

POLYMER  
STRUCTURE AND  
CHARACTERIZATION

Professor John A. Nairn

Fall 2007

# TABLE OF CONTENTS

<b>1</b>	<b>INTRODUCTION</b>	<b>1</b>
1.1	Definitions of Terms . . . . .	2
1.2	Course Goals . . . . .	5
<b>2</b>	<b>POLYMER MOLECULAR WEIGHT</b>	<b>7</b>
2.1	Introduction . . . . .	7
2.2	Number Average Molecular Weight . . . . .	9
2.3	Weight Average Molecular Weight . . . . .	10
2.4	Other Average Molecular Weights . . . . .	10
2.5	A Distribution of Molecular Weights . . . . .	11
2.6	Most Probable Molecular Weight Distribution . . . . .	12
<b>3</b>	<b>MOLECULAR CONFORMATIONS</b>	<b>21</b>
3.1	Introduction . . . . .	21
3.2	Nomenclature . . . . .	23
3.3	Property Calculation . . . . .	25
3.4	Freely-Jointed Chain . . . . .	27
3.4.1	Freely-Jointed Chain Analysis . . . . .	28
3.4.2	Comment on Freely-Jointed Chain . . . . .	34
3.5	Equivalent Freely Jointed Chain . . . . .	37
3.6	Vector Analysis of Polymer Conformations . . . . .	38
3.7	Freely-Rotating Chain . . . . .	41
3.8	Hindered Rotating Chain . . . . .	43
3.9	More Realistic Analysis . . . . .	45
3.10	Theta ( $\Theta$ ) Temperature . . . . .	47
3.11	Rotational Isomeric State Model . . . . .	48
<b>4</b>	<b>RUBBER ELASTICITY</b>	<b>57</b>
4.1	Introduction . . . . .	57
4.2	Historical Observations . . . . .	57
4.3	Thermodynamics . . . . .	60
4.4	Mechanical Properties . . . . .	62
4.5	Making Elastomers . . . . .	68
4.5.1	Diene Elastomers . . . . .	68

4.5.2	Nondiene Elastomers . . . . .	69
4.5.3	Thermoplastic Elastomers . . . . .	70
<b>5</b>	<b>AMORPHOUS POLYMERS</b>	<b>73</b>
5.1	Introduction . . . . .	73
5.2	The Glass Transition . . . . .	73
5.3	Free Volume Theory . . . . .	73
5.4	Physical Aging . . . . .	73
<b>6</b>	<b>SEMICRYSTALLINE POLYMERS</b>	<b>75</b>
6.1	Introduction . . . . .	75
6.2	Degree of Crystallization . . . . .	75
6.3	Structures . . . . .	75

# Chapter 1

## INTRODUCTION

The topic of polymer structure and characterization covers molecular structure of polymer molecules, the arrangement of polymer molecules within a bulk polymer material, and techniques used to give information about structure or properties of polymers. The subjects are logically combined because understanding how structure affects properties, as measured in characterization, is a key element of polymer materials science and engineering. The subject of polymer structure and characterization is typically a second course in polymer science. As such it will be assumed that all students have completed, as a prerequisite, an introduction to polymer materials course.

We choose to subdivide polymer structure into two areas. The first area is analysis of individual polymer molecules. Molecular structure involves the detailed description of polymer molecules, their molecular weights, and their molecular configurations and conformations. Polymers are random-coil molecules that can exist in a variety of lengths, configurations, and conformations. We can learn much about polymer materials purely by theoretical analysis of their conformations. Many of the theoretical results can be verified by experiment, but most of our insight is gained by the process of doing the theoretical analysis and not by learning about techniques used to verify the analysis. The second area is the study of how individual polymer molecules pack into a solid material to make a bulk polymer. Polymer solids are either amorphous or semicrystalline. An amorphous polymer means a non-crystalline material. A semicrystalline polymer means a mixture of polymer single crystals (polymer lamellae) and amorphous polymer. These components combine into supramolecular structures that pack into the bulk material. A polymer's properties are strongly affected by whether or not it is semicrystalline. For semicrystalline polymers, the properties are strongly affected by the amount of crystalline material and the arrangement of the supramolecular structures.

Polymer characterization involves measuring any kind of property of a polymer material. It includes both molecular characterization, such as molecular weight, microstructural information, degree of crystallinity, *etc.*, and macroscopic property measurement, such as thermal properties,

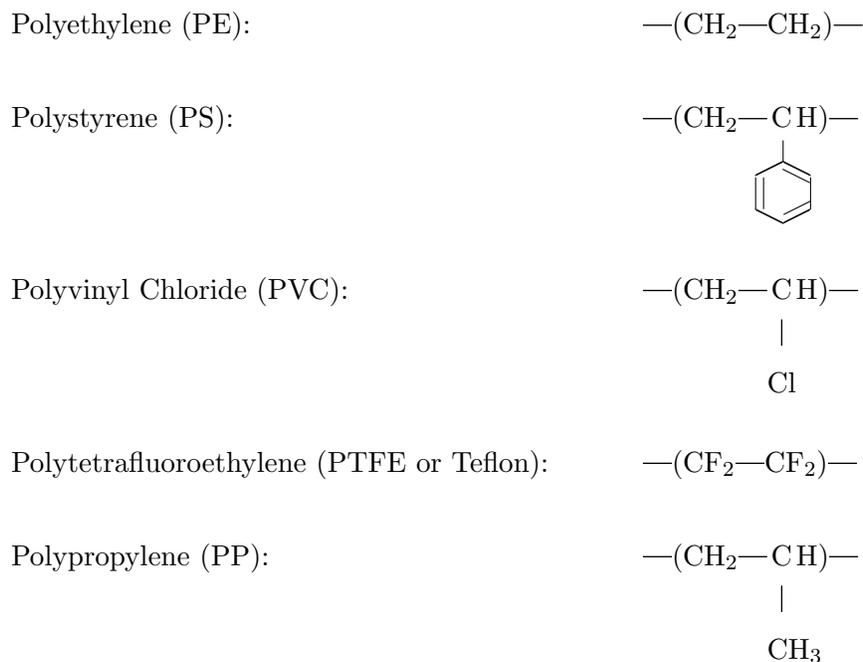
mechanical properties, microstructural information, time dependence of properties, *etc.*. Polymer characterization is done with a variety of experimental approaches. Molecular characterization uses common methods from physical chemistry and often involves polymer solutions. Sometimes spectroscopic methods can be used. Some common spectroscopic techniques are UV-visible absorption spectroscopy, infrared spectroscopy (IR), Raman spectroscopy, nuclear magnetic resonance (NMR), electron spin resonance (ESR), and mass spectrometry (MS). These techniques are usually aimed at getting information about the chemical structure of polymer materials. Macroscopic property measurement is what might be referred to as conventional polymer characterization. It involves taking a macroscopic polymer specimen, often in the final solid form, and doing experiments that give information about properties of that polymer. Some of the more important properties include thermal properties, mechanical and failure properties, melt viscosity, viscoelasticity properties, friction and wear properties, and electrical properties.

## 1.1 Definitions of Terms

The most basic definition is that of a polymer. A *polymer* is molecule formed by covalent chemical bonds between atoms (or groups of atoms) to give a large structure (linear chains, branched chains, or cross-linked networks). The key word is “large.” The word *polymer* is usually reserved for high molecular weight molecules. Historically, the fact that polymers are molecules with ordinary chemical bonds (*i.e.*, with chemical bonds identical to those found in low molecular weight molecules) was not recognized and polymers were once thought to be a distinct state of matter. Because this old thinking was wrong and instead polymers are large molecules (or macromolecules), we will find that most of the principles of chemistry (*e.g.*, chemical reactions) and physics (*e.g.*, physical properties) apply to polymers just as they do to conventional molecules. In the field of polymer characterization, we can therefore draw on all the knowledge of the physical chemistry of small molecules. Before applying any traditional physical chemistry analysis, however, we must first ask about the effect that large molecular size has on the traditional analysis and then correct for those effects. In one sense, physical chemistry of polymers and polymer characterization can be thought of as a subset of physical chemistry. Fortunately the effect of large molecular size is of enough significance that polymer science is not a trivial subset of physical chemistry — it is a challenging and important subset.

Two types of polymers are *natural* polymers and *synthetic* polymers. Natural polymers are, as expected, naturally occurring macromolecules. Natural polymers include DNA, RNA, proteins, enzymes, cellulose, collagen, silk, cotton, wool, and natural rubber. Cellulose is the most abundant polymer, natural or synthetic, on the earth. Despite the unquestioned importance of natural polymers, most of the polymer and chemical industry is based on *synthetic* polymers or polymers that can be synthesized by polymerization of low molecular weight monomers. Some example

synthetic polymers are



Other examples of synthetic polymers include nylon, polycarbonate, polymethyl methacrylate (lucite), epoxy, polyethylene terephthalate (polyester, mylar), and polyoxymethylene.

The above structures show the *repeat unit* of the polymer. The repeat unit is usually the smallest piece of the polymer that can be said to “repeat” periodically to give the polymer chain. In polyvinyl chloride the repeat unit is  $-(\text{CH}_2-\text{CHCl})-$ . In PE, the repeat unit listed above is  $-(\text{CH}_2-\text{CH}_2)-$ . From a topological point of view, the PE repeat unit could be  $-(\text{CH}_2)-$ , but because PE is polymerized from ethylene or  $\text{CH}_2=\text{CH}_2$ , it is common practice to call  $-(\text{CH}_2-\text{CH}_2)-$  the repeat unit although it is not the smallest periodically repeating unit.

The word polymer literally means many “mers” or many *monomers*. Monomers are the starting materials used in synthesizing polymers. Polymers are made by combining many monomers. The repeat unit and the monomer are usually closely related. Sometimes (*e.g.*, in condensation and most step-reaction polymers) some atoms are lost (*e.g.*, a molecule of water ( $\text{H}_2\text{O}$ )) from the monomer during polymerization and the repeat unit will differ slightly from the monomer. The names of polymers often indicate the starting monomer material. Thus polytetrafluoroethylene is a polymer made by polymerizing tetrafluoroethylene monomers.

If a polymer is made from only one type of monomer or if it has a single repeat unit, it is called a *homopolymer*. If a polymer is made from more than one type of monomer or has more than a single repeat unit, it is called a *copolymer*. Some polymers are made up of alternating monomers or alternating repeat units. Such polymers are often made from two types of monomers and thus are formally copolymers. However, it is possible to consider two consecutive monomer units in the polymer chain as a single repeat unit. As there is then only one type of repeat unit, it is common

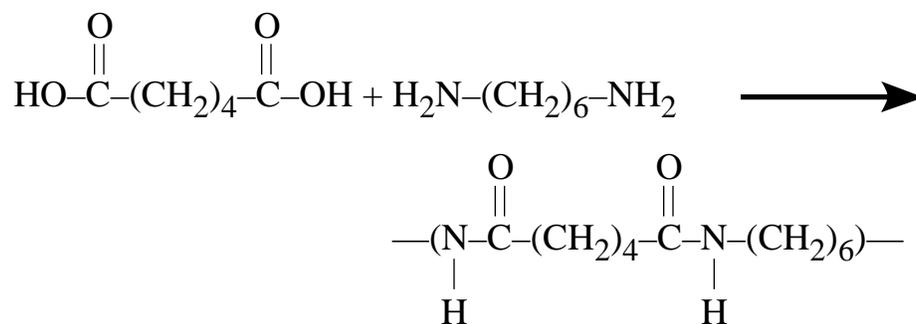


Figure 1.1: Copolymerization of the two monomers, adipic acid and hexamethyl diamine, result in synthesis of the polymer Nylon 6/6.

practice to refer to such alternately copolymers as homopolymers. A good example is Nylon 6/6. The polymerization of Nylon 6/6 is shown in Fig. 1.1. Nylon 6/6 is actually an alternating copolymer polymerized from monomers of adipic acid and hexamethyl diamine. Although it is a copolymer, the structure on the right side Fig. 1.1 can be viewed as the single repeat unit for Nylon 6/6. The “6/6” in the polymer name denotes the number of carbon atoms in each of the two monomers. The first gives the number of carbon atoms in the amine; the second gives the number of carbon atoms in the acid. Besides Nylon 6/6, other commercial nylons include Nylon 6/12, Nylon 6/11, Nylon 6/9 and Nylon 4/6. Some nylons are followed by a single number as in Nylon 6. These nylons are made from  $\omega$ -amino acids (a methylene chain with an amine group on one end and an acid group on the other) and the single number is the number of carbon atoms in the  $\omega$ -amino acid. Some examples of such commercial nylons are Nylon 6 and Nylon 11.

The repeat unit can also be called the *structural unit*. Structural units can be connected to make *linear*, *branched*, or *cross-linked* polymers. Cross-linked polymers are also called *network* polymers. Figure 1.2 shows the various ways in which structural units “A” can be connected to make a polymer molecule. The way in which structural units are connected has a profound effect on polymer properties such as toughness, viscosity, glass transition temperature, *etc.*.

Besides the way the units are connected, the total number of units also has a profound effect on polymer properties. The more units that are connected, the higher the molecular weight. A polymer must have a high molecular weight before it has useful properties, especially mechanical properties. The number of monomers, or sometimes the number of repeat units, in a polymer is called the *degree of polymerization*.

Polymers are often characterized as being *thermoplastic* or *thermoset*. A thermoplastic polymer will soften as it is heated (*i.e.*, *thermal* treatment leads to *plastic* flow). This behavior has important implications about processing such polymers. Thermoplastic polymers can usually be molded and are typically used as injection molding resins. In brief, the polymer is heated until it softens and then is injected into a mold where it cools and solidifies into a solid part. Thermoplastic behavior is



Figure 1.2: A schematic view of monomer “A” connected to make a linear, a branched, or a cross-linked polymer.

a *physically* change that is reversible; the polymer can be heated and soften and cooled and solidified many times. In contrast, a thermoset polymer *sets* up when heated. Thermoset polymers undergo irreversible *chemical* reactions on heating. Such polymers cannot be reheated and soften; instead they normally degrade when reheated. They are never processed by thermal injection molding, but instead required other processing methods such as liquid casting or reaction injection molding.

Thermoplastic polymers typically have linear polymers with few or no cross links. Thermoset polymers are typically highly cross-linked or are network polymers. It is the cross linking reactions that cause the “setting” at high temperatures. An important use of the thermoplastic and thermoset terminology is to decide how to process a given polymer. Thermoplastic polymers are processed by heating, molding, and solidification; thermoset polymers are processed by liquid or gel methods followed by chemical reactions. Some polymers fall between these two categories. For example, some polymers with no cross linking may have very high melting points and may undergo thermal degradation before they soften enough to allow molding. With regards to polymer structure, such polymers have more in common with thermoplastic polymers than with thermoset polymers. They require, however, different processing methods than thermoplastic polymers. For example, Kevlar<sup>®</sup> aramid polymer is a linear polymer, but it cannot be processed by molding. It is processed into high-modulus and high-strength fibers by a solution, fiber-spinning method.

## 1.2 Course Goals

These notes will emphasize polymer structure and characterization of high molecular weight synthetic polymers. The focus on high molecular weight is because high molecular weight is a prerequi-

site for an organic material to have useful physical properties. It takes high molecular weight before a polymer has sufficient stiffness or strength to be useful for making things ranging from clothing to airplanes. One finds high molecular weight polymers in plastic parts, synthetic fibers (both textile fibers and high performance fibers), elastomers (synthetic rubbers), glues, and composites. These uses are the ones that are important to most of the polymer industry and thus these notes focus on polymers of commercial interest. Likewise, the focus on synthetic polymers reflects the current emphasis of the polymer and chemical industry. In fact, synthetic polymers not only dominate the polymer industry, they even dominate the chemical industry as a whole. This dominance is illustrated by the fact that more than half the chemists and chemical engineers employed in this country are involved with polymers. Although the emphasis is on synthetic polymers, most of the methods work for natural polymers too. Natural polymers, however, sometimes require additional considerations to get valid results.

The ultimate goal of polymer structure and characterization is to understand polymer properties, how those properties relate to polymer structure, and how they relate to potential polymer applications. Someone well versed in polymer structure and characterization should be able to take any polymer and decide whether or not that polymer is suitable for some contemplated application. A long-range goal of polymer structure and characterization is also to design new polymer materials. With knowledge of how various polymer structures translate into polymer properties (as measured using polymer characterization), the astute polymer engineer could recommend molecular and structural modifications that could be used to create new and more useful polymers.

## Problems

- 1-1. What are the repeat units for the following polymers: Nylon 6, Nylon 11, Polymethyl methacrylate, and polypropylene?
- 1-2. What is the difference between *natural* polymers and *synthetic* polymers?
- 1-3. What is the difference between a *branched* polymer and a *cross-linked* polymer?
- 1-4. What is the difference between a *thermoplastic* polymer and a *Thermoset* polymer?
- 1-5. Search the Internet and find the top five *synthetic* polymers on the basis of volume sold.
- 1-6. Search the Internet and find product information on two commercial copolymers. Give the chemical structures of the monomers used to synthesize the polymer.

## Chapter 2

# POLYMER MOLECULAR WEIGHT

### 2.1 Introduction

Polymer molecular weight is important because it determines many physical properties. Some examples include the temperatures for transitions from liquids to waxes to rubbers to solids and mechanical properties such as stiffness, strength, viscoelasticity, toughness, and viscosity. If molecular weight is too low, the transition temperatures and the mechanical properties will generally be too low for the polymer material to have any useful commercial applications. For a polymer to be useful it must have transition temperatures to waxes or liquids that are above room temperature (*i.e.*, be a solid at room temperature) and it must have mechanical properties sufficient to bear design loads.

For example, consider the property of tensile strength. Figure 2.1 shows a typical plot of strength as a function of molecular weight. At low molecular weight, the strength is too low for the polymer material to be useful. At high molecular weight, the strength increases eventually saturating to the infinite molecular weight result of  $S_\infty$ . The strength-molecular weight relation can be approximated by the inverse relation

$$S = S_\infty - \frac{A}{M} \quad (2.1)$$

where  $A$  is a constant and  $M$  is the molecular weight. Many properties have similar molecular weight dependencies. They start at a low value and eventually saturate at a high value that is characteristic for infinite or very large molecular weight.

Unlike small molecules, however, the molecular weight of a polymer is not one unique value. Rather, a given polymer will have a distribution of molecular weights. The distribution will depend on the way the polymer is produced. For polymers we should not speak of a molecular weight, but rather of the distribution of molecular weight,  $P(M)$ , or of the average molecular weight,  $\langle M \rangle$ .

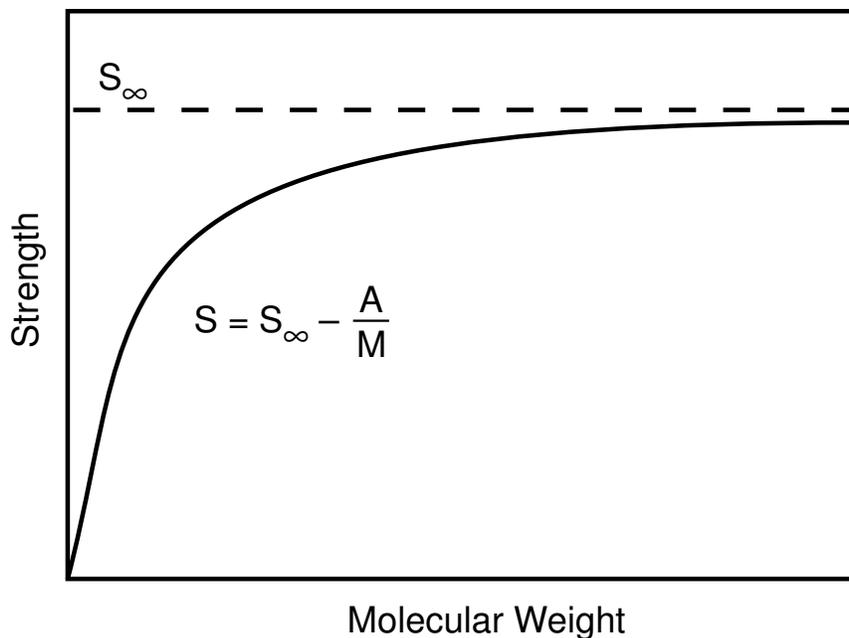


Figure 2.1: A typical plot of tensile strength as a function of molecular weight.

Polymer physical properties will be functions of the molecular weight distribution function as in

$$S = S_{\infty} - \frac{A}{F[P(M)]} \quad (2.2)$$

where  $F[P(M)]$  is some function of the complete molecular weight distribution function. For some properties,  $F[P(M)]$  may reduce to simply an *average* molecular weight. The property will thus be a function of the average molecular weight,  $\langle M \rangle$ , and insensitive to other the details of the molecular weight distribution function:

$$S = S_{\infty} - \frac{A}{\langle M \rangle} \quad (2.3)$$

There are many ways, however, to calculate an average molecular weight. The question therefore is how do you define the average molecular weight for a given distribution of molecular weights. The answer is that the type of property being studied will determine the desired type of average molecular weight. For example, strength properties may be influenced more by high molecular weight molecules than by low molecular weight molecules and thus the average molecular weight for strength properties should be weighted to emphasize the presence of high molecular weight polymer. In this chapter we consider several ways of calculating molecular weights. We also consider the meanings of those averages. Finally, we consider typical distributions of molecular weights.

## 2.2 Number Average Molecular Weight

Consider a property which is only sensitive to the number of molecules present — a property that is not influenced by the size of any particle in the mixture. The best example of such properties are the colligative properties of solutions such as boiling point elevation, freezing point depression, and osmotic pressure. For such properties, the most relevant average molecular weight is the total weight of polymer divided by the number of polymer molecules. This average molecular weight follows the conventional definition for the mean value of any statistical quantity. In polymer science, it is called the number average molecular weight —  $\overline{M}_N$ .

To get a formula for  $\overline{M}_N$ , we must first realize that the molecular weight distribution is not a continuous function of  $M$ . Rather, only discrete values of  $M$  are allowed. The possible values of  $M$  are the various multiples of the monomer molecular weight —  $M_0$ . By monomer molecular weight we mean the weight per monomer that appears in the polymer chain. For condensation reactions, for example, where molecules of water are typically lost from the monomers during reaction, we will take  $M_0$  as the monomer molecular weight less any weight loss due to the polymerization reaction. The possible values of  $M$  make up a set of numbers with discrete values labeled  $M_i$ . Let  $N_i$  be the number of polymers with molecular weight  $M_i$ . Then the total weight of all polymers is

$$\text{Total Weight} = \sum_{i=1}^{\infty} N_i M_i \quad (2.4)$$

and the total number of polymer molecules is

$$\text{Total Number} = \sum_{i=1}^{\infty} N_i \quad (2.5)$$

As discussed above, the number average molecular weight is

$$\overline{M}_N = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i} = \frac{\text{Total Weight}}{\text{Number of Polymers}} = \frac{\text{Weight}}{\text{Polymer}} \quad (2.6)$$

The term  $N_i / \sum N_i$  is physically the number fraction of polymers with molecular weight  $M_i$ . If we denote number fraction as  $X_i$  (*i.e.*, mole fraction) the number average molecular weight is

$$\overline{M}_N = \sum_{i=1}^{\infty} X_i M_i \quad (2.7)$$

In lab experiments it is more common to measure out certain weights of a polymer rather than certain numbers of moles of a polymer. It is thus useful to derive an alternate form for  $\overline{M}_N$  in terms of weight fraction of polymers with molecular weight  $M_i$  denoted as  $w_i$ . First we note that the concentration of polymer species  $i$  is (in weight per unit volume):

$$c_i = \frac{N_i M_i}{V} \quad (2.8)$$

Inserting  $c_i$  for  $N_i M_i$  and expressing  $N_i$  in terms of  $c_i$  results in

$$\overline{M}_N = \frac{\sum_{i=1}^{\infty} c_i}{\sum_{i=1}^{\infty} \frac{c_i}{M_i}} \quad (2.9)$$

Dividing numerator and denominator by  $\sum c_i$  results in

$$\overline{M}_N = \frac{1}{\sum_{i=1}^{\infty} \frac{w_i}{M_i}} \quad (2.10)$$

where  $w_i$  is the weight fraction of polymer  $i$  or the weight of polymer  $i$  divided by the total polymer weight:

$$w_i = \frac{N_i M_i}{\sum_{i=1}^{\infty} N_i M_i} = \frac{c_i}{\sum_{i=1}^{\infty} c_i} \quad (2.11)$$

## 2.3 Weight Average Molecular Weight

Consider of polymer property which depends not just on the number of polymer molecules but on the size or weight of each polymer molecule. A classic example is light scattering. For such a property we need a weight average molecular weight. To derive the weight average molecular weight, replace the appearance of the number of polymers of molecular weight  $i$  or  $N_i$  in the number average molecular weight formula with the weight of polymer having molecular weight  $i$  or  $N_i M_i$ . The result is

$$\overline{M}_W = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i} \quad (2.12)$$

By noting that  $N_i M_i / \sum N_i M_i$  is the weight fraction of polymer with molecular weight  $i$ ,  $w_i$ , an alternative form for weight average molecular weight in terms of weight fractions

$$\overline{M}_W = \sum_{i=1}^{\infty} w_i M_i \quad (2.13)$$

Comparing this expression to the expression for number average molecular weight in terms of number fraction (see Eq. (2.7)) we see that  $\overline{M}_N$  is the average  $M_i$  weighted according to number fractions and that  $\overline{M}_W$  is the average  $M_i$  weighted according to weight fractions. The meanings of their names are thus apparent.

## 2.4 Other Average Molecular Weights

To get  $\overline{M}_W$  from  $\overline{M}_N$  we replaced  $N_i$  by  $N_i M_i$ . We can generalize this process and replace  $N_i$  by  $N_i M_i^k$  to get an average molecular weight denoted as  $\overline{M}_k$ :

$$\overline{M}_k = \frac{\sum_{i=1}^{\infty} N_i M_i^{k+1}}{\sum_{i=1}^{\infty} N_i M_i^k} \quad (2.14)$$

Thus  $\overline{M}_0 = \overline{M}_N$ , and  $\overline{M}_1 = \overline{M}_W$ . Several other  $\overline{M}_k$  forms appear in experiments. Two examples are  $\overline{M}_2 = \overline{M}_z$  and  $\overline{M}_3 = \overline{M}_{z+1}$  which are used in analysis of ultracentrifugation experiments.

One average molecular weight which does not fit into the mold of  $\overline{M}_k$  is the viscosity average molecular weight or  $\overline{M}_v$ . It is defined by

$$\overline{M}_v = \left( \frac{\sum_{i=1}^{\infty} N_i M_i^{1+a}}{\sum_{i=1}^{\infty} N_i M_i} \right)^{\frac{1}{a}} \quad (2.15)$$

where  $a$  is a constant that depends on the polymer/solvent pair used in the viscosity experiments. Viscosity average molecular weight and viscosity experiments are discussed in Chapter ??.

For any molecular weight distribution, the various average molecular weights always rank in the order

$$\overline{M}_N \leq \overline{M}_v \leq \overline{M}_W \leq \overline{M}_z \leq \overline{M}_{z+1} \leq \overline{M}_4 \leq \dots \quad (2.16)$$

The equalities hold only when the polymer is monodisperse; *i.e.*, only when all molecules have the same molecular weight. For monodisperse polymers all molecular weight averages are the same and equal to the one molecular weight. For polydisperse polymers, the average molecular weights will all be different and will rank in the above order. Historically this fact was not always recognized thus it was sometimes difficult to reconcile conflicting experimental results. Say two scientists measured average molecular weight, but one used a colligative property which yields  $\overline{M}_N$  and the other used light scattering which yields  $\overline{M}_W$ . Until it was recognized that  $\overline{M}_N \neq \overline{M}_W$ , it was difficult to explain differing experimental results on the same polymer solution.

## 2.5 A Distribution of Molecular Weights

Schematically, a typical molecular weight distribution might appear as in Fig. 2.2. It resembles a probability distribution curve. The various average molecular weights are indicated in their expected rank.

The spread of any distribution function can be characterized by its standard deviation, or equivalently by its coefficient of variation. We can express the standard deviation of molecular weight in terms of  $\overline{M}_N$  and  $\overline{M}_W$ . The definition of variance,  $\sigma^2$ , is

$$\sigma^2 = \langle M^2 \rangle - \langle M \rangle^2 \quad (2.17)$$

where angle brackets (*e.g.*,  $\langle M \rangle$ ) denote conventional averaging. In terms of  $N_i$  and  $M_i$  the variance is

$$\sigma^2 = \frac{1}{N} \sum_{i=1}^{\infty} N_i M_i^2 - \left( \frac{1}{N} \sum_{i=1}^{\infty} N_i M_i \right)^2 = \frac{\sum_{i=1}^{\infty} N_i M_i^2 \sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i \sum_{i=1}^{\infty} N_i M_i} - \overline{M}_N^2 \quad (2.18)$$

which in terms of  $\overline{M}_N$  and  $\overline{M}_W$  is

$$\sigma^2 = \overline{M}_W \overline{M}_N - \overline{M}_N^2 = \overline{M}_N^2 \left( \frac{\overline{M}_W}{\overline{M}_N} - 1 \right) \quad (2.19)$$

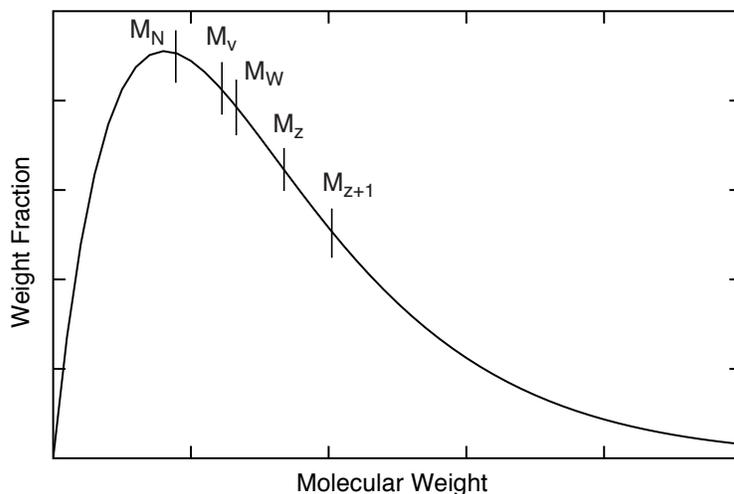


Figure 2.2: A schematic plot of a distribution of molecular weights along with the rankings of the various average molecular weights.

or the standard deviation is

$$\sigma = \overline{M}_N \sqrt{\frac{\overline{M}_W}{\overline{M}_N} - 1} \quad (2.20)$$

The coefficient of variation is the mean divided by the standard deviation. Because  $\overline{M}_N$  is also the conventional mean

$$\text{C.V.} = \frac{\sigma}{\overline{M}_N} = \sqrt{\frac{\overline{M}_W}{\overline{M}_N} - 1} \quad (2.21)$$

A key term in the coefficient of variation is  $\frac{\overline{M}_W}{\overline{M}_N}$ . This term is known as the polydispersity index. For the coefficient of variation to be real (as it must), the polydispersity index must be greater than or equal to one. When it is equal to one, the coefficient of variation is zero which means that the distribution is monodisperse. For all real polymers it is greater than one and the amount that it is greater than one is a measure of the polydispersity of that polymer.

## 2.6 Most Probable Molecular Weight Distribution

Many condensation polymers are synthesized by the polymerization of bifunctional monomers. If we denote two functional groups as  $A$  and  $B$  then a bifunctional monomer would have an  $A$  group on one end and a  $B$  group on the other and be denoted  $A-B$ . The polymerization reaction of  $A-B$  is



For example if  $A$  is an acid group ( $-\text{COOH}$ ) and  $B$  is an alcohol group ( $-\text{OH}$ ), the  $A-B$  monomer can polymerize to a polyester. Or, if  $A$  is an acid group ( $-\text{COOH}$ ) and  $B$  is an amine group ( $-\text{NH}_2$ ) the  $A-B$  monomer can polymerize to a polyamide. Flory considered the polymerization

of  $A$ — $B$  type monomers and used simple statistical arguments to calculate the expected, or most probable distribution of molecular weights. His results give us insight into typical molecular weight distributions.

We define  $p$  as the fraction of functional groups of type  $A$  that have reacted at a given stage of polymerization. Because  $A$  reacts by reacting with  $B$ , the fraction of functional groups of type  $B$  that have reacted at the same stage of polymerization is also  $p$ . We define  $p$  in mathematical terms but note that in practical terms it is often easily accessible by measurement. For example, to find the fraction of reacted acid  $A$  groups of type  $-\text{COOH}$ , one could use simple acid/base titration experiments. Next, after some amount of polymerization (*i.e.*,  $p \neq 0$ ) we select a molecule at random. We begin at one end of the molecule which will be an unreacted  $A$  group. The probability that the adjacent  $B$  group is also unreacted is simply  $(1 - p)$  — one minus the probability that a  $B$  group has reacted. Thus the probability that the randomly selected molecule is a monomer is

$$P(i = 1) = (1 - p) \quad (2.23)$$

The probability that the randomly selected molecule is a dimer is equal the product of the independent probabilities that the first group is reacted ( $p$ ) and the second is unreacted ( $1 - p$ ):

$$P(i = 2) = p(1 - p) \quad (2.24)$$

Continuing on by induction, the probability that the randomly selected molecule has a degree of polymerization  $i$  is

$$P(i) = p^{i-1}(1 - p) \quad (2.25)$$

The  $p^{i-1}$  term is for the  $i - 1$  reacted functional groups in the chain and the  $1 - p$  term is for the terminal unreacted functional group.

If there are  $N$  molecules in the polymerizing mixture, then the number of polymer chains of length  $i$  is  $N$  times the probability of having length  $i$ :

$$N_i = Np^{i-1}(1 - p) \quad (2.26)$$

$N$  is related to the initial number of monomers  $N_0$  by  $N = N_0(1 - p)$ . This relation can easily be derived by realizing that each reaction of a functional group reduces the total number of molecules by one. For extent of reaction  $p$ , the total number of molecules is reduced by  $N_0p$ . Now, in terms of known quantities  $N_i$  is

$$N_i = N_0p^{i-1}(1 - p)^2 \quad (2.27)$$

The above equation for  $N_i$  describes the complete polymer distribution. It is called the most probable distribution or the Flory Distribution. Virtually all condensation polymers no matter how they are formed will end up with a distribution resembling the most probable distribution. Plots of  $N_i$  for various values of  $p$  are given in Fig. 2.3. At all values of  $p$ , all molecular weights are present

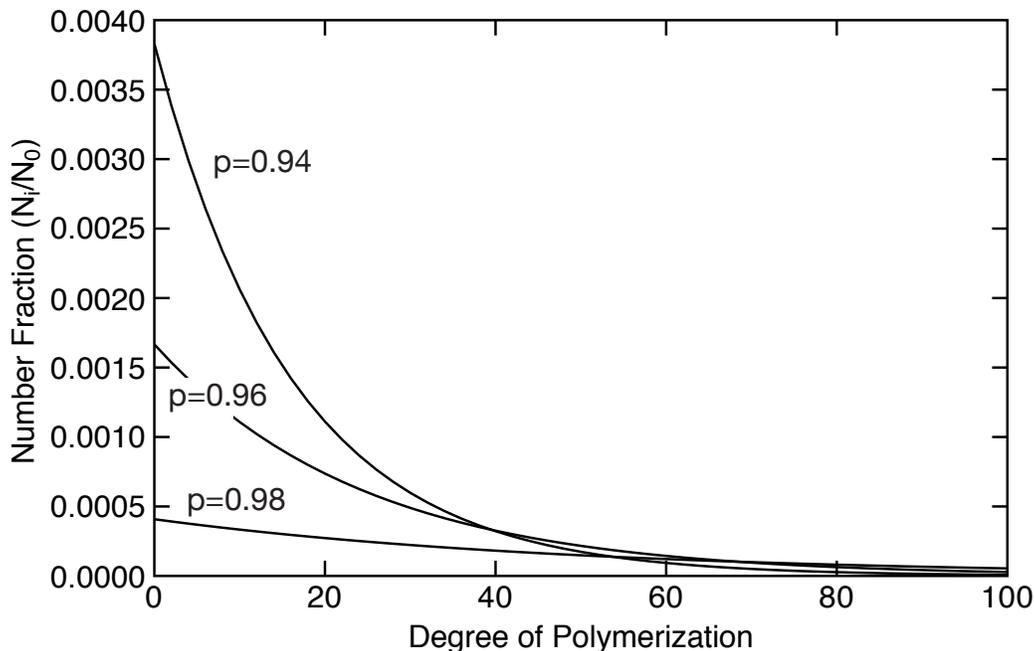


Figure 2.3: The number fraction as a function of degree of polymerization for the most probable molecular weight distribution. The three curves are for three values of  $p$ .

to some extent. The surprising result is that at all values of  $p$ , the most probable species is the monomer. This monotonically decreasing function is not the type commonly drawn to illustrate distribution functions.

A more familiar distribution function results if we consider the weight fraction of polymer with length  $i$ . Weight fraction is defined by

$$w_i = \frac{iM_0N_i}{N_0M_0} = \frac{iN_i}{N_0} = ip^{i-1}(1-p)^2 \quad (2.28)$$

where  $M_0$  is the monomer molecular weight. When the repeat of the polymer has lower molecular weight than the monomer, because of reaction products such as  $H_2O$  loss due to condensation,  $M_0$  should be the molecular weight of the monomer that makes it into the polymer. In other words,  $M_0$  is the repeat unit molecular weight,  $iM_0$  is the molecular weight of a polymer of length  $i$ , and  $N_0M_0$  is the total weight of monomer that ends up in a polymer. Some plots of weight fraction for various values of  $p$  are given in Fig. 2.4. The most prevalent species is no longer the monomer. Although there will be a lot of monomers, each monomer weighs very little. As time of reaction increases, which increases  $p$ , the peak in the weight fraction shifts to higher values and the distribution curve broadens. The peak molecular weight turns out to be very close to  $\overline{M}_N$  especially as  $p$  is close to 1 (see problem 3 at end of this chapter)

Now that we have a complete distribution function (*i.e.*, an equation for  $N_i$ ) we can calculate  $\overline{M}_N$  and  $\overline{M}_W$ . We can calculate  $\overline{M}_N$  for the most probable distribution using two methods. First

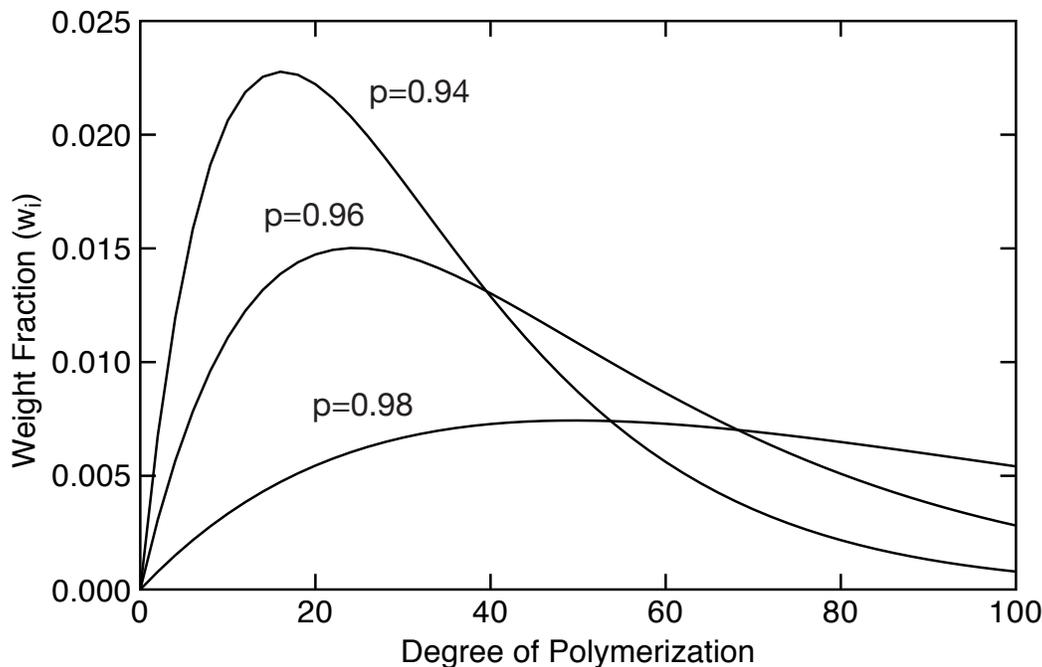


Figure 2.4: The weight fraction as a function of degree of polymerization for the most probable molecular weight distribution. The three curves are for three values of  $p$ .

we evaluate the sums in the number average molecular weight formula:

$$\overline{M}_N = \frac{\sum_{i=1}^{\infty} iM_0N_i}{\sum_{i=1}^{\infty} N_i} = M_0(1-p) \sum_{i=1}^{\infty} ip^{i-1} \quad (2.29)$$

The evaluation of the sum is nontrivial. The sum, however, can be expressed as the derivative of another sum which is simpler to evaluate.

$$\sum_{i=1}^{\infty} ip^{i-1} = \frac{d}{dp} \sum_{i=1}^{\infty} p^i = \frac{d}{dp} \left( \frac{p}{1-p} \right) \quad (2.30)$$

Evaluating the derivative gives

$$\sum_{i=1}^{\infty} ip^{i-1} = \frac{1}{(1-p)^2} \quad (2.31)$$

Multiplying by  $M_0(1-p)$  gives

$$\overline{M}_N = \frac{M_0}{1-p} \quad (2.32)$$

An alternative and simpler method to  $\overline{M}_N$  is to realize that, by conservation of mass, the total weight of material is always  $M_0N_0$ . From above, the total number of polymers is  $N_0(1-p)$ . Thus

$$\overline{M}_N = \frac{\text{Total weight of polymer}}{\text{Total number of polymers}} = \frac{M_0N_0}{N_0(1-p)} = \frac{M_0}{1-p} \quad (2.33)$$

To get  $\overline{M}_W$  for the most probable distribution we use the weight average molecular weight formula in terms of weight fractions:

$$\overline{M}_W = \sum_{i=1}^{\infty} w_i i M_0 = M_0 (1-p)^2 \sum_{i=1}^{\infty} i^2 p^{i-1} \quad (2.34)$$

We evaluate the sum using the trick used to find  $\overline{M}_N$  and some additional work.

$$\sum_{i=1}^{\infty} i^2 p^{i-1} = \frac{d}{dp} \sum_{i=1}^{\infty} i p^i = \frac{d}{dp} \left( p \sum_{i=1}^{\infty} p^{i-1} \right) = \frac{d}{dp} \left( \frac{p}{(1-p)^2} \right) \quad (2.35)$$

The last step uses the result from the  $\overline{M}_N$  calculation. Evaluating the derivative gives

$$\sum_{i=1}^{\infty} i^2 p^{i-1} = \frac{1+p}{(1-p)^3} \quad (2.36)$$

Multiplying by  $M_0(1-p)^2$  gives the final result:

$$\overline{M}_W = M_0 \frac{1+p}{1-p} \quad (2.37)$$

Combining the results for  $\overline{M}_N$  and  $\overline{M}_W$ , the polydispersity index for the most probable distribution is

$$\frac{\overline{M}_W}{\overline{M}_N} = 1+p \quad (2.38)$$

As the reaction nears completion,  $p$  approaches one and the polydispersity index approaches 2. That is the coefficient of variation of the most probable distribution is 100%. That large of a coefficient of variation means that the molecular weight distribution is relatively broad.

We also notice that as  $p$  approaches one, both  $\overline{M}_N$  and  $\overline{M}_W$  approach infinity. This limit means that all the monomers will be in a single polymer molecule. It is usually not desirable to have molecular weights that are too high. Such polymers would not be processible; they would not flow when melted. To avoid unprocessable polymers, it is desirable to use methods to control molecular weight. One way to control molecular weight would be to freeze the reaction at some  $p$  less than one. This scheme, however, can produce a material that is unstable with time. Instability occurs if over long times, there are more reactions (albeit at a slow rate) which cause  $p$  to increase. When  $p$  increases, the polymer properties change with time and might eventually give a molecular weight that is too high to be processible.

One solution to molecular weight control is to polymerize the two monomers  $A-A$  and  $B-B$  instead of the single monomer  $A-B$ . If the two monomers are mixed in equal proportions, the analysis will be identical to the one above and there will be no molecular weight control (note: although the analysis is the same, the meaning of  $M_0$  has to be changed to be *half* the repeat unit molecular weight to account for the fact that the synthesis is from two monomers ( $A-A$  and

$B-B$ ) instead of from one monomer ( $A-B$ ). If the proportions are unequal and  $r = N_A/N_B < 1$  then the results are different. A more complicated analysis gives the following  $\overline{M}_N$ :

$$\overline{M}_N = \frac{M_0(1+r)}{1+r-2rp} \approx \frac{M_0(1+r)}{1-r} \quad (2.39)$$

where, as explained above,  $M_0$  is half the repeat unit molecular weight. The second part of this equation assumes  $p$  is equal to one. Sample calculations for various values of  $r$  give

$$\begin{array}{ll} r = 1.00 & \overline{M}_N = \infty \\ r = 0.99 & \overline{M}_N = 199M_0 \\ r = 0.95 & \overline{M}_N = 39M_0 \\ r = 0.90 & \overline{M}_N = 19M_0 \end{array}$$

By selecting  $r$ , we see it is possible to control molecular weight to some finite value. Physically what happens is that the monomer mixture runs out of  $A-A$  and all polymers are end capped with  $B-B$  monomers. Because  $B$  can only react with  $A$  and no unreacted  $A$  remains, the reaction stops at a finite molecular weight. The only problem is that small changes in  $r$  lead to large changes in  $\overline{M}_N$ . For example a 5% deviation of  $r$  from 1.00 reduces the molecular weight from infinite to  $39M_0$ . But,  $39M_0$  is not a very high molecular weight and may not be high enough to be useful. To prevent polymerization from stopping at low molecular weights, you must have accurate control over  $r$ . Also you must account for any side reactions and monomer volatility which might remove monomer of one type and effectively change  $r$ .

## Problems

2-1. Suppose you have  $n$  batches of polydisperse polymers. Let  $N_{i,j}$  be the number of polymers of type  $j$  with degree of polymerization  $i$  and  $M_{i,j}$  be the molecular weight of that polymer. The basic  $\overline{M}_N$  and  $\overline{M}_W$  equations for the total mixture of polymers now require double sums:

$$\overline{M}_N = \frac{\sum_{j=1}^n \sum_i N_{i,j} M_{i,j}}{\sum_{j=1}^n \sum_i N_{i,j}} \quad \text{and} \quad \overline{M}_W = \frac{\sum_{j=1}^n \sum_i N_{i,j} M_{i,j}^2}{\sum_{j=1}^n \sum_i N_{i,j} M_{i,j}} \quad (2.40)$$

Now, assume that the number average and weight average molecular weights of batch  $j$  are  $\overline{M}_{Nj}$  and  $\overline{M}_{Wj}$ , and that you mix a weight  $w_j$  of each batch to make a new polymer blend.

- a. Starting from the above basic number average molecular weight definition, show that the number average molecular weight of the blend is

$$\overline{M}_N = \frac{w_1 + w_2 + \cdots + w_n}{\frac{w_1}{\overline{M}_{N1}} + \frac{w_2}{\overline{M}_{N2}} + \cdots + \frac{w_n}{\overline{M}_{Nn}}}$$

In other words, show that  $\overline{M}_N$  of the blend can be calculated from the individual  $\overline{M}_{Nj}$  of the components of the blend. Here  $\overline{M}_{Nj}$  has the usual definition of

$$\overline{M}_{Nj} = \frac{\sum_i N_{i,j} M_{i,j}}{\sum_i N_{i,j}} \quad (2.41)$$

or a sum over just the polymers of component  $j$ .

- b Starting from the above basic weight average molecular weight definition, show that the weight average molecular weight of the blend is

$$\overline{M}_W = \frac{w_1 \overline{M}_{W1} + w_2 \overline{M}_{W2} + \cdots + w_n \overline{M}_{Wn}}{w_1 + w_2 + \cdots + w_n}$$

In other words, show that  $\overline{M}_W$  of the blend can be calculated from the individual  $\overline{M}_{Wj}$  of the components of the blend. Here  $\overline{M}_{Wj}$  has the usual definition of

$$\overline{M}_{Wj} = \frac{\sum_i N_{i,j} M_{i,j}^2}{\sum_i N_{i,j} M_{i,j}} \quad (2.42)$$

or a sum over just the polymers of component  $j$ .

- 2-2. Calcium stearate ( $Ca(OOC(CH_2)_{16}CH_3)_2$ , molecular weight = 607) is sometimes used as a lubricant in the processing of poly(vinyl chloride). A sample of pure PVC polymer with a polydispersity index of 2.8 is modified by the addition of 3% by weight of calcium stearate. The mixture of PVC and calcium stearate is found to have  $\overline{M}_N = 15,000$  g/mol.

- What is the  $\overline{M}_N$  of the PVC part of the compound? (Hint: use the blend  $\overline{M}_N$  result from the previous problem.)
- What is the  $\overline{M}_W$  of the blend?
- What effect does the calcium stearate have on the light scattering and osmotic pressure properties of the polymer? (Hint: light scattering measures  $\overline{M}_W$  while osmotic pressure measures  $\overline{M}_N$ )
- What is the highest possible  $\overline{M}_N$  for a polymer containing 3% by weight of calcium stearate?

- 2-3. Consider the most probable molecular weight distribution:

- Derive an expression for  $P(M)$  where  $P(M)$  is the probability that a randomly selected polymer chain as molecular weight  $M$ . Express your result in terms of  $M$  (and not degree of polymerization  $i$ ).
- What molecular weight has the maximum probability?
- Derive an expression for  $w(M)$  where  $w(M)$  is the weight fraction of polymer that has molecular weight  $M$ . Again, express your answer in terms of  $M$  (and not  $x$ ).
- What molecular weight has the largest weight fraction? Express your answer in terms of the number average molecular weight.

- 2-4. Calculate the percentage conversion of functional groups required to obtain a polyester with a number-average molecular weight of 24,000 g/mol from the monomer  $HO(CH_2)_{14}COOH$ .

- 2-5. A polyamide was prepared by bulk polymerization of hexamethyl diamine (9.22 g and molecular weight 116) and adipic acid (13.2 g and molecular weight 166) at 280°C. Analysis of the whole reaction product showed that it contained  $2.6 \times 10^{-3}$  moles of carboxylic acid groups. Evaluate  $\overline{M}_N$  of the mixture. Assume it has a “most probable distribution” and also evaluate  $\overline{M}_W$ .



## Chapter 3

# MOLECULAR CONFORMATIONS

### 3.1 Introduction

Polymers can exist in various *conformations* and various *configurations*. Two polymers which differ only by rotations about single bonds are said to be two different conformations of that polymer. A schematic view of two polymer conformations is shown in Fig. 3.1. Two polymers which have the same chemical composition but can only be made identical (*e.g.*, superposable) by breaking and reforming bonds are said to be two configurations of that polymer. Two examples in Fig. 3.2 are polymers that contain asymmetric carbon atoms or that contain double bonds. Asymmetric carbon atoms can exist in *d* or *l* states while double bonds can exist in *cis* or *trans* states. No manner of rotations about single bonds can turn polymers in different configuration states into superposable polymers.

The above definitions of *conformation* and *configuration* are standard, but they have not always been rigorously followed in the literature. For example, Paul Flory, who won a Nobel prize for studies of polymer conformations, used configuration in his writings when he meant conformation. Fortunately a writer's meaning is usually obvious from context. It is recommended that you strive to use the correct terminology as defined above. These notes strive to follow that convention.

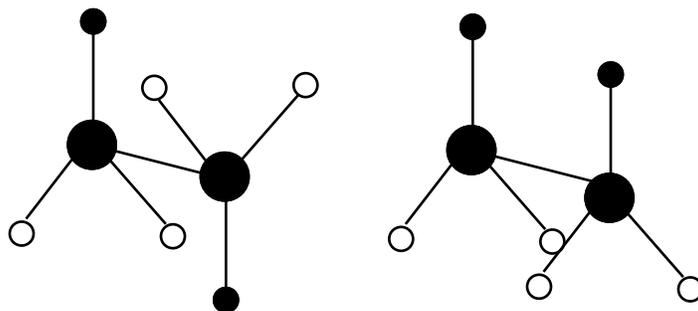


Figure 3.1: Two molecules with different conformations. These two molecules can be made identical with a rotation of  $180^\circ$  about the central single bond.

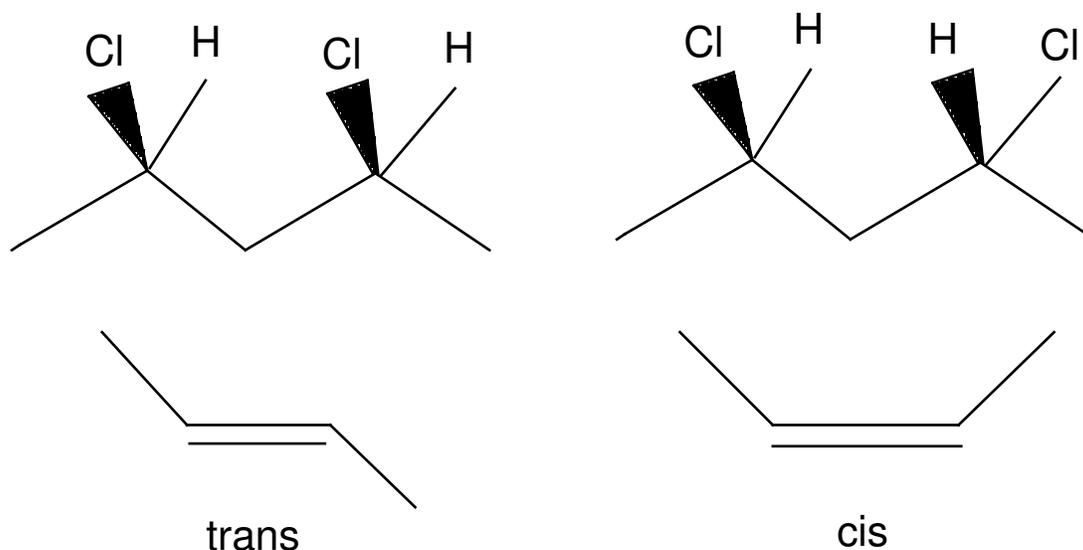


Figure 3.2: Two distinct configurations of polymers can exist at asymmetric carbon atoms (top) and across double bonds (bottom).

To understand polymers, we must understand the shape or the form that polymers have in solution as well as in solid state. We will therefore spend some time studying the conformations of isolated polymer chains. An isolated polymer chain is clearly a good model for a gas phase or a dilute solution polymer. It turns out that the description of an isolated polymer chain is also a good description for polymer chains in concentrated solutions, or even in the solid state.

The first thing to realize about polymers is that they are usually very long and are best described as resembling a *random coil*. In a collection of polymers (gas phase, solution, or solid state), the various individual polymer molecules will assume many possible conformations. Each conformation will be a different variation on a random coil. The different conformations arise by thermal energy and the relatively low barrier to rotations about single bonds. The shapes of the possible conformations have a direct bearing on the physical properties of the polymer. Some properties that can be influenced included solution viscosity, solution light scattering, and mechanical properties. For example, rigid rod polymers generally assume more extended conformations than polymers with more flexible backbones. These more extended shapes give rigid rod polymers very different properties. To be specific, rigid rod polymers are generally stiffer and have a higher glass-transition temperature.

Figure 3.3 shows an extended chain polymer and a random coil polymer. The extended chain picture is the way we might choose to draw a polymer structure. The random coil picture, however, is a more realistic view of the shape of real polymer molecules. In this chapter we will discuss various theoretical methods for characterizing the shape of random coil polymers. The major results will be predictions of the end-to-end distance for linear polymers. The ideas that enter into the analysis give insight about the shape of polymers. As discussed in the Introduction chapter (chapter 1),

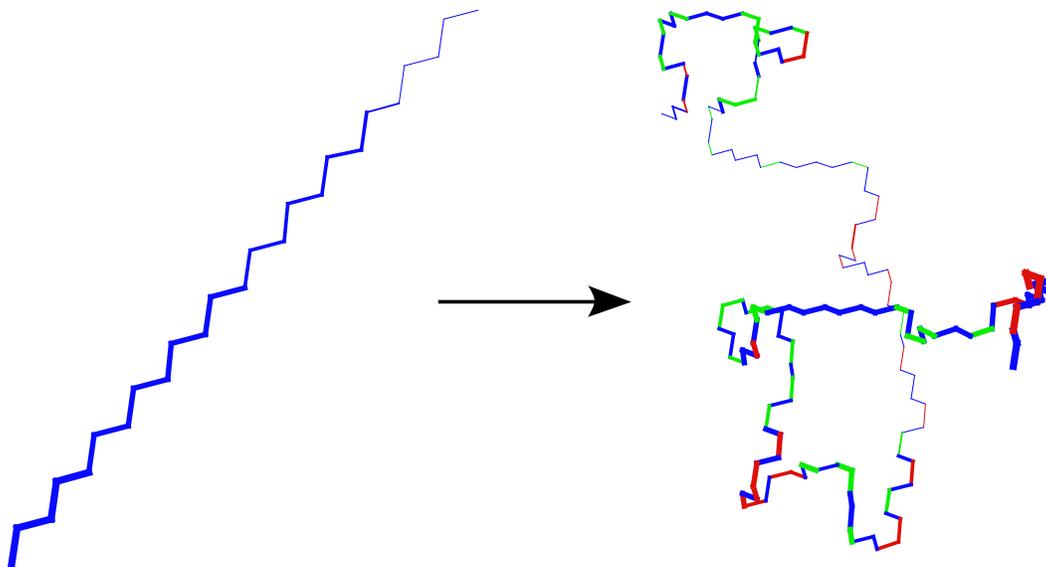


Figure 3.3: Extended chain polymer on the left. A more realistic picture of a polymer as a random coil on the right. The colors indicate rotation angle about each bond. Blue is for trans bonds while red and green are for gauche bonds.

this type of polymer characterization is theoretical characterization.

## 3.2 Nomenclature

We will restrict ourselves to linear polymers and we will consider all their possible conformations. To describe any given conformation we must first define a nomenclature or coordinate system. We begin with a polymer having  $n$  bonds. These  $n$  bonds connect  $n + 1$  backbone atoms. We can thus define any conformation by giving the  $3(n + 1)$  Cartesian coordinates of the  $n + 1$  atoms along the polymer backbone. This nomenclature works but is normally more cumbersome than desired and we thus make some simplifications.

We begin with the bond length ( $l$ ). In many polymers the bonds in the polymer backbone are all identical and therefore have a constant bond length. For example, in PE the bonds are all carbon-carbon bonds and they are all typically about  $1.53\text{\AA}$  long. For simplicity we will restrict ourselves to polymers with constant bond lengths. A generalization to non-constant bond lengths can be made later if necessary. With constant bond lengths, we can consider a polymer conformation as a 3D random walk of  $n$  steps where each step has length  $l$ . Instead of listing absolute coordinates of each atom in the backbone, we choose to describe a polymer by listing the *relative* directions of each step in the random walk.

Directions in space are most conveniently described using polar angles. Figure 3.4 shows an arbitrary direction in space emanating from the origin of a coordinate system. The angle with respect to the  $z$  axis is called the polar angle and is usually denoted by  $\theta$ . The angle that the

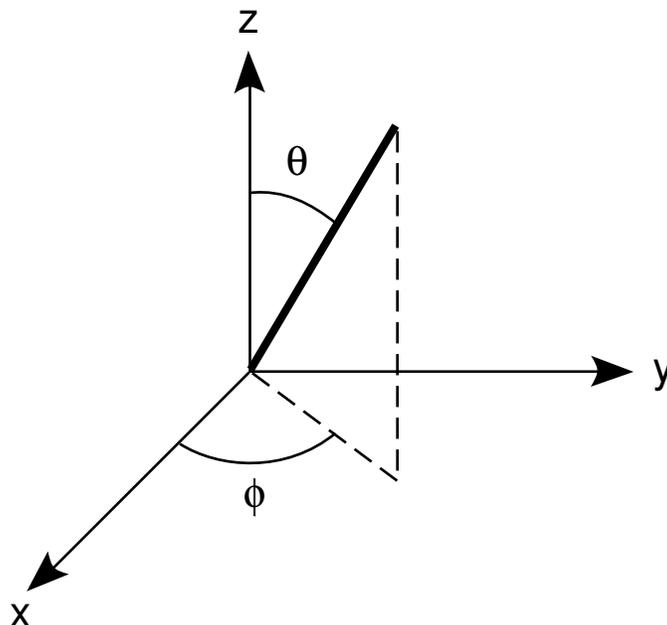


Figure 3.4: Definitions of the polar angle  $\theta$  and the azimuthal angle  $\phi$  for any vector in a right-handed coordinate system.

projection of the direction onto the  $x$ - $y$  plane makes with any consistently chosen reference point in that plane is called the azimuthal angle and is usually denoted by  $\phi$ . All possible directions in space can be spanned by choosing  $\theta$  from 0 to  $\pi$  and  $\phi$  from 0 to  $2\pi$ . In other words, any direction from the origin can be defined by a unique pair of  $\theta$  and  $\phi$ .

We will represent a polymer as a 3D random walk of  $n$  steps where  $n$  is the number of bonds (note that  $n$  is not necessarily the same as the degree of polymerization or the number of repeat units; some repeat units have more than one bond and for  $n$  we count all of these bonds). In the random walk, each step can be described by polar and azimuthal angles,  $\theta$  and  $\phi$ , where those angles are given with respect to an axis system centered on the atom at the start of that bond. For  $n$  bonds, each bond will have its own angles,  $\theta_i$  and  $\phi_i$ , and the complete chain will be described with the 3 original coordinates for the first atom and the  $2n$  angles for the steps of the random walk. We thus require  $2n + 3$  variables to specify a conformation of a polymer with constant bond length.

Normally we will not be concerned with the absolute location in space of the polymer chain. If we do everything relative to the location of the first bond, then we do not need to know the 3 original coordinates nor the 2 polar angles of the first bond. Subtracting these five variables, we can define an arbitrary polymer conformation with  $2n - 2$  or  $2(n - 1)$  variables. The  $2(n - 1)$  variables are the polar and azimuthal angles for each bond except the first bond. If we ever generalize to different  $l$ 's for each bond, we must add to these  $2(n - 1)$  variables,  $n$  new variables which specify the length of each bond.

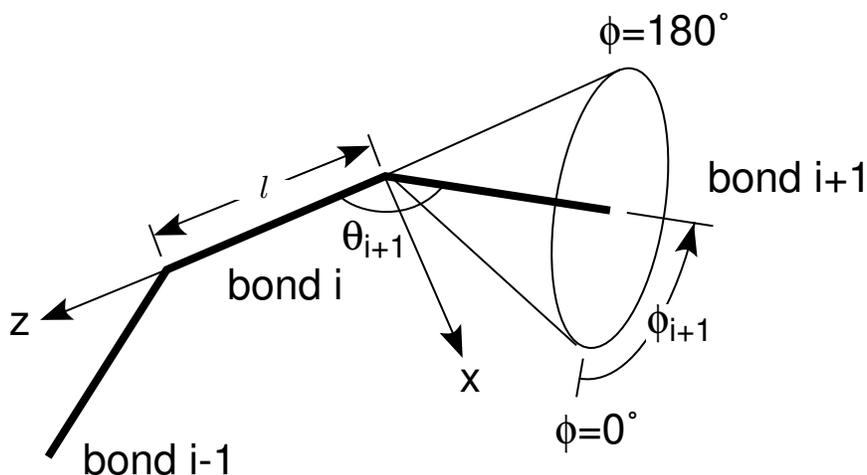


Figure 3.5: Definition of polar and azimuthal angles for bond  $i$ . With the illustrated selection of  $x$ ,  $y$ , and  $z$  axes, the polar angle is the bond angle for bond  $i + 1$  and the azimuthal angle is the dihedral angle for bond  $i + 1$ .

It is convenient to choose a coordinate system that lends physical interpretations to the polar and azimuthal angles of each bond in the polymer chain. As illustrated in Fig. 3.5, we consider the central bond as bond  $i$  and take the  $z$  axis to point back along bond  $i$ . With this choice for the  $z$  axis, the polar angle for bond  $i + 1$  is just the bond angle between bond  $i$  and bond  $i + 1$  (see Fig. 3.5). From now on, we will refer to the polar angle as the bond angle. The possible orientations for bond  $i + 1$  when the bond angle is  $\theta_{i+1}$  sweep out the cone illustrated in Fig. 3.5. The azimuthal angle ( $\phi$ ) for bond  $i + 1$  is the counter-clockwise angle around that cone from some suitably selected reference point. We choose the  $x$  axis to define the reference point such that the azimuthal angle for bond  $i + 1$  is  $180^\circ$  when bond  $i$  is a *trans* bond. This choice is arbitrary, but is consistent with the bulk of the modern literature (note: Flory choose  $\phi = 0$  to correspond to *trans* bonds which makes his results shifted by  $180^\circ$  from these notes). Another term for such an azimuthal angle is the *dihedral* angle for bond  $i + 1$  — a term that we will adopt throughout these notes. Finally, the  $y$  axis is chosen to be perpendicular to the  $x$  and  $z$  axes and directed to make the  $x$ - $y$ - $z$  coordinates a right-handed coordinate system.

### 3.3 Property Calculation

The goal of theoretical characterization of polymers is to be able to predict certain properties of those polymers. When a polymer exists in a single conformation, the task is simple — we merely calculate the property for that conformation. Random coil polymers, however, can exist in many different conformations. An observed macroscopic property of an ensemble of polymer chains will be an average value of that property over the range of polymer conformations. We denote the average value of any property over an ensemble of random coil polymer chains as  $\langle Property \rangle$ .

The way to find  $\langle Property \rangle$  is to examine a large number of polymer chains by considering a large number of random walks. For the simplest models (models of short chains) we will be able to examine all possible random walks. When we can consider all possible random walks we can assign to each random walk a probability which equals the probability that that conformation will be selected when one polymer is selected from an ensemble of random coils. Assuming we can calculate some polymer property (*e.g.*, size, stiffness, etc.) for each specific conformation, we can average them to get the average of that property for the bulk polymer sample. The average property is defined by

$$\langle Property \rangle = \sum_i Property(conf\ i) \times Probability(conf\ i) \quad (3.1)$$

where  $Property(conf\ i)$  is the value of the property calculated for conformation  $i$  and  $Probability(conf\ i)$  is the probability of that conformation occurring.

For small molecules you can often do the above averaging process exactly. In other words you can enumerate all possible conformations, find the probability and property of each conformation, and then find the average property by averaging the results. Some small molecules have only one conformation and the task is relatively simple — the average property is equal to the property of the single conformation. Other molecules have only a few conformations and the task is still relatively simple. For a non chemistry example, consider the roll of a single dice and consider the property of the number of pips showing on each role. A die has six faces which represent six possible conformations of the die after each roll. When counting pips, the  $Property(conf\ i) = i$ . Assuming the die is a fair die (*i.e.*, not loaded) the probability of each conformation is the same and equal to  $1/6$  (thus  $Probability(conf\ i) = 1/6$ ). The property of the number of pips therefore has the exact average value of

$$\langle pips \rangle = \sum_i^6 i \times \frac{1}{6} = \frac{1}{6} + \frac{2}{6} + \frac{3}{6} + \frac{4}{6} + \frac{5}{6} + \frac{6}{6} = 3.5 \quad (3.2)$$

For polymer calculations there will usually be too many conformations to make the above exact calculation procedure possible. Instead we will select conformations at random and use a Monte Carlo procedure to get the average property. By the Monte Carlo procedure, if the probability of selecting a particular conformation at random is proportional to the actual probability of conformation  $i$  (selection probability  $\propto Probability(conf\ i)$ ), then the average property for a polymer sample can be approximated by

$$\langle Property \rangle \approx \frac{1}{N} \sum Property(sample\ i) \quad (3.3)$$

where  $N$  is the number of randomly generated polymer chains. The larger  $N$ , the more accurate will be the calculated average property.

We can illustrate the Monte Carlo method with the dice problem. A Monte Carlo solution to the dice problem would be to roll a die many times, total the pips, and divide by the number of

rolls. If the die was rolled sufficiently many times and if the die was fair (*i.e.*, symmetric and not loaded), the Monte Carlo solution would be very close to the exact answer of 3.5. After a few rolls, the answer might differ from 3.5. After many rolls, however, the answer would be very unlikely to show much deviation from 3.5.

The success of the Monte Carlo procedure is dependent on one's ability to select polymer conformations with realistic probabilities that accurately reflect the true distribution of conformations. This problem is easily solved in the dice problem by rolling a die. Unfortunately for polymer problems we cannot physically select real polymers. Instead we have to generate conformations mathematically or in a computer. The problem we must solve is the development of rules or algorithms for realistically generating conformations. We will approach this problem in a series of steps. We will begin with the simplest possible rules. At each subsequent step we will add more realism to the procedure used to generate the random conformations. The final results can be used to accurately predict many polymer properties.

### 3.4 Freely-Jointed Chain

In a freely-jointed chain all  $2(n - 1)$  angular variables are allowed to assume any values with equal probability. In other words the direction of any bond is equally likely to occur in any of the possible directions of space — the joints at each bond thus move freely to allow all these possible orientations.

Let's begin with one particular property — the polymer size. Size can be characterized by calculating the end-to-end distance,  $r$ , or the radius of gyration,  $s$ . As an average property, these properties are usually calculated as a root mean squared end-to-end distance (or a root mean squared radius of gyration). End-to-end distance is the distance from the beginning of the chain to the end of the chain (see Fig. 3.6). The root mean squared end-to-end distance is the square root of the average of the squared end-to-end distances:

$$\text{rms } r = \sqrt{\langle r^2 \rangle} = \sqrt{\frac{1}{N} \sum_{i=1}^N r_i^2} \quad (3.4)$$

where  $N$  is the total number of possible conformations and  $r_i$  is the end-to-end distance for conformation  $i$ . The radius of gyration is the average of the distances of each of the atoms in the polymer chain to the center of mass of the polymer. The root mean squared radius of gyration is the square root of the average of the squared radius of gyration:

$$\text{rms } s = \sqrt{\langle s^2 \rangle} = \sqrt{\frac{1}{N} \sum_{i=1}^N s_i^2} \quad (3.5)$$

where  $s_i$  is the radius of gyration for conformation  $i$ .

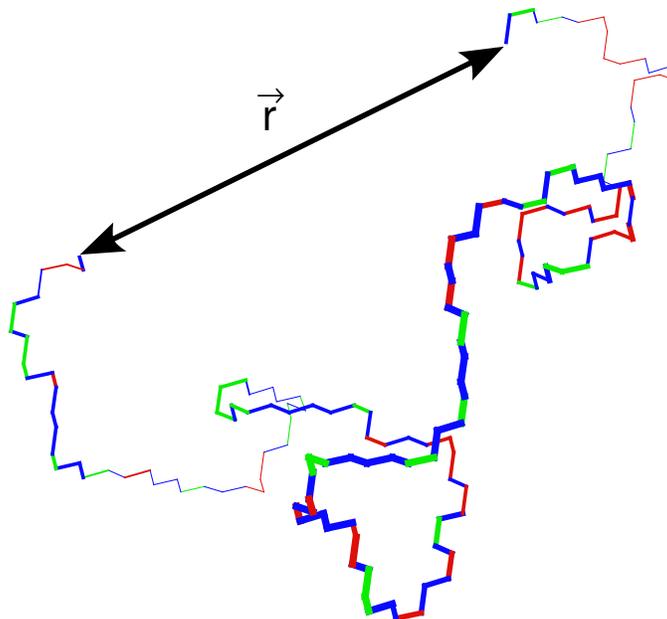


Figure 3.6: The length of a vector ( $\vec{r}$ ) from the first atom to the last atom on a linear polymer chain is the end-to-end distance for that polymer conformation. This figure shows the end-to-end vector.

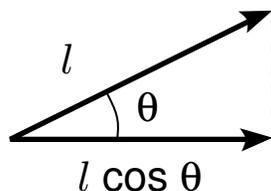


Figure 3.7: The projection of a bond of length  $l$  onto the  $z$  axis is  $l_z = l \cos \theta$  where  $\theta$  is the angle between the bond and the  $z$  axis.

### 3.4.1 Freely-Jointed Chain Analysis

We begin our analysis of the freely-jointed chain by analyzing a single direction in space — we will analyze the  $z$  axis direction. For any of the bonds in the chain (or steps in the random walk), the bond length along the  $z$  axis is  $l_z = l \cos \theta$  (see Fig. 3.7) where  $\theta$  is the angle between the bond direction and the  $z$ -axis direction.  $\theta$  is also the polar angle in the coordinate system defined in Fig. 3.5 in which the  $z$  axis is along the previous bond. The average value of  $l_z$  is found by integrating over all possible bond projections or all possible bond directions:

$$\langle l_z \rangle = \int_{-l}^l l_z p(l_z) dl_z = \int \int l \cos \theta p(\theta, \phi) dS \quad (3.6)$$

where  $p(\theta, \phi)$  is the probability that any given bond has directional angles of  $\theta$  and  $\phi$ . The integration is over the surface of a sphere centered on the origin and  $dS$  is the differential of surface area.

For a freely-jointed chain all angles are all equally likely and therefore  $p(\theta, \phi)$  must be a constant;

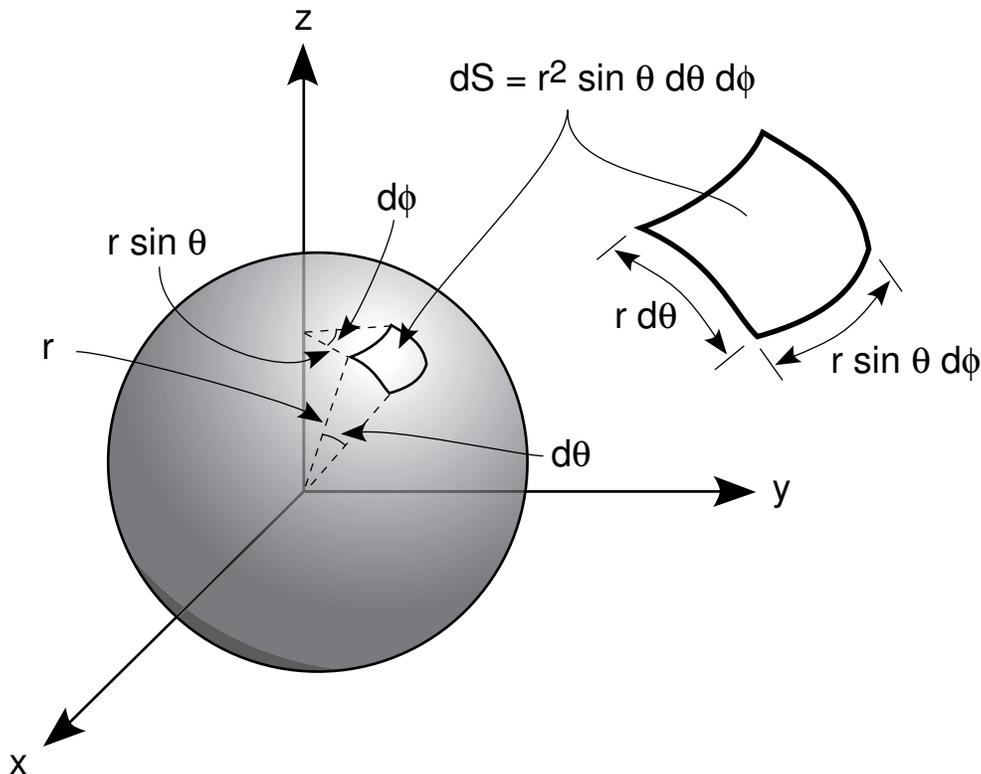


Figure 3.8: The differential of surface integration for polar coordinates is the area of the surface element on the right side of the figure which is a top view of the left side. For small angles this area is  $dS = r^2 \sin \theta d\theta d\phi$ .

we call it  $k$ . To find  $k$ , we integrate over the surface of sphere, which represents all possible directions in space, and note that the integral over  $p(\theta, \phi)$ , which is a probability distribution function, must be 1. Because  $dS$  for surface integration over a sphere is  $r^2 \sin \theta d\theta d\phi$  (see Fig. 3.8) we can integrate over the unit sphere ( $r = 1$ ) to get:

$$1 = k \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta = 4\pi k \quad (3.7)$$

or

$$k = p(\theta, \phi) = \frac{1}{4\pi} \quad (3.8)$$

We can now insert  $p(\theta, \phi)$  into the expression for  $\langle l_z \rangle$  and integrate. The result is

$$\langle l_z \rangle = \int_0^{2\pi} d\phi \int_0^\pi d\theta \frac{l \cos \theta \sin \theta}{4\pi} = \frac{l}{2} \int_0^\pi \cos \theta \sin \theta d\theta = 0 \quad (3.9)$$

This result could have been anticipated. When random walk steps in all directions are equally likely, we are equally likely to jump in the positive direction as in the negative directions. These equally likely jumps cancel out to give zero average jump size.

A simple average step size is not useful and we therefore instead consider the average *squared* step length. It is for this reason that we constantly work with root-mean-squared end-to-end

distances in our discussion of polymer size. Squaring each step length makes all step size positive and we are guaranteed to get a nonzero result. With the known  $p(\theta, \phi)$  function, we can easily calculate the mean squared jump size:

$$\langle l_z^2 \rangle = \int_0^{2\pi} d\phi \int_0^\pi d\theta \frac{l^2 \cos^2 \theta \sin \theta}{4\pi} = \frac{l^2}{2} \int_0^\pi \cos^2 \theta \sin \theta d\theta \quad (3.10)$$

$$= \frac{l^2}{2} \left[ -\frac{1}{3} \cos^2 \theta \right]_0^\pi = \frac{l^2}{3} \quad (3.11)$$

The root mean squared distance per step is:

$$\sqrt{\langle l_z^2 \rangle} = \frac{l}{\sqrt{3}} \quad (3.12)$$

The above result gives as an average jump size per step, but we are concerned with the total  $z$  axis root-mean-squared end-to-end distance. The solution to this problem is approached by considering a set of typical jump directions. For a chain of  $n$  bonds, some of the bonds will point in the positive  $z$  direction and some will point in the negative  $z$  direction. If  $n$  is large, the root mean squared length of all positive jumps will be the same as that of all negative jumps and each will be equal to the average of all jumps. We let  $n_+$  be the total number of jumps in the positive direction and  $n_-$  be the total number of jumps in the negative direction. Then the root-mean-squared distance traveled in the  $z$  direction, denoted by  $z$ , is

$$z = (n_+ - n_-) \sqrt{\langle l_z^2 \rangle} = (n_+ - n_-) \frac{l}{\sqrt{3}} \quad (3.13)$$

To solve for  $z$  we must determine  $(n_+ - n_-)$ . The factor  $(n_+ - n_-)$  is like the result of a coin toss experiment. Each step is considered a coin toss, if  $z$  increases on the step the coin toss result is heads, if  $z$  decreases, the coin toss result is tails. In the coin toss results, the expected result is to have equal numbers of heads and tails. If a large number of coin tosses are made the distribution of  $(n_+ - n_-)$  will be a Gaussian function centered at zero (mean of zero). We can thus represent the factor  $(n_+ - n_-)$ , or more usefully the distance in the  $z$  direction, with the following Gaussian distribution function:

$$W(z)dz = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{z^2}{2\sigma^2}} dz = \frac{\beta}{\sqrt{\pi}} e^{-\beta^2 z^2} dz \quad (3.14)$$

where  $\sigma$  is the standard deviation in  $z$ -direction distance and the term  $\beta$  is defined in terms of standard deviation by

$$\beta = \frac{1}{\sqrt{2\sigma^2}} \quad (3.15)$$

The freely-jointed chain problem is solved if we can find the standard deviation in  $z$ -direction distance. For a *single* step the variance, or the standard deviation squared, follows simply from the formula for variance:

$$\sigma_1^2 = \langle l_z^2 \rangle - \langle l_z \rangle^2 = \langle l_z^2 \rangle \quad (3.16)$$

Statistical analysis tells us that for  $n$  steps, the standard deviation in  $z$  is  $n$  times the standard deviation for a single step or

$$\sigma^2 = n\sigma_1^2 = n\langle l_z^2 \rangle \quad (3.17)$$

Substituting the above result for  $\langle l_z^2 \rangle$  gives

$$\beta = \frac{1}{\sqrt{2n\langle l_z^2 \rangle}} = \sqrt{\frac{3}{2nl^2}} \quad (3.18)$$

An alternate route to finding  $\beta$  is to find the variance by integration (*i.e.*, find the average value of  $z^2$  and subtract the square of the average value of  $z$ , which we know to be zero). The result is

$$\frac{\langle z^2 \rangle}{n} = \langle l_z^2 \rangle = \frac{\lambda^2}{3} = \frac{1}{n} \int_{-\infty}^{\infty} z^2 W(z) dz = \frac{1}{2n\beta^2} \quad (3.19)$$

Solving for  $\beta$  again gives

$$\beta = \sqrt{\frac{3}{2nl^2}} \quad (3.20)$$

The expression for  $\beta$  together with the Gaussian distribution function give the distribution function for chain length in one direction. Now we need to solve the three-dimensional problem. Because the chain is freely jointed, the three axes are independent of each other. From probability theory, the probability that a given polymer chain jumps distances of  $x$ ,  $y$ , and  $z$  in each of the three Cartesian directions is the product of the probabilities for each of the axes considered separately. The probability that a chain has an end-to-end distance characterized by a vector  $(x, y, z)$  is thus

$$W(x, y, z) dx dy dz = W(x)W(y)W(z) dx dy dz \quad (3.21)$$

Because the analysis for  $W(z) dz$  given above applies equally well to the  $x$  and  $y$  directions, we have

$$W(x, y, z) dx dy dz = \left( \frac{\beta}{\sqrt{\pi}} \right)^3 e^{-\beta^2 r^2} dx dy dz \quad (3.22)$$

where  $r^2 = x^2 + y^2 + z^2$  is the square of the distance from the origin to the end of the chain at  $(x, y, z)$ .

As stated above,  $W(x, y, z) dx dy dz$  gives the probability that a chain's end-to-end vector is characterized by a vector  $(x, y, z)$ . In other words, it is the probability that a chain that begins at the origin ends in a box center at the point  $(x, y, z)$  or size  $dx dy dz$  (see Fig. 3.9). One dimension of  $W(x, y, z) dx dy dz$  is plotted in Fig. 3.9. The function is a Gaussian distribution function centered at the origin or centered about the mean value of zero.

The function  $W(x, y, z) dx dy dz$  solves the freely-jointed chain problem, but it is not in the most useful form. We are normally not concerned with absolute end of the chain (*i.e.*, location  $(x, y, z)$ ), but rather with the end-to-end distance  $r$ . To find this result we sum up all possible  $(x, y, z)$  coordinates that give the same  $r$  value. In other words, we integrate over the volume element  $V$

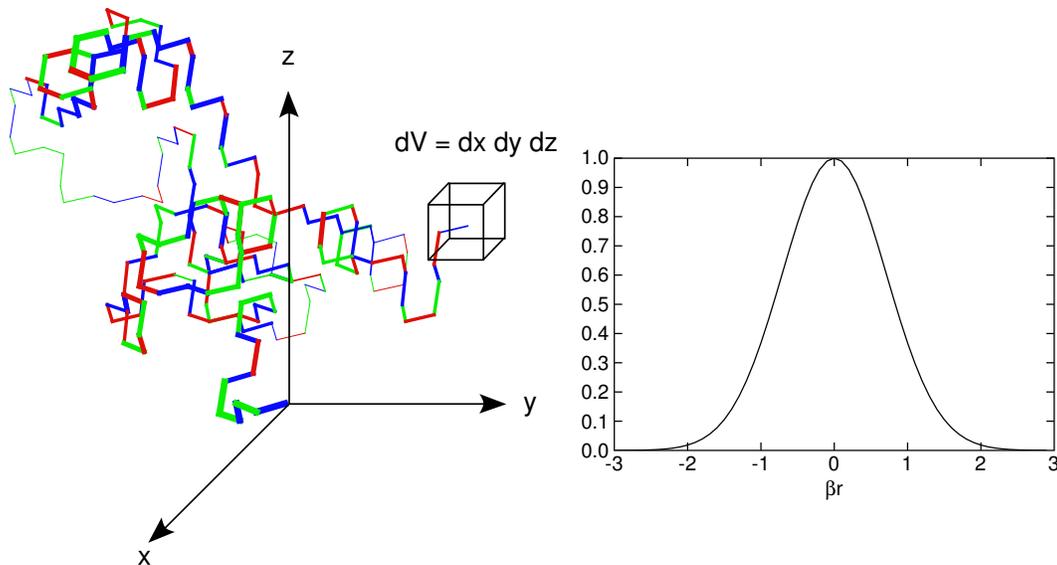


Figure 3.9: The left side shows a chain that starts at the origin and ends in a box centered a  $(x, y, z)$ . The right side is a one-dimensional plot of  $W(x, y, z)dx dy dz$ .

of width  $dr$  where  $\sqrt{x^2 + y^2 + z^2}$  is between  $r$  and  $r + dr$ . The volume element of constant  $r$  is a spherical shell as shown in Fig. 3.10. Integrating over this volume element yields a probability distribution in terms of the end-to-end distance  $r$ :

$$W(r)dr = \int_V W(x, y, z)dx dy dz = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 4\pi r^2 e^{-\beta^2 r^2} dr \quad (3.23)$$

This type of distribution function is called a *radial* distribution function.

Figure 3.11 schematically plots the end-to-end distance distribution function,  $W(r)dr$ . We can characterize the distribution function by finding some key points. The function  $W(r)dr$  always increases to some maximum and then decrease towards zero. The peak value is found by finding where the derivative of  $W(r)dr$  is zero. The maximum value,  $r_{max}$ , occurs at

$$r_{max} = \frac{1}{\beta} = l\sqrt{\frac{2n}{3}} = 0.82l\sqrt{n} \quad (3.24)$$

The average value of  $r$ ,  $\langle r \rangle$ , is found by integrating  $W(r)dr$ :

$$\langle r \rangle = \int_0^\infty rW(r)dr = \frac{2}{\beta\sqrt{\pi}} = l\sqrt{\frac{8n}{3\pi}} = 0.92l\sqrt{n} \quad (3.25)$$

Likewise, the mean-squared value of  $r$ ,  $\langle r^2 \rangle$ , is

$$\langle r^2 \rangle = \int_0^\infty r^2W(r)dr = \frac{3}{2\beta^2} = l^2n \quad (3.26)$$

and the root mean squared end-to-end distance is

$$\sqrt{\langle r^2 \rangle} = l\sqrt{n} \quad (3.27)$$

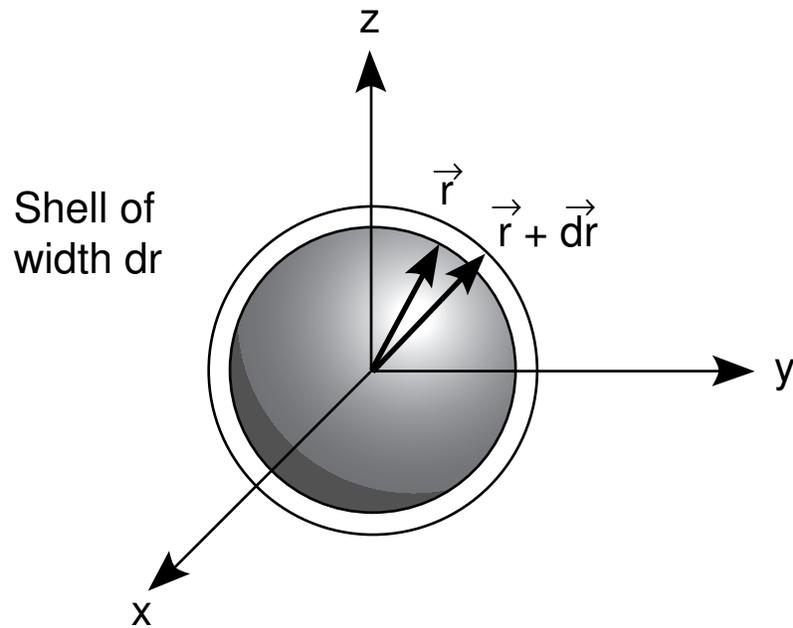


Figure 3.10: Cross section of a spherical shell between radii of  $r$  and  $r + dr$ .

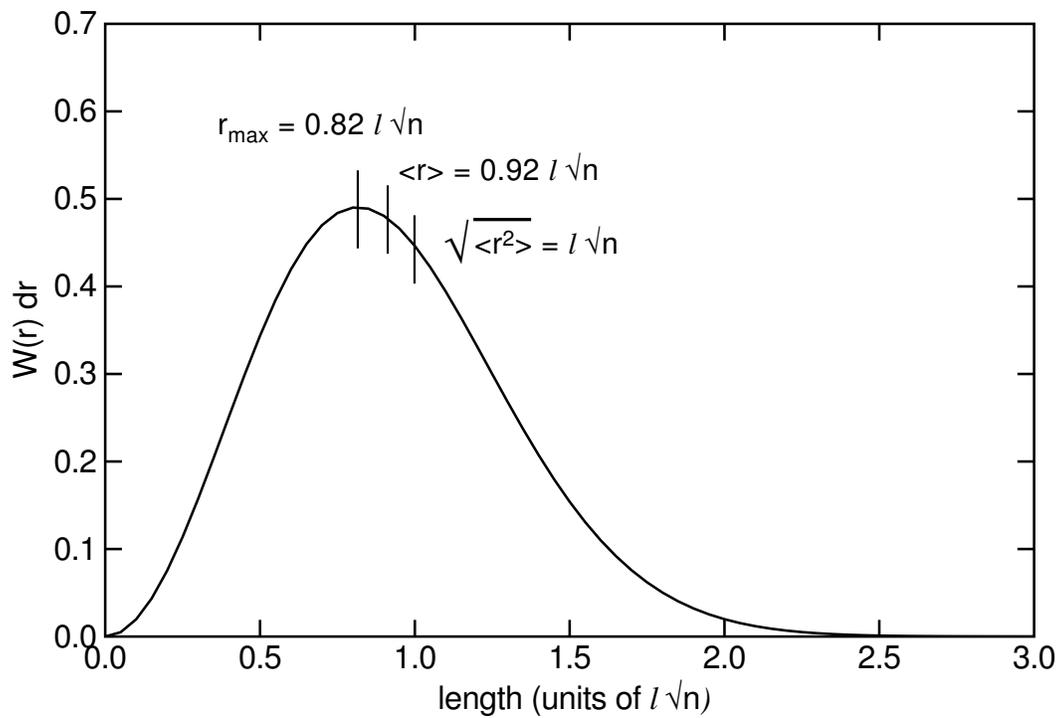


Figure 3.11: A typical plot of  $W(r)dr$ . The key values  $r_{\max}$ , average  $r$  or  $\langle r \rangle$ , and root-mean-squared  $r$  are indicated on the figure.

The above key values are indicated in Fig. 3.11. For constant  $l$  and  $n$ , they always rank in the order  $r_{max} < \langle r \rangle < \langle r^2 \rangle$ .

The variance in the end-to-end distance can be found from the mean and mean-squared end-to-end distances:

$$\sigma^2 = \langle r^2 \rangle - \langle r \rangle^2 = \frac{3}{2\beta^2} - \frac{4}{\beta^2\pi} = \frac{0.23}{\beta^2} = 0.15nl^2 \quad (3.28)$$

From this results, the coefficient of variation (standard deviation divided by the mean) is

$$CV = \frac{\sigma}{\langle r \rangle} = 42\% \quad (3.29)$$

This result can be characterized as a fairly large coefficient of variation.

### 3.4.2 Comment on Freely-Jointed Chain

We only used two facts in deriving  $W(r)$ . First we assumed that the chain can be simulated by a random walk. Second, we assumed there are enough steps to make the random walk a Gaussian distribution. To find the Gaussian curve we therefore only had to find the mean (mean = 0) and the standard deviation ( $\sigma = \sqrt{n\langle l_z^2 \rangle}$ ). The final result predicts that the root-mean-squared end-to-end distance is

$$\sqrt{\langle r^2 \rangle} = l\sqrt{n} \quad (3.30)$$

In other words the root mean squared end-to-end distance is proportional to the square root of the number of bonds and linear in the bond length.

The linear dependence on bond length is a trivial result. It is merely a scaling parameter. Thus if we double all bond lengths we double the end-to-end distance. It can also be thought of as a consequence of units. If we solve the problem in inches and then in millimeters, we should get answers that differ only by the units conversion factor for inches to millimeters of 25.4. This expected result will only occur if the end-to-end distance is linear in bond length.

The dependence of root-mean-squared end-to-end distance on the square root of the number of bonds is a profound, or at least a non-trivial, result. Let's consider the origins of the square root dependence on bond length. Our analysis is one of a completely random three dimensional random walk. The square root of  $n$  dependence comes from the expression for the standard deviation of the walk which contains  $\sqrt{n}$ . If we repeated the analysis for one- or two-dimensional random walks we would find the same result. The root-mean-squared end-to-end distance is

$$\sqrt{\langle r^2 \rangle} = l\sqrt{n} \quad (3.31)$$

in any dimension. We thus conclude that the square root of  $n$  dependence is a property of the random walk nature of polymers and unrelated to geometrical effects. Only polymer features that alter the random walk nature of the chain can alter the square root dependence on  $n$ .

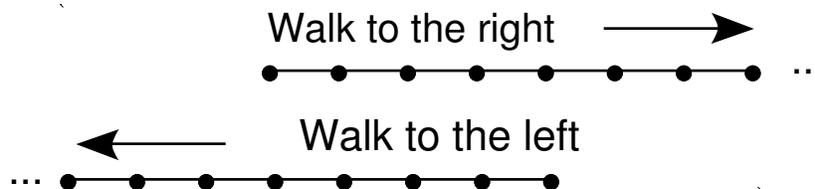


Figure 3.12: The only two possible one-dimensional, self-avoiding random walks.

To anticipate a future result that does alter the random walk nature of polymers, we consider self-avoiding random walks. In self-avoiding random walks, the path cannot revisit any spot that was previously visited. Because no two atoms in a polymer chain can occupy the same space, a self-avoiding random walk is a better model for a polymer chain than the completely random walk discussed previously. A self-avoiding random walk, however, is not a completely random walk because some steps may be influenced by previous steps. In other words, some steps may be biased away from moving in a given direction because doing so would revisit a previous part of the random walk.

The exact analysis of two- and three-dimensional self-avoiding random walks is not possible. One-dimensional, self-avoiding random walks, however, are trivial to analyze. As shown in Fig. 3.12 there are only two possible one-dimensional, self-avoiding random walks. A one-dimensional random walk must begin with one step to the left or to the right. If the first step is to the left, the next step must also be to the left because a step to the right would revisit the starting location. Continuing on, the chain that starts to the left must make all steps to the left. The other possible chain is the one that starts with its first step to the right. This chain can only continue with repeated steps to the right. There are thus only two possible chains. One makes all  $n$  steps to the left and its length is  $nl$ . The other makes all  $n$  steps to the right and its length is also  $nl$ . Averaging over all possible chain conformations, the root-mean-squared end-to-end distance for a one-dimensional, self-avoiding random walk is

$$\sqrt{\langle r^2 \rangle} = nl \quad (3.32)$$

In contrast to the completely random walk, this result is now linear in  $n$ . Because of scaling requirements it remains *linear* in  $l$ .

In two- and three-dimensional random walks, the effect of imposing self avoiding characteristics will be less dramatic. A one-dimensional, self-avoiding, random walk is hardly random. All steps (except the first one) are determined by the requirement of being self avoiding and not by random chance. Two- and three-dimensional, self-avoiding random walks will not be restricted as much. Some steps will be influenced by self-avoiding requirements, but most will have other options than can be reached by random chance. Without proof, we state that the end-to-end distance for two- and three-dimensional random walks will be proportional to  $n$  to some power between 0.5 and 1.0. The two extremes are completely random walks (power equal to 0.5) and self-avoiding random

walks in which every step is determined by the self-avoiding requirement (power of 1.0). The former extreme is the random walk result from above; the later extreme is the one-dimensional, self-avoiding random walk result.

We now return to the random walk analysis and its assumption that the polymer chains are long enough such that a Gaussian distribution function accurately represents the results. How big do the chains have to be to be large enough? The Gaussian distribution was applied to the factor  $(n_+ - n_-)$ . For large chains with random  $n_+$  and  $n_-$  jumps, we require  $|n_+ - n_-| \ll n$ .  $W(r)dr$  is accurate as long as this inequality is true.  $W(r)dr$ , however, is supposed to work for all values of  $r$  which includes  $r$  near  $r_{max} = nl$ . The maximum value of  $r$  can only occur when all jumps are in the same direction which means either  $n_+ = n$  and  $n_- = 0$  or  $n_- = n$  and  $n_+ = 0$ . In each of these cases  $|n_+ - n_-| = n$  and the requirement that  $|n_+ - n_-|$  be much less than  $n$  is violated. In other words, as  $r$  gets large, the chain becomes less Gaussian and  $W(r)dr$  becomes increasing inaccurate.

To assess the accuracy of  $W(r)dr$ , some researchers have constructed more detailed analyses that account for deviations from Gaussian behavior at large  $r$ . One published result is

$$W(r)dr = (\text{Const})4\pi r^2 \exp \left\{ -\beta^2 r^2 \left[ 1 + \frac{3}{10} \left( \frac{r}{r_{max}} \right)^2 + \dots \right] \right\} dr \quad (3.33)$$

The first term within the square brackets is 1 which is the previous result for a Gaussian distribution. The rest of the terms within the square brackets are correction terms that are small for small  $r$  and become more significant for large  $r$ . Only the first and largest correction term is given. Let's consider a chain of  $n$  bonds and say that the uncorrected  $W(r)dr$  is adequate as long as the correction term is less than 0.01 (or less than 1%).  $W(r)dr$  will then be good for a chain that is up to  $f$  times larger than the root-mean-squared end-to-end distance (*i.e.*, good for  $r \leq f\sqrt{\langle r^2 \rangle}$ ) as long as

$$\frac{3}{10} \left( \frac{f\sqrt{\langle r^2 \rangle}}{r_{max}} \right)^2 = \frac{3f^2}{10n} < 0.01 \quad \text{or} \quad f = \sqrt{\frac{n}{30}} \quad (3.34)$$

For example consider a chain of  $n = 100$  bonds (a fairly short polymer chain). Solving this equation for  $f$  results in  $f = 1.83$ . Therefore the first correction term in  $W(r)dr$  is less than 1% for  $0 < r < 1.83l\sqrt{n} = 18.3l$ . When  $18.3l < r < nl = r_{max} = 100l$  the first correction term is greater than 1%.

We can relate the range of small correction terms to the standard deviation in root mean squared end-to-end distance. The upper limit in  $r$  for small corrections is  $fl\sqrt{n}$  where  $l\sqrt{n}$  is the root mean squared end-to-end distance. From above, the standard deviation in end-to-end distance is  $0.15l\sqrt{n}$ . Therefore the upper limit in  $r$  for small corrections is

$$\frac{fl\sqrt{n} - l\sqrt{n}}{0.15l\sqrt{n}} = \frac{\sqrt{\frac{n}{30}} - 1}{0.15} \quad (3.35)$$

standard deviations above the mean. For the above example with  $n = 100$  bonds, this equation shows the  $W(r)dr$  is accurate as long as  $r$  is less than 5.50 standard deviations above the mean. In

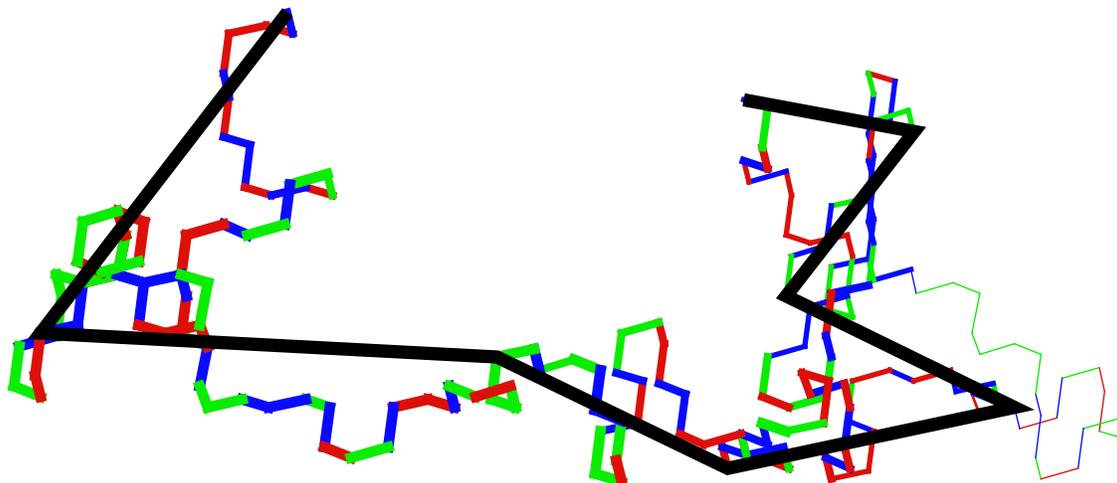


Figure 3.13: The thin lines are a real polymer chain of  $n$  bonds. The thick lines are the superposed equivalent freely-jointed chain of  $n' = n/m$  bonds.

a normal distribution very few chains will be more than 5.50 standard deviations above the mean. Thus even for a relatively short 100 bond chain, the correction factor is insignificant. We conclude that the correction factors are insignificant for most real polymer chains.

### 3.5 Equivalent Freely Jointed Chain

Real polymers are not freely jointed; the bond directions  $\theta$  and  $\phi$  are not free but are restricted by local environment to be biased towards specific values. The major restrictions are caused by nearby bonds. In other words, the conformation of any bond is correlated with the conformations of nearby bonds. As the distance between any two bonds increases, the correlation decreases with the conformations of distant bonds eventually becoming uncorrelated. Say that it takes  $m$  bonds for the correlation to drop to zero and then construct from an  $n$  bond chain an  $n'$  bond chain with  $n' = n/m$ . Let the average length of each new bond be  $l'$  which will be proportional to  $l$  (or  $l' = kl$ ). We call the new chain of  $n'$  bonds of average length  $l'$  the equivalent freely-jointed chain for the original  $n$  bond chain. An example equivalent freely-jointed chain is shown in Fig. 3.13.

Because the bond conformations are uncorrelated over long distances, the random walk steps in this new chain are freely-jointed. Using the freely-jointed chain result the root-mean-squared end-to-end distance is

$$\sqrt{\langle r^2 \rangle} = l' \sqrt{n'} = l \sqrt{Cn} \quad (3.36)$$

where

$$C = \frac{k}{\sqrt{m}} \quad (3.37)$$

By using the equivalent freely-jointed chain, we have shown that the end-to-end distance of a realistic chain is proportional to  $l\sqrt{n}$ . The proportionality constant is  $\sqrt{C}$ .  $C$  is normally greater

than one and therefore  $\sqrt{C}$  is sometimes called the expansion factor and sometimes denoted as  $\alpha$ . It tells how much the real chain is expanded relative to a freely jointed chain. The square of the expansion factor, or  $C$ , is known as the characteristic ratio. It is defined by

$$C = \frac{\langle r^2 \rangle}{nl^2} \quad (3.38)$$

In the freely-jointed chain,  $C = 1$ . In real polymers the characteristic ratio is a function of  $n$  or the number of bonds and is usually greater than 1. It is customary to write the bond-dependent characteristic ratio as  $C_n$ . In relatively ideal polymers  $C_n$  approaches a limiting constant value for large  $n$ . The value of  $C_n$  at large  $n$  for such polymers characterizes the random coil nature of that polymer. Low values of  $C_n$  correspond to tightly coiled polymers and high values of  $C_n$  correspond to polymers that are loosely coiled or extended.

In real polymers, self-avoiding requirements or excluded volume effects, to be described later, cause  $C_n$  to increase without bound as  $n$  increases without bound. A scaling law derived by deGennes states that for large  $n$ ,  $C_n$  increases in proportion to  $n^{0.2}$ . Thus we have

$$C_n = \frac{\langle r^2 \rangle}{nl^2} \propto n^{0.2} \quad (3.39)$$

or

$$\sqrt{\langle r^2 \rangle} \propto ln^{0.6} \quad (3.40)$$

This result agrees with the previous discussion of self-avoiding random walks which claimed that the power-law dependence on  $n$  for a real chain is between 0.5 (for a completely random chain) and 1.0 (for a chain with all steps controlled by self-avoiding requirements).

Our discussion on the equivalent freely-jointed chain shows that any real polymer can be reduced to any expression for end-to-end distance that is proportional to  $l\sqrt{n}$  (provided we ignore, for the moment, excluded volume effects). The thing that distinguishes one polymer from another is the characteristic ratio  $C$ . We thus embark on a series of models whose main purpose is to use theoretical arguments for calculating the characteristic ratio.

### 3.6 Vector Analysis of Polymer Conformations

We will find it useful to develop an alternate approach to the analysis of end-to-end distance in polymers. The new analysis will be based on vectors and analytical geometry. We associate with each bond a vector. Let the vectors  $\vec{u}_1$  to  $\vec{u}_n$  be the vectors along the  $n$  bonds. Then a vector from one end of the chain to the other is simply the sum of these vectors:

$$\vec{r} = \sum_{i=1}^n \vec{u}_i \quad (3.41)$$

The mean squared end-to-end distance is

$$\langle r^2 \rangle = \langle \vec{r} \cdot \vec{r} \rangle = \left\langle \sum_{i=1}^n \vec{u}_i \cdot \sum_{j=1}^n \vec{u}_j \right\rangle \quad (3.42)$$

Expanding this expression for a polymer chain with a constant bond length,  $l$ , results in

$$\langle r^2 \rangle = \sum_{i=1}^n \vec{u}_i \cdot \vec{u}_i + 2 \sum_{i < j} \langle \vec{u}_i \cdot \vec{u}_j \rangle \quad (3.43)$$

where the sum over  $i < j$  means all combinations of  $i$  and  $j$  such that  $i$  is less than  $j$ . The factor of 2 in front of the sum includes, by symmetry, the terms when  $i$  is greater than  $j$ . The dot product of a vector with itself is simply the square of the length of the vector. Thus we can write

$$\langle r^2 \rangle = nl^2 + 2l^2 \sum_{i < j} \langle \cos \theta'_{ij} \rangle \quad (3.44)$$

where  $\theta'_{ij}$  is the angle between the vectors along bond  $j$  and along bond  $i$ . If vector  $j$  is equal to  $i + 1$  (*i.e.*, the bond next to bond  $i$ ) then  $\theta'_{ij}$  is the supplement of the bond angle between bonds  $i$  and  $i + 1$ .

For the freely-jointed chain, the bond directions are uncorrelated and  $\langle \cos \theta'_{ij} \rangle$  is zero which yields  $\sqrt{\langle r^2 \rangle} = l\sqrt{n}$  as before. This result was obtained with less work than the previous analysis. The previous analysis, however gave a full distribution function (a Gaussian distribution) while this one only gives the root-mean-squared end-to-end distance. For more complicated models, we will need to evaluate the term  $\langle \cos \theta'_{ij} \rangle$ .

We can use a vector analysis to investigate the relation between end-to-end distance and radius of gyration -  $s$ . In vector notation, we can write an expression for  $s^2$  in which  $\vec{r}_i$  is the location of the  $i^{\text{th}}$  atom along the polymer chain and  $\vec{z}$  is the location of the center of mass:

$$s^2 = \frac{1}{n} \sum_i (\vec{r}_i - \vec{z}) \cdot (\vec{r}_i - \vec{z}) \quad (3.45)$$

Expanding this sum results in

$$ns^2 = \sum_i r_i^2 + nz^2 - 2\vec{z} \cdot \sum_i \vec{r}_i \quad (3.46)$$

where  $r_i$  is the distance from the origin to atom  $i$  and  $z$  is the distance from the origin to the center of mass. The definition of the center of mass is

$$\vec{z} = \frac{1}{n} \sum_i \vec{r}_i \quad \text{or} \quad \sum_i \vec{r}_i = n\vec{z} \quad (3.47)$$

Substituting this expression in to the above results gives

$$ns^2 = \sum_i r_i^2 - nz^2 = \sum_i r_i^2 - n(\vec{z} \cdot \vec{z}) = \sum_i r_i^2 - \frac{1}{n} \sum_i \sum_j \vec{r}_i \cdot \vec{r}_j \quad (3.48)$$

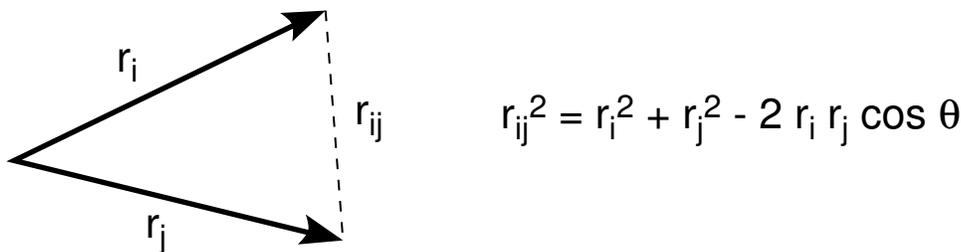


Figure 3.14: A triangle framed by vectors  $\vec{r}_i$  and  $\vec{r}_j$ . The vector  $\vec{r}_{ij}$  connects the two ends of vectors  $\vec{r}_i$  and  $\vec{r}_j$ .

To evaluate the vector dot product  $\vec{r}_i \cdot \vec{r}_j$ , consider the triangle in Fig. 3.14. By the cosine law the length of the vector  $\vec{r}_{ij}$  connecting the ends of vectors  $\vec{r}_i$  and  $\vec{r}_j$  is

$$r_{ij}^2 = r_i^2 + r_j^2 - 2r_i r_j \cos \theta = r_i^2 + r_j^2 - 2\vec{r}_i \cdot \vec{r}_j \quad (3.49)$$

Solving for  $\vec{r}_i \cdot \vec{r}_j$  gives

$$\vec{r}_i \cdot \vec{r}_j = \frac{r_i^2 + r_j^2 - r_{ij}^2}{2} \quad (3.50)$$

The expression for the radius of gyration then simplifies to:

$$s^2 = \frac{1}{2n^2} \sum_j \sum_i r_{ij}^2 = \frac{1}{n^2} \sum_j \sum_{i < j} r_{ij}^2 \quad (3.51)$$

In this step we made use of symmetry ( $r_{ij} = r_{ji}$ ) and the fact that  $r_{ii} = 0$ .

Because the vectors  $\vec{r}_i$  are the coordinates of the atoms in the polymer chain, the distance  $r_{ij}$  is the end-to-end distance for a sub-polymer chain of  $j - i$  bonds. By the discussion in the section on the equivalent freely-jointed chain, we can write this distance as

$$r_{ij}^2 = C(j - i)l^2 \quad (3.52)$$

We do not know the value of  $C$  but it is the characteristic ratio for the polymer under consideration and may depend on  $j - i$  (especially for small  $j - i$ ). Ignoring the  $j - i$  dependence of  $C$ , inserting this result, and reordering the summation over  $i$  yields:

$$s^2 = \frac{Cl^2}{n^2} \sum_{j=1}^n \sum_{i=1}^{j-1} i = \frac{Cl^2}{n^2} \sum_{j=1}^n \frac{j(j-1)}{2} \approx \frac{Cl^2}{2n^2} \sum_{j=1}^n j^2 = \frac{Cl^2}{2n^2} \frac{n(n+1)(2n+1)}{6} \quad (3.53)$$

For large polymer chains (large  $n$ ) this result simplifies to

$$\sqrt{\langle s^2 \rangle} = \sqrt{\frac{Cnl^2}{6}} = \sqrt{\frac{\langle r^2 \rangle}{6}} \quad (3.54)$$

We conclude that whenever  $\langle r^2 \rangle = Cnl^2$  for a polymer, that the radius of gyration is directly proportional to (and smaller than) the end-to-end distance. This result holds for large molecules

when  $C_n$  is independent of  $n$ . An important corollary to this result is that everything we learn while studying the end-to-end distance also applies to the radius of gyration. The reverse is also true. Any analysis or experiments that give us information about the radius of gyration also give us information about the end-to-end distance.

The approximations used to relate radius of gyration to end-to-end distance can be understood using a matrix representation. Using the equivalent freely-jointed chain approximation, the radius of gyration squared is the sum of all terms above the diagonal of the following matrix:

$$\begin{pmatrix} 0 & Cl^2 & 2Cl^2 & 3Cl^2 & 4Cl^2 & \dots \\ - & 0 & Cl^2 & 2Cl^2 & 3Cl^2 & \dots \\ - & - & 0 & Cl^2 & 2Cl^2 & \dots \\ - & - & - & 0 & Cl^2 & \dots \\ - & - & - & - & 0 & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix} \quad (3.55)$$

The terms near the diagonal are random walk, long-chain approximations for short chains and may be inaccurate. If the matrix is large, however, there will be many more terms far from the diagonal than close to the diagonal. For large matrices, the inaccuracies in the terms close to the diagonal will have only a negligible effect on the sum of all terms. Thus the relation between  $\langle s^2 \rangle$  and  $\langle r^2 \rangle$  derived above will be accurate. In order for the derived relation, rewritten here as

$$\frac{\langle r^2 \rangle}{\langle s^2 \rangle} = 6 \quad (3.56)$$

to be accurate, the chain must be slightly larger than is required for  $\langle r^2 \rangle$  to be equal to  $Cnl^2$ . The relation will be inaccurate for short chains or for chains that are not random walk coils (*e.g.*, extended chain polymers).

### 3.7 Freely-Rotating Chain

Commonly the bond angles in polymers are fixed or narrowly fixed to constant values. For example, in polyethylene the bonds angles are all close to  $112^\circ$ . It takes much more energy to distort bond angles than it does to induce rotations about single bonds. We therefore consider a random walk where all bond angles,  $\theta_i$ , are constant and equal to one value  $\theta$ . The more easily moved dihedral or rotational angles are considered to all be equally likely. Thus there is free rotation about each bond and hence we call this model the “freely-rotating chain” model. The conformation of a given chain is reduced to specifying the dihedral angles for  $n - 1$  bonds (all bonds except the first bond).

To analyze the freely-rotating chain we use the vector approach outlined in the previous section. By taking successive projections of one bond onto another, we can show (See Flory book) that  $\langle \cos \theta'_{ij} \rangle = \cos^m \theta'$  where  $m = |j - i|$  where  $\theta' = \pi - \theta$  is the supplement of the fixed bond angle.

The resulting vector analysis becomes

$$\langle r^2 \rangle = nl^2 + 2l^2 \sum_{i < j} \cos^{j-i} \theta' \quad (3.57)$$

This expression can be imagined as the sum of all the terms in the matrix of size  $n \times n$  in which the element at row  $i$  and column  $j$  is  $\cos^{|j-i|} \theta'$ :

$$l^2 \times \begin{pmatrix} 1 & \cos \theta' & \cos^2 \theta' & \cos^3 \theta' & \dots & \cos^{n-1} \theta' \\ \cos \theta' & 1 & \cos \theta' & \cos^2 \theta' & \dots & \cos^{n-2} \theta' \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \cos^{n-1} \theta' & \cos^{n-2} \theta' & \dots & \cos^2 \theta' & \cos \theta' & 1 \end{pmatrix} \quad (3.58)$$

The  $n$  diagonal terms sum to  $n$  which give the first term ( $nl^2$ ) in the  $\langle r^2 \rangle$  expression. Writing out the required terms for the summation term by inspection of this matrix gives

$$\langle r^2 \rangle = nl^2 + 2l^2 [(n-1) \cos \theta' + (n-2) \cos^2 \theta' + \dots + (n-(n-1)) \cos^{n-1} \theta'] \quad (3.59)$$

which can be written as

$$\langle r^2 \rangle = nl^2 + 2l^2 \sum_{i=1}^{n-1} (n-i) \cos^i \theta' \quad (3.60)$$

We rewrite this summation in simpler terms by letting  $x = \cos \theta'$ :

$$\langle r^2 \rangle = nl^2 + 2l^2 (nS_1 - xS_2) \quad (3.61)$$

where

$$S_1 = \sum_{i=1}^{n-1} x^i \quad \text{and} \quad S_2 = \sum_{i=1}^{n-1} ix^{i-1} \quad (3.62)$$

The terms  $S_1$  and  $S_2$  can be evaluated in closed form for all values of  $n$ . For polymer problems, we are normally concerned with large  $n$  for which these sums converge to constant values and we can treat the two sums as infinite series. The infinite geometric series  $S_1$  has the well known result

$$S_1 \approx \sum_{i=1}^{\infty} x^i = x (1 + x + x^2 + x^3 + \dots) = \frac{x}{1-x} \quad (3.63)$$

For  $S_2$ , we use a trick by noticing that

$$S_2 = \frac{d}{dx} \sum_{i=1}^{n-1} x^i = \frac{dS_1}{dx} \quad (3.64)$$

For large  $n$  we thus have

$$S_2 \approx \frac{d \left( \frac{x}{1-x} \right)}{dx} = \frac{1}{(1-x)^2} \quad (3.65)$$

Substituting  $S_1$  and  $S_2$  into the expression for  $\langle r^2 \rangle$  gives

$$\langle r^2 \rangle = nl^2 + 2l^2 \left[ \frac{nx}{1-x} - \frac{x}{(1-x)^2} \right] \quad (3.66)$$

For large  $n$ , the second term in the brackets quickly becomes negligible and we have

$$\langle r^2 \rangle = nl^2 + \frac{2nl^2x}{1-x} = nl^2 \frac{1+x}{1-x} \quad (3.67)$$

Finally we substitute for  $x$  and note that  $\cos \theta = -\cos \theta'$  (where  $\theta$  is the bond angle and  $\theta' = \pi - \theta$  is the supplement of the bond angle). We get

$$\langle r^2 \rangle = nl^2 \frac{1 - \cos \theta}{1 + \cos \theta} \quad (3.68)$$

The root-mean-squared end-to-end distance for large, freely-rotation chains is

$$\sqrt{\langle r^2 \rangle} = l\sqrt{n} \sqrt{\frac{1 - \cos \theta}{1 + \cos \theta}} \quad (3.69)$$

The characteristic ratio is

$$C_n = \frac{\langle r^2 \rangle}{nl^2} = \frac{1 - \cos \theta}{1 + \cos \theta} \quad (3.70)$$

Note that the characteristic ratio is independent of  $n$ . This independence is a consequence of our assumption of large  $n$ . It is possible to evaluate  $S_1$  and  $S_2$  for any value of  $n$  and get an exact result. The exact result gives a  $C_n$  that depends on  $n$  but rapidly converges to the above result for large  $n$ .

For an example we consider polyethylene. All carbon bonds are in approximately tetrahedral geometries. We can thus approximate all bond angles by the tetrahedral angle of  $\theta = 109.47^\circ$  or  $\cos \theta = -1/3$  (note: it is easier to remember the tetrahedral angle as the  $\cos^{-1}(-1/3)$  than it is to remember it as  $109.47^\circ$ ). For a freely-rotating polyethylene chain

$$\sqrt{\langle r^2 \rangle} = l\sqrt{2n} \quad (3.71)$$

and the characteristic ratio is  $C_n = 2$ . Real polyethylene is not totally symmetric and thus the C—C—C bonds deviate slightly from  $109.47^\circ$  to  $112^\circ$ . The C—C—H and H—C—H bonds shrink slightly to compensate. This slight increase in bond angle increases the characteristic ratio by 10% to  $C_n = 2.20$ .

### 3.8 Hindered Rotating Chain

The dihedral angle is clearly not free to assume all possible values. Instead the angle is restricted by steric interactions. Consider the potential energy for rotation about the central C—C bond in butane ( $\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—CH}_3$ ) shown in Fig. 3.15. The rotations about the central C—C bond

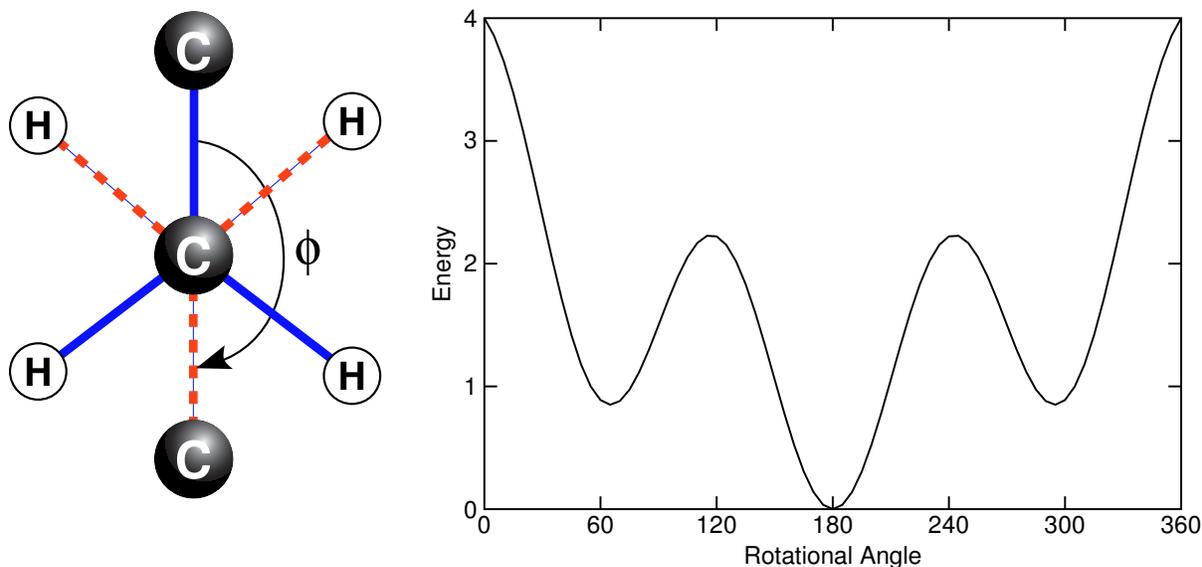


Figure 3.15: Left side is an end view of the central C—C bond in butane. The right side plots to potential energy as a function of angle with  $\phi = 180^\circ$  defined as the *trans* position illustrated on the left side.

in butane are a reasonable model for the C—C rotations in polyethylene. A preferred analogy would be higher molecular weight alkanes. Those experiments and their analysis have been done, but with more effort and less accuracy than available for butane.

The *trans* state illustrated on the left side of Fig. 3.15 is the lowest energy state. It is lowest because the two CH<sub>3</sub> groups, which are larger than the H atoms, are as far apart as possible. As rotations occur the groups appended to each of the central C atoms come into closer proximity and the steric energy increases. There are local maxima at  $\phi = \pm 120^\circ$ . These maxima occur when the CH<sub>3</sub> groups are aligned with H atoms on the other carbon atom. There are local minima when  $\phi = \pm 60^\circ$ . These minima occur when all the groups are staggered (as in the left of Fig. 3.15) but the CH<sub>3</sub> groups are adjacent to each other rather than opposite each other as in the *trans* state. These local minima are called the *gauche+* and *gauche-* states. Finally there is a local maximum at  $\phi = 0^\circ$ , which occurs when the two CH<sub>3</sub> groups on either end of the butane chain are aligned and as close together as possible.

When rotations are hindered by potential energy functions such as those shown in Fig. 3.15, it is clear that the rotations will not be free. All rotational angles are perhaps possible, but the dihedral angles will have a preference for the low energy states. For butane, most bonds will be at or near the *trans* state ( $\phi = 180^\circ$ ) or at or near the local *gauche* minima ( $\phi = \pm 60^\circ$ ). Thermal energy will allow the angles to deviate from these states and to overcome the barriers to transitions from one state to another. The populations of all rotational angles, however, will not be equal. We thus replace the freely-rotating chain with a more realistic hindered-rotating chain model.

End-to-end distance for a hindered-rotation chain is more difficult to find than the freely-

rotating chain model. We omit the details and give the results. The final equation is found using the vector analysis and averaging the dot products  $\vec{u}_i \cdot \vec{u}_j$ , while accounting for unequal populations of the possible rotational angles. The result is

$$\sqrt{\langle r^2 \rangle} = l\sqrt{n} \sqrt{\frac{1 - \cos \theta}{1 + \cos \theta}} \sqrt{\frac{1 - \langle \cos \phi \rangle}{1 + \langle \cos \phi \rangle}} \quad (3.72)$$

where  $\langle \cos \phi \rangle$  is the average value of the rotational angle. The characteristic ratio is

$$C_n = \frac{\langle r^2 \rangle}{nl^2} = \frac{1 - \cos \theta}{1 + \cos \theta} \frac{1 - \langle \cos \phi \rangle}{1 + \langle \cos \phi \rangle} \quad (3.73)$$

Note that if this hindered-rotation chain becomes freely-rotating chain then  $\langle \cos \phi \rangle = 0$  and the results reduce to the freely-rotating chain results.

For a detailed example, let's consider polyethylene with  $l = 1.53\text{\AA}$ ,  $n = 5000$  bonds, and  $\theta = 112^\circ$ . The simplest model, the freely-jointed chain model, gives

$$\sqrt{\langle r^2 \rangle} (\text{freely jointed}) = 108\text{\AA} \quad (3.74)$$

and a characteristic ratio of 1. The next most realistic model, the freely-rotating chain model, gives

$$\sqrt{\langle r^2 \rangle} (\text{freely rotating}) = 108\sqrt{2.20}\text{\AA} = 160\text{\AA} \quad (3.75)$$

and a characteristic ratio of 2.20. For the hindered-rotation chain model we need to know  $\langle \cos \phi \rangle$ . We thus need some new information. For example, we will say that experiments show that 60% of the bonds have  $\phi = 180^\circ$  (*trans*) and 20% each have  $\phi$ 's of  $+60^\circ$  or  $-60^\circ$  (*gauche+* or *gauche-*). Then the average dihedral angle gives

$$\langle \cos \phi \rangle = -0.6 + 0.2 \times (0.5) + 0.2 \times (0.5) = -0.4 \quad (3.76)$$

The end-to-end distance for the hindered-rotation chain is

$$\sqrt{\langle r^2 \rangle} (\text{hindered rotation}) = 108\sqrt{2.20}\sqrt{2.33}\text{\AA} = 245\text{\AA} \quad (3.77)$$

and the characteristic ratio is  $C_n = 5.13$ . We can compare this result to the experimental result for polyethylene which is 6 to 7 (depending on temperature). The hindered rotating chain gives a result that is close to the correct results, but is still too low. In the next section we consider improvements on the hindered rotating chain model.

### 3.9 More Realistic Analysis

We can list two general factors that influence the end-to-end distance, but are not included in the hindered rotation chain model — short range interactions and long range interactions. The next step in our analysis is to include some, or preferable all, of these effects.

We consider short-range interactions as interactions with neighboring bonds that affect the relative probabilities of the dihedral angle. When we include short range interactions we cannot take a simple average of  $\cos \phi$  as in the hindered rotation model. We need to account for the effect of neighboring bonds. In its simplest implementation we might assume that the conformation of one bond depends on relative energies that are influenced by the conformation of the previous bond. Each step of the random walk then requires an adjustment of the jump-direction probabilities according to the conformation of the previous bond. Some probability analysts call such models Markov chains instead of random walks. After we develop a model that does a good job of accounting for short-range interactions, we will have a good model for polymer conformations that are unperturbed by the long-range interactions described below. We will call the polymers generated by this modified random walk or Markov chain process “unperturbed polymer conformations.” The end-to-end distance of these chains will be called the unperturbed end-to-end distance and will be denoted with a subscript zero —  $\langle r^2 \rangle_0$ .

Long-range interactions are all interactions that are not short-range interactions. To be more specific, long-range interactions are interactions between atoms or molecular units that are not covalently bonded to each other. Defined this way, long range interactions include interactions between two parts of the polymer that are separated by many bonds or between the polymer and solvent molecules. We discuss three types of long-range interactions.

The first important perturbation to random walks is that while random walks can cross their own path, a polymer conformation cannot — random walks used to simulate polymer chains should be self-avoiding random walks. This new feature is called the effect of *excluded volume*. The elements of the chain exclude other elements from their occupied volume. If included in the analysis, excluded volume will perturb the end-to-end distance and cause it to increase. Besides increasing the end-to-end distance, excluded volume will cause the root-mean-squared end-to-end distance to no longer be proportional to  $\sqrt{n}$ . When excluded volume effects are significant, we can assume that  $\langle r^2 \rangle$  is proportional to some power of  $n$  such as  $p$  (where  $p > 0.5$ ):

$$\langle r^2 \rangle \propto n^p l^2 \quad (3.78)$$

According to deGennes,  $p = 1.2$  and therefore the characteristic ratio increases as  $n^{0.2}$ :

$$C_n = \frac{\langle r^2 \rangle}{nl^2} \propto n^{0.2} \quad (3.79)$$

A second long-range interaction is interactions between the polymer and the solvent. A solvent can cause the unperturbed end-to-end distance to increase or decrease. A good solvent will cause it to increase. In effect the polymer will prefer interactions with the solvent over interactions with itself and therefore will expand to maximize polymer-solvent interactions. A poor solvent will cause the unperturbed end-to-end distance to contract. The polymer wants to avoid the solvent and thus will contract on itself to avoid polymer-solvent interactions. In the extreme case, a poor solvent will

cause the polymer to completely contract and precipitate out of solution. This extreme example of a poor solvent is better characterized as a non-solvent.

The last types of long-range interactions are specific interactions. By specific interactions we mean identifiable interactions between remote parts of the chains. Two examples are hydrogen bonding and ionic interactions.

After considering both short-range and long-range interactions we are led to split the problem of theoretical polymer characterization into two parts. The first part is the study of the unperturbed end-to-end distance. We plan to modify the hindered rotation chain model to correctly account for short-range interactions and thereby calculate the correct unperturbed end-to-end distance. After solving this problem we will consider what influence the long-range interactions (including excluded volume effects) have on the results. Let's define  $\alpha$  to be the factor by which the linear dimension expands ( $\alpha > 1$ ) or contracts ( $\alpha < 1$ ) due to long-range interactions:

$$\sqrt{\langle r^2 \rangle} = \alpha \sqrt{\langle r^2 \rangle_0} \quad (3.80)$$

The solution to the long-range interaction problem is to find  $\alpha$ .

### 3.10 Theta ( $\Theta$ ) Temperature

We also need to consider temperature effects. Temperature can affect all types of interactions. It can affect short-range interactions by influencing the relative probabilities of the various dihedral angles. Rotations about single bonds are influenced by the presence of thermal energy and thus higher temperature will make it more likely to find conformations in higher-energy rotational angles. Temperature affects long-range interactions mainly through polymer-solvent interactions. In general increasing the temperature improves solvent quality and lowering it decreases solvent quality.

As discussed in the previous section, we will first attempt to solve the short-range interaction problem. The first problem we encounter is how do we know when we have the right answer? Real polymers have long-range interactions and short-range interactions. Thus real polymers have a mean-squared end-to-end distance of  $\langle r^2 \rangle$  and not  $\langle r^2 \rangle_0$ . If we compare our theoretical analysis to experimental results we will normally find disagreement, regardless of whether the analysis to find  $\langle r^2 \rangle_0$  was correct or not. Fortunately there is an experimental solution to this problem called the theta ( $\Theta$ ) temperature. For any given polymer-solvent pair, there is a specific temperature, called the  $\Theta$  temperature, for which the true end-to-end distance is equal to the unperturbed end-to-end distance. Thus experiments at the  $\Theta$  temperature can be used to measure  $\langle r^2 \rangle_0$  which can be compared to experimental predictions.

The concept of  $\Theta$  temperature can be understood by considering the effect of temperature on polymer-solvent interactions. In general the polymer-solvent interactions for a given polymer-

solvent pair is an increasing function of temperature. As the polymer-solvent interaction increases the solvent becomes a better solvent. Thus increasing temperature leads to a better solvent and to a higher  $\alpha$ ; decreasing temperature leads to a poorer solvent and a lower  $\alpha$ . For a given polymer-solvent pair, there will be some temperature for which  $\alpha = 1$ . That temperature is called the theta ( $\Theta$ ) temperature. At the  $\Theta$  temperature  $\langle r^2 \rangle = \langle r^2 \rangle_0$  and experiments at the  $\Theta$  temperature can be used to measure  $\langle r^2 \rangle_0$ .

Besides measuring  $\langle r^2 \rangle_0$ , the  $\Theta$  temperature has other useful properties. At the  $\Theta$  temperature, some physical properties (*e.g.*, osmotic pressure) obey ideal laws up to high concentrations. Thus simple theories for analysis of a physical property that do not account for long-range interactions will still work well at the  $\Theta$  temperature. There is an analogy between the  $\Theta$  temperature and the Boyle point of a gas. The Boyle point is the temperature where the repulsion between gas molecules due to excluded volume is exactly compensated by their mutual attraction. At the Boyle point, the ideal gas laws are obeyed to very high pressures. Note that conformity to ideal laws is one way of determining the  $\Theta$  temperature. The temperature can be varied until the measurements obey ideal laws. That temperature is the  $\Theta$  temperature.

Despite the advantages of the  $\Theta$  temperature, we note that working in theta solvents is often impractical. To get  $\alpha$  down to one, you need a solvent that is sufficiently poor. The solvent may become so poor the precipitation becomes imminent. It is often better to work in a good solvent and correct the results to the unperturbed results. For measurements of physical properties, this correction involves correcting ideal laws for large molecules or long-range interactions.

### 3.11 Rotational Isomeric State Model

The rotational isomeric state model will be our solution to the problem of accounting for short-range interactions and some long range interactions (*e.g.*, the effect of excluded volume). In general, any polymer conformation is defined by a set of bond lengths,  $l_i$ , bond angles,  $\theta_i$ , and dihedral angles,  $\phi_i$ . In the rotational isomeric state model, we assume that the polymer is restricted to certain types of conformations or to certain isomeric states. Bond lengths are likely to vary only  $\pm 3\%$  and thus as before we consider them to be fixed at  $l$ . Likewise, bond angles are likely to vary only  $\pm 5$  degrees and we consider them to be fixed at  $\theta$ . The dihedral angles are not allowed to assume any possible angle, but instead are assumed to be restricted to a small number of discrete values. The possible discrete dihedral angles define the set of rotational isomeric states for each bond.

We will illustrate with polyethylene. These ideas will be extended to other polymers latter. Due to symmetry of polyethylene there are three possible rotational isomeric states (see Fig. 3.16). The *trans* state ( $\phi = +180^\circ$ ), the *gauche+* state ( $\phi = +60^\circ$ ) and the *gauche-* state ( $\phi = -60^\circ$ ). In the rotational isomeric state model, each bond of polyethylene is assumed to be in one of these three states. No other values of  $\phi$  are allowed. In reality, thermal fluctuations about the minima in

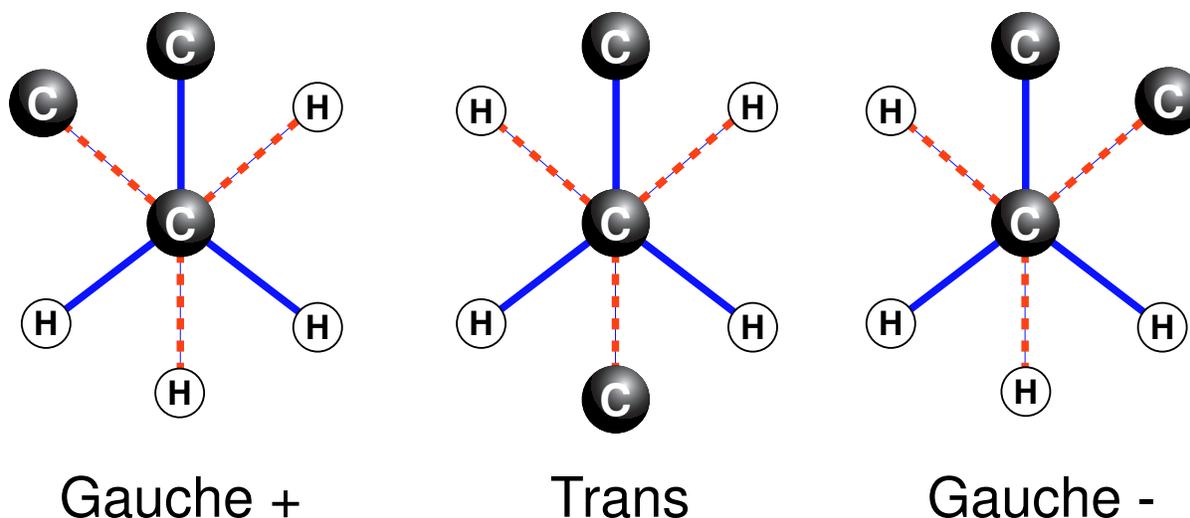


Figure 3.16: The three rotational isomeric states in polyethylene. The dihedral angle,  $\phi$ , is defined as the angle between to white circles.

potential energy will lead to a distribution in  $\phi$ 's around these three local minima. The rotational isomeric state model asserts that we can realistically simulate a polymer chain by ignoring variations in  $\phi$  around the local minima.

In our random walk analysis of the rotational isomeric state, the probability of any bond existing in one of the rotational state  $i$  characterized by angle  $\phi_i$ , is given by a Boltzman factor:

$$P(\phi_i) = \frac{e^{-E(\phi_i)/RT}}{Z} \quad (3.81)$$

where  $Z$  is a normalizing factor or the sum of the Boltzman energy factors for all possible angles:

$$Z = \sum_{i=1}^3 e^{-E(\phi_i)/RT} \quad (3.82)$$

where  $E(\phi_i)$  is the energy associated with the state at dihedral angle  $\phi_i$  and the sum is over the three possible states in Fig. 3.16 (Note: this equation can easily be generalized to more than three rotational isomeric states) Because of short-range interactions discussed above, this probability factor is expected to be affected by neighboring bonds. The simplest model is to assume that the energy,  $E(\phi_i)$ , is affected by the bond conformation of the previous bond. This important nearest-neighbor interaction is ignored in the hindered rotation chain model. Its inclusion in the rotational isomeric state model is the major advance in realism in this new model.

To account for nearest neighbor interactions, we must consider all bond pairs and all possible conditional probabilities of the form  $P(\phi_i|\phi_{i-1})$ , which gives the conditional probability that bond  $i$  has angle  $\phi_i$  given that the previous bond or bond  $i - 1$  has angle  $\phi_{i-1}$ . By analogy with the previous probability factor

$$P(\phi_i|\phi_{i-1}) = \frac{e^{-E(\phi_{i-1}\phi_i)/RT}}{Z(\phi_{i-1})} \quad (3.83)$$

where  $Z(\phi_{i-1})$  is a normalizing factor or the sum of the Boltzman energy factors for all angles  $\phi_i$  given that  $\phi_{i-1}$  is fixed:

$$Z = \sum_{j=1}^3 e^{-E(\phi_{i-1}\phi_j)/RT} \quad (3.84)$$

In these equations,  $E(\phi_{i-1}\phi_i)$  is the energy associated with two consecutive bonds with dihedral angles  $\phi_{i-1}$  and  $\phi_i$ . In this section we are restricting ourselves to three rotational states of *trans* ( $t$ ), *gauche+* ( $g^+$ ), and *gauche-* ( $g^-$ ). The energy factors we care about are  $E(tt)$ ,  $E(tg^+)$ ,  $E(tg^-)$ , etc.. The conditional probabilities we are concerned with can conveniently be tabulated in a matrix called the weighting factor matrix. For polyethylene (or for any three-state polymer) we write can write a weighting factor matrix as

$$U = \begin{pmatrix} P(t|t) & P(g^+|t) & P(g^-|t) \\ P(t|g^+) & P(g^+|g^+) & P(g^-|g^+) \\ P(t|g^-) & P(g^+|g^-) & P(g^-|g^-) \end{pmatrix} \quad (3.85)$$

For example, the matrix element  $P(t|g^+)$  gives the probability that the next bond is *trans* given that the previous bond was *gauche+*.

Let's begin with the first row and arbitrarily assign the  $tt$  state to the ground state. Thus we assume  $E(tt) = 0$ . The  $tg^+$  and  $tg^-$  bond pairs will each be higher in energy than the  $tt$  bond pair. In polyethylene, the excess energy associated with the two possible *gauche* bonds will be the same. We let that excess energy be  $E_g$  or the extra energy associated with a *gauche* bond. We further define

$$\sigma = e^{-E_g/RT} \quad (3.86)$$

and we can quickly derive  $Z(t) = 1 + 2\sigma$  and

$$P(t|t) = \frac{1}{1+2\sigma} \quad P(g^+|t) = \frac{\sigma}{1+2\sigma} \quad P(g^-|t) = \frac{\sigma}{1+2\sigma} \quad (3.87)$$

$Z(t)$  appears in the denominator of each probability as a normalizing factor.

For the second row, we might just consider the energy associated with all the *gauche* bonds and assume  $E(g^+t) = E_g$  and  $E(g^+g^+) = E(g^+g^-) = 2E_g$ . The probabilities would become

$$P(t|g^+) = \frac{\sigma}{\sigma+2\sigma^2} \quad P(g^+|g^+) = \frac{\sigma^2}{\sigma+2\sigma^2} \quad P(g^-|g^+) = \frac{\sigma^2}{\sigma+2\sigma^2} \quad (3.88)$$

This simple analysis ignores an important short-range interaction that occurs when two consecutive bonds are  $g^+g^-$  or  $g^-g^+$ . Figure 3.17 illustrates a  $g^+g^-$  conformation. Two parts of the polymer chain separated by four bonds are in close proximity which causes a large steric interaction. This interaction is known as the *pentane* effect and causes the energy of  $g^+g^-$  or  $g^-g^+$  conformations to be much higher than that  $g^+g^+$  or  $g^-g^-$  conformations. If we let  $E_p$  be the energy of the pentane effect interaction then  $E(g^-g^+) = 2E_g + E_p$  whereas  $E(g^+g^+) = 2E_g$ . Defining

$$\omega = e^{-E_p/RT} \quad (3.89)$$

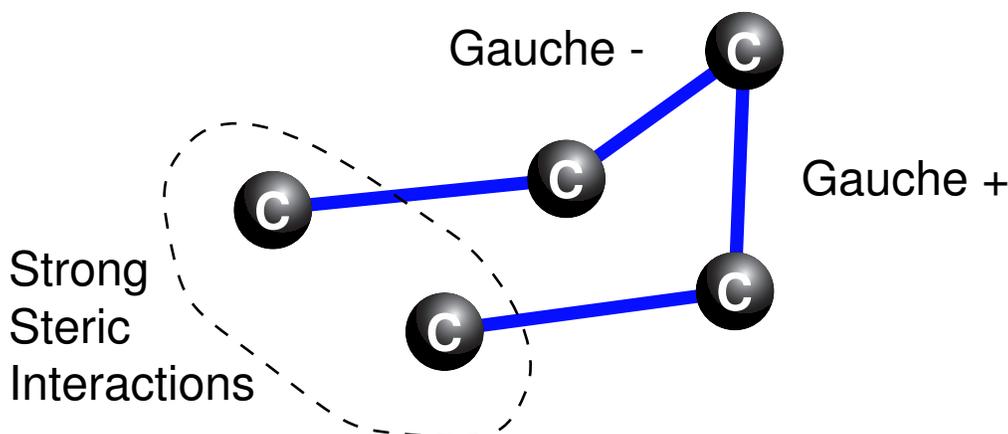


Figure 3.17: The steric interactions caused by the pentane effect when two consecutive bonds are  $g^+|g^-$  or  $g^-|g^+$ .

we derive the conditional probabilities for the second row of  $U$  to be

$$P(t|g^+) = \frac{\sigma}{\sigma + \sigma^2 + \sigma^2\omega} = \frac{1}{1 + \sigma + \sigma\omega} \quad (3.90)$$

$$P(g^+|g^+) = \frac{\sigma^2}{\sigma + \sigma^2 + \sigma^2\omega} = \frac{\sigma}{1 + \sigma + \sigma\omega} \quad (3.91)$$

$$P(g^-|g^+) = \frac{\sigma^2\omega}{\sigma + \sigma^2 + \sigma^2\omega} = \frac{\sigma\omega}{1 + \sigma + \sigma\omega} \quad (3.92)$$

Analyzing the third row similarly to the second row and collecting all probabilities in the matrix we arrive at

$$U = \begin{pmatrix} \frac{1}{1+2\sigma} & \frac{\sigma}{1+2\sigma} & \frac{\sigma}{1+2\sigma} \\ \frac{1}{1+\sigma+\sigma\omega} & \frac{\sigma}{1+\sigma+\sigma\omega} & \frac{\sigma\omega}{1+\sigma+\sigma\omega} \\ \frac{1}{1+\sigma+\sigma\omega} & \frac{\sigma}{1+\sigma+\sigma\omega} & \frac{\sigma\omega}{1+\sigma+\sigma\omega} \end{pmatrix} \quad (3.93)$$

It usually suffices to work with relative probabilities rather than absolute probabilities. By convention we normalize each row to the first element in that row. For a simple polymer like polyethylene, we write the weighting matrix of relative probabilities as

$$U = \begin{pmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{pmatrix} \quad (3.94)$$

By theory and experiment, the energy terms for polyethylene are well known. The best results give  $E_g = 2100$  J and  $E_p = 8400$  J. At  $300^\circ\text{C}$  these lead to weighting factors of

$$\sigma = e^{-2100\text{J}/RT} = 0.43 \quad \text{and} \quad \omega = e^{-8400\text{J}/RT} = 0.081 \quad (3.95)$$

Thus gauche bonds are only about 46% as likely as trans bonds ( $2\sigma/(1 + 2\sigma)$ ) and  $g^+|g^-$  conformations are only about 2.4% as likely ( $\sigma\omega/(1 + \sigma + \sigma\omega)$ ).

We next consider how to use the rotational isomeric state model to predict polymer properties. Imagine a polymer chain of  $n$  bonds. A polymer conformation of this chain is determined by setting the states of each bond; each bond can be  $t$ ,  $g^+$ , or  $g^-$ . We can ignore the first two bonds and thus we need to set the states of the terminal  $n - 2$  bonds. The first bond can be ignored because it only serves to locate the start of the polymer in space. The second bond direction is determined by the rotational state of bond 1, but this state only serves to locate the initial direction of the random walk. The remaining  $n - 2$  bonds need to be determined.

There are two possible solutions to the rotational isomeric state model. Because each bond has a small number of discrete states, the total number of polymer conformations is finite. For a polymer with  $n$  bonds of which each bond can be in one of three states, the total number of polymer conformations is  $3^{n-2}$ . One possible approach is to enumerate all possible conformations and calculate properties using the exact process discussed earlier in this chapter. This exact solution can be done for small  $n$ , but soon becomes impractical for large  $n$ 's typical of real polymers. When  $n$  is large the total number of conformations is too large to enumerate, even on the fastest supercomputer.

For large polymers, a preferred approach is to use the Monte Carlo method. We generate a large number of chains using a random walk or Markov chain process. For each bond the probabilities of the next bond being in a given state are determined by the weighting matrix like the one given above and by the state of the previous bond. For each chain we can calculate a property of interest (*e.g.*, end-to-end distance, radius of gyration, *etc.*). The average value of that property after generating sufficiently many chains will be our Monte Carlo solution to the problem.

The above Monte Carlo random walk process requires a computer. The computer program Lattice™ discussed in class is an example of a program that can do Monte Carlo simulations using the rotational isomeric state model. Programs like Lattice™ are, in effect, computer experiments. You set polymer properties by selecting weighting factors, excluded volume, temperature, *etc.*. Then you run the program and calculate the end-to-end distance or the radius of gyration. These computer experimental results can be compared to real experimental results. If the two results agree, you have evidence that the rotational isomeric state is a valid model for polymers. Furthermore the physical concepts of the rotational isomeric state model give you insight about the polymer molecules and the factors that control conformations.

The following pseudo computer code is the program logic, or flow chart, of the main part of any program that does Monte Carlo solutions using the rotational isomeric state model. This flow chart assumes a three rotational isomeric states, but it could easily be generalized to handle any number of states.

```
let v = (1,0,0) or the first bond is t
for bond=2 to number of bonds-1
```

```

let q=Uv be a vector giving the probabilities for t, g+, and g-
pick a random number between 0 and q1+q2+q3
if (random number is between 0 and q1) then
    next bond is t and v = (1,0,0)
else if (random number is between q1 and q2) then
    next bond is g+ and v = (0,1,0)
else if (random number between q2 and q3) then
    next bond is g- and v = (0,0,1)
end if

if desired, check for excluded volume effects
    if jump to occupied site, try another site, reject the entire
        chain, or reject several previous bonds
    if all sites occupied start new chain
end if

next bond

Now have set of n-2 bond conformations which completely define the chain
Calculate properties (e.g. end-to-end distance, radius of gyration, etc.)
Start over with another chain and continue until results converge

```

The key part of this loop is calculating the properties of each generated chain. You can calculate any property that can be reliably calculated for a given polymer conformation. The simplest and most reliable properties are size properties. The program Lattice™ calculates the following properties:

1. Last  $r$  (end-to-end distance of current chain)
2. rms  $r$
3.  $\langle r \rangle$
4. rms  $s$
5.  $\frac{r^2}{nl^2}$  — the characteristic ratio (equal to  $C_n$ )
6.  $\frac{r^2}{s^2}$  — how close is it to 6?
7. % trans
8. Number of rejected steps
9. Relative entropy

In addition to the above calculations, Lattice™ can also plot many results. It can plot each generated polymer in a three-dimensional view. These stick figures give a feel for typical polymer conformations. It can plot the distribution of end-to-end distances and compare them to the radial Gaussian function calculated for in the freely-jointed chain analysis.

There is one important aspect of Lattice™ and many rotational isomeric state solutions that requires discussion. As implied by its name, Lattice™ generates chains on a tetrahedral lattice. This requires all bonds angles to be the tetrahedral bond angle of  $109.47^\circ$ . Because it is a regular lattice, it also requires all bonds lengths to be the same. This type of simulation is reasonably accurate for polyethylene and for many other carbon-backbone polymers. Lattice simulations, however, cannot give you information about the effect of bond angle (*e.g.*,  $112^\circ$  in real polyethylene *vs.* the  $109.47^\circ$  in a tetrahedral lattice) and cannot simulate polymers with different bond lengths. The advantage of lattice simulations is that they are fast. They can do most of the work with integer arithmetic which is much faster in computers. The use of a lattice makes it possible to do meaningful simulations in personal computers such as Macintoshes. An off-lattice calculation on a Macintosh would be limited to much more rudimentary work and to much shorter chains.

We can simulate many polymers using the rotational isomeric state model. Some interesting polymers are:

1. Polyethylene (see above)
2. Polytetrafluoroethylene (PTFE)
3. Copolymers
4. Polyoxymethylene (POM) (Delrin, Celcon, *etc.*)
5. Polypropylene (PP) — a vinyl polymer

Some results from these types of polymers are discussed in the Lattice™ manual and will be covered in class.

## Problems

3-1. The radial distribution function for the freely-jointed chain model was shown in class to be

$$W(r)dr = \left(\frac{\beta}{\sqrt{\pi}}\right)^3 4\pi r^2 e^{-\beta^2 r^2} dr \quad (3.96)$$

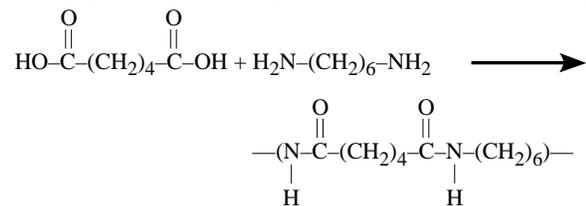
where

$$\beta = \sqrt{\frac{3}{2nl^2}} \quad (3.97)$$

Because the form of the radial distribution function even for non-freely-jointed chains is similar to the freely-jointed chain result (except with a different value for  $\beta$ ) it is worth studying this function.

- a. Show that the maximum in  $W(r)dr$  occurs at  $r = \frac{1}{\beta}$
  - b. Show that the mean value of  $r$  is  $\langle r \rangle = \frac{2}{\beta\sqrt{\pi}}$ .
  - c. Show that the average value of  $r^2$  is  $\langle r^2 \rangle = \frac{3}{2\beta^2}$
  - d. What is the standard deviation in  $r$ ?
  - e. Express the answers to *a* through *d* in terms of number of bonds ( $n$ ) and bond length ( $l$ ).
- 3-2. Pretend that linear polyethylene (PE or  $-(\text{CH}_2-\text{CH}_2)_n-$ ) can be modeled as a freely-jointed chain in which each bond is  $1.53\text{\AA}$  long. Using the results from problem 2-1, evaluate the following quantities:
- a. How many bonds are in a 500,000 g/mole PE polymer chain?
  - b. What is the maximum length of the chain?
  - c. What is the most likely end to end distance?
  - d. What is the mean end-to-end distance
  - e. What is the root mean squared end-to-end distance?
  - f. What is the standard deviation in  $r$ ?
  - g. Plot the radial distribution function for this polymer chain and indicate on your plot the answers to *c*, *d*, and *e*.
- 3-3. Polymer *A* contains  $x$  freely jointed segments each of length  $l_a$  and polymer *B* contains  $y$  freely jointed segments each of length  $l_b$ . One end of *A* is connected to one end of *B* to form a two block, block copolymer.
- a. What is the root-mean-squared end-to-end distance of this block copolymer?
  - b. If segments of *A* are randomly interspersed with segments of *B* and the segments are still freely jointed, what would be the root-mean-squared end-to-end distance of the random copolymer?
- 3-4. How do each of the following affect the radius of gyration?
- a. Decreasing the molecular weight.
  - b. Decreasing the polymer-solvent interaction.
  - c. Adding the effects of excluded volume.
  - d. Reducing the hindrance to rotations about bonds.

- 3-5. Many polymers have more than one type of bond the different types of bonds may have more the one value for bond length. One example is Nylon 66 whose repeat unit structure is



This polymer has  $N-CH_2$  bonds,  $N$ -carbonyl bonds, carbonyl- $CH_2$  bonds, and  $CH_2-CH_2$  bonds. Explain, in general terms, how you would use the rotational isomeric state model to calculate the characteristic ratio of Nylon 66.

## Chapter 4

# RUBBER ELASTICITY

### 4.1 Introduction

The mechanical properties that define a *rubber elastic* material are:

1. High elongation (often 5-10× or more elongation before failure)
2. Much of the elongation is recoverable (it returns to its original shape when unloaded)
3. The force required to elongate is low

Many polymers exhibit such *rubber elasticity* over some range in temperatures. Those polymers that exhibit rubber elasticity at room temperature are called *elastomers*. Furthermore, it is only polymeric materials that can be elastomers (with some commercially-unimportant exceptions in inorganic gels). Since the main unique feature of polymers is that they are large molecules, it is logical to assume that rubber elasticity is a potential property of large, covalently bonded molecules. But, what is it about polymers that makes it possible for them to be elastomers? What are the mechanical properties of elastomers? How does one design new and improved elastomers? Those questions are discussed in this chapter.

### 4.2 Historical Observations

Rubbery materials have been around longer than the polymer industry. The first commercial use of rubbers was developed by Charles Goodyear in 1830's. He *invented* the process of rubber vulcanization<sup>2</sup> that converted natural rubber to a true elastomer with properties suitable for his intended use as rubberized fabric. His "invention" is now an important part of polymer science. At the time, however, researchers did not even understand the existence of polymer molecules. He discovered vulcanization by chance and it was used for many years before its scientific basis became clear.

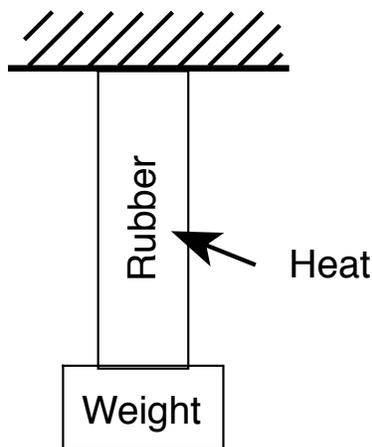


Figure 4.1: A specimen of rubber loaded under a constant weight and then heated. Upon heating the specimen decreases in length.

Prior to vulcanized rubber, natural rubber from various sources existed and was studied in the literature. In 1805, John Gough described a series of experiments on caoutchouc or Indian rubber.<sup>3</sup> His first experiment was to monitor the temperature during elongation. He did not have elaborate equipment, but was able to observe a temperature rise by stretching a rubber and bringing the specimen into contact with his lips:

“For the resin evidently grows warmer the further it is extended; and the edges of the lips possess a high degree of sensibility, which enables them to discover these changes with greater facility than other parts of the body.”

The expectation for an *elastic* material (*i.e.*, a material that recovers its shape when unloaded), is that all the energy put into a specimen is stored as mechanical energy and then recovered when the sample is unloaded. During such reversible unloading, it is unexpected to experience heat. Thus, the behavior of rubber is unusual compared to other materials. Even though rubber increases in temperature on elongation, it is still able to be reversible because it cools when unloaded.

Gough’s second experiment was to hang a weight on a piece of rubber (*i.e.*, load a piece of rubber at constant force) and then heat the specimen (see Fig. 4.1). The result of heating was that the sample *decreased* in length. All other types of materials get slightly longer when heated due to thermal expansion. In fact even a piece of rubber will thermally expand when it is not under load. Rubber specimens under load, however, have the unusual property of getting shorter when heated.

Gough’s final experiments were to stretch rubber samples under water at different temperatures. The elastomeric nature of the rubbers was preserved in warm water but was impaired in cold water. It is not unusual for the elongation of materials to depend on temperature, but rubbery materials depend dramatically on temperature. In fact the rubber elasticity effects disappear at sufficiently low temperature. A common science demonstration is to bounce a rubber ball, dip it in liquid nitrogen, and then show that it shatters like glass when bounced again. This effect is loss of

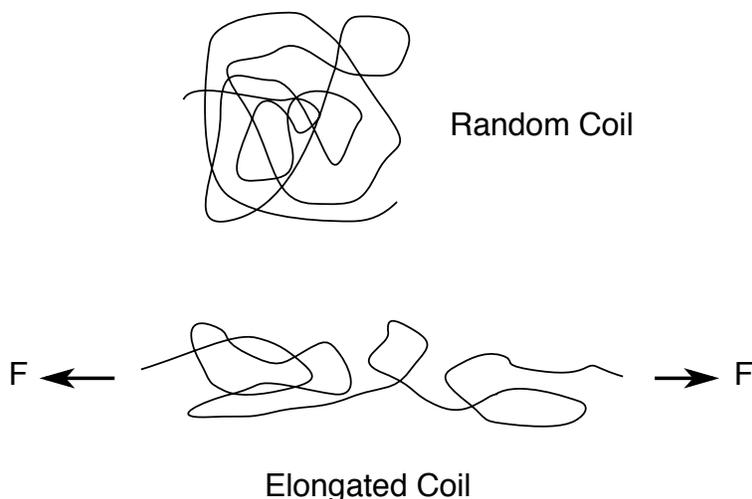


Figure 4.2: A single polymer molecule in the random coil state and in a more-ordered state when elongated by a force.

rubber elasticity at lower temperature. The shattering like glass is a consequence of the polymer now being well below its glass transition.

All these experiments on rubber, and more, can be explained as a consequence of changes in entropy while stretching a rubber. Polymers are random coils. When they are stretched in one direction, it is possible for the coil to become more ordered. This higher-order state is less random and thus has less entropy. The process is illustrated in Fig. 4.2. In other words, the change in entropy,  $\Delta S$ , is negative upon loading ( $\Delta S < 0$ ). The restoring force in rubbery materials is a result of this entropy decrease. For this reason, elastomers are accurately called “entropy springs.” Now all materials must follow the laws of thermodynamics and thus the restoring force in all materials is consequence of both internal energy change and entropy change. In virtually all materials, the internal energy change dominates and entropy effects can be ignored. Rubber elastic materials are unique in that it is the internal energy effects that are small and the entropy effects dominate.

We can outline the three requirements for a polymer molecule to be rubber elastic:

1. The polymer must be above its glass transition or  $T_g$
2. The polymer must be a non-crystalline or amorphous material
3. The polymer molecules must be lightly crosslinked. The cross links may be either chemical cross links or physical entanglements between large polymer molecules.

The first two criteria relate to the need for the polymer chain to be mobile and the need for internal energy effects to be small. The only way entropy effects can be large is when the polymer chains become ordered on elongation such as in Fig. 4.2. This ordering is only possible when the polymer is at sufficiently high temperature. For polymers, the characteristic temperature is the glass transition temperature or  $T_g$ . By definition,  $T_g$  is the temperature where molecular motions become slow and

difficult. Thus whenever  $T > T_g$  molecular motions are easy and rubber elasticity is possible. The requirement to be an amorphous material is similar. A crystalline structure is not mobile and deformations of crystals result in internal energy changes that impair rubber elasticity. The last criteria is less obvious. The need for cross linking is to make the material a solid rather than a liquid. After all, many materials are highly mobile and non-crystalline but are still not rubber elastic; they are liquids. To be rubber elastic, a liquid-like material has to be cross linked to prevent viscous flow. It is the cross links that allow the material to recover when unloaded. Goodyear's invention of vulcanization was actually an invention of a process for cross linking natural rubber. Natural rubber, in its native state, is slightly crystalline and too fluid for significant commercial uses. By cross linking using vulcanization, the crystallinity disappears and the mechanical properties become much more useful. Finally, it is the need for cross linking that makes polymers the only materials that can be elastomers. They are the only liquid-like materials that can be readily cross linked.

### 4.3 Thermodynamics

The deformation of elastomers and how they differ from most other materials can be understood by simple (albeit non-rigorous) thermodynamics analysis for uniaxial loading. The first law of thermodynamics is

$$dQ + dW = dU \quad (4.1)$$

where  $dQ$  is heat added to the sample,  $dW$  is work done on the sample, and  $dU$  is the change in internal energy. (Note that chemical engineers frequently define work done *by* a sample and thus the  $dW$  term changes sign. In mechanics, it is more natural to think in terms of work done *on* a sample). In a reversible process (such as loading an elastic material), the heat term is  $dQ = T dS$  where  $T$  is absolute temperature and  $dS$  is the change in entropy. The work term is

$$dW = F d\ell - P dV \quad (4.2)$$

The first term is work of extension (force  $F$  times distance of extension or change in length  $d\ell$ ). The second term is expansion work, but it is generally very small during uniaxial loading. Substitution into the first law of thermodynamics gives

$$T dS + F d\ell = dU + P dV = dH \quad (4.3)$$

where  $dH$  is the enthalpy change (by definition  $dH = dU + P dV$ ). Finally, solve for the force of elongation gives

$$F = \left( \frac{\partial H}{\partial \ell} \right)_{T,P} - T \left( \frac{\partial S}{\partial \ell} \right)_{T,P} \quad (4.4)$$

The first term in the extension force is the force due to enthalpy change, which is very close to the internal energy change (since  $P dV$  is small). For nearly all engineering materials, such as

metals, ceramics, polymers (with  $T < T_g$ ), *etc.*, this first term dominates as the force is equal to the internal energy change per unit length change. For elastomers, however, the converse is true. The internal energy change is small while the entropy change is large. Thus for elastomers, the force of extension is

$$F \approx -T \left( \frac{\partial S}{\partial \ell} \right)_{T,P} \quad (4.5)$$

Because extension ( $\partial \ell > 0$ ) causes a decrease in entropy ( $\partial S < 0$ ), the negative sign is correct and leads to a positive force. Conventional engineering materials and elastomers are two extremes of the force equation in which one of the two terms dominates. It is possible for materials to be between these two extremes where the internal energy and entropy terms are of similar magnitude, but such materials are uncommon.

To explain temperature effects in Gough's experiments<sup>3</sup> requires slightly more advanced thermodynamics. The free energy change,  $dG$ , on extension is:<sup>1</sup>

$$dG = V dP - S dT + F d\ell \quad (4.6)$$

Using reciprocity relations in thermodynamics, this relation leads to

$$-\left( \frac{\partial S}{\partial \ell} \right)_{T,P} = \left( \frac{\partial F}{\partial T} \right)_{\ell,P} \quad (4.7)$$

Thus, when an elastomer is stretched ( $\partial \ell > 0$ ) causing the entropy to decrease ( $\partial S < 0$ ), the left hand side (with the minus sign) is positive. This result implies that whenever the force increases ( $\partial F > 0$ ) that the temperature must increase too ( $\partial T > 0$ ). This relation thus explains Gough's first experiment. Gough's second experiment is length as a function of temperature at constant force. This experiment can be explained by more involved thermodynamics,<sup>1</sup> but will not be discussed here.

Actually, Eq. (4.7) is true for any material, but it is only elastomers for which the decrease in entropy is sufficient to cause an easily observable temperature increase. Equation (4.7) gives a simple experiment to verify this dominant role of entropy in elastomers. The experiment is to measure force as a function of temperature at constant length and pressure. The slope of the results is  $(\partial F/\partial T)_{\ell,P}$ , which by Eq. (4.7) is equal to  $-(\partial S/\partial \ell)_{T,P}$ . Substitution of this entropy result into Eq. (4.4) provides simultaneous measurement of enthalpy (or approximately internal energy) change during elongation. The results for such experiments on elastomers and conventional materials are shown schematically in Fig. 4.3. For elastomers, the slope is large and positive and the energy terms can be shown to be small. For most other materials the slope is close to zero. As shown in Fig. 4.3, most materials have a slightly negative slope due to thermal expansion. As the material expands when held at fixed length, it expands against the grips and therefore reduces the force. Such experiments can prove the dominance of entropy effects in elastomers and their absence in other materials.

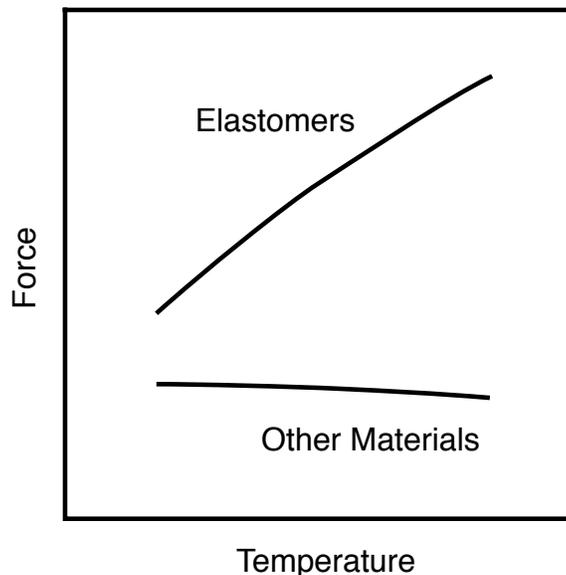


Figure 4.3: Force as a function of temperature for a specimen held at constant length and external pressure.

#### 4.4 Mechanical Properties

We can combine concepts of entropy dominated elongation in the previous section with the analysis of polymer chain conformations in Chapter 3 to derive a theoretical expression for the force as a function of elongation for an elastomer. According to statistical thermodynamics, entropy is given by

$$S = k \ln \Omega \quad (4.8)$$

where  $k$  is Boltzman's constant and  $\Omega$  is the number of possible configurations. The number of configurations per unit volume is equal to the distribution function for random-coil chain end:

$$\Omega \propto W(x, y, z) = \left( \frac{\beta}{\sqrt{\pi}} \right)^3 e^{-\beta^2 r^2} \quad (4.9)$$

where  $W(x, y, z)$  is the probability that a polymer chain starting at the origin ends at location  $(x, y, z)$  which is a distance  $r = \sqrt{x^2 + y^2 + z^2}$  from the origin. The derivation of this equation was given in Chapter 3. The distribution is picture in Fig. 4.4, which is repeated from the Chapter 3.  $W(x, y, z)$  is the probability that the random coil on the left starts at the origin and ends in the box centered on  $(x, y, z)$ . Substitution into the entropy equation gives the entropy of a single chain as

$$S = c - k\beta^2 r^2 \quad (4.10)$$

where  $c$  is a constant (that will drop out later).

We next assume this single polymer molecule is subjected to an "affine" deformation, which is defined as proportional scaling in all directions. In other words, let  $L_{x0}$ ,  $L_{y0}$ , and  $L_{z0}$  be the initial

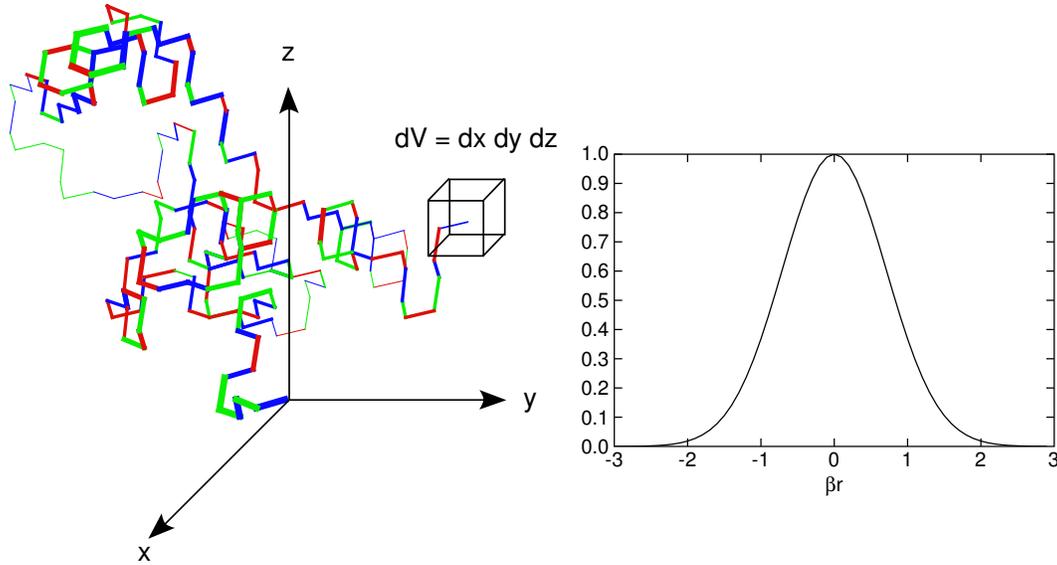


Figure 4.4: The left side shows a chain that starts at the origin and ends in a box centered a  $(x, y, z)$ . The right side is a one-dimensional plot of  $W(x, y, z)dx dy dz$ .

lengths in the  $x$ ,  $y$ , and  $z$  directions before deformation and  $L_x$ ,  $L_y$ , and  $L_z$  be the lengths after deformation. Now define elongation ratios

$$\lambda_x = \frac{L_x}{L_{x0}}, \quad \lambda_y = \frac{L_y}{L_{y0}}, \quad \text{and} \quad \lambda_z = \frac{L_z}{L_{z0}} \quad (4.11)$$

An “affine” deformation means that each location in space transforms the same way as the global lengths. Thus a point initially at  $(x, y, z)$  will be at  $(\lambda_x x, \lambda_y y, \lambda_z z)$  in the deformed space. Thus the entropy of a single chain will change from

$$S_i = c - k\beta^2(x^2 + y^2 + z^2) \quad (4.12)$$

to

$$S_i = c - k\beta^2(\lambda_x^2 x^2 + \lambda_y^2 y^2 + \lambda_z^2 z^2) \quad (4.13)$$

The change in entropy for the deformed random coil becomes

$$\Delta S_i = -k\beta^2 \left[ (\lambda_x^2 - 1)x^2 + (\lambda_y^2 - 1)y^2 + (\lambda_z^2 - 1)z^2 \right] \quad (4.14)$$

The total entropy change per unit volume is found by integrating the single-chain result over all space using the random coil distribution function

$$\Delta S = N \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Delta S_i W(x, y, z) dx dy dz \quad (4.15)$$

where  $N$  is the number of random coils per unit volume. Using the integration result that

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \beta^2 x^2 W(x, y, z) dx dy dz = \frac{1}{2} \quad (4.16)$$

the entropy change per unit volume simplifies to

$$\Delta S = -\frac{1}{2}Nk(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3) \quad (4.17)$$

But, what is the meaning of  $N$  in an elastomer which is a cross-linked, network polymer? It is the number of random coils between the cross links per unit volume, rather than the number of molecules. It is also known as the *cross link density*. A more physical number for characterization of elastomers is the *molecular weight between cross links* or  $M_c$ .  $N$  and  $M_c$  are related by

$$N = \frac{\rho L}{M_c} \quad (4.18)$$

where  $\rho$  is density and  $L$  is Avagadro's number. We can thus write

$$\frac{1}{2}Nk = \frac{\rho Lk}{2M_c} = \frac{\rho R}{2M_c} = \frac{G_0}{2T} \quad (4.19)$$

where  $R = Lk$  is the gas constant and  $G_0$  is defined by

$$G_0 = \frac{\rho RT}{M_c} \quad (4.20)$$

Here  $G_0$  is just a defined constant, but as discussed below it is equal to the shear modulus of the elastomer. The key molecular property that affects  $G_0$  is  $M_c$  and that property is a function of the amount of cross-linking. As the amount of cross linking increases, the distance between cross links, and therefore also  $M_c$ , decreases. The shear modulus therefore increases. Thus, a lightly cross-linked elastomer will have a low shear modulus (or stiffness). As the amount of cross linking increases, it will get stiffer. If the amount gets too high, it will eventually become a non-elastomeric, rigid polymer. A key requirement when making elastomers is to get the ideal amount of cross linking.

We can apply the above entropy change result to analysis of deformation experiments on elastomers. First consider uniaxial loading of extension  $\lambda = \lambda_x$ . Under such loading the specimen will contract in the  $y$  and  $z$  directions. For an isotropic material, the contractions will be the same or  $\lambda_y = \lambda_z = \lambda_T$ . After elongation, the new volume will be  $V = \lambda\lambda_T^2 V_0$  where  $V_0 = L_{x0}L_{y0}L_{z0}$  is the initial volume. All experiments with elastomers shows that the volume change is always very small. In other words  $V = V_0$ , which for uniaxial loading implies  $\lambda\lambda_T^2 = 1$ . Uniaxial loading in the  $x$  direction is thus represented by one variable,  $\lambda$  using:

$$\lambda_x = \lambda, \quad \lambda_y = \frac{1}{\sqrt{\lambda}}, \quad \text{and} \quad \lambda_z = \frac{1}{\sqrt{\lambda}} \quad (4.21)$$

From Eq. (4.5), the force for uniaxial loading of a collection of networked random coils is

$$F = -TV \left( \frac{d\Delta S}{dL_x} \right) \quad (4.22)$$

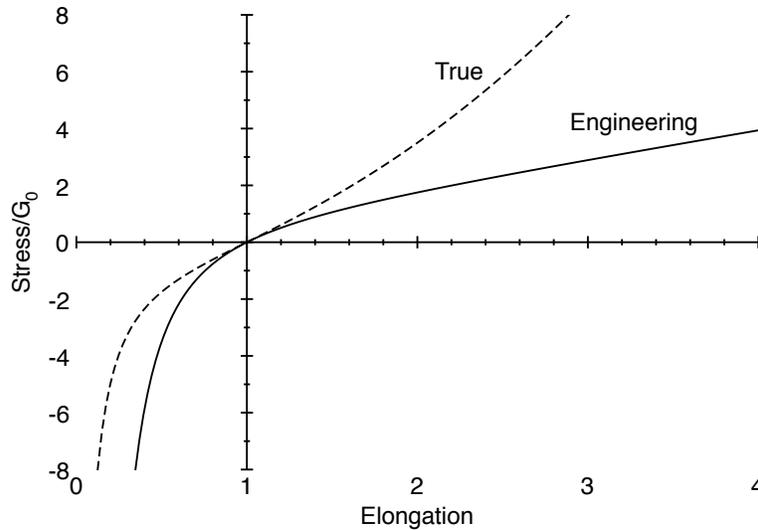


Figure 4.5: Theoretical predictions for engineering and true stress as a function of elongation for a networked polymer of random coils. The force is assumed to be due solely to entropy change on elongation.

The  $V$  is needed because  $\Delta S$  was derived per unit volume. Substituting  $L_x = \lambda L_{x0}$ ,  $V = L_{x0}L_{y0}L_{z0}$  (and constant), and  $\Delta S$  gives

$$F = L_{y0}L_{z0} \frac{G_0}{2} \frac{d}{d\lambda} \left( \lambda^2 + \frac{2}{\lambda} - 3 \right) = L_{y0}L_{z0}G_0 \left( \lambda - \frac{1}{\lambda^2} \right) \quad (4.23)$$

Now  $L_{y0}L_{z0} = A_0$  or the initial cross-sectional area normal to the loading direction. The definition of engineering stress,  $\sigma$ , is the force divided by the initial area or

$$\sigma = \frac{F}{A_0} = G_0 \left( \lambda - \frac{1}{\lambda^2} \right) \quad (4.24)$$

The definition of true stress is the force divided by the current area  $A = L_yL_z = \lambda_y\lambda_zL_{y0}L_{z0} = A_0/\lambda$ . Thus true stress is

$$\sigma^{true} = \frac{\lambda F}{A_0} = G_0 \left( \lambda^2 - \frac{1}{\lambda} \right) \quad (4.25)$$

Plots of engineering and true stress predicted for an elastomer are in Fig. 4.5. The curves are nonlinear. The engineering stress has decreasing slope as the elongation increases. The true stress increases more rapidly due the decreasing cross sectional area. Both curves get stiff in compression because compression elongation can never reach zero. Real elastomers have similar curves at modest elongation but differ at very high elongations. At very high elongations, the molecular chains can become sufficiently aligned that the sample gets much stiffer. The curves thus turn up to very high stress just prior to failure. This transition is due to molecular alignment rather than entropy effects and thus is not reproduced in entropy elasticity theories.

Shear Loading can be pictured as pulling in one direction (say the  $x$  direction) while pushing in a perpendicular direction (say the  $y$  direction) by the same amount. If the equal stresses are

equal to  $\sigma$ , it produces a pure shear stress state with  $\tau = \sigma/2$ . This pure shear deformation state is represented by elongation ratios

$$\lambda_x = \lambda, \quad \lambda_y = \frac{1}{\lambda}, \quad \text{and} \quad \lambda_z = 1 \quad (4.26)$$

The  $\lambda_x$  and  $\lambda_y$  values are for equal, but opposite forces. The  $\lambda_z$  value is required by the criterion for zero volume change. The equal and opposite stresses are

$$\sigma = \frac{F}{A_0} = \frac{G_0}{2} \frac{d}{d\lambda} \left( \lambda^2 - 2 + \frac{1}{\lambda^2} \right) = \frac{G_0}{2} \frac{d}{d\lambda} \left( \lambda - \frac{1}{\lambda} \right)^2 = G_0 \left( \lambda - \frac{1}{\lambda} \right) \left( 1 + \frac{1}{\lambda^2} \right) \quad (4.27)$$

The shear stress is

$$\tau = \frac{\sigma}{2} = \frac{G_0}{2} \left( \lambda - \frac{1}{\lambda} \right) \left( 1 + \frac{1}{\lambda^2} \right) \quad (4.28)$$

It is interesting to consider experiments at small strain or for  $\lambda$  close to 1. Under these conditions, the tensile strain is  $\varepsilon = \lambda - 1$  and the shear strain can be shown to be

$$\gamma = \lambda - \frac{1}{\lambda} \quad (4.29)$$

Expressing the tensile test in terms of  $\varepsilon$  and the shear test in terms of  $\gamma$ , taking the limits as  $\lambda \rightarrow 1$  (*i.e.*, as  $\varepsilon \rightarrow 0$  and  $\gamma \rightarrow 0$ ), and keeping only the linear terms results in

$$\sigma = 3G_0\varepsilon \quad \text{and} \quad \tau = G_0\gamma \quad (4.30)$$

In other words,  $G_0$  is the shear modulus of an elastomer or the slope of the shear stress-strain curve around  $\lambda = 1$ . Similarly, the tensile modulus, or the slope of the tensile stress-strain curve around  $\lambda = 1$ , is  $E = 3G_0$ . For an isotropic, linear elastic material,  $E$  and  $G_0$  are related by

$$\frac{E}{G_0} = 2(1 + \nu) \quad (4.31)$$

where  $\nu$  is the low-strain Poisson's ratio of the material. Using the ratio of 3 implies  $\nu = 1/2$ . A Poisson ratio of  $1/2$  is characteristic for a material with no volume change upon deformation as was assumed above for elastomers.

The section concludes with some example calculations. Consider an elastomer with density  $\rho = 900 \text{ kg/m}^3$  and molecular weight between cross links of  $M_c = 20,000 \text{ g/mol}$ . What is the shear modulus at  $0^\circ\text{C}$ ? The shear modulus is equal to  $G_0$ , which is defined by

$$G_0 = \frac{\rho RT}{M_c} = \frac{900 \text{ kg/m}^3 \cdot 8.31 \text{ J/(K} \cdot \text{mol)} \cdot 273 \text{ K}}{20 \text{ kg/mol}} = 1.02 \times 10^5 \text{ Pa} = 0.1 \text{ MPa} \quad (4.32)$$

A typical engineering polymer with  $T < T_g$  will have  $G_0 \approx 1000 \text{ MPa}$ . Thus, this elastomer with  $T > T_g$  is 10,000 times less stiff than a typical engineering plastic. This problem solved for modulus as a function of  $M_c$ .

The previous example can be inverted. In other words, a good way to determine the molecular weight between cross links is to measure the shear modulus and then use

$$M_c = \frac{\rho RT}{G_0} \quad (4.33)$$

For example, consider a piece of rubber that is 12.7 mm × 1 mm × 40 mm with a shear modulus of  $G_0 = 2$  MPa at 25° C and  $\rho = 900$  kg/m<sup>3</sup>. What is the molecular weight between cross links? Substitution gives

$$M_c = \frac{\rho RT}{G_0} = \frac{900 \text{ kg/m}^3 \cdot 8.31 \text{ J/(K} \cdot \text{mol)} \cdot 298 \text{ K}}{2 \times 10^6 \text{ Pa}} = 1.114 \text{ kg/mol} = 1114 \text{ g/mol} \quad (4.34)$$

How much work would it take to extend this specimen to  $\lambda = 3$ ? By the first law of thermodynamics, and because internal energy change for an elastomer is zero

$$\Delta W = -\Delta Q = -TV\Delta S = \frac{VG_0}{2} \left( \lambda^2 + \frac{2}{\lambda} - 3 \right) = \frac{508 \text{ mm}^3 \cdot 2 \text{ N/mm}^2}{2} \left( \frac{20}{3} \right) \quad (4.35)$$

or

$$\Delta W = 3.387 \text{ J} \quad (4.36)$$

Finally, estimate the temperature rise of the specimen during this experiment (*i.e.*, Gough's first experiment). Assume the heat capacity of the elastomer is typical for a polymer or  $C_p = 1.5$  J/(g · K). The total heat is

$$\Delta Q = -\Delta W = -3.382 \text{ J} \quad (4.37)$$

The heat is less than zero since  $\Delta Q$  is defined as heated *added* to the sample. For an elastomer during elongation, the sample heats up and thus the specimen *releases* heat. This heat will raise the sample temperature by

$$\Delta T = -\frac{\Delta Q}{mC_p} \quad (4.38)$$

where  $m$  is the mass of the specimen:

$$m = \rho V = 0.9 \text{ g/cm}^3 \cdot 508 \times 10^{-3} \text{ cm}^3 = 0.4572 \text{ g} \quad (4.39)$$

The temperature rise is then

$$\Delta T = \frac{3.382 \text{ J}}{0.4572 \text{ g} \cdot 1.5 \text{ J/(g} \cdot \text{K)}} = 4.93^\circ\text{C} = 8.88^\circ\text{F} \quad (4.40)$$

This temperature rise is easily detectable (such as by touching the sample with your lips). In non-elastomeric materials, the internal energy change is nearly equal to the work and thus heat during deformation, from the first law of thermodynamics, is

$$\Delta Q = \Delta U - \Delta W \approx 0 \quad (4.41)$$

In other words, there is no noticeable temperature rise for most materials during elongation.

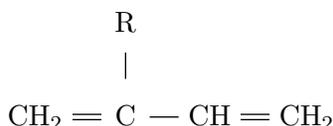
## 4.5 Making Elastomers

Many polymers can be made into elastomers. The first step is to find a polymer with  $T < T_g$ . If the selected polymer is not amorphous, the next step is to make it amorphous. The most common approach to breaking up crystallinity is to copolymerize with a second monomer. If these first two steps are achieved, the final step is to cross link. The three common strategies to cross linking are:

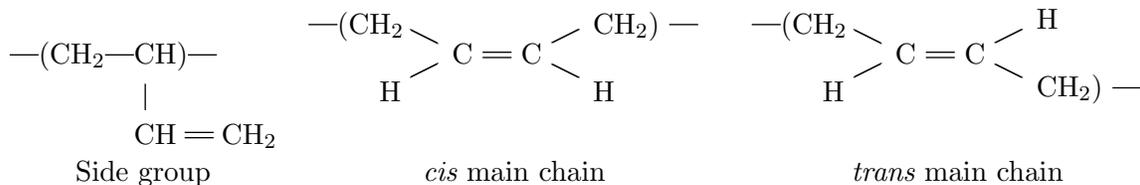
1. Diene elastomers - if the main polymer chain has double bonds, they can act as reaction sites to add cross links between chains.
2. Nondiene elastomers - if the main chain does not have any double bonds, cross linking has to be done by other methods. One common approach is to copolymerize with a small amount of a monomer having main-chain dienes and cross linking at those diene sites. This approach might be considered a diene elastomer, but since most of the network is mostly a nondiene monomer, they are still called nondiene elastomers.
3. Thermoplastic elastomers - these elastomers do not have chemical cross links. They rely on physical entanglements to act like cross links. As long as the cross links maintain connection on the time scale of deformation, they are just as effective as chemical cross links. An advantage of physical cross links is that the material can be melted and processed by typical thermoplastic means such as injection molding or extrusion.

### 4.5.1 Diene Elastomers

A common building block for many commercial diene elastomers is the diene monomer



When  $\text{R} = \text{H}$ , the monomer is butadiene; when  $\text{R} = \text{CH}_2$ , the monomer is isoprene; when  $\text{R} = \text{Cl}$ , the monomer is chloroprene. When butadiene is polymerized by non-specific methods, it generates a mixture of three different polymers depending on how the double bond reacts and the location of the double bond that remains in the polymer:



Each polymer in the mixture has one remaining double bond per repeat unit. The second step in making butadiene rubber is to use those double bonds to cross link the chains. Although it can

be done with a mixture of stereochemistries, it is usually preferable to start with a pure polymer (e.g., all *cis* or all *trans*) by using a stereo-specific polymerization process. A common cross linking process is sulfur vulcanization invented by Goodyear.<sup>2</sup> The process is to heat in the presence of sulfur and various additives (fatty acids, ZnO<sub>2</sub>, and accelerators). This step creates S<sub>x</sub> linkages between polymer chains. The process is run until light cross linking is achieved. Too little cross linking and the product will be too soft. Too much cross linking and it will lose rubber elasticity. Besides sulfur vulcanization, other methods of cross linking include using peroxides or ionizing radiation.

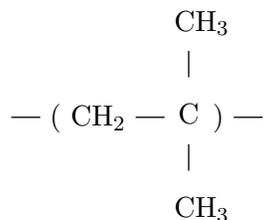
Elastomers made with butadiene include butadiene rubber (BR), styrene-butadiene rubber (SBR), and nitrile rubber (NBR). SBR starts with a copolymer of styrene (10-25%) and butadiene. The addition of styrene makes the rubber cheaper and improves wear resistance. One application is for tires. NBR starts with a copolymer of acrylonitrile (15-40%) and butadiene. The addition of acrylonitrile improves the solvent resistance. One application is for gaskets.

The monomer for natural rubber (NR) is isoprene. Like butadiene, non-specific polymerization of isoprene results in a mixture of polymers. In contrast, natural rubber from plants is stereospecific. The all *trans* version of polyisoprene is known as *Hevea* rubber. When vulcanized, it is used in tires. The all *cis* version is known as *Gutta Percha* rubber. When vulcanized, it is harder than *Hevea* rubber. One application is in covers for golf balls. Unvulcanized natural rubber is crystalline due to the stereoregular nature of the polymers. The vulcanization breaks up the crystallization as well as creating the cross links - the two things need to create the low-*T<sub>g</sub>* polyisoprene into an elastomer. Synthetic versions of natural rubber are possible, but they require use of stereospecific polymerization methods to start with all *trans* or all *cis* polyisoprene polymers.

Rubbers starting with polychloroprene are called Neoprene rubber (CR). These rubbers have improved solvent resistance. Common applications are for gaskets and O-rings.

#### 4.5.2 Nondiene Elastomers

Numerous polymers based on aliphatic hydrocarbon chains (e.g., polyethylene, polypropylene, etc.) are inexpensive and have low *T<sub>g</sub>*, but are not elastomeric unless further processed. For example, polyisobutylene has the repeat unit



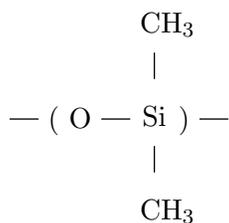
The main chain has no double bonds and therefore this polymer can not be cross linked by standard double bond methods. The solution is to copolymerize with a small amount of isoprene. This comonomer adds double bonds to the main chain which can be reactive sites for cross linking.

Even though cross linking is done with dienes, this rubber is called a non-diene rubber because most of the main chain lacks double bonds. The resulting elastomer is called Butyl Rubber. It has lower permeability to oxygen than other elastomers and therefore has application in inner tubes (*e.g.*, bicycle tires) and weather stripping.

Polyethylene and polypropylene are two of the most widely-produced synthetic polymers. They are both inexpensive and have  $T_g$ 's well below room temperature. Both, however, are highly crystalline (otherwise they would not be commercially significant polymers due to their low  $T_g$ 's). The first step to using them for elastomers, is to eliminate the crystallinity. This step can be achieved by an ethylene-polypropylene random copolymer. The random arrangement of monomers breaks up the regularity needed for crystallization. The next step is to cross link. The copolymer can be cross linked using peroxides. The resulting elastomer is ethylene-propylene rubber (EPR or EPM). An alternative is the approach taken with butyl rubber to copolymerize with a third diene monomer, such as isoprene, and cross link at the added double bond sites. The resulting elastomer is called ethylene-propylene-diene rubber (EPDM).

If all, or most, of the hydrogens in the above olefinic elastomers are replaced by fluorine (*e.g.*, replace ethylene and propylene monomers with tetrafluoroethylene and hexafluoropropylene), the polymers still have low  $T_g$ 's, but have much higher temperature resistance and improved solvent resistance. When these polymers are lightly cross linked they produce fluoroelastomers. Common applications are hoses, O-rings, gaskets, tubing, and hydraulics.

Silicone elastomers are made from polymers derived from polysiloxanes with repeat unit



They have good low-temperature properties, good electrical properties, good resistance to solvents (*e.g.*, oil), and weather well. Cross linking is done by copolymerizing with silanes that have functional groups or with peroxides.

### 4.5.3 Thermoplastic Elastomers

An alternative to chemical cross linking is to prevent flow by physical cross links. Two types of physical cross links are shown in Fig. 4.6. The top of the figure shows two entangled polymers being pulled apart. As long as the chains do not break, this arrangement is an *effective* cross link that will prevent flow. In real polymers, one does not pull individual molecules, but the result is similar if the molecular weight is sufficiently high. Given enough time, such entanglements will unravel allowing flow. On time scales much shorter than this time, the polymer will act like an elastomer. In fact all amorphous polymers have a region above  $T_g$  up to some higher temperature

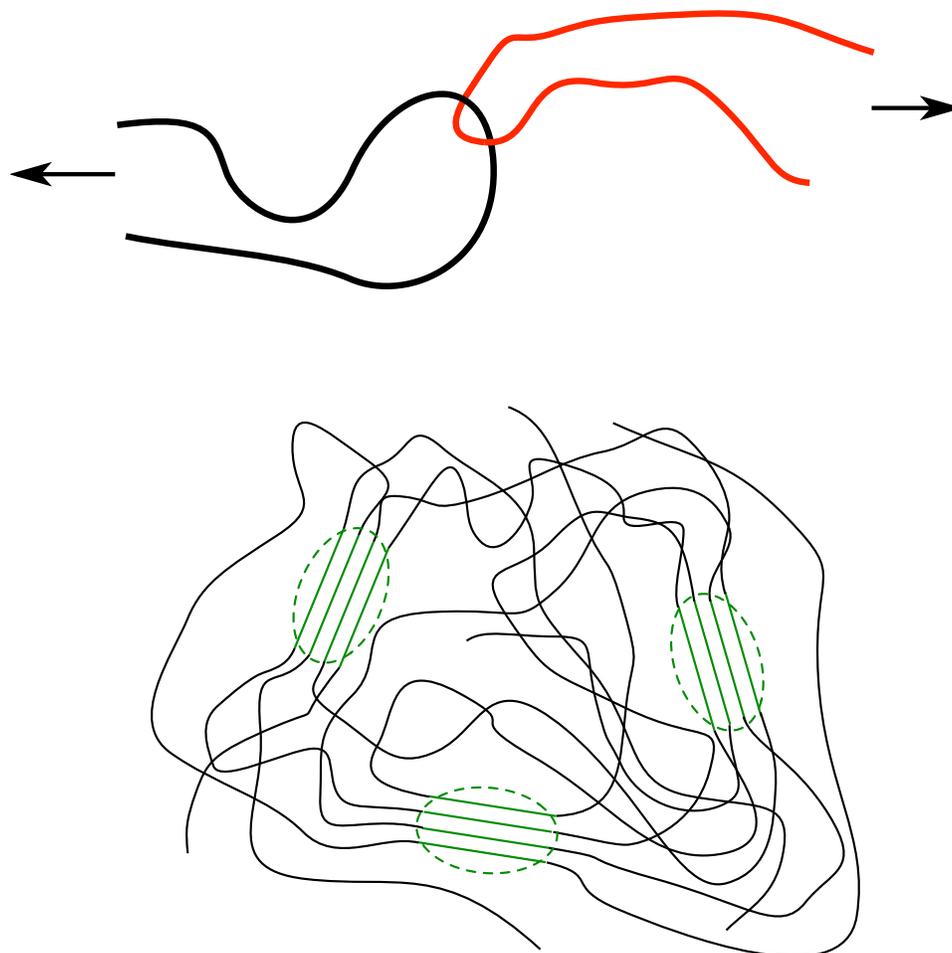


Figure 4.6: The top shows two polymer molecules entangles. A short time scales this molecules will not pull apart and the entanglement will act like a cross link. The bottom shows a block copolymer with flexible blocks and semicrystalline blocks. The semicrystalline blocks can organize to create regions that act like cross links.

with elastomeric properties known at the “rubbery plateau.” The rubbery plateau gets longer as the molecular weight gets higher. Thus any high molecular weight, amorphous polymer with  $T_g$  below room temperature, will have some elastomeric properties or some temperature and time range without adding chemical cross links.

The bottom half of Fig. 4.6 shows a different type of physical cross linking and an important type in the polymer industry. This schematic diagram is for a block copolymer having soft segments (low  $T_g$  amorphous polymer) and hard segments (a semicrystalline polymer). When copolymerized into a block copolymer, the hard segments can segregate in to crystalline regions that act as cross links for the remaining soft material. It is crucial that the two blocks are from incompatible polymers such that they segregate into separate regions when solidified. If this polymer is heated above the melting point of the crystalline region, the cross links will melt and the polymer will flow. Thus, there elastomers are known as *thermoplastic elastomers*. When heated then can be molded

or melt spun into fibers. When they cool down, the cross links form again to make an elastomer. One example is Lycra<sup>®</sup> spandex fibers.

## Problems

- 4-1. a. Give three characteristics that a polymer must have for it to have elastomeric properties at room temperature
- b. For each of the characteristics listed in part a, give a physical explanation of why it is needed for elastomeric properties.
- 4-2. A rubber consists of a cross-linked network of chains with the molecular weight between cross links equal to  $M_c = 15,000$  g/mol. The density of the specimen is  $0.92$  g/cm<sup>3</sup>.
- a. Calculate the shear modulus at 25°C.
- b. If a cube of this rubber of initial length 10 cm was loaded in uniaxial tension, calculate the load required to double its length.
- c. Give a processing method you could use to increase the shear-modulus of this rubbery material.
- 4-3. Polyethylene (PE) is highly crystalline and not elastomeric at room temperature. By copolymerizing with two other monomers and further processing it can be converted into an elastomeric product (olefinic rubbers).
- a. Describe two co-monomers and the further processing that can be used to convert PE into olefinic rubber. Explain the reasons for each co-monomer and for the extra processing.
- a. If the resulting elastomer is found to have a shear modulus of 100 kPa at 25°C and a density of  $0.95$  g/cm<sup>3</sup>, find the molecular weight between cross links and the cross link density of the polymer.
- 4-4. Imagine an elastomer subjected to biaxial loading in the  $x$  and  $y$  directions such that  $\lambda_x = \lambda_y = \lambda$ . Find the stress-elongation curve and compare to the result for uniaxial loading.

## Chapter 5

# AMORPHOUS POLYMERS

### 5.1 Introduction

Polymer solids

### 5.2 The Glass Transition

Thermo and kinetics of T<sub>g</sub>

### 5.3 Free Volume Theory

Apply to T<sub>g</sub>

### 5.4 Physical Aging

Analysis with free volume theory



## Chapter 6

# SEMICRYSTALLINE POLYMERS

### 6.1 Introduction

Polymer solids

### 6.2 Degree of Crystallization

Measure and why

### 6.3 Structures

Unit cell, lamallae, spherulites, etc.



# Bibliography

1. P. J. Flory. *Principles of Polymer Chemistry*. Cornell University Press, 1953.
2. C. Goodyear. Vulcanized rubber: Improvements in India-rubber fabrics. US Patent No. 3633, 1844.
3. J. Gough. A description of a property of caoutchouc or Indian rubber. *Memoirs of the Literary and Philosophical Society of Manchester*, I:288–295, 1805.