KUHN-GRÜN TYPE APPROXIMATIONS FOR POLYMER CHAIN DISTRIBUTIONS

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1. Introduction

Polymer physics offers many problems of interest to applied probabilists because of the essentially statistical basis of many of the characteristic phenomena associated with polymers. They arise from the fact that the polymer molecules are long, more or less flexible chains which can have many configurations. In the early development of the theory it was adequate to regard polymer chains as three dimensional random walks and to use a simple Gaussian approximation to the relevant distributions. As the theory became more refined, attention had to be paid to the effect of the actual structure of the polymer chains on the distribution. Excellent accounts of the recent state of the theory are given by Volkenstein [17], Birshtein and Ptitsyn [1], and Flory [7].

Many physical properties are explainable from a knowledge of the moments, usually the second moment, of the vector length of the chain molecules, and in such cases the Gaussian approximation or some Edgeworth type expansions based on it is a suitable description of the distribution. But there are other properties, such as the elastic behavior of rubber under large strains, which require the vector length distribution to be known with comparable relative accuracy over the whole of its range, a much stronger condition which is appropriate for "large deviations." It is the latter type of property which motivates the discussion given here. The first approximation of this kind was given in a famous paper by Kuhn and Grün [14]—hence, the title of the present paper.

Apart from "stiffness" caused by the interaction of neighboring elements of the chain, we shall ignore excluded volume effects arising from the space taken up by the chain. The effect of the selfavoiding nature of the chain on the distribution of vector length is a subject of much current discussion, but the mathematical difficulties are such that only the simplest chain models can be considered. In contrast, we are concerned with distributions associated with chain models approximating to real polymer molecules.

Much of the paper is an exposition of the history and background of the subject for the benefit of applied probabilists wishing to enter the field. However, the asymptotic result sketched in Section 7 for the behavior of the distribution in the extreme tail is new and by no means fully worked out. Also, the integral equation approach is offered as a practical way of validating and generalizing the method of calculation currently in favor, which is based on the so called rotational isomeric approximation.