

Chapter 1

Introduction

1.1 Overview

A polymer is a large molecule made up of many small chemical units, joined together by chemical bond. The most famous polymer in living cell is DNA. Which is an extremely long molecule made up of up to 10^7 nucleotides. This giant molecule occurs naturally in living organisms. Polymers are also synthetically produced and used all around us, for example plastics, rubber, etc. These polymers are a repetitive sequence of a particular atomic group, called monomers, or repeating units. The number of units in the sequence is called degree of polymerization. It is possible to have polymers containing over 10^5 units. There are even naturally occurring polymers with the degree of polymerization exceeding 10^9 .

Polymeric materials display properties different from other materials, especially, in mechanical properties. As we have known polymeric liquids (chewing gum, egg white for example) show quite distinct flow behaviours from the usual liquids like water. A polymeric liquid is usually quite viscous and has visible elasticity. This property is called the viscoelasticity. This is just one of many distinctive properties of polymeric liquids. In order to understand the properties of polymeric materials we must consider a large assembly of molecules. However, in the case of polymers, the molecules themselves are very large, and we need to use statistical mechanics to calculate the characteristics of even an isolated polymer. One way to investigate the properties of a single polymer is to place it

in a very dilute solution, thus interactions between polymers can be neglected. Experimentally, such dilute polymer solutions are used to determine the size and molecular weight of the molecule.

As mentioned above, to understand the properties of polymeric materials, we need to reduce the problem to an isolated polymer problem. However, this problem is still very complicated. It is of the same form and difficulty as the general many body problem, first discussed by Kuhn (1934). The modern development was initiated by Flory (1949). A great deal of work has been done on this problem (Doi and Edwards, 1986). The main problem is to find the size of a single polymer chain in the dilute solution. This problem has become a well-developed subject since 1965 (Edwards, 1965), when Edwards had proposed a model for self-avoiding polymer chain that bears his name "Edwards Hamiltonian". This new formulation was very successful and it suddenly enabled many theoretical approaches, which had been previously very difficult. Edwards' model is a continuous model composing of two terms. The first term describes the connectivity which he took as a Wiener process. The second term is a non-local pseudo-potential that describes the interaction between the monomers. Edwards formally showed that polymer statistics boils down to summing over all possible paths weighted by the Hamiltonian given by the sum of the "kinetic energy" (representing chain connectivity) and the pseudo-potential. The resulting path-integral is non-Markovian which is a reflection of the nature of the excluded volume interactions (self-avoiding walk). The formal analogy to path-integral allowed the use of many systematic approximations devised in the context of quantum mechanics to problems in polymers.

The problem of a polymer chain was developed by Flory (1949) and con-

tinuously used up to now. Flory used a simple theory to calculate the size of polymer chain. The results obtained by Flory were also identical with those from experiment. However, some errors were found with the application of that theory due to simple estimation used. Nevertheless, this theory developed by Flory can be considered as the original theory of the mean field theory further developed by Edwards (1965). The mean field theory can be used to predict many interesting features of the excluded volume chain, effectively. In 1972 de Gennes further developed a correlation to predict the size of polymer by renormalization group theory. Later on in 1979, Edwards and Singh used the method called "Effective step length technique" to predict the size of polymer. It should be noted that among those theories, the most famous theory was perturbation theory used by Fixman (1955), Yamakawa and Tanaka (1967), etc. It has been known that, the most acceptable theory was further developed by Muthukumar and Nickel (1984).

As mentioned earlier, a polymer chain problem can be written in path-integral. This approach can be extended to the problem of polymer melts or correspondingly concentrated polymer solutions. In this problem, excluded volume correlations are now not only taking place within one single chain, but an increasing number of contact points from other chains. Increasing polymer concentration yields additional excluded volume effect.

Besides a single polymer chain in dilute solution and polymer melts or concentrated polymer solutions, Edwards' Hamiltonian has been developed to the problem of a polymer chain in random potential. Edwards and Muthukumar (1988) used replica method to predict the size of a polymer chain in random media. For very short-range correlation, at small chain lengths, the polymer chain behaves like a free chain. However, at large chain lengths, the polymer size

is independent of its length. It is localized to a certain size. For the long-range correlation Shiferaw and Goldschmidt (2000) had shown that the polymer chain behaves like a free chain for all value of chain length.

1.2 Our Work

The aim of our work is to consider the problem of a single polymer chain in random media with long range interactions. We shall generalize the model proposed by Edwards and Muthukumar (1988) for short-range correlation to finite correlation. Instead of using the idea of a replica method, we employ the Feynman path-integral method by modeling the polymer Hamiltonian as a model of non-local quadratic trial Hamiltonian. This non-local trial Hamiltonian is essential as it will reflect the translation invariant of the origin Hamiltonian. The calculation is proceeded by considering the difference between the polymer Hamiltonian and the trial Hamiltonian as the first cumulant approximation. The variational principle is used to find the optimal values of the variational parameters and the mean square end-to-end distance is obtained.

1.3 Outline of the Thesis

This thesis is organized as follows. In the next chapter (Chapter 2), the basic notation is introduced. Therefore, we introduce the random walk model for a polymer chain, the Wiener-Edwards integral, a polymer chain under an external field, the self-avoiding polymer chain or excluded volume effect and some theoretical approaches to the self-avoiding polymer chain. In Chapter 3, some theoretical approaches to a polymer chain in random media are presented. We review Edwards and Muthukumar (1988) approach for very short-range correlation

and Shiferaw and Goldschmidt (2000) approach for long-range correlation. In Chapter 4, we generalize Edwards' model to finite correlation. The path-integral with one parameter model is calculated to find the size of the polymer chain in random media. The results are discussed and concluded in Chapter 5. Finally, in order to be able to carry out the calculation arising in Chapter 5, an appendix gives a detailed derivation of a characteristic functional corresponding to the trial Hamiltonian.