CHAPTER 5

Theoretical Models and Simulations of Polymer Chains

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5.1 INTRODUCTION

In the first part of this article the review of various theoretical models for polymer chains is given. The models of freely jointed chains, freely rotating chains (including wormlike chains), and chains with fixed bond angles and independent rotational potentials and with interdependent potentials, including rotational isomeric state approximation, are presented.

In the second part various theories of polymer networks are presented. The affine network model, phantom network, and theories of real networks are discussed. Scattering from polymer chains is also briefly presented.

The third part of this article covers computer simulations of polymer chains. Methods of simulation of chains on lattices are presented and the equivalence between lattice chains and off-lattice chain models is discussed. The simulation of excluded volume effect is examined. The polymer chain collapse from random coil to dense globular state, and simulations of dense polymer systems are discussed.

This article describes models for linear chains of homopolymers and for unimodal, unfilled polymer networks.

Theoretical models for other systems, such as star, branched, and ring polymers, random and alternating copolymers, graft and block copolymers are discussed in the book by Mattice and Suter [1]. Block copolymers are discussed in Chap. 32 of this Handbook [2]. Theories of branched and ring polymers are presented in the book by Yamakawa [3]. Liquid–crystalline polymers are discussed in the book by Grosberg and Khokhlov [4], and liquid crystalline elastomers in the recent book of Warner and Terentjev [5]. Bimodal networks are discussed by Mark and Erman [6,7]. Molecular theories of filled polymer networks are presented by Kloczkowski, Sharaf and Mark [8] and recently by Sharaf and Mark [9].

This first part of this article deals only with treatment of "bonded" interactions of polymer chains, appropriate only for modeling chains under Θ-point conditions. Problems connected with effects of excluded volume are presented at the end of this chapter. The excluded volume effect for chains in good solvents are also presented in Chaps. IIB [10] and IIID [11] of this handbook and in books by Freed [12], de Gennes [13], des Cloizeaux and Jannink [14], and

Forsman [15]. More information about computer modeling of polymers is provided by Binder [16,17], Baumgartner [18], Kolinski and Skolnick [19], and most recently by Kotelyanskii and Therodorou [20].

5.2 THE FREELY JOINTED CHAIN

The freely jointed chain model (known also as random flight model) was proposed for polymers by Kuhn in 1936. The chain is assumed to consist of n bonds of equal length l, jointed in linear succession, where the directions (θ, ϕ) of bond vectors may assume all values $(0 \le \theta \le \pi; 0 \le \phi \le 2\pi)$ with equal probability (see Fig. 5.1).

This means that directions of neighboring bonds are completely uncorrelated. The freely jointed chain model corresponds to a chain with fixed bond lengths and with unconstrained, free to adjust valence angles and with free torsional rotations. The mean square end-to-end vector $\langle r^2 \rangle_0$ in the unperturbed state (denoted by subscript 0) for the freely jointed chain is

$$\langle r^2 \rangle_0 = \langle (\sum_{i=1}^{n} \mathbf{l}_j) \cdot (\sum_{j=1}^{n} \mathbf{l}_j) \rangle_0 = nl^2 \tag{5.1}$$

because

$$\langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle_0 = 0 \quad \text{for } i \ne j. \tag{5.2}$$

It is convenient to compare real polymer chains with freely jointed chain by using the concept of the characteristic ratio defined as the ratio of the mean-square end-to-end vectors of a real chain and freely jointed chain with the same number of bonds

$$C_n = \frac{\langle r^2 \rangle_0}{nl^2}. \tag{5.3}$$

The characteristic ratio is a measure of chain flexibility. Flexible chains have C_n close to unity, while semiflexible and rigid polymers have usually much larger values of C_n. The mean-square radius of gyration for freely jointed chain is:

$$\langle s^2 \rangle_0 \equiv \frac{\sum_{0 \le I < j \le n} \langle r_{ij}^2 \rangle_0}{(n+1)^2} = \frac{(n+2)nl^2}{6(n+1)}. \tag{5.4}$$

For longer chains (in the limit $n \to \infty$) we have

$$\frac{\langle s^2 \rangle_0}{\langle r^2 \rangle_0} = \frac{1}{6}. \tag{5.5}$$

The freely jointed chain model has an exact analytical solution for the distribution function of the end-to-end vector. The probability that the chain of n bonds has the end-to-end vector $\mathbf{r}$ is

$$P(\mathbf{r}, n) = \int d\mathbf{l}_1 d\mathbf{l}_2 \ldots d\mathbf{l}_n \delta[(\sum_{i=1}^{n} \mathbf{l}_i) - \mathbf{r}] \prod_{j=1}^{n} \exp\left(\frac{-u(\mathbf{l}_j)}{kT}\right), \tag{5.6}$$

where T is the absolute temperature, k is the Boltzmann constant, $u(\mathbf{l}_j)$ is the potential energy of two segments connected by the j-th bond $\mathbf{l}_j$, and δ denotes Dirac delta function. For the freely jointed chain model we have

$$\exp\left(\frac{-u(\mathbf{l}_j)}{kT}\right) = \frac{1}{4\pi l^2} \delta(|\mathbf{l}_j| - \ell). \tag{5.7}$$

By using the Fourier representation of the δ function we obtain

$$P(\mathbf{r}, n) = \frac{1}{8\pi^3} \int d\mathbf{k} \, e^{-i\mathbf{k}\cdot\mathbf{r}} \left[\frac{\sin(kl)}{kl}\right]^n$$

$$= \frac{1}{2\pi^2 r} \int_0^\infty \sin(kr) \left[\frac{\sin(kl)}{kl}\right]^n k\, dk. \tag{5.8}$$

The solution of Eq. (5.8) is

$$P(\mathbf{r}, n) = \frac{1}{2^{n+1}\pi l^2 r(n-2)!} \sum_{i=0}^{i \le (n-r/l)/2} (-1)^i \frac{n!}{i!(n-i)!} (n - 2i - r/l)^{n-2}. \tag{5.9}$$
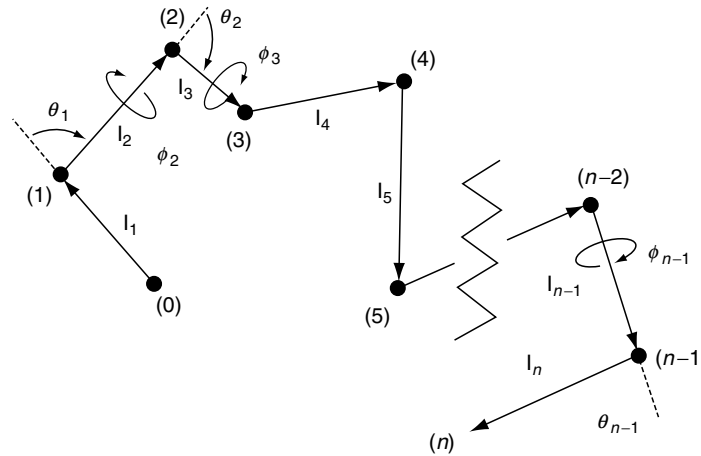

FIGURE 5.1. Polymer chain composed of n bonds. Angles θ are defined as complementary angles.