frac{(2R)^2}{r_{nm}^3} \left(1 - \frac{3}{2} \frac{(2R)^2}{r_{nm}^2} + \ldots\right) \right]$$ \hfill (3–62)

$$= \frac{f_x}{8\pi\eta} \left[ - \frac{2R^2}{r_{nm}^3} + 0(r_{nm}^4) \right].$$ \hfill (3–63)

Thus,

$$(v_n)_x \propto \frac{R^2}{r_{nm}^3}.$$ \hfill (3–64)

For the $y$ component

$$(v_n)_y = \frac{f_x}{8\pi\eta} \left[ \frac{X_{nm} Y_{nm}}{r_{nm}^3} - \frac{X_{nm'} Y_{nm'}}{r_{nm'}^3} \right]$$ \hfill (3–65)

$$= \frac{f_x}{8\pi\eta} \left[ \frac{X_{nm'} Y_{nm'}}{r_{nm'}^3} \right]$$ \hfill (3–66)

$$= \frac{f_x}{8\pi\eta} \left[ \frac{2R r_{nm}}{\left((r_{nm})^2 + (2R)^2\right)^{\frac{3}{2}}} \right]$$ \hfill (3–67)

$$= \frac{f_x}{8\pi\eta} \left[ \frac{2R}{r_{nm}^2} \left(1 - \frac{3}{2} \frac{(2R)^2}{r_{nm}^2} + \ldots\right) \right]$$ \hfill (3–68)

$$= \frac{f_x}{8\pi\eta} \left[ \frac{2R}{r_{nm}^2} + 0(r_{nm}^3) \right].$$ \hfill (3–69)
Thus,
\[(v_n)_y \propto \frac{R^2}{r_{nm}^2}. \tag{3–70}\]

Similarly,
\[(v_n)_z = \frac{f_x}{8 \pi \eta} \left[ \frac{X_{n,m}Z_{n,m}}{r_{nm}^3} - \frac{X_{n,m'}Z_{n,m'}}{r_{nm'}^3} \right]. \tag{3–71}\]

We have placed monomers \(m, m'\) and \(n\) in the \(z = 0\) plane, so that \(Z_{n,m} = 0, Z_{n,m'} = 0\) and \((v_n)_z = 0\). If the monomers were in the \(y = 0\) plane, a similar treatment would show that \((v_n)_z \propto \frac{R^2}{r_{nm}^2}\).

This rough calculation shows that velocity component along the line of the pair of forces is proportional to \(\frac{1}{r_{nm}}\) and the velocity in the perpendicular direction is \(\propto \frac{R^2}{r_{nm}^2}\). Thus, for a pair of forces, \(v_n \propto \frac{R^2}{r_{nm}^2} + 0(\frac{1}{r_{nm}})\). Since for a Gaussian chain \(r_{nm}^2 \propto |n - m|\), the velocity field at monomer \(n\) for a pair of equal and opposite forces at monomer \(m\) is \(\propto \frac{1}{|n - m|}\).

The solution of Zimm model, which includes the hydrodynamic interaction, uses the following Oseen tensor for a Gaussian chain [13]

\[H_{nm} = \frac{I}{6 \pi^3 |n - m|^{\frac{1}{2}} \eta b} = h(n - m)I. \tag{3–72}\]

In terms of normal modes the equation of motion in Zimm model is

\[\frac{\partial \mathbf{X}_p}{\partial t} = \sum h_{pq} (-k_q \mathbf{X}_q + f_q), \tag{3–73}\]

where

\[h_{pq} = \frac{1}{N^2} \int_0^N \int_0^N dn \int_0^N dm \cos \left( \frac{p \pi n}{N} \right) \cos \left( \frac{q \pi m}{N} \right) h(n - m). \tag{3–74}\]

This can be written as

\[h_{pq} = \sum_{-\infty}^{\infty} h(m) \cos \left( \frac{p \pi m}{N} \right). \tag{3–75}\]

As in Zimm model if we take \(h(m) = m^{-\frac{1}{2}}\), then

\[\sum \frac{\cos \left( \frac{p \pi m}{N} \right)}{m^{\frac{1}{2}}} \propto \left( \frac{N}{\rho} \right)^{\frac{1}{2}}. \tag{3–76}\]
Consider the pair of forces, \( h(m) = m^{-1} \), which gives
\[
\sum \frac{\cos \left( \frac{p \pi m}{N} \right)}{m} \propto -\ln \left( 2 \sin \left( \frac{p \pi}{2N} \right) \right). \tag{3–77}
\]

Since the right side of Equation 3–77 is negligible compared to \( \left( \frac{N}{p} \right)^{\frac{1}{2}} \), the hydrodynamic interaction due to a pair of equal and opposite forces is negligible compared to the hydrodynamic interaction from a single random force. Therefore, we can safely say that the momentum transfer from monomer to monomer is direct and does not involve solvent. Thus, the mechanism of internal friction in vacuum is applicable in solutions as well.

In summary, we have shown first-principles calculations of internal friction. For polymers in vacuum, the dynamics of a single chain can be described by the Langevin equation where the random forces are correlated. The friction constant for different normal modes obtained by this treatment shows that correlations between different \( X_p \)'s do not vanish. For polymers in solution, the Langevin equation contains two random force terms. One arising from the solvent particles and the other from collisions with other monomers, and these two are utterly uncorrelated. We have shown that hydrodynamic interaction term for random forces caused by collisions between monomers is negligible compared to the term that arises due to solvent particles. Therefore, the dynamics in solution can be described by the Zimm model with an extra friction term which is internal; extrapolation of solvent viscosities to zero would reveal this residual dissipation.
CHAPTER 4
SHEAR THINNING NEAR THE ROUGH BOUNDARY IN A VISCOELASTIC FLOW

4.1 Dynamics of polymer melts

Interest in this dissertation research originated while studying the properties of polymer melt flow in thin capillaries. Polymer melts in thin capillaries show some unusual properties [34–38], requiring investigation of boundary effects. Chapter 4 is about the dissipation rate near the boundary.

Chapter 4 describes the shear thinning effect of a polymer melt near a corrugated boundary. First, the main ideas used to describe the dynamics of polymer melts are introduced [9] [13].

Polymer melts are noodle-like materials containing aggregations of many chains. In the melt monomers are space-filling. Since chains cannot cross each other, the motion of a single chain is restricted by the topological constraints imposed on it by its neighbors. For a molecular view of topological constraints, consider a test chain as shown in Figure 4-1.

![Figure 4-1. Two-dimensional view of a single chain in the melt. Movement of a chain in melt is restricted by topological constraints. Here the dots represent other chains. In the melt, a chain is forced to move in a tube-like region.](image)

Assuming for a moment that other chains (dots in the figure) cannot move, the motion of the test chain is restricted in a tube-like region. It cannot move in a direction perpendicular to the tube axis but can easily creep along the tube. In reality other chains are also moving, thereby renewing the tube, but the effect of tube renewal is insignificant. Therefore, as a result of topological constraints, the chains in melts are
forced to move in a tube-like region. This type of motion along a tube is called reptation, and polymer melt dynamics is described by the reptation model [39–41].

Figure 4-2. Contact between two chains in the melt. Here the contact should not be taken as topological constraint, because in this state monomers can easily push each other aside.

The first question is: what can be the diameter of the tube? The tube is created because the chains cannot cross each other. Since monomers are space-filling, each monomer in the melt comes into contact with several monomers from other chains. If the radius of a monomer is $R$ and every contact with other monomers is considered impenetrable, then the tube diameter would be $R$. But this is not the case, because the boundary of the tube is not created by all direct contacts with other monomers coming from different chains. Some contacts cause only weak topological constraints as shown in Figure 4-2.

Figure 4-3. Topological contact between two chains in the melt. This contact should be taken as a topological constraint. This type of contact is known as entanglement, but this entanglement is not the same as topologic entanglement of ring polymers.
As shown in Figure 4-3, some contacts impose heavy constraints and contribute to the formation of the tube. These types of contacts are called entanglements, and the tube is created only by entanglement contacts. This can be described quantitatively by introducing a parameter $N_e$ which is the average number of monomers or links in a chain between two consecutive entanglements. Because exact calculation of this parameter is very complicated, in modern theories $N_e$ is treated as a phenomenological parameter. Quantitatively, $N_e$ shows the ability of a polymer chain to entangle with other chains.

![Figure 4-4. Tube formed by entanglements. Inside the tube there are $\frac{N}{N_e}$ blobs placed one after another. Inside each blob, the segments follow Gaussian statistics.]

Because excluded volume interactions are screened in the melt, a polymer chain follows ideal chain statistics. If $b$ is a Kuhn segment length, the distance between two entanglements would be $bN_e^{\frac{1}{2}}$. We can take this characteristic scale as the tube diameter, because the tube is formed by entanglements. On a length scale smaller than the tube diameter $d$, the chain’s motion is not affected by entanglements, but for a length scale larger than $d$, the motion is restricted. The shortest line connecting the tube ends is called the primitive path. The tube is composed of blobs with diameter $d$, inside which the segments follow Gaussian statistics. The total contour length of the tube is obtained by adding these blobs one after another. Because there are $\frac{N}{N_e}$ such blobs with diameter...
\( d \), the contour length is given by

\[
L = \frac{N}{N_e} d = \frac{Nb}{N_e^2}. \tag{4-1}
\]

The dynamics can be described by the diffusion of individual chains along their confining tubes. First it is necessary to determine the diffusion constant. One important aspect of polymer melts is that the hydrodynamic interaction is totally screened. So if the friction constant for a segment is \( \zeta \), then the friction constant for the entire chain would be \( N\zeta \). A similar result is shown in the Rouse model (Section 2.2), where the hydrodynamic interaction is neglected. Thus, the diffusion constant for reptation along the tube would be

\[
D_t \approx \frac{k_B T}{N\zeta}. \tag{4-2}
\]

In reptational diffusion, a chain abandons some sections of the original tube and creates new sections, which are created by the motion of the end segments. Because these motions are random and do not depend on the original tube conformations, when a chain abandons the entire section of the old tube, it starts a new life, i.e., it forgets everything about the previous tube conformation. The average time \( \tau_* \), for a chain to creep out from the initial tube can be obtained with knowledge of the diffusion constant and is given by

\[
\tau_* = \frac{L^2}{D_t} = \frac{\zeta b^2}{N_e k_B T} N^3. \tag{4-3}
\]

A rigorous approach is used to determine the time correlation of the end-to-end vector. If \( R(s) \) denotes the coordinate of a point at a distance \( s \) along the primitive path from one of its ends, the end-to-end vector is \( P(t) \equiv R(L, t) - R(0, t) \).

As shown in Figure 4-5, the chain is in a tube \( ABCD \) at time \( t = 0 \). As it reptates, at a later time \( t \) it lies inside a different tube \( A'B'C'D' \). The part \( BC \) of the old tube remains in the new tube. To calculate the end-to-end vector we write \( P(0) \) and \( P(t) \) as

\[
P(0) = AB + BC + CD, \tag{4-4}
\]
Figure 4-5. Reptation of a chain in the melt. At time $t = 0$, the chain was inside the tube $ABCD$. Due to the random movements of end segments, some part of the chain left the original tube. Here $A'B$ and $CD'$ are not correlated with $ABCD$.

\[
P(t) = A'B + BC + CD'. \tag{4–5}
\]

Because the vectors $A'B$ and $CD'$ are not correlated with $P(0)$,

\[
\langle P(t) \cdot P(0) \rangle = \langle BC^2 \rangle = d\langle \sigma(t) \rangle, \tag{4–6}
\]

where $\sigma(t)$ is the contour length of $BC$. To find $\sigma(t)$ we can consider a certain segment $s$ of the original tube. This segment will disappear when any end of the primitive chain reach this point. If $\psi(s, t)$ is the probability that this segment remains in the tube at time $t$, the average of $\sigma(t)$ would be

\[
\langle \sigma(t) \rangle = \int_0^L ds \psi(s, t). \tag{4–7}
\]

Let $\Psi(\xi, t; s)$ be the probability that the primitive chain moves a distance $\xi$ before the ends reach the segment $s$. Because the chain can creep either to the right or to the left, this corresponds to a diffusion problem in one dimension, and the probability $\Psi(\xi, t; s)$ satisfies the one-dimensional diffusion equation

\[
\frac{\partial \psi}{\partial t} = D_t \frac{\partial^2 \psi}{\partial \xi^2}, \tag{4–8}
\]

with the initial condition $\Psi(\xi, 0; s) = \delta(\xi)$. $\Psi$ will satisfy the following boundary condition:

\[
\Psi(\xi, t; s) = 0 \text{ for } \xi = s \text{ and } \xi = s - L. \tag{4–9}
\]
When $\xi = s$, the segment $s$ is reached by the end and $\Psi$ vanishes. Similarly when $\xi = s - L$, the segment is reached by the other end and $\Psi$ vanishes. Because the parameter $L$ appears in the boundary condition, the solution of Equation 4–8 is a function of $D_t$ and $L$:

$$\Psi(\xi, t; s) = \sum_{p=1}^{\infty} \frac{2}{L} \sin \left( \frac{p\pi s}{L} \right) \sin \left( \frac{p\pi (s - \xi)}{L} \right) \exp \left( -\frac{p^2 t}{\tau_{\text{rep}}} \right), \quad (4–10)$$

where $\tau_{\text{rep}} = \frac{4L^2}{\pi^2 \kappa T}$. If the segments remain inside the tube then $\xi$ can be anywhere between $s - L$ and $s$, so that

$$\psi(s, t) = \int_{s-L}^{s} \Psi(\xi, t; s) d\xi. \quad (4–11)$$

From Equations 4–6, 4–7, 4–11 we get [9]

$$\langle \mathbf{P}(t) \cdot \mathbf{P}(0) \rangle = N b^2 \sum_{1,3,5,\ldots} \frac{8}{\pi^2 p^2} \exp \left( -\frac{p^2 t}{\tau_{\text{rep}}} \right), \quad (4–12)$$

which is the most important result of the reptation model. In this correlator, the longest relaxation time is $\tau_{\text{rep}}$, which is similar to the term $\tau^*$ in Equation 4–3. Therefore, the maximum relaxation time in entangled polymer melts is the average time for a chain to creep entirely out from the initial tube. The correlation in Equation 4–12 can be compared with the correlation in Rouse model. In the Rouse model the relaxation time is

$$\tau_r = \frac{\zeta N^2 b^2}{3\pi^2 k_B T}. \quad (4–13)$$

The relaxation time for reptation is

$$\tau_{\text{rep}} = \frac{\zeta N^3 b^4}{3\pi^2 k_B T d^2}. \quad (4–14)$$

In both cases individual chain behaves ideally and the hydrodynamic interaction is screened. But $\tau_r \propto N^2$ and $\tau_{\text{rep}} \propto N^3$. So $\tau_{\text{rep}} \gg \tau_r$ for long chains. The presence of entanglement causes a significant slowing of the relaxation process.
Since the maximum relaxation time is proportional to the cube of the length of the polymer, \( \tau_{\text{rep}} \) is very long and is responsible for many properties, such as the unusual viscoelasticity of polymer melts. If the characteristic time of an external action is less than \( \tau_{\text{rep}} \), then the chains do not have sufficient time to relax and the melt behaves as an elastic body. If the characteristic time of the external action is larger than \( \tau_{\text{rep}} \), then viscous flow is observed.

4.2 Stress relaxation modulus for different time Scales

This section treats the viscoelastic properties of polymer melts.

For a perfectly elastic solid, the shear modulus is the ratio of stress to strain:

\[
G = \frac{\sigma}{\gamma}. \quad (4\text{–}15)
\]

For a Newtonian liquid, the shear viscosity is the ratio of stress to strain rate:

\[
\eta = \frac{\sigma}{\dot{\gamma}}. \quad (4\text{–}16)
\]

Figure 4-6. Maxwell model to represent viscoelasticity. For a given strain, initially stress comes only from elastic element. As time proceeds, this elasticity is lost due to its attachment to viscous element.

Polymer melts are viscoelastic; i.e., they have intermediate properties between perfectly elastic solids and Newtonian liquids. A simple model of viscoelasticity is Maxwell model. In this model, a perfect elastic element is added to a viscous element in
series as shown in Figure 4-6. Since the elements are in series, the total strain is

$$\gamma = \gamma_e + \gamma_v, \quad (4-17)$$

and the stress is the same in both elements:

$$\sigma = G\gamma_e = \eta\gamma'. \quad (4-18)$$

From this equation, a characteristic time scale for the viscoelastic material, corresponding to the relaxation time, is given

$$\tau = \frac{\eta}{G}. \quad (4-19)$$

When a step strain is applied, the stress relaxation modulus is defined as the ratio of stress at time $t$ to the magnitude of the step strain:

$$G(t) = \frac{\sigma(t)}{\gamma}. \quad (4-20)$$

Using Equations 4–17 and 4–18,

$$G(t) = G_0 \exp\left(-\frac{t}{\tau}\right). \quad (4-21)$$

In the regime of linear response, the Boltzmann superposition principal applies, and the stress at a time $t$ is the sum of the strain at different times:

$$\sigma(t) = \sum_i G(t - t_i)\delta\gamma_i. \quad (4-22)$$

For a strain rate $\gamma' = \frac{\delta\gamma}{\delta t}$, $\sigma(t)$ is given by

$$\sigma(t) = \sum_i G(t - t_i)\gamma'_i\delta t_i, \quad (4-23)$$

and in a continuum limit:

$$\sigma(t) = \int_{-\infty}^{t} G(t - t')\gamma'(t')dt'. \quad (4-24)$$

This is the constitutive equation that relates stress to the strain rate.
Considering the following shear flow:

\[ v_x(r, t) = k(t) r_y, \quad v_y = v_z = 0, \]  

(4–25)

the constitutive equation is

\[ \sigma_{xy} = \int_{-\infty}^{t} G(t - t') k(t') dt'. \]  

(4–26)

If \( k(t) = \) constant, then

\[ \sigma = k \int_{-\infty}^{t} G(t - t') dt'. \]  

(4–27)

But \( k(t) \) is the strain rate, so that

\[
\begin{align*}
\sigma &= \gamma' \int_{-\infty}^{t} G(t - t') dt' \\
&= \gamma' \int_{0}^{\infty} dt G(t).
\end{align*}
\]

(4–28)

(4–29)

Thus,

\[
\frac{\sigma}{\gamma'} = \int_{0}^{\infty} dt G(t).
\]

(4–30)

This is the steady state shear viscosity.

For oscillatory flow:

\[ k(t) = k_0 \cos \omega t = k_0 [\text{Re} \exp(i\omega t)]. \]  

(4–31)

The stress can be written as

\[ \sigma_{xy} = k_0 \text{Re} \left[ \frac{G^*(\omega)}{i\omega} \exp(i\omega t) \right]. \]  

(4–32)

Since

\[
\begin{align*}
\sigma_{xy} &= k_0 \text{Re} \left[ \int_{-\infty}^{t} G(t - t') \exp(i\omega t') dt' \right] \\
&= k_0 \text{Re} \left[ \exp(i\omega t) \int_{0}^{\infty} G(t') \exp(-i\omega t') dt' \right].
\end{align*}
\]

(4–33)

(4–34)
$G^*(\omega)$ is given by

\[ G^*(\omega) = i\omega \int_0^\infty G(t') \exp(-i\omega t') dt' \]
\[ = G'(\omega) + iG''(\omega), \] (4–35)

where $G'(\omega)$ is the storage modulus and $G''(\omega)$ is the loss modulus:

\[ G'(\omega) = \omega \int_0^\infty G(t') \sin \omega t' dt', \] (4–37)

\[ G''(\omega) = \omega \int_0^\infty G(t') \cos \omega t' dt'. \] (4–38)

Thus, the stress can be written as

\[ \sigma_{xy} = k_0 \text{Re} \left[ \frac{G' + G''}{i\omega} \exp(i\omega t) \right] \]
\[ = k_0 \left[ \frac{G'}{\omega} \sin \omega t + \frac{G''}{\omega} \cos \omega t \right]. \] (4–39)

If $G(t) = G_0 \exp(-t/\tau)$ then from Equations 4–37 and 4–38,

\[ G'(\omega) = G_0 \int_0^\infty \omega \sin \omega t' \exp(-t'/\tau) dt' = G_0 \frac{(\omega \tau)^2}{1 + (\omega \tau)^2}, \] (4–41)

\[ G''(\omega) = G_0 \int_0^\infty \omega \cos \omega t' \exp(-t'/\tau) dt' = G_0 \frac{\omega \tau}{1 + (\omega \tau)^2}. \] (4–42)

For $\omega \tau \gg 1$, $G'(\omega) \gg G''(\omega)$.

For $\omega \tau \ll 1$, $G'(\omega) \ll G''(\omega)$.

So at $T \sim \tau$, where $T$ is the time period of the oscillatory shear, there is a crossover from elastic to viscous regime. Equation 4–38 gives an important relation between the loss modulus and the steady state shear viscosity:

\[ \eta = \int_0^\infty G(t') dt' = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega}. \] (4–45)
As shown in Section 4.1, the motion of chain segments involves different time scales in polymer melts. In this dissertation research, the dissipation rate near a corrugated boundary was calculated for different slip velocities. Section 4.3 will show how the strain rate frequency depends on slip velocity. Since by changing pressure gradient we can achieve a wide range of slip velocities, we need to consider in detail the dynamics of polymer melts in all time scales, from the relaxation time of a Kuhn segment to the reptation relaxation time. This section considers the stress relaxation modulus for different time scales.

To evaluate the stress relaxation modulus for different time scales, it is useful to start with chains for which \( N < N_e \) for two reasons. First, we will know how chains with large \( N \) behave in short time scales. Second, it gives guidance about how to find \( G(t) \) for long chains. When \( N < N_e \), the topological constraints do not affect chains motion. Since hydrodynamic interactions are screened in the melt and there is no volume interaction, the dynamics of a chain can be described by the Rouse model if \( N < N_e \). First, evaluation of \( G(t) \) for \( N < N_e \) will be considered.

If a stepwise shear strain is applied, the ratio of stress to strain at time \( t \) gives storage modulus \( G(t) \). So, to obtain \( G(t) \) we need a molecular expression of the stress tensor for the deformed state of the polymer melts. Since Rouse model considers only interactions between neighbors, the stress in the melt is caused by these interactions. The stress tensor for a Rouse chain with length \( N \) is \( \sigma_{\alpha\beta} \), where \( \alpha \) is the component of force per unit area perpendicular to the axis \( \beta \).

Considering a hypothetical plane perpendicular to the \( y \) axis as shown in Figure 4-7, the stress tensor \( \sigma_{xy} \) would be

\[
\sigma_{xy} = \frac{C}{N} \sum_{n=1}^{N-1} \langle f_n \left( R_{n+1,y} - R_{n,y} \right) \rangle,
\]

(4–46)
Figure 4-7. Stress tensor for polymeric liquids. If monomers $n$ and $m$ are on different sides of the plane represented by the dashed line, and if their $x$ components are different, then there would be a force along the $x$ direction. This is the origin of the microscopic stress tensor.

where $f_{nx}$ is the force link $n + 1$ applies on link $n$ along the $x$ direction, $c$ is the number of links per unit volume, and $R_{n,y}$ is the $y$ component of $R_n$. For a Rouse chain

$$f_{nx} = \frac{3k_B T}{b^2} (R_{n+1,x} - R_{n,x}).$$ \hspace{1cm} (4–47)

In the continuum limit,

$$\sigma_{xy} = \frac{c}{N} \frac{3k_B T}{b^2} \int_0^N \langle \frac{\partial R_{n,x}}{\partial n} \frac{\partial R_{n,y}}{\partial n} \rangle \, dn. \hspace{1cm} (4–48)$$

In a generic form:

$$\sigma_{\alpha\beta} = \frac{c}{N} \frac{3k_B T}{b^2} \int_0^N \langle \frac{\partial R_{n,\alpha}}{\partial n} \frac{\partial R_{n,\beta}}{\partial n} \rangle \, dn. \hspace{1cm} (4–49)$$

Using the Rouse coordinate $R_n = 2 \sum X_p(t) \cos \left( \frac{p \pi n}{N} \right)$, Equation 4–49 can be written as

$$\sigma_{\alpha\beta} = \frac{c}{N} \frac{3k_B T}{b^2} \sum_p \sum_q 4 \left( \frac{p \pi}{N} \right) \left( \frac{q \pi}{N} \right) \langle X_{p\alpha}(t)X_{q\beta}(t) \rangle \int_0^N dn \sin \left( \frac{p \pi n}{N} \right) \sin \left( \frac{q \pi n}{N} \right). \hspace{1cm} (4–50)$$

To determine the stress for the shear flow given by

$$v_x(r, t) = k(t)r_y, \hspace{0.2cm} v_y = v_z = 0, \hspace{1cm} (4–51)$$
we need to know $X_p(t)$. In a shear flow the friction force on a monomer would be proportional to $\zeta(v_n - v(r))$ [9], and the equation for $X_{px}$ is

$$\zeta_p \frac{\partial X_{px}(t)}{\partial t} = -\frac{6 \pi^2 k_B T p^2}{Nb^2} X_{px}(t) + f_{px}(t) + \zeta_p k(t) X_{py}(t). \quad (4-52)$$

Because there is no shear flow along the $y$ direction,

$$\zeta_p \frac{\partial X_{py}(t)}{\partial t} = -\frac{6 \pi^2 k_B T p^2}{Nb^2} X_{py}(t) + f_{py}(t). \quad (4-53)$$

Equations 4–52 and 4–53 can be used to give

$$\zeta_p \frac{\partial}{\partial t} \langle X_{px} X_{py} \rangle = -\frac{12 \pi^2 k_B T p^2}{Nb^2} \langle X_{px} X_{py} \rangle + \zeta_p k(t) \langle X^2_{py} \rangle. \quad (4-54)$$

If the shear is small, $\langle X^2_{py} \rangle$ can be replaced by $\langle X^2_{py} \rangle_0$, where $\langle \rangle_0$ denotes average for $k = 0$. For an immobile liquid $\langle X^2_{py} \rangle_0 = \frac{Nb^2}{6 \pi^2 p^2}$, and Equation 4–54 becomes

$$\frac{\partial}{\partial t} \langle X_{px} X_{py} \rangle = -\frac{6 \pi^2 k_B T p^2}{N^2 \zeta b^2} \langle X_{px} X_{py} \rangle + k(t) \frac{Nb^2}{6 \pi^2 p^2}. \quad (4-55)$$

This is similar to the equation $\zeta \frac{\partial x}{\partial t} = -kx + f(t)$. The solution of Equation 4–55 is

$$\langle X_{px} X_{py} \rangle = \frac{Nb^2}{6 \pi^2 p^2} \sum_{p=1}^{\infty} \int_{-\infty}^{t} dt' k(t') \exp \left( -\frac{2(t - t')}{\tau_{px}} \right), \quad (4-56)$$

where $\tau_{px}$ is the Rouse relaxation time: $\tau_{px} = \frac{\zeta N^2 b^2}{3 \pi^2 k_b T}$. Using Equation 4–56 in Equation 4–50 gives

$$\sigma_{xy} = \frac{c k_B T}{N} \sum_{p=1}^{\infty} \int_{-\infty}^{t} dt' k(t') \exp \left( -\frac{2(t - t')}{\tau_{px}} \right). \quad (4-57)$$

Using the definition of $G$ in Equation 4–24,

$$G(t) = \frac{c k_B T}{N} \sum_p \exp \left( -\frac{2t}{\tau_{px}} \right)$$

$$= \frac{c k_B T}{N} \sum_p \exp \left( -\frac{2tp^2}{\tau_r} \right). \quad (4-58)$$
where \( \tau_r \) is the maximum Rouse relaxation time. For constant \( k(t) \), Equation 4–57 gives
\[
\sigma_{xy} = k \int_0^\infty G(t) \, dt.
\]
(4–59)

Since \( k \) is the strain rate, \( \sigma_{xy}/k \) is the steady state shear viscosity, and the expression for the steady state shear viscosity \( \eta \) is
\[
\eta = \int_0^\infty G(t) \, dt
\]
(4–60)
\[
= \frac{ck_B T}{N} \sum_p \exp \left( -\frac{2tp^2}{\tau_r} \right) \]
(4–61)
\[
= \frac{ck_B T \pi^2 \tau_r}{N \cdot 12}.
\]
(4–62)

This is the molecular origin of intrinsic viscosity. To keep a constant strain rate, the interactions between neighboring chains in a deformed state must be overcome. This elaborate derivation was needed to learn how the molecular expression of the stress tensor depends on the strain rate and at what condition the steady state shear viscosity can be used in the Navier-Stokes equation.

The function \( G(t) \) describes how the stress relaxes after a step strain. For \( t \ll \tau_r \), the sum in Equation 4–58 can be replaced by an integral to give
\[
G(t) = \frac{ck_B t}{N} \left( \frac{\tau_r}{t} \right)^{\frac{3}{2}}.
\]
(4–63)

Since for \( t \gg \tau_r \) only \( p = 1 \) contribute,
\[
G(t) = \frac{ck_B T}{N} \exp \left( -\frac{2t}{\tau_r} \right).
\]
(4–64)

So far we have considered the special case of \( N < N_e \). For long chains, this same \( G(t) \) can be used if the time scale is small. A long chain in a melt does have two characteristic times, \( \tau_e \) and \( \tau_{\text{rep}} \), where \( \tau_e \) is the relaxation of the entanglement strand of \( N_e \) monomers, and \( \tau_{\text{rep}} \) is the relaxation time of the entire chain. For \( t < \tau_e \) the motion is not affected by topological constraints, and \( G(t) \) will be similar to the stress modulus.
of the Rouse chain. Since $\tau_e$ is proportional to $N_e^0$, it is much smaller than the longest Rouse relaxation time, $\tau_r$, which is proportional to $N^2$. As we are considering motion for $t < \tau_e$, Equation 4–63 can be used because $\tau_e \ll \tau_r$. Thus, the storage modulus for a chain with length $N$ is

$$G(t) = \frac{c k_B T}{N} \left( \frac{\tau_e}{t} \right)^{\frac{1}{2}}.$$  \hfill (4–65)

For $t > \tau_e$, the topological constraints affect the motion. After applying a small step strain at $t = 0$, at time $t \leq \tau_e$, the major part of the polymer chain would be confined in a deformed tube. At a later time the parts of the polymer near the ends will disengage themselves from the tube as they are reptating in a random fashion. Only the segments that are still inside the original tube would be oriented and would contribute to the stress as shown in Figure 4-8.

![Figure 4-8](image-url)

Figure 4-8. Contribution to stress from the fraction of the chain remaining in the original tube. If a step strain is applied, the confining tube will be deformed. At a later time, some part of the chain will leave this tube. Only the fraction which remains in the original tube would contribute to the stress. Here the oblique lines indicate the deformed part.

Since the stress is caused by residual orientation, it can be assumed that the stress would be proportional to the fraction $\psi(t)$ of links remaining in the original tube. Thus, the relaxation modulus for $t > \tau_e$ is

$$G(t) = G^0_n \psi(t).$$  \hfill (4–66)
In Equation 4–66, $G_N^0$ is a constant that can be evaluated by comparing $G(t)$ with the storage modulus of Rouse chains in melts. The function $\psi(t)$ was considered in Section 4.1:

$$\psi(t) = \sum_{p; \text{odd}} \frac{8}{\pi^2 p^2} \exp \left( -\frac{p^2 t}{\tau_{\text{rep}}} \right).$$  \hfill (4–67)

Now $G(t)$ from Equation 4–66 must agree with $G(t)$ from Equation 4–65 at $t \sim \tau_e$. Since $\tau_e \ll \tau_{\text{rep}}$, we can take $\psi(t) = 1$ in Equation 4–66. Thus,

$$G(t) = \frac{ck_B T}{N_e} \left( \frac{\tau_r}{\tau_e} \right)^{\frac{1}{2}} \hfill (4–68)$$

$$= \frac{ck_B T}{N_e},$$  \hfill (4–69)

where $\tau_r = \frac{\zeta k_B N_e^2}{5\pi^2 k_B T}$ and $\tau_e = \frac{\zeta k_B N_e^2}{5\pi^2 k_B T}$. Finally, the stress modulus for $t > \tau_e$ is

$$G(t) = \frac{ck_B T}{N_e} \sum_{p; \text{odd}} \frac{8}{\pi^2 p^2} \exp \left( -\frac{p^2 t}{\tau_{\text{rep}}} \right).$$ \hfill (4–70)

$G(t)$ can be drawn for all time scales involved from Equations 4–65 and 4–70. For a Rouse chain, elasticity arises due to the deformation of each chain. Thus, we have a factor $\frac{c}{N}$ for Rouse chain (Equation 4–65) which is the total number of chain in unit volume. The quantity $\frac{1}{N_e}$ in Equation 4–70 shows that elasticity depends on the number of entanglement strands per unit volume.

Now the storage and loss modulus for an oscillatory shear can be derived. If the frequency is $\omega$, then for $\omega \tau_e \ll 1$, the storage and loss modulus are (Equations 4–41 and 4–42)

$$G'(\omega) = \frac{ck_B T}{N_e} \sum_{p=1,3,5\ldots} \frac{8}{\pi^2 p^2} \frac{(\omega \tau_{\text{rep}})^2}{p^4 + (\omega \tau_{\text{rep}})^2}. \hfill (4–71)$$

$$G''(\omega) = \frac{ck_B T}{N_e} \sum_{p=1,3,5\ldots} \frac{8}{\pi^2 p^4} \frac{\omega \tau_{\text{rep}}}{p^4 + (\omega \tau_{\text{rep}})^2}. \hfill (4–72)$$

For $\omega \gg \frac{1}{\tau_{\text{rep}}}$, $G'(\omega) \gg G''(\omega)$, and the polymer melt behaves like an elastic body when the period is smaller than $\tau_{\text{rep}}$. If $\omega \ll \frac{1}{\tau_{\text{rep}}}$, then $G''(\omega) \gg G'(\omega)$, i.e., the loss modulus dominates over the storage modulus.
The steady state shear viscosity is given by
\[ \int_0^\infty G(t)dt. \]
The integral from 0 to \( \tau_e \) would be very small for a chain where \( N \gg N_e \). In that case, steady state shear viscosity would be

\[
\eta = \frac{ck_B T}{N_e} \int_0^\infty \psi(t)dt \\
= \frac{\pi^2 \ c k_B T}{12 \ N_e \ \tau_{rep}} \\
= cb^2 \zeta \frac{N^3}{N_e^2}.
\]

Thus, the steady state shear viscosity follows the power law \( \eta \propto N^3 \).

Figure 4-9. Plot of \( \ln G \) as a function of \( \ln t \). Stress modulus behaves differently on different time scales. For \( t < \tau_e \), it can be obtained from the Rouse model. For \( t > \tau_e \), entanglement comes into play and \( G \) is obtained from reptation model.

Figure 4-9 summarizes the behavior of \( G \). Since \( \tau_{rep} \) is very large, the relaxation modulus is virtually constant over a wide interval of time, extending from \( \tau_e \) to \( \tau_{rep} \) as shown in Equation 4–70. \( \tau_e \) is proportional to \( N_e^2 \) and does not depend on \( N \). On the other hand \( \tau_{rep} \propto N^3 \). So the plateau region extends as the chain length grows. In this region, stress is proportional to strain. At \( t > \tau_{rep} \), it starts to drop again. If we have a oscillatory shear, then loss modulus would be larger than the storage modulus in this region.

4.3 Dissipation rate near a corrugated boundary

When polymer melts flow along a solid surface, there may exist a nonzero velocity \( \nu \) at the surface which is known as the slip velocity \([42–48]\). If melts flow under a shear
stress $\sigma$ then

$$\sigma = f v_x = \eta \frac{dv_x}{dy} |_{y=0}, \quad (4-76)$$

where $\eta$ is the melt viscosity, and $f$ is the friction constant. This equation can be used to calculate a quantity called the slippage length $b$,

$$b = \frac{v_x}{\frac{dv_x}{dy} |_{y=0}} = \frac{\eta}{f}. \quad (4-77)$$

Figure 4-10. Plug flow. In Plug-type flow, there is a flat velocity profile, and $v_x$ does not depend on $y$.

The flow pattern can be described in terms of this slip length. For a smooth solid surface, $f$ comes from weak friction due to interactions between the wall and the monomers: $f = f_m$, where $f_m$ is the friction for monomeric liquid. On the other hand, $\eta$ for an entangled melt is huge, and so $b$ can be as large as $100 \mu m$. This leads to Plug flow as shown in Figure 4-10. If some roughness is introduced on the surface, $f$ will be larger, $b$ will drop and the familiar Poiseuille flow is observed as shown in Figure 4-11. This section treats this friction constant $f$.

Figure 4-11. Poiseuille flow. $v_x$ is maximum at the center and decreases as it approaches the boundary.
At first, the velocity field near a corrugated boundary for slip boundary condition will be derived. If the slip speed is \( V_0 \), then the boundary conditions are:

\[
\hat{n} \cdot \mathbf{V} = 0, \quad (4-78)
\]
\[
\hat{t} \cdot \mathbf{V} = V_0. \quad (4-79)
\]

![Figure 4-12. Perturbation at the surface. The flat velocity field can be disturbed by introducing a perturbation, which is controlled by the parameter \( \epsilon \).](image)

We will perturb a smooth surface by \( \epsilon g(x) \), as shown in Figure 4-12. Since \( \epsilon \) is small, corrugation will slightly perturb the velocity and pressure fields. The velocity and pressure can be written in perturbation series:

\[
\mathbf{V} = \mathbf{V}'_0 + \epsilon \mathbf{v}_1 + \epsilon^2 \mathbf{v}_2 + \epsilon^3 \mathbf{v}_3 + \ldots, \quad (4-80)
\]
\[
P = P'_0 + \epsilon p_1 + \epsilon^2 p_2 + \epsilon^3 p_3 + \ldots, \quad (4-81)
\]

where \( \mathbf{V}'_0 \) and \( P'_0 \) are velocity and pressure for smooth boundary. Since velocity and pressure will satisfy the following equations:

\[
\nabla \cdot \mathbf{v} = \eta \nabla^2 \mathbf{v}, \quad (4-82)
\]
\[
\nabla \cdot \mathbf{V} = 0, \quad (4-83)
\]

\( \mathbf{v}_1 \) and \( p_1 \) will satisfy the following relations:

\[
\frac{\partial p_1}{\partial x} = \eta \left[ \frac{\partial^2 v_{1x}}{\partial x^2} + \frac{\partial^2 v_{1x}}{\partial y^2} \right], \quad (4-84)
\]
\[
\frac{\partial p_1}{\partial y} = \eta \left[ \frac{\partial^2 v_{1y}}{\partial x^2} + \frac{\partial^2 v_{1y}}{\partial y^2} \right], \quad (4-85)
\]
\[ \frac{\partial v_{1x}}{\partial x} + \frac{\partial v_{1y}}{\partial y} = 0. \] (4–86)

Taking \( g(x) = \cos kx \), the following solutions can be considered:

\[ v_{1x} = f_1(y) \cos kx, \] (4–87)

\[ v_{1y} = f_2(y) \sin kx, \] (4–88)

\[ p_1 = f_3(y) \sin kx. \] (4–89)

Using these in Equations 4–84, 4–85 and 4–86, we will get

\[ \eta (-k^2 f_1 + f_1'') = kf_3, \] (4–90)

\[ \eta (-k^2 f_2 + f_2'') = f_3', \] (4–91)

\[ -kf_1 + f_2' = 0. \] (4–92)

These three equations can be used to get a fourth-order equation for \( f_1 \):

\[ f_1''' - 2k^2 f_1'' + k^4 f_1 = 0. \] (4–93)

The solution for \( f_1 \) is:

\[ f_1 = A \exp(ky) + B \exp(-ky) + C y \exp(ky) + D y \exp(-ky), \] (4–94)

so that

\[ v_{1x} = \left[ (A + Cy) \exp(ky) + (B + Dy) \exp(-ky) \right] \cos kx. \] (4–95)

Since \( v_{1x} \) must have an upper bound, constants \( A \) and \( C \) must be zero, giving

\[ v_{1x} = (B + Dy) \exp(-ky) \cos kx. \] (4–96)
From Equation 4–92 we get

\[
f_2 = k \int f_1 dy \tag{4–97}
\]

\[
= -\left( B + Dy + \frac{D}{k} \right) \exp(-ky). \tag{4–98}
\]

Thus,

\[
v_{1y} = -\left( B + Dy + \frac{D}{k} \right) \exp(-ky) \sin kx. \tag{4–99}
\]

The boundary conditions can be used to evaluate the constants \( B \) and \( D \). Any line of a boundary can be represented by a function \( f(x, y) \), and from the gradient of \( f(x, y) \), the normal at any point can be obtained. In this case, \( f(x, y) = y - \varepsilon g(x) \), and the normal is

\[
\hat{n} = \frac{\nabla (y - \varepsilon g(x))}{|\nabla (y - \varepsilon g(x))|} \tag{4–100}
\]

\[
= \frac{\hat{y} - \varepsilon g'(x)\hat{x}}{\left[1 + (\varepsilon g'(x))^2\right]^{\frac{1}{2}}} \tag{4–101}
\]

\[
= \hat{y} - \varepsilon g'(x)\hat{x} + 0(\varepsilon^2). \tag{4–102}
\]

Using the boundary condition \( \hat{n} \cdot V = 0 \), the following is obtained:

\[
\hat{n} \cdot V|_{y=\varepsilon g(x)} = 0 \tag{4–103}
\]

\[
= \left[(\hat{y} - \varepsilon g'(x)\hat{x}) \cdot (V_x\hat{x} + V_y\hat{y})\right]|_{y=\varepsilon g(x)} \tag{4–104}
\]

\[
= [V_y - \varepsilon g'(x)V_x]|_{y=\varepsilon g(x)}. \tag{4–105}
\]

The velocities can be expanded around \( y = 0 \):

\[
V_x = V_x|_{y=0} + \varepsilon g(x) \frac{\partial V_x}{\partial y}|_{y=0} + 0(\varepsilon^2). \tag{4–106}
\]

\[
V_y = V_y|_{y=0} + \varepsilon g(x) \frac{\partial V_y}{\partial y}|_{y=0} + 0(\varepsilon^2). \tag{4–107}
\]
From Equation 4–105,

\[ V_y|_{y=0} + \epsilon g(x) \frac{\partial V_y}{\partial y}|_{y=0} - \epsilon g'(x) V_x|_{y=0} = 0. \] (4–108)

Use of Equation 4–80 gives

\[ V'_{0y}|_{y=0} + \epsilon v_{1y}|_{y=0} + \epsilon g(x) \frac{\partial V'_{0y}}{\partial y}|_{y=0} - \epsilon g'(x) V'_{0x}|_{y=0} = 0. \] (4–109)

This is the boundary condition for the normal component.

Considering the tangential component, \( \hat{n} \cdot \hat{t} = 0 \), so that

\[ \hat{t} = \frac{\hat{x} + \epsilon g'(x)\hat{y}}{\left[1 + (\epsilon g'(x))^2\right]^\frac{1}{2}} \] (4–110)

\[ = \hat{x} + \epsilon g'(x)\hat{y} + 0(\epsilon^2). \] (4–111)

Since there is slip along the boundary with speed \( V_0 \),

\[ V_0 = \hat{t} \cdot V|_{y=\epsilon g(x)} \] (4–112)

\[ = (\hat{x} + \epsilon g'(x)\hat{y}) \cdot (V_x\hat{x} + V_y\hat{y})|_{y=\epsilon g(x)} \] (4–113)

\[ = [V_x + \epsilon g'(x)V_y]|_{y=\epsilon g(x)} \] (4–114)

\[ = V_x|_{y=0} + \epsilon g(x) \frac{\partial V_x}{\partial y}|_{y=0} + \epsilon g'(x)V_y|_{y=0} \] (4–115)

\[ = V'_{0x}|_{y=0} + \epsilon v_{1x}|_{y=0} + \epsilon g(x) \frac{\partial V'_{0x}}{\partial y}|_{y=0} + \epsilon g'(x)V'_{0y}|_{y=0}. \] (4–116)

As described above, Plug flow is expected for a small diameter capillary. If \( V'_0 = V_0\hat{x} \),

then

\[ V'_{0x} = V_0, \] (4–117)

\[ \frac{\partial V'_{0x}}{\partial y} = 0, \] (4–118)

\[ V'_{0y} = 0, \] (4–119)

\[ \frac{\partial V'_{0y}}{\partial y} = 0. \] (4–120)
Equation 4–109 becomes
\[ v_{1y}|_{y=0} + kV_0 \sin kx = 0. \]  
(4–121)

Using this result in Equation 4–99 gives
\[ - (B + \frac{D}{k}) + kV_0 = 0. \]  
(4–122)

From Equation 4–116 we have
\[ V_0 + \epsilon v_{1x}|_{y=0} = V_0. \]  
(4–123)

Thus, \( v_{1x}|_{y=0} = 0 \), and from Equation 4–96,
\[ B = 0. \]  
(4–124)

Thus, Equation 4–122 gives
\[ D = k^2 V_0, \]  
(4–125)

and the velocity fields are
\[ v_{1x} = Dy \exp(-ky) \cos kx, \]  
(4–126)
\[ v_{1y} = -(Dy + \frac{D}{k}) \exp(-ky) \sin kx, \]  
(4–127)

where \( D = k^2 V_0 \).

From the pressure and velocity fields, the friction force is given by
\[ \Sigma_x(\hat{n}) = [\sigma_{xy} - \epsilon g'(x)\sigma_{xx}]|_{y=g(x)} \]  
(4–128)
\[ = \sigma_{xy}|_{y=0} + \epsilon g(x) \frac{\partial \sigma_{xy}}{\partial y}|_{y=0} - \epsilon g'(x) \sigma_{xx}|_{y=0}, \]  
(4–129)

in this case,
\[ \sigma_{xy} = \eta \left( \frac{\partial V_x}{\partial y} + \frac{\partial V_y}{\partial x} \right) \]  
(4–130)
\[ = \eta \left( \frac{\partial v_{1x}}{\partial y} + \frac{\partial v_{1y}}{\partial x} \right). \]  
(4–131)
From Equations 4–126 and 4–127, \( \sigma_{xy} \propto \cos kx \). Thus the average would be zero. Similarly,

\[
\frac{\partial \sigma_{xy}}{\partial y} = \eta \left( \frac{\partial^2 V_x}{\partial y^2} + \frac{\partial^2 V_y}{\partial y \partial x} \right) \tag{4–132}
\]

\[
= \eta \varepsilon \left( \frac{\partial^2 v_{1x}}{\partial y^2} + \frac{\partial^2 v_{1y}}{\partial y \partial x} \right) \tag{4–133}
\]

From Equations 4–126 and 4–127, \( \frac{\partial \sigma_{xy}}{\partial y} \propto \cos kx \). Thus, the average of this term is also zero. So only the pressure term \( \sigma_{xx} \) contributes to the force. The pressure can be obtained from Equation 4–90, and the friction constant \( f \) is given by

\[
f = \frac{1}{2} \eta \varepsilon^2 k^3. \tag{4–134}
\]

This result was initially obtained by P. G. de Gennes [49]. This paper [49] shows only the final result, not the derivations of the velocity and pressure fields. The elaborate derivations of the velocity field presented above clearly shows at what points the condition of first-order perturbation is applied. This velocity field will now be used to determine the total dissipation rate.

The friction term in Equation 4–134 is obtained by solving Navier-Stokes equation. Since we are considering steady flow, the fluid element at any point is under steady shear, so that the shear rate is constant. The term \( \eta \) in the Navier-Stokes equation is the steady state shear viscosity.

The derivations above have shown how corrugation perturbs the velocity field. When a chain moves near the boundary, it experiences different strain field, which is actually an oscillatory shear, as it moves. Because the polymer melt is viscoelastic, it retains its elastic energy as it passes through an oscillatory shear. If the total dissipation rate is calculated using this oscillatory shear, the total dissipation rate will be different from the dissipation using steady state shear.

The total dissipation using an oscillatory strain rate will be obtained and subsequently related to the friction term. Since small slip velocity corresponds to an approximately
constant strain rate on a chain, for very small slip velocities the new friction term must
match the friction term obtained using steady state shear viscosity.

From Equations 4–126 and 4–127, the velocity field near the boundary is given by

\[ v_1(r, t) = D_1 y \exp(-ky) \cos kx \hat{x} - (D_1 y + \frac{D_2}{k}) \exp(-ky) \sin kx \hat{y}, \tag{4–135} \]

where \( D_1 = \epsilon k^2 V_0 \). As a chain moves, it experiences a changing velocity field. For
a steady flow, within first-order perturbation, if at time \( t = 0 \) the chain experiences
the velocity field around point \( x \), then at time \( t \) it will experience the field around point
\( x + V_0 t \). From the viewpoint of a single chain the velocity field is

\[ v(r, t) = D_1 y \cos \left[ k (x + V_0 t) \right] \exp(-ky)\hat{x} \]

\[ - (D_1 y + \frac{D_2}{k}) \sin \left[ k (x + V_0 t) \right] \exp(-ky)\hat{y}. \tag{4–136} \]

The viscoelastic properties of a material can be entirely characterized by the
constitutive equation which gives the stress tensor \( \sigma_{\alpha\beta}(t) \) in terms of the velocity gradient
tensor \( k_{\alpha\beta} \). In an ordinary fluid, the constitutive equation is

\[ \sigma_{\alpha\beta}(t) = \eta [k_{\alpha\beta}(t) + k_{\beta\alpha}(t)], \tag{4–137} \]

but in a polymeric liquid this constitutive equation becomes complicated, because the
stress depends on the history of velocity gradient tensor. If the perturbation by the
velocity gradient is small, the relation between the stress and velocity gradient would be
linear and the constitutive equation can be written as

\[ \sigma_{\alpha\beta}(t) = \int_{-\infty}^{t} dt' G(t - t') \left[ k_{\alpha\beta}(t') + k_{\beta\alpha}(t') \right], \tag{4–138} \]

where the stress modulus \( G(t - t') \) relates the strain rate at time \( t' \) to the stress at time
\( t \).
The velocity gradients can be obtained from Equation 4–136:

\[
k_{xy}(t') = \frac{\partial v_x(t')}{\partial y} \tag{4–139}
\]

\[
= [D_1 \exp(-ky) - D_1 k y \exp(-ky)] \cos[k(x + V_0 t)] \tag{4–140}
\]

\[
= [D_1 - D_1 k y] \exp(-ky) \cos[k(x + V_0 t)], \tag{4–141}
\]

\[
k_{yx}(t') = \frac{\partial v_y(t')}{\partial x} \tag{4–142}
\]

\[
= - [D_1 y + \frac{D_1}{k}] \exp(-ky)(k) \cos[k(x + V_0 t)] \tag{4–143}
\]

\[
= (-D_1 k y - D_1) \exp(-ky) \cos[k(x + V_0 t)]. \tag{4–144}
\]

Thus,

\[
k_{xy}(t') + k_{yx}(t') = -2D_1 k y \exp(-ky) \cos[k(x + V_0 t)]. \tag{4–145}
\]

This is an oscillatory strain, which can be written as

\[
\gamma(t) = k_{xy}(t') + k_{yx}(t') \tag{4–146}
\]

\[
= \gamma_0 \cos[k(x + V_0 t)] \tag{4–147}
\]

\[
= \gamma_0 \cos kx \cos(kV_0 t) - \gamma_0 \sin kx \sin(kV_0 t), \tag{4–148}
\]

where \( \gamma_0 = -2D_1 k y \exp(-ky) \). Letting \( \omega = kV_0 \), \( \gamma_1 = \gamma_0 \cos kx \), and \( \gamma_2 = \gamma_0 \sin kx \), Equation 4–148 becomes

\[
\gamma(t) = \gamma_1 \cos \omega t - \gamma_2 \sin \omega t, \tag{4–149}
\]

and the constitutive equation becomes

\[
\sigma_{xy}(t) = \int_{\infty}^{t} dt' G(t - t') \gamma(t'). \tag{4–150}
\]

As shown in Section 4.2, when an oscillatory strain is applied, the stress can be written as storage and loss modulus (Equation 4–39). So from Equations 4–149 and 4–150, \( \sigma_{xy} \)
can be written as
\[
\sigma_{xy} = \left[ \gamma_1 \frac{G'(\omega)}{\omega} \sin \omega t + \gamma_1 \frac{G''(\omega)}{\omega} \cos \omega t \right]
- \left[ \gamma_2 \frac{G'(\omega)}{\omega} \cos \omega t + \gamma_2 \frac{G''(\omega)}{\omega} \sin \omega t \right].
\] (4–151)

Because the dissipation corresponds to the product of this stress and the strain rate, the dissipation rate \(D''\) is
\[
D'' = \left[ \left( \gamma_1 \frac{G'(\omega)}{\omega} \sin \omega t + \gamma_1 \frac{G''(\omega)}{\omega} \cos \omega t \right) - \left( \gamma_2 \frac{G'(\omega)}{\omega} \cos \omega t + \gamma_2 \frac{G''(\omega)}{\omega} \sin \omega t \right) \right]
\left[ \gamma_1 \cos \omega t - \gamma_2 \sin \omega t \right].
\] (4–152)

Averaging over a time period gives the dissipation rate \(D''\) as
\[
D'' = \gamma_1^2 \frac{G''(\omega)}{\omega} \langle \cos^2 \omega t \rangle - \gamma_1^2 \frac{G'(\omega)}{\omega} \langle \cos^2 \omega t \rangle
- \gamma_1 \gamma_2 \frac{G'(\omega)}{\omega} \langle \sin^2 \omega t \rangle + \gamma_2^2 \frac{G''(\omega)}{\omega} \langle \sin^2 \omega t \rangle.
\] (4–153)

Substituting the values of \(\gamma_1\) and \(\gamma_2\) into Equation 4–153 and averaging over a wavelength gives
\[
D'' = \gamma_0^2 \frac{G''(\omega)}{\omega} \langle \cos^2 kx \rangle \langle \cos^2 \omega t \rangle
- \gamma_0^2 \frac{G'(\omega)}{\omega} \langle \cos kx \sin kx \rangle \langle \cos^2 \omega t \rangle
- \gamma_0^2 \frac{G'(\omega)}{\omega} \langle \cos kx \sin kx \rangle \langle \sin^2 \omega t \rangle
+ \gamma_0^2 \frac{G''(\omega)}{\omega} \langle \sin^2 kx \rangle \langle \sin^2 \omega t \rangle
= \frac{1}{2} \gamma_0^2 \frac{G''(\omega)}{\omega}.
\] (4–154)

Because \(\gamma_0 = -2D_1 ky \exp(-ky)\) (Equation 4–148),
\[
D''(y) = 2D_1^2 k^2 y^2 \exp(-2ky) \frac{G''(\omega)}{\omega}.
\] (4–155)
Integration over $y$ gives the total dissipation rate $D_t$ as
\[
D_t = \int_0^\infty D''(y)dy
\]  
(4–156)
\[
= 2D_1^2k^2 \frac{G''(\omega)}{\omega} \int_0^\infty y^2 \exp(-2ky)dy
\]  
(4–157)
\[
= 2D_1^2k^2 \frac{G''(\omega)}{\omega} \frac{1}{4k^3}
\]  
(4–158)
\[
= \frac{1}{2} \frac{D_1^2}{k} \frac{G''(\omega)}{\omega}.
\]  
(4–159)
Since the value of $D_1$ is (Equation 4–135)
\[
D_1 = \epsilon k^2 V_0,
\]  
(4–160)
$D_t$ becomes
\[
D_t = \frac{1}{2} \epsilon^2 k^3 \frac{G''(\omega)}{\omega} V_0^2.
\]  
(4–161)
The dissipation rate can be related to the friction force as
\[
D_t = FV_0.
\]  
(4–162)
Therefore, the friction force is given by
\[
F = \frac{1}{2} \epsilon^2 k^3 \frac{G''(\omega)}{\omega} V_0.
\]  
(4–163)
Writing the friction force as $F = fV_0$, the friction constant $f$ is
\[
f = \frac{1}{2} \epsilon^2 k^3 \frac{G''(\omega)}{\omega},
\]  
(4–164)
in which the frequency $\omega$ is $kV_0$. As the chain moves with velocity $V_0$, the period of the strain rate that it experiences is $T_s = \frac{2\pi}{kV_0}$. If $V_0$ is small so that $T_s > \tau_e$, then the reptation model must be used for the value of $G''(\omega)$ and $f$ would be
\[
f = \frac{1}{2} \epsilon^2 k^3 \frac{1}{\omega} \frac{ck_B T}{N_e} \sum_{p=1,3,5...} \frac{8}{\pi^2} \frac{\omega\tau_{rep}}{p^4 + (\omega\tau_{rep})^2}.
\]  
(4–165)
When $V_0 \to 0$, then $\omega \to 0$. From Equation 4–45, the relation between the steady state viscosity and loss modulus is given by

$$ \eta = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega}. \quad (4–166) $$

Substitution into Equation 4–164 gives

$$ f_{V_0 \to 0} = \frac{1}{2} \frac{k^3}{\omega} \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \quad (4–167) $$

$$ = \frac{1}{2} \eta \epsilon^2 k^3. \quad (4–168) $$

Equations 4–134 and Equation 4–168 were determined from two different viewpoints. To obtain Equation 4–134, we use the viewpoint of a laboratory coordinate and see a steady flow with every point in the fluid under constant strain rate. For a given boundary condition, the Navier-Stokes equation, $\nabla p = \eta \nabla^2 \mathbf{v}$, can be solved using the steady state shear viscosity and the resulting velocity and pressure fields are used to obtain the friction constant $f$.

For Equation 4–168 we use the viewpoint of a single chain, which experiences an oscillatory strain rate as it moves. The stress is obtained using a constitutive equation which takes into account the viscoelastic property of the chain. This stress is subsequently used to obtain the dissipation and ultimately the friction constant. When the chain moves very slowly, the time period of strain rate is so large that we can treat the chain as if it is under constant strain rate. Thus, these two viewpoints will overlap to each other as the velocity becomes smaller, and for $V_0 \to 0$ the friction constants from these two viewpoints exactly match each other.
CHAPTER 5
CONCLUSION TO THE SHEAR THINNING PROBLEM

Equation 4–164 can be used to obtain the friction constant for different slip velocities. For \( T_s = \frac{2\pi}{k V_0} > \tau_e \), the reptation model is used, and Equation 4–165 gives

\[
f = \frac{1}{2} \epsilon^2 k^3 \left[ \left( \frac{c k_B T}{N_e} \right) \tau_{\text{rep}} \right] \sum_{p=1,3,5...} \frac{8}{\pi^2} \frac{1}{p^4 + (\omega \tau_{\text{rep}})^2}.
\] (5–1)

From Equation 4–74, \( \left( \frac{\pi}{\omega n} \right) \left[ \left( \frac{c k_B T}{N_e} \right) \tau_{\text{rep}} \right] = \eta \), and

\[
f = \frac{1}{2} \eta \epsilon^2 k^3 \left( \frac{12}{\pi^2} \right) \sum_{p=1,3,5...} \frac{8}{\pi^2} \frac{1}{p^4 + (\omega \tau_{\text{rep}})^2}.
\] (5–2)

As shown in Chapter 4, if \( k V_0 \tau_{\text{rep}} \ll 1 \), i.e., \( T_s \gg \tau_{\text{rep}} \), then

\[f \propto \eta \epsilon^2 k^3.\] (5–3)

When \( T_s < \tau_e \), Rouse model is used, and the loss modulus in Equation 4–164 is given by

\[
f = \frac{1}{2} \epsilon^2 k^3 \frac{c k_B T}{N} \sum_{p=1} \frac{\omega \tau_{pr}}{1 + (\omega \tau_{pr})^2},
\] (5–4)

where \( \tau_{pr} = \frac{\eta}{p^2} \). Thus,

\[
f = \frac{1}{2} \epsilon^2 k^3 \left[ \left( \frac{c k_B T}{N} \right) \tau_{r} \right] \sum_{p=1} \frac{p^2}{p^4 + (\omega \tau_{r})^2}.
\] (5–5)

In this case, \( \left[ \left( \frac{c k_B T}{N} \right) \tau_{r} \right] \) is the steady state viscosity for Rouse model, \( \eta_r \). Thus,

\[
f = \frac{1}{2} \eta_r \epsilon^2 k^3 \sum_{p=1} \frac{p^2}{p^4 + (\omega \tau_{r})^2}.
\] (5–6)

For \( T_s < \tau_e \), the relaxation time for entanglement strands is much smaller than the largest Rouse relaxation time. Thus, \( T_s \ll \tau_r \), i.e., \( \omega \tau_r \gg 1 \), and the sum in Equation 5–6 can be replaced by the integral:

\[
\int_0^\infty \frac{p^2 dp}{p^4 + (\omega \tau_r)^2}.
\] (5–7)
This is a standard integral and its value is \( \approx \frac{1}{\sqrt{\omega \tau}} \). Therefore \( f \) is given by

\[
f = \frac{1}{2} \frac{\eta_r}{\tau_r} \epsilon^2 k^3 \frac{1}{\sqrt{k V_0}},
\]

\( f \propto \frac{1}{(k V_0)^{3/2}} \). \hfill (5–8)

\[
f \propto \frac{\eta}{(k V_0)^{1/2}} \propto \sum_p \frac{\eta}{k^{1/2}} \propto (k V_0)^{1/2}\]

\( f \propto \eta \). \hfill (5–9)

Figure 5-1. Friction constant \( f \) for different slip velocities. Here \( T_s = \frac{2\pi}{k V_0} \), \( \eta \) is the steady state shear viscosity of polymer melt, and \( \eta_r \) is the steady state shear viscosity for the Rouse model. The figure shows how \( f \) depends on \( V_0 \). As the slip velocity is changed, the frequency of the strain rate changes. \( G \) behaves differently for different time scales, resulting in different loss modulus for different slip velocities. Hence the friction constant varies with \( V_0 \).

The Figure 5-1 summarizes the results for different slip velocities. For \( \nu \to 0 \), friction is independent of velocity. As the velocity increases, friction constant decreases. If \( T_s \) is smaller than \( \tau_{rep} \), then friction is a function of \( V_0^2 \). If \( T_s < \tau_e \), then \( f \propto \frac{1}{V_0^3} \).

Since there is less dissipation for large velocities, the phenomenon of shear thinning of the viscoelastic flow is observed for polymer melts near a corrugated boundary.
APPENDIX A

CALCULATION OF I

\[ I_1 = \int_2^N du \frac{\sin^2 p'u}{u(\ln u)^2} \int_u^{2N-u} dv \sin^2 p'v \]
\[ = \frac{1}{2} \int_2^N du \frac{\sin^2 p'u}{u(\ln u)^2} \int_u^{2N-u} dv (1 - \cos 2p'v) \]
\[ = \frac{1}{2} \int_2^N du \frac{\sin^2 p'u}{u(\ln u)^2} \left\{ \int_u^{2N-u} dv - \int_u^{2N-u} dv \cos 2p'v \right\} \]
\[ = \frac{1}{2} \int_2^N du \frac{\sin^2 p'u}{u(\ln u)^2} \left\{ 2N - u - u - \frac{1}{2p'} [\sin 2p'v]_{u=2N-u} \right\} \]
\[ = \frac{1}{2} \int_2^N du \frac{\sin^2 p'u}{u(\ln u)^2} 2N - \frac{1}{2} \int_2^N du \frac{\sin^2 p'u}{u(\ln u)^2} 2u \]
\[ - \frac{1}{4p'} \int_2^N du \frac{\sin^2 p'u}{u(\ln u)^2} \{ \sin 2p'(2N - u) - \sin 2p'u \} \]
\[ = N \int_2^N du \frac{\sin^2 p'u}{u(\ln u)^2} - \int_2^N du \frac{\sin^2 p'u}{u(\ln u)^2} + 1 \int_2^N du \frac{\sin^2 p'u \sin 2p'u}{u(\ln u)^2}. \tag{A-1} \]

\[ I_2 = \int_{-N}^{-2} du \frac{\sin^2 p'u}{|u|(\ln |u|)^2} \int_{-u}^{-u+2N-u} dv \sin^2 p'v \]
\[ = N \int_{-N}^{-2} du \frac{\sin^2 p'u}{|u|(\ln |u|)^2} + \int_{-N}^{-2} du \frac{\sin^2 p'u}{|u|(\ln |u|)^2} \frac{1}{u} \]
\[ - \frac{1}{4p'} \int_{-N}^{-2} du \frac{\sin^2 p'u}{|u|(\ln |u|)^2} \{ \sin 2p'(2N + u) + \sin 2p'u \} \]
\[ = N \int_{-N}^{-2} du \frac{\sin^2 p'u}{|u|(\ln |u|)^2} + \int_{-N}^{-2} du \frac{\sin^2 p'u}{|u|(\ln |u|)^2} \frac{1}{u} - \frac{1}{2p'} \int_{-N}^{-2} du \frac{\sin^2 p'u \sin 2p'u}{|u|(\ln |u|)^2} \]
\[ = N \int_{-N}^{N} du \frac{\sin^2 p'u}{u(\ln u)^2} - \int_{-N}^{N} du \frac{\sin^2 p'u}{u(\ln u)^2} + \frac{1}{2p'} \int_{-N}^{N} du \frac{\sin^2 p'u \sin 2p'u}{u(\ln u)^2}. \tag{A-2} \]

\[ l = l_1 + l_2 \]
\[ = 2N \int_{-N}^{N} du \frac{\sin^2 p'u}{u(\ln u)^2} - 2 \int_{-N}^{N} du \frac{\sin^2 p'u}{u(\ln u)^2} + 1 \int_{-N}^{N} du \frac{\sin^2 p'u \sin 2p'u}{u(\ln u)^2} \]
\[ = 2N \int_{-N}^{N} du \frac{\sin^2 p'u}{u(\ln u)^2} + 1 \int_{-N}^{N} du \frac{\sin 2p'u}{u(\ln u)^2} - 1 \int_{-N}^{N} du \frac{\sin 4p'u}{u(\ln u)^2}. \tag{A-3} \]
APPENDIX B
CALCULATION OF THE DIAGONAL ELEMENTS

\[ l_1 = \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} \int_{u}^{2N-u} dv \sin^2 p'v \]
\[ = \frac{1}{2} \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} \int_{u}^{2N-u} dv (1 - \cos 2p'v) \]
\[ = \frac{1}{2} \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} \left\{ \int_{u}^{2N-u} dv - \int_{u}^{2N-u} dv \cos 2p'v \right\} \]
\[ = \frac{1}{2} \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} \left\{ 2N - u - u - \frac{1}{2p'} \sin^2 p'v \right\} \]
\[ = \frac{1}{2} \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} \left\{ 2N - \frac{1}{2} \int_{1}^{N} du \frac{\sin^2 p'u}{u^2} \right\} \]
\[ - \frac{1}{4p'} \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} \left\{ \sin 2p' \left( 2N - u \right) - \sin 2p'u \right\} \]
\[ = N \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} - \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} + \frac{1}{2p'} \int_{1}^{N} du \frac{\sin^2 p'u \sin 2p'u}{u^3}. \]  

\[ b_2 = \int_{-N}^{-1} du \frac{\sin^2 p'u}{|u|^{\frac{3}{2}}} \int_{-u}^{2N+u} dv \sin^2 p'v \]
\[ = N \int_{-N}^{-1} du \frac{\sin^2 p'u}{|u|^{\frac{3}{2}}} + \int_{-N}^{-1} du \frac{\sin^2 p'u}{|u|^{\frac{3}{2}}} \]
\[ - \frac{1}{4p'} \int_{-N}^{-1} du \frac{\sin^2 p'u}{|u|^{\frac{3}{2}}} \left\{ \sin 2p' \left( 2N + u \right) + \sin 2p'u \right\} \]
\[ = N \int_{-N}^{-1} du \frac{\sin^2 p'u}{|u|^{\frac{3}{2}}} + \int_{-N}^{-1} du \frac{\sin^2 p'u}{|u|^{\frac{3}{2}}} - \frac{1}{2p'} \int_{-N}^{-1} du \frac{\sin^2 p'u \sin 2p'u}{|u|^{\frac{3}{2}}} \]
\[ = N \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} - \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} + \frac{1}{2p'} \int_{1}^{N} du \frac{\sin^2 p'u \sin 2p'u}{u^3}. \]

\[ l = l_1 + b_2 \]
\[ = 2N \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} - \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} + \frac{1}{p'} \int_{1}^{N} du \frac{\sin^2 p'u \sin 2p'u}{u^3} \]
\[ = 2N \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} - \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} + \frac{1}{2p'} \int_{1}^{N} du \frac{\sin^2 p'u}{u^3} - \frac{1}{4p'} \int_{1}^{N} du \frac{\sin^2 p'u}{u^3}. \]

(B–3)
APPENDIX C
CALCULATION OF THE NON DIAGONAL ELEMENTS

\[ l = \sum_{u=1}^{N} \frac{\sin(p'u)\sin(q'u)}{|u|^3} \sum_{v=u}^{2N-u} \sin(p'v)\sin(q'v) \]
\[ + \sum_{u=-N}^{-1} \frac{\sin(p'u)\sin(q'u)}{|u|^3} \sum_{v=-u}^{2N+u} \sin(p'v)\sin(q'v). \]

(C–1)

\[ l_1 = \int_1^N du \frac{\sin(p'u)\sin(q'u)}{|u|^3} \int_u^{2N-u} dv \sin(p'v)\sin(q'v) \]
\[ = \frac{1}{4} \int_1^N du \frac{\cos(p' - q')u - \cos(p' + q')u}{|u|^3} \int_u^{2N-u} dv [\cos(p' - q')v - \cos(p' + q')v] \]
\[ = l_3 + 4. \]

(C–2)

where

\[ l_3 = \frac{1}{4} \int_1^N du \frac{\cos(p' - q')u - \cos(p' + q')u}{|u|^3} \]
\[ \left( \frac{1}{p' - q'} \right) \{\sin(p' - q')(2N - u) - \sin(p' - q')u\} \]
\[ = \frac{1}{4(p' - q')} \int_1^N \frac{du}{u^3} [\cos(p' - q')u - \cos(p' + q')u] \]
\[ [\sin 2N(p' - q')\cos(p' - q')u - \cos 2N(p' - q')\sin(p' - q')u - \sin(p' - q')u] \]
\[ = \frac{1}{8(p' - q')} [(-1)^{p-q} + 1] \int_1^N \frac{du}{u^3} [\cos(p' - q')u - \cos(p' + q')u] [-2\sin(p' - q')u] \]
\[ = \frac{1}{8(p' - q')} [(-1)^{p-q} + 1] \int_1^N \frac{du}{u^3} [\sin 2p'u - \sin 2q'u - \sin 2(p' - q')u], \]

(C–3)
and

\[
l_4 = \frac{1}{4} \int_1^N \frac{du}{|u|^{3/2}} \cos(p' - q')u - \cos(p' + q')u \times \\
\left( \frac{1}{p' + q'} \right) \{\sin(p' + q')(2N - u) - \sin(p' + q')u\} \\
= - \frac{1}{4(p' + q')} \int_1^N \frac{du}{u^3} \left[ \cos(p' - q')u - \cos(p' + q')u \right] \\
[\sin 2N(p' + q') \cos(p' + q')u - \cos 2N(p' + q') \sin(p' + q')u - \sin(p' + q')u] \\
= - \frac{1}{8(p' + q')} \left[ (-1)^{p+q+1} \right] \int_1^N \frac{du}{u^3} \left[ \cos(p' - q')u - \cos(p' + q')u \right] \left[ -2 \sin(p' + q')u \right] \\
= - \frac{1}{8(p' + q')} \left[ (-1)^{p+q+1} \right] \int_1^N \frac{du}{u^3} \left[ \sin 2(p' + q')u - \sin 2q'u - \sin 2p'u \right].
\]

(C-4)

\[
l_2 = l_5 + k_3,
\]

(C-5)

where

\[
k_5 = \frac{1}{4} \int_{-N}^{-1} du \frac{|u|^{3/2}}{\cos(p' - q')u - \cos(p' + q')u} \times \\
\left( \frac{1}{p' - q'} \right) \{\sin(p' - q')(2N + u) + \sin(p' - q')u\} \\
= \frac{1}{4(p' - q')} \int_{-N}^{-1} \frac{du}{|u|^{3/2}} \left[ \cos(p' - q')u - \cos(p' + q')u \right] \\
[\sin 2N(p' - q') \cos(p' - q')u + \cos 2N(p' - q') \sin(p' - q')u + \sin(p' - q')u] \\
= \frac{1}{8(p' - q')} \left[ (-1)^{p+q+1} \right] \int_{-N}^{-1} \frac{du}{|u|^{3/2}} \left[ \cos(p' - q')u - \cos(p' + q')u \right] \left[ 2 \sin(p' - q')u \right] \\
= \frac{1}{8(p' - q')} \left[ (-1)^{p+q+1} \right] \int_{-N}^{-1} \frac{du}{|u|^{3/2}} \left[ \sin 2(p' - q')u - \sin 2p'u + \sin 2q'u \right] \\
= \frac{1}{8(p' - q')} \left[ (-1)^{p+q+1} \right] \int_1^N \frac{du}{u^3} \left[ \sin 2p'u - \sin 2q'u - \sin 2(p' - q')u \right] \\
= k_3,
\]

(C-6)
and

\[ l_6 = \frac{1}{4} \int_{-N}^{1} du \frac{\cos(p' - q')u - \cos(p' + q')u}{|u|^{\frac{3}{2}}} \]
\[ \left( \frac{1}{p' + q'} \right) \{ \sin(p' + q')(2N + u) + \sin(p' + q')u \} \]
\[ = -\frac{1}{4(p' + q')} \int_{-N}^{1} du \left[ \cos(p' - q')u - \cos(p' + q')u \right] \]
\[ \left[ \sin 2N(p' + q') \cos(p' + q')u + \cos 2N(p' + q') \sin(p' + q')u + \sin(p' + q')u \right] \]
\[ = -\frac{1}{8(p' + q')} \left[ (-1)^{p+q} + 1 \right] \int_{-N}^{1} du \left| \frac{u}{|u|^{\frac{3}{2}}} \right| \left[ \cos(p' - q')u - \cos(p' + q')u \right] \left[ 2 \sin(p' + q')u \right] \]
\[ = -\frac{1}{8(p' + q')} \left[ (-1)^{p+q} + 1 \right] \int_{-N}^{1} du \left| \frac{u}{|u|^{\frac{3}{2}}} \right| \left[ \sin 2p'u + \sin 2q'u - \sin 2(p' + q')u \right] \]
\[ = -\frac{1}{8(p' + q')} \left[ (-1)^{p+q} + 1 \right] \int_{1}^{N} du \left| \frac{u}{u^2} \right| \left[ \sin 2(p' + q')u - \sin 2p'u - \sin 2q'u \right] \]
\[ = l_4. \quad (C-7) \]

\[ l = l_3 + l_4 + l_5 + l_6 \]
\[ = 2(l_3 + l_4) \]
\[ = \frac{1}{4(p' - q')} \left[ (-1)^{p-q} + 1 \right] \int_{1}^{N} du \left| \frac{u}{u^2} \right| \left[ \sin 2p'u - \sin 2q'u - \sin 2(p' - q')u \right] \]
\[ + \frac{1}{4(p' + q')} \left[ (-1)^{p+q} + 1 \right] \int_{1}^{N} du \left| \frac{u}{u^2} \right| \left[ \sin 2p'u + \sin 2q'u - \sin 2(p' + q')u \right]. \quad (C-8) \]
REFERENCES


BIOGRAPHICAL SKETCH

Sayed Hasan was born in Gaibandha, Bangladesh. After completing the Bachelor in Science degree from the Department of Physics, University of Dhaka, he moved to Gainesville, FL for graduate studies at the University of Florida. In 2007, he joined Professor Sergei Obukhov’s group in theoretical condensed matter physics and completed his Ph.D in the summer of 2012. In the future, Sayed intends to remain involved in condensed matter physics research.