INTRODUCTION

The conformational freedom of a polymer chain in an elastomeric network is severely restricted by the presence of neighboring chains. Two monomer units cannot occupy the same space, and two chains cannot pass through each other. These entanglement constraints are not easy to introduce into the theory of rubber elasticity though many attempts have been made.

In our opinion, a fruitful procedure can be found in modifications of the classical theory. The description of an elastomer as an assembly of polymer chains has reproduced qualitatively most of the physical properties normally associated with a rubbery material.

For example, the phantom network model of James and Guth (1,2) gave a recipe for predicting the deformation of a polymer network by an applied stress, and allowed predictions of the change in chain dimensions as a function of network expansion or distortion. In an effort to make the phantom model more realistic, and to fit the model to a variety of experimental results, P.J. Flory and collaborators (3,4,5) proposed that the fluctuation of crosslink junction points calculated by the James-Guth method should be very much restricted by chain entanglements. Ronca and Allegra (6), and Flory, and Flory and Erman (5) pointed out the probable anisotropy of these fluctuations in an oriented elastomer, and these considerations have been in good accord with a considerable number of experimental investigations (7).

Nevertheless, the Flory-Erman theory has left a number of questions unanswered, and it has become evident that it is not possible to take account of all the physical effects of chain entanglements by considering
fluctuations of crosslink junctions alone. We discuss some of the problems below.

EXPERIMENTAL ANOMALIES

High Moduli

The elastic modulus of a rubber according to the phantom network theory is much lower than the modulus of the same network with all junction fluctuations suppressed. If the fluctuations are partially suppressed, the calculated modulus lies between these limits. In fact, in many cases, the measured modulus is many times greater than predicted by fixed junction models (8,9).

Memory of the Crosslinking Condition

Alfrey and Lloyd (10,11) have studied the swelling of networks prepared in solution in a variety of solvents. The swelling of these networks prepared at several dilutions differed from each other as well as from networks prepared in bulk.

Kramer, Ferry and collaborators (12,13) prepared networks from linear polymers which had been stretched, frozen, crosslinked and reheated. The anisotropy of the network crosslinked in the stretched state remained in part in the crosslinked polymer, and the mechanical properties of the network depended to a considerable degree on the degree of orientation of the polymeric sample when the network was formed.

Both the experiments of Alfrey and Lloyd and the studies of Ferry and Kramer are inexplicable by a phantom network model. Incorporation of constraints on junction fluctuations cannot account for the memory of the conditions of crosslinking. Ferry and Kramer use a two network model proposed earlier by Flory (14) to explain their results.

Small Angle Neutron Scattering (SANS) of Polymer Networks

Direct measurements of chain deformation in rubbers or other polymer networks can be carried out in a SANS experiment on a material containing some labeled (by deuterium) chains. The radius of gyration of the chain is obtained, and if the chain is assumed to follow random flight Gaussian statistics, the change in radius of gyration with network deformation is easy to compute from the usual assumption that the vector connecting the chain ends is distorted in the same manner as the macroscopic distortion. The result depends on whether junction points fluctuate or not, but, given a prescription for the magnitude of the fluctuation, the calculation can be performed. There have been many experiments, not all of which are reliable, but it has become clear that no simple relation between network deformation and chain expansion can be found (15,16,17,18,19).