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## A Note on "Modified Chain Displacement Function of Gaussian Networks" by A. H. Crossland

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### ABSTRACT

Crossland claims that the development of the conventional Gaussian theory of rubber elasticity does not take into account the requirement that the polymer chain end-to-end vector must be equal in direction to the network junction-to-junction vector. Reintroducing the directional probability, he develops a novel Gaussian strain-energy function. If correct, Crossland's work is a significant contribution, resulting in notable improvements in important models in rubber elasticity and polymer rheology. Unfortunately, there is an error in Crossland's analysis. Correction of the error reduces Crossland's results to those of the conventional Gaussian theory and shows that the conventional theory does correctly account for the directional probability. The "improved" strain-energy function, therefore, has no theoretical basis and, at best, must be considered purely empirical.

A strain-energy function for the Gaussian theory of rubber elasticity can be derived if one can calculate a Gaussian chain displacement function. The chain displacement function can be calculated from knowledge of the probability that a polymeric chain reaches from one cross-link junction to a second where this probability is given by the probability that the chain's end-to-end vector is equal in magnitude and direction to the junction-to-junction vector.

In his paper, Crossland [ 1 ] argues that conventional Gaussian theories do not account for the equality in direction required, and he reintroduced the directional probability. His analysis led to a novel strain-energy function which he showed to be in qualitative and quantitative agreement with reversible deformation data in extension and pure shear. The strain-energy function of Crossland is significantly better in its ability to describe the qualitative features of experimental data than the strain-energy function resulting for the conventional Gaussian analysis.

In a landmark development in rheology, Lodge [ 2 ] idealized a concentrated polymer solution as a temporary Gaussian network, in which the junction points are formed by physical entanglements and local secondary forces between chain molecules, and the strain-energy function is of the form given by the conventional Gaussian theory of rubber elasticity. On this basis he developed the important "rubberlike liquid" constitutive equation which describes qualitatively many of the distinctive features of polymer liquid flows. Unfortunately, it also predicts qualitatively incorrect features, e.g., viscosity and other material functions independent of shear rate.

Paralleling Lodge's development and using Crossland's Gaussian strain-energy function, the authors [ 3 ] derived a "viscoelastic liquid" model which is a significant improvement on the "rubberlike liquid" model. In addition to correctly predicting the same features satisfactorily described by the "rubberlike liquid" model, the "viscoelastic liquid" model gave qualitatively correct and quantitatively reasonable predictions of the rate-dependence of the viscosity and several other material functions.

If correct, Crossland's analysis is an important contribution resulting in notable improvements in important models in the areas of rubber elasticity and polymer rheology. Unfortunately, there is an error in Crossland's analysis, and correction for the error reduces his results to those of the conventional Gaussian theory. Therefore, his novel strain-energy function has no theoretical basis and it appears to be purely fortuitous that it yields much better results than the correct Gaussian strain-energy function. The clearest way to show the error in Crossland's derivation is to present a standard development of the appropriate probability relations here and compare them with Crossland's results.

Consider a polymer molecule of  $n$  segments, each of length  $\ell$ . Fix one end at the origin of a hypothetical coordinate system. Find the probability that the other end is in a volume element  $dx dy dz$  at position  $x, y, z$ . The probability is calculated via random walk statistics and is generalized from the 1-dimensional random walk result to give

$$\begin{aligned} p(x, y, z)dx dy dz &= p(x)p(y)p(z) dx dy dz \\ &= \beta^3 \pi^{-3/2} \exp \{ - \beta^2 r^2 \} dx dy dz \end{aligned} \quad (1)$$

where the end-to-end distance  $r$  is given by

$$r^2 = x^2 + y^2 + z^2 \tag{2}$$

$$\beta^2 = \frac{3}{2n\ell^2} = \frac{3}{2r^2} \tag{3}$$

and  $p(x)$ ,  $p(y)$ ,  $p(z)$  are the probability densities in the three coordinate directions, and are independent of one another.

Equation (1) gives the probability that the other end of the molecule is in a volume element  $dV_1 = dx dy dz$  located at some particular values of  $x$ ,  $y$ ,  $z$ . In the sense that this locates the other end at a particular distance and orientation relative to the fixed end, this is a vector probability.

$p(x, y, z)$  is the probability density and is symmetric, i.e., a function of  $r$  only and not a function of  $x$ ,  $y$ ,  $z$  in any other way.

Now if we want the probability that the end-to-end length is  $r$ , then we want the sum of probabilities for all  $x$ ,  $y$ ,  $z$  combinations giving  $r$ . Heuristically, it is clear that this is simply the probability density in Eq. (1) (which is constant for a given  $r$ ) multiplied by the differential volume element of thickness  $dr$  at  $r$ , i.e.,  $dV_2 = 4\pi r^2 dr$ . This gives

$$p(r) dr = 4\beta^3 \pi^{-1/2} r^2 \exp \{-\beta^2 r^2\} dr \tag{4}$$

Equation (4) gives the probability that the second end of the molecule lies in the volume element  $dV_2$  located at some particular value of  $r$ . It is the scalar probability that the length of the end-to-end vector is  $r$ . Considering a collection of chains, an alternate interpretation of Eq. (4) is that it gives the fraction of chains having end-to-end length  $r$  in a collection of chains with average end-to-end length  $\bar{r}$ . Therefore, if we have  $\nu$  chains, then  $\nu p(r) dr = d\nu$  is the number of chains having end-to-end length  $r$ . Comparing Crossland's Eq. (5) with our Eq. (1), it is clear that his  $P(r = r_j)$  not only is not the probability that  $\underline{r}$  has length  $r_j$ , it is not even a probability; it is essentially the probability density  $p(x, y, z)$ . His  $P(x)$ ,  $P(y)$ ,  $P(z)$ , and  $P(\underline{r} = \underline{r}_j)$  are also probability densities, not probabilities.

The correct probability that the end-to-end vector has a particular length  $r$  and a particular orientation, i.e., such that one end is located at  $x$ ,  $y$ ,  $z$  relative to a coordinate system with origin at the other end, is given by Eq. (1). Using our Eq. (4), the correct probability that the end-to-end distance is  $r$ , and the directional probability given by Crossland, we have

$$\begin{aligned}
 \underline{P}(\underline{r}) &= \frac{\delta A}{4\pi r^2} 4\beta^3 \pi^{-1/2} r^2 \exp\{-\beta^2 r^2\} dr \\
 &= \beta^3 \pi^{-3/2} \exp\{-\beta^2 r^2\} \delta A dr = p(x, y, z) \delta A dr \quad (5)
 \end{aligned}$$

instead of his Eq. (9). To the extent that  $\delta A dr$  approximates  $dx dy dz$ , this merely brings us back to Eq. (1).

The remainder of Crossland's development, therefore, is invalid, being based on his Eq. (9) which is erroneous. Correctly using our Eq. (1) merely yields the conventional Gaussian theory of rubber elasticity and, therefore, also Lodge's "rubberlike liquid" rheological model. As the conventional Gaussian theory of rubber elasticity does account correctly for the directional probability, the "improved" models of Crossland and ourselves have no theoretical validity and, at best, must be regarded as arbitrary, empirical models.

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