

# On orientation functions in a network of short chains

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Recent investigations into the development of molecular orientation on straining in the glass transition range and above (e.g. refs. 1 and 2) have led to interpretation of results in terms of rubber elasticity theory, discrepancies being accounted for via a strain-dependent entanglement molecular weight. It has been shown recently that experimental orientation functions can also be adequately described by a model involving two components of strain (extensional and orientational)<sup>3</sup>; nevertheless, it might be wondered whether part of the above-mentioned discrepancy could stem from an inadequacy of the rubber-elasticity theory in the case of short-chain molecules, i.e. chains in which the number of statistical segments is too small for statistical methods to apply. This work was undertaken in order to compare orientation functions obtained using alternative models with those derived from classical theories.

(Keywords: molecular orientation; rubber elasticity; network; deformation)

## INTRODUCTION

The theory of orientation functions in rubbery networks of long chains is well established. In this theory, the orientation function  $\langle P_{2n} \rangle$  of the statistical segments with respect to the principal strain directions is obtained by convolution of the orientation function ( $C_{2n}$ ) of statistical segments with respect to end-to-end vectors of strands joining crosslinks with that ( $P_{2n}$ ) of end-to-end vectors with respect to the principal strain directions<sup>4</sup>.  $C_{2n}$  relates to the most probable orientation distribution, which was obtained by Kuhn and Gr $\ddot{u}$  n for long-chain molecules, in which the probability distribution of end-to-end lengths is given by the Langevin function<sup>6</sup>.

Experimental data on rubbers, and on thermoplastics in the rubbery state, can be fitted to the random-chain affine result only by allowing the number of statistical segments per chain to depend on strain and temperature<sup>1,2</sup>. Various two-parameter theories have been proposed (e.g. refs. 3 and 7), giving a more adequate description of experimental results. However, an alternative possibility exists that the source of the inadequacy of the classical theory lies in the fact that K $\ddot{u}$  hn and Gr $\ddot{u}$  n's approximation is valid only for long chains. Intuitively, one expects short chain behaviour to lie somewhere between the random-chain affine and pseudo-affine limits, which is precisely the situation for experimental data. (In the pseudo-affine model, the anisotropic unit rotates like a rigid rod in an affinely deforming isotropic matrix.) The purpose of this paper is to model short-chain behaviour using hopefully more appropriate models than the Langevin approximation.

First, as shown by Treloar<sup>8</sup>, the Langevin approximation does not give a correct description of the probability distribution of end-to-end distances in the case of short chains. The orientation distribution derived from Treloar's 'exact' distribution for short chains<sup>9</sup> will first be compared with the classical solution.

An alternative approach is to consider a real chain with fixed valence angles, and look for a relationship between the orientation distribution and the chain length in terms of the internal rotation angle. The resulting orientation function, obtained using an approximation to Volkenstein's relations for real chains<sup>10</sup>, will also be compared with classical theory.

Discussion will be restricted to the second moment of the orientation distribution, which is appropriate for birefringence.

## GENERAL THEORY

In this section, Roe and Krigbaum's theory of orientation functions will be outlined, and its limitations and possible extensions discussed.

Consider a structural unit, anisotropic in a material property,  $p$ . The orientation of the axis of the structural unit can be defined in a reference frame, fixed in the sample, by polar coordinates  $(\theta, \phi)$ . An additional coordinate  $\Psi$  defines the orientation of the structural unit about its axis. (Coordinates  $\theta$ ,  $\phi$  and  $\Psi$  are simply the Euler angles defining a reference frame fixed in the structural unit with respect to a reference frame fixed in the sample.) Sample anisotropy will depend on anisotropy of the structural unit and on the orientation distribution.

If the property  $p$  is a tensor (e.g. polarizability, sonic modulus, thermal expansivity), the contribution of each structural unit to the macroscopic anisotropy will depend on the products of the direction cosines defining the structural unit; in other terms, the macroscopic anisotropy is determined by an average of second-order spherical harmonics over the orientation distribution. For other properties, (n.m.r. second moment, polarized fluorescence, Raman spectroscopy) the contribution of each structural unit can be expressed in terms of squares of spherical harmonics, or of linear combinations of

spherical harmonics of order 0, 2 and 4. In general,

$$\langle P_l^m \rangle = \int_0^{2\pi} \int_{-1}^{+1} f(\cos\theta, \phi) P_l^m(\cos\theta) \exp(-im\phi) d\cos\theta d\phi \quad (1)$$

where  $f(\cos\theta, \phi)$  is the orientation distribution of the structural units.

The structural unit chosen by Roe and Krigbaum<sup>4</sup> is the average strand joining crosslinks in a rubbery network. In this case, the spherical harmonic  $P_l^m(\cos\theta)\exp(-im\phi)$  appearing in equation (1) is replaced by an expansion, in terms of spherical harmonics, of the distribution of orientations of segments with respect to the strand's end-to-end vector; the coefficients of the expansion are:

$$C_l^m = \int_0^{2\pi} \int_{-1}^{+1} g(\cos\theta, \phi, \cos\alpha, \psi) P_l^m(\cos\alpha) \exp(-im'\psi) d\cos\alpha d\psi \quad (2)$$

where  $g(\cos\theta, \phi, \cos\alpha, \psi)$  is the distribution function of orientations of segments (defined by  $\alpha, \psi$ ), about the end-to-end vector defined by  $\theta, \phi$ .

Roe and Krigbaum restrict their attention to the situation where both the sample and the strand exhibit transverse isotropy. In this case  $g$  becomes independent both of  $\phi$  and  $\psi$ , so that the integrals in equations (1) and (2) vanish except when  $m$  and  $m' = 0$ ; equivalently, the spherical harmonics reduce to Legendre polynomials of order  $l$ , and the distribution functions are independent of  $\phi$  and  $\psi$ . In this case equation (1), for the second moment, reduces to:

$$P_2 = \int_{-1}^{+1} C_2(\cos\theta) f(\cos\theta) \left( \frac{3\cos^2\theta - 1}{2} \right) d\cos\theta \quad (3)$$

where  $C_2(\cos\theta)$  is the coefficient of the second-order Legendre polynomial in the expansion of the distribution of segmental orientation. A solution is obtained when:

(a) the end-to-end vectors  $\vec{r}$  joining crosslinks undergo an affine transformation:

$$f(\cos\theta) = \frac{\lambda^3}{2(\lambda^3 - \cos^2\theta(\lambda^3 - 1))^{3/2}} \quad (4)$$

and

$$\delta = \frac{r}{r_0} = \frac{\lambda}{(\lambda^3 - \cos^2\theta(\lambda^3 - 1))^{1/2}} \quad (5)$$

(b) the end-to-end distance  $r_0$  in the unstrained state is equal to the root-mean-square length of the free chain:

$$r_0 = N^{1/2}l$$

where  $l$  is the length of a statistical segment and  $N$  the number of segments per strand;

(c) the segmental orientation distribution is given by Kuhn and Grün's equation<sup>5</sup>:

$$g(\cos\theta, \cos\alpha) = \frac{\beta}{2\sinh\beta} \exp(\beta\cos\alpha) \quad (6)$$

where

$$\coth\beta - \frac{1}{\beta} = \frac{r}{Nl} = \frac{\lambda}{(N(\lambda^3 - \cos^2\theta(\lambda^3 - 1)))^{1/2}} \quad (7)$$

On introducing equation (5) into equation (2), the following expression is obtained for the second-order orientation function, averaged over all segments in a strand:

$$C_2 = 1 - \frac{3t}{\beta} \quad (8)$$

$$= 0.6t + 0.2t^4 + 0.2t^6 \quad (9)$$

where Treloar's approximation (equation (9)) is accurate to within 1%<sup>11</sup>. On introducing this expression into equation (1):

$$\langle P_2 \rangle = \frac{0.6}{3N} \left( \lambda^2 - \frac{1}{\lambda} \right) + \frac{0.2}{5N^2} \left( \lambda^4 + \frac{\lambda}{3} - \frac{4}{3\lambda^2} \right) + \frac{0.2}{7N^3} \left( \lambda^6 + \frac{3\lambda^3}{5} - \frac{8}{5\lambda^3} \right) \quad (10)$$

The reader is referred to refs. 4 and 5 for expressions for higher-order orientation functions.

The major limitation of Roe and Krigbaum's treatment is that it is restricted to the case of transverse isotropy, both of the sample and of the structural unit. Since the purpose of the present work is to evaluate the validity of the Langevin approximation, this is not a serious restriction. Solutions have been obtained for a more general deformation, and applied to birefringence<sup>12</sup> and to broadline n.m.r.<sup>13</sup>.

Another restriction is that equation (10) would appear to apply only if the orientation of segments in a strand is given by the Kuhn and Grün equation. In fact, equation (9) is quite general, and its solution is of the form given by equation (10) whenever the orientation function can be expressed as

$$C_2 = at^2 + bt^4 + ct^6 \quad (11)$$

The coefficients in equation (10) are simply replaced by  $a/3\lambda_M^2$ ,  $b/5\lambda_M^4$  and  $c/7\lambda_M^6$  respectively, where  $\lambda_M$  is the maximum extension of the chain (i.e. the extension at which  $C_2 = 1$ ).

## ORIENTATION FUNCTIONS FOR SHORT CHAINS

### n freely-jointed segments

It has been shown by Treloar<sup>7</sup> that the Langevin approximation for the probability density of end-to-end lengths  $r$  ceases to be a useful approximation when the number of segments is small (less than 25). If the limiting extension is identified with  $N^{1/2}$ , the validity of equation (10) for polymers having a natural draw ratio of 2.5 or even less is questionable.

In this section, an expression for  $C_2$  will be obtained from Treloar's 'exact' distribution of lengths for short chains.

Consider a strand of end-to-end vector  $\bar{r}$ , made up of  $n$  statistical segments of length  $l$ . The projection of a link onto the unit vector  $\bar{l}$ , is:

$$OX = l \cos \alpha$$

where  $\alpha$  is the angle between the link and the end-to-end vector. We are interested in the probability of finding  $OX$  between  $x$  and  $x + dx$ , subject to the condition that the length of the end-to-end vector be  $OR$ . Referring to Figure 1, and introducing reduced coordinates  $x = \frac{OX}{l}$ ,  $r = \frac{OR}{l}$ ,

$\rho = \frac{LR}{l}$ , the following probabilities can be defined:

(i)  $f_n(x)dx$ , that the projection of a given segment falls between  $x$  and  $x + dx$ , subject to the condition that the end-to-end length of the strand of  $n$  segments is  $r$ ;

(ii)  $f_n(r)dr$ , that the end-to-end length of the strand is between  $r$  and  $r + dr$ , irrespective of direction;

(iii)  $p(x)dx$  is the *a priori* probability that  $x$  will fall between  $x$  and  $x + dx$ .

The probability that the projection of a given segment (represented as the first in Figure 1) will be  $x$ , and that the end of the strand  $Z$  will be found in an elemental volume  $dV$  about  $R$  can be found in two ways: it is the probability of finding  $OR/l$  between  $r$  and  $r + dr$ , of finding  $OR$  inside a cone defined by  $dS = dV/dr$  on the sphere of radius  $r$  and centre  $O$ , and of finding  $OX/l$  between  $x$  and  $x + dx$  subject to the condition that the strand's length is  $r$ . It is also the *a priori* probability of finding  $OX/l$  between  $x$  and  $x + dx$ , and at the same time of having the end-to-end length of the  $n - 1$  remaining segments between  $\rho$  and  $\rho + d\rho$ , the direction being defined by  $dS' = dV/d\rho$  on the sphere of radius  $\rho$  and centre  $L$ . This is expressed by:

$$p(x)dx f_{n-1}(\rho)d\rho \frac{dS'}{4\pi\rho^2} = f_n(x|r)dx f_n(r)dr \frac{dS}{4\pi r^2} \quad (12)$$

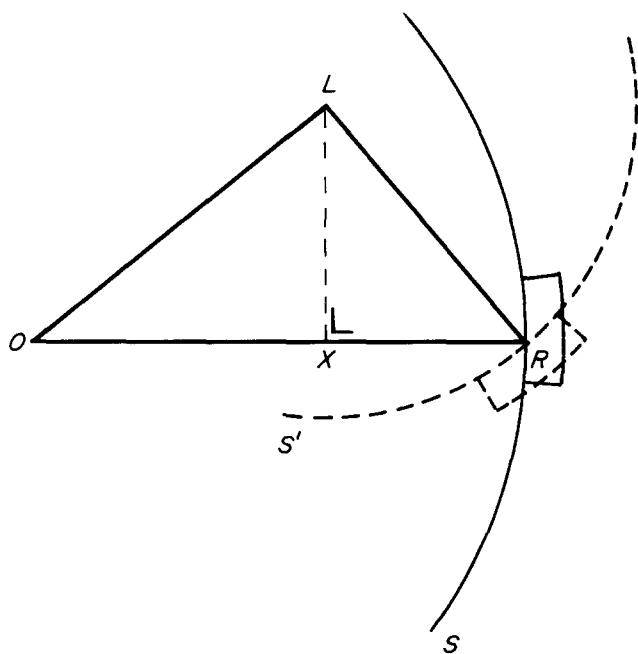


Figure 1 Definition of geometrical variables used in derivation of probability distribution of orientations

Since the *a priori* probability is isotropic,

$$p(x) = \frac{1}{2} \quad (|x| < 1) \\ = 0 \quad (|x| > 1) \quad (13)$$

and, taking into account that  $dV = dS'd\rho = dSdr$ ,

$$f_n(x|r)dx = \frac{f_{n-1}(\rho)d\rho r^2}{2f_n(r)\rho^2} \quad (14)$$

Referring to Figure 1, it can be seen that

$$\rho^2 = (r - x)^2 + 1 - x^2 \quad (15)$$

$$\text{or} \quad x = \frac{r^2 + 1 - \rho^2}{2r} \quad (16)$$

$$\text{and} \quad dx = -\frac{\rho}{r}d\rho$$

and finally

$$f(x|r)dx = \frac{f_{n-1}(\rho)d\rho r}{2f_n(r)\rho} \quad (17)$$

Treloar's distribution function is<sup>8</sup>:

$$f_n(r) = \frac{r}{2} \sum_{s=0}^k (-1)^s \frac{n! \binom{n-r-s}{2}^{n-2}}{(n-s)!s!(n-2)!} \quad (18)$$

where  $k$  is an integer defined by

$$k \leq \frac{n-r}{2} \leq k+1 \quad (19)$$

This distribution is applicable for a chain of  $n$  freely rotating segments.

The second-order orientation function of the statistical segments with respect to the end-to-end vector is:

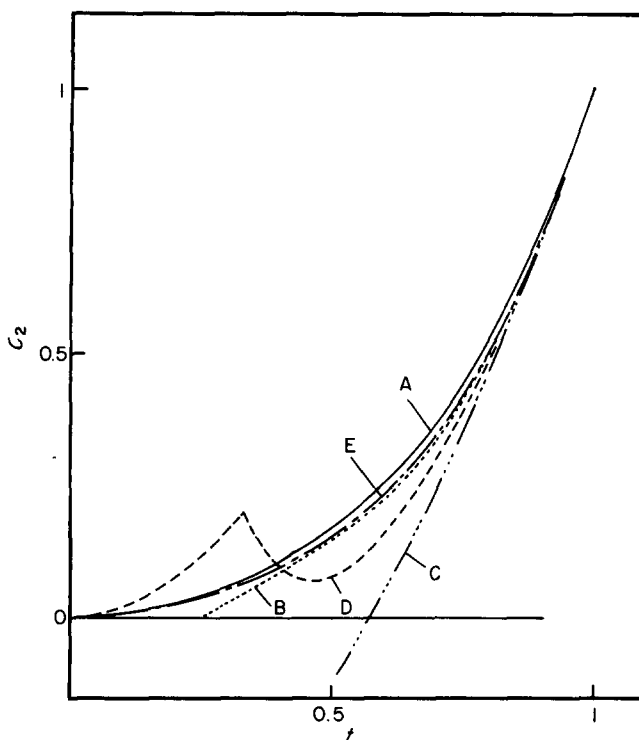
$$C_2 = \frac{3\langle x^2 \rangle - 1}{2} = \int_{-1}^{+1} \frac{3x^2 - 1}{2} f(x|r) dx \\ = \frac{3}{4} \int_{r-1}^{r+1} \frac{(r^2 + 1 - \rho^2)^2 r f_{n-1}(\rho) d\rho}{4r^2 \rho f_n(r)} - \frac{1}{2} \quad (20)$$

Introducing equation (18) into equation (20) it can be shown, after some tedious but elementary algebra, that:

$$C_2 = 1 - \frac{6}{r^2} \left\{ \sum_{s=0}^k \frac{(-1)^s n!}{(n-s)!s!} \left[ \frac{A_s^{n-1}}{(n-1)!} r \binom{r^2}{n} - 1 \right] + \frac{2A_s^n}{n!} \left( \frac{3r^2}{n} - 1 \right) \right. \\ \left. + \frac{24A_s^{n+1}}{(n+1)!} \frac{r}{n} + \frac{48A_s^{n+2}}{n(n+2)!} \right\} / \sum_{s=0}^k \frac{(-1)^s n!}{(n-s)!s!} \frac{A_s^{n-2}}{(n-2)!}$$

where  $A_s = \frac{n-r}{2} - s$ .

Equation (21) is plotted in Figure 2 for various values of  $n$ , together with the long-chain approximation, equation (8). The resulting variation of the global orientation function  $P_2$  with draw ratio is given in Figure 3. It can be



**Figure 2** Plot of orientation factor  $C_2$  versus fractional extension  $t$ . A, (—) Langevin approximation, equation (8); B, (---) rotational isomer model, equation (30); Treloar's distribution, equation (21); C, (-·-·-)  $n=2$ ; D, (····)  $n=3$ ; E, (----)  $n=6$

seen that, even for very short chains, the result obtained using Treloar's distribution is not fundamentally different from that obtained using Kuhn and Gr $\ddot{u}$  n's distribution.

#### $n_r$ rigid segments with fixed valence angles

It might be objected that the very concept of the statistical segment breaks down for very short chains, and that the analysis in the previous section might well be irrelevant.

In this section the orientation function will be found for chains formed of  $n_r$  rigid segments with fixed valence angles  $\Phi$  and internal rotation angle  $\phi$  ( $n_r$  is not equivalent to the number of  $n$  of statistical segments per chain). This model is, hopefully, more realistic than the preceding one.

The anisotropy of a segmental property  $p$  and the average end-to-end length are given by Volkenstein<sup>9</sup>:

$$\Delta p = \frac{6\cos\Phi}{5\sin^2\Phi} \left(1 + \frac{2}{3}\cos\Phi\right) \frac{1+\eta}{1-\eta} \left(p_1 - \frac{p_2+p_3}{2}\right) - \left(\frac{2\gamma}{5(1-\gamma)} + \frac{6\eta}{5(1-\eta^2)}\right) \left(p_2 - \frac{p_1+p_3}{2}\right) \quad (22)$$

where  $\eta = \overline{\cos\Phi}$ ,  $\gamma = \overline{\cos^2\Phi}$ ,  $p_1$  is the value of the property along the segment axis,  $p_2$  and  $p_3$  are its values transverse to the segment axis. If free rotation of the segment about its axis can be assumed, effective transverse isotropy is obtained and:

$$\Delta p = \left[ \frac{6\cos\Phi}{5\sin^2\Phi} \left(1 + \frac{2}{3}\cos\Phi\right) \frac{1+\eta}{1-\eta} + \left(\frac{\gamma}{5(1-\gamma)} + \frac{3\eta}{5(1-\eta^2)}\right) \right] (p_{\parallel} - p_{\perp}) \quad (23)$$

where  $p_{\parallel}$  and  $p_{\perp}$  are the values  $p$  takes respectively parallel and perpendicular to the segment axis.

The end-to-end distance  $r$  is given by:

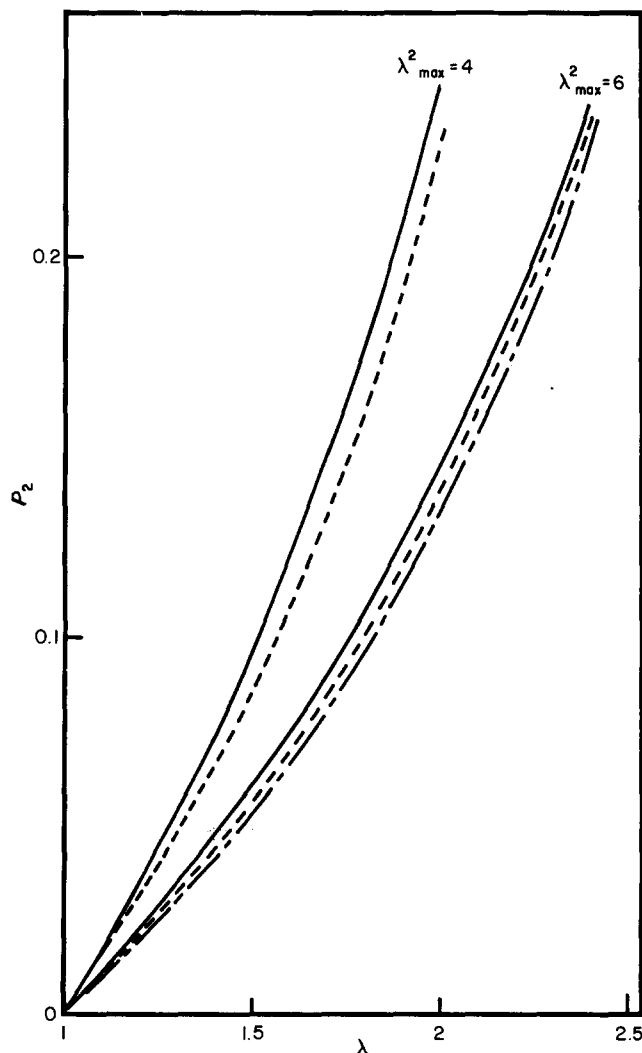
$$r^2 = n_r l^2 \frac{1 + \cos\Phi}{1 - \cos\Phi} \frac{1 + \eta}{1 - \eta} \quad (24)$$

Expressions (23) and (24) are both approximations, valid only at low extensions (i.e. low  $\eta$ ). Better approximations for  $r^2$  are given by Volkenstein, but none are valid over a useful range of  $\eta$  for short chains (i.e.  $n_r < 500$ ). The exact expression for  $r^2$  is, to say the least, unmanageable. Also, no better approximation than equation (22) is given for the chain anisotropy. In order to obtain a relationship between anisotropy and extension ratio, the following empirical expressions are used, which reduce to equations (23) and (24) at low draw ratios,

$$\Delta p = \Delta p_1 (1 - \eta^{x_a}) \quad \text{and} \quad r^2 = r_1^2 (1 - \eta^{x_r}) \quad (25)$$

where  $\Delta p_1$  and  $r_1^2$  are given by equations (23) and (24) and  $x_a$  and  $x_r$  will be found below in order for equations (25) to give the correct values of anisotropy and length at full chain extension.

In order for a relationship to be obtained between  $\Delta p$  and  $r$  from equations (25), a relationship is required between  $\gamma$  and  $\eta$ . This relationship will, of course, depend



**Figure 3** Average orientation function versus global extension ratio. (—) Langevin approximation, equation (10); (---) Treloar's distribution, from equation (21); (-·-·-) rotational isomer model, equation (31)

on the distribution of internal rotation angles. Assuming tetrahedral bond angles ( $\cos\Phi = \frac{1}{3}$ ), and restricting accessible rotational isomers to one *trans* ( $\cos\Phi = 1$ , weight  $f$ ) and two *gauche* ( $\cos\Phi = -\frac{1}{2}$ , with equal weights  $\frac{1-f}{2}$ ):

$$\eta = \frac{3f-1}{2} \quad \text{and} \quad \gamma = \frac{3f+1}{4} \quad (26)$$

and the anisotropy and end-to-end length can be expressed in terms of the fraction of *trans* conformers as:

$$\Delta p = \frac{5(3f-1)^2 + 28(3f-1) + 20}{20(1-f)(1+3f)} \left( 1 - \left( \frac{3f-1}{2} \right) x_a \right) (p_{\parallel} - p_{\perp}) \quad (27)$$

$$r^2 = 2n_r l^2 \frac{1+3f}{3(1-f)} \left( 1 - \left( \frac{3f-1}{2} \right) x_r \right) \quad (28)$$

When  $f=1$ ,  $\Delta p = \frac{n_r}{2}(p_{\parallel} - p_{\perp})$  and  $r^2 = \frac{2n_r^2 l^2}{3}$ , giving:

$$x_a = \frac{n_r}{3.6} \quad \text{and} \quad x_r = \frac{n_r}{6} \quad (29)$$

On eliminating  $f$  between equations (27) and (28), a relationship between  $C_2 = \Delta p / \Delta p_{\max}$  and  $t = r / r_{\max}$  can be found for a given  $n_r$ . This relationship is evaluated for  $n_r = 20$ , which corresponds to the number of rigid segments between entanglements in polycarbonate ( $M_e = 2500$ , monomer = 258, two rigid segments per monomer). This choice was made in order to compare results with those of the preceding section. Most other polymers have entanglement molecular weights corresponding to several hundred rigid bonds, or in other terms, a 'statistical segment' is made up of several monomers. The relationship between  $C_2$  and  $t$  is then indistinguishable from the inverse Langevin expression, equation (8).

For  $n_r = 20$ , elimination of  $f$  between equations (27) and (28) gives a relationship which is numerically very close to:

$$C_2 = 0.45t^2 + 0.425t^4 + 0.125t^6 \quad (30)$$

(In the region of interest, the absolute error is less than 0.003 and the relative error is generally better than 1%.)

The second-order orientation function is then:

$$P_2 = \frac{0.15}{\lambda_{\max}^2} \left( \lambda^2 - \frac{1}{\lambda} \right) + \frac{0.085}{\lambda_{\max}^4} \left( \lambda^4 + \frac{\lambda}{3} - \frac{4}{3\lambda^2} \right) + \frac{0.125}{7\lambda_{\max}^6} \left( \lambda^6 + \frac{3\lambda^3}{5} - \frac{8}{5\lambda^3} \right) \quad (31)$$

This expression is compared with those derived from Treloar's distribution and from the inverse Langevin distribution in Figure 3, taking  $\lambda_{\max}^2 = 6$ . The resulting orientation functions can be seen to be remarkably close to each other.

## DISCUSSION

It might appear somewhat unexpected that three fundamentally different models should yield such similar representations of the development of orientation on stretching. The reasons for this behaviour are several.

First, the orientation function  $C_2$  for a single chain obtained using Treloar's distribution of end-to-end lengths is itself remarkably close to that derived from the inverse Langevin function, for as few as six statistical segments, although the probability distributions of end-to-end lengths are themselves quite dissimilar. This can be understood in the following manner.

A chain of end-to-end length  $r$  is made up of  $n$  segments of length  $l$ ; let  $\alpha$  be the angle between any individual segment and the end-to-end vector. The following equations then hold:

$$\frac{r}{nl} = \overline{\cos\alpha} \quad (32)$$

$$C_2 = \frac{3\overline{\cos^2\alpha} - 1}{2} = \frac{3(\overline{\cos\alpha})^2 + 3\sigma^2 - 1}{2} \quad (33)$$

where  $\sigma^2$  is the variance of the distribution of  $\cos\alpha$ . The upper and lower bounds for  $C_2$  at a given  $\overline{\cos\alpha}$  will now be sought following Bower's method<sup>14</sup>. The lower limit for  $C_2$  is obtained for  $\sigma^2 = 0$ , corresponding to  $n = 2$  (only one value of  $\alpha$  compatible with the given end-to-end distance). The upper limit is obtained when  $\cos\alpha = \pm 1$ , i.e. all segments lying either parallel or antiparallel to the end-to-end vector, giving  $C_2 = 1$  for any  $r$ . In principle, the relationship between  $t$  and  $C_2$  could lie anywhere between these extremes. In practice, however, limitations on accessible configurations, resulting in a narrow distribution and low variance, will be unimportant except for very small  $n$ ; and extreme configurations giving a high variance usually have a low weight unless  $n$  is very small. For example, when  $n = 3$  and  $r = 1$ , one segment is parallel to the end-to-end vector and the other two are parallel to each other. The orientation distribution is bimodal, resulting in a maximum in variance at this point. (Incidentally, this includes configurations in which the first segment lies along the end-to-end vector, and the other two fold back on each other; this is an impossible configuration in a real chain. Clearly, segments are not indistinguishable at this level. In this sense, Treloar's distribution is no more 'exact' than the Langevin 'approximation'.) At high extensions, few configurations are accessible so that all distributions merge. The most probable orientation function will thus be fairly insensitive to details of the configurational model.

On averaging  $C_2$  to obtain the global orientation function  $P_2$ , the largest contribution comes from those chains with the highest draw ratios: these chains have a high weight (probability proportional to  $\delta^3$ , where the local extension ratio  $\delta$  is given by equation (5)) and are strongly oriented towards the draw direction, (factor  $(3x^2 - 1)/2$ ), so that the effect of differences in segmental orientation functions, which are preponderant only at low extensions, is further reduced. The resulting orientation functions are therefore very similar, whatever the model, even for very short chains.

This means that the Langevin approximation and the concept of a statistical segment are both 'useful', even for

extremely limited chain extensibilities. Just how useful will now be discussed.

The orientation-strain relationship obtained using Treloar's 'exact' distribution has been shown above to be close to that derived from the Langevin approximation; however, the probability distributions of end-to-end lengths are quite dissimilar. This means that the variation of entropy with strain obtained with the Langevin approximation will probably be in error for short chains: although orientation-strain relationships derived from the Langevin approximation are probably acceptable, stress-strain and orientation-stress relationships are unlikely to be useful.

Whether a better description of stress-strain behaviour can be derived from Treloar's 'exact' distribution is, however, open to question: in chains made up of freely rotating 'statistical segments' strain can be accommodated not only by rotation of segments, but also by extension of the segments themselves. The statistical segment is equivalent to a certain number of real links, the number being chosen so that orientations of successive segments are uncorrelated. On straining a real chain, the probability distribution of internal rotation angles is altered at all bonds, so that the 'statistical segment' cannot be thought of as rigid. Also, as pointed out above, Treloar's distribution includes some impossible configurations, with a non-negligible weight in the case of very short chains. Clearly, a strong decrease in orientation with increasing draw ratio as obtained in the case of three freely rotating segments using Treloar's distribution, is physically unrealistic.

It might at first sight appear preferable to model the behaviour of the chain as a whole, as outlined in the section dealing with ' $n$ , rigid segments with fixed valence angles'. In fact, the underlying hypotheses are extremely restrictive: equations (23) and (24) are valid only if there is no correlation of internal rotation angles between successive bonds; very low extensions cannot be reached if only three conformations are allowed; and the upper range of extension ratios can be covered only by using an interpolation formula whose sole justification is that it reduces to the correct expressions at both ends. Since the resulting orientation falls slightly below the theoretical lower limit at high extension ratios, it is evidently too low (this would imply a negative variance, which is, of course, impossible). A realistic model with coarse, albeit inevitable, approximations will evidently do no better than a rigorous solution to an approximate model. These limitations are relatively unimportant for the orientation function because the major contribution comes from the region where the approximations are most likely to be adequate; it is, however, unlikely that a useful expression for the entropic force can be derived.

In conclusion, then, the description of the orientation-strain behaviour is insensitive to details of the conformational model; this is a consequence of the averaging procedure. On the other hand, it appears unlikely that any available model can give a realistic detailed description of stress-strain behaviour.

One point remains to be discussed: how well do any of

the models given above describe orientation data in real polymers? This point will not be discussed in detail, as work in this field will be published shortly. As shown by Brown and Mitchell<sup>15,16</sup>, experimental behaviour of rubbers, or of PMMA in the rubbery state, can be fitted to the description resulting from the Langevin approximation only by using a strain-dependent value of  $n$ , the number of segments between entanglements or crosslinks. This adjustment is required because of the initial downward curvature of the orientation-strain curve. All models given in this paper give a positive curvature, so that refining the mathematics does not appear to be able to improve the description of behaviour of real polymers. The basic assumptions of the random chain affine model require reassessment: either deformation of end-to-end vectors is not affine, or chain conformation between entanglements (crosslinks) is not random. Mitchell<sup>17</sup> has successfully applied Brown and Windle's two-component model<sup>3</sup> to orientation-strain behaviour of crosslinked rubbers; an alternative model, applicable to the glassy state, will be compared with experiment in a following paper.

## CONCLUSIONS

Two models of orientation-strain behaviour have been presented as alternatives to the Kuhn and Gr $\ddot{u}$ n model in the case of short chains. The resulting orientation-strain relationships are very close to the Langevin approximation, which is therefore a valid approximation for random-chain affine behaviour even for chains having extremely limited maximum extension, and which is preferable to the alternative models in view of its mathematical simplicity. The non-applicability of the Kuhn and Gr $\ddot{u}$ n theory to real chains does not stem from the Langevin approximation itself, but from inadequacy of the hypothesis of random chain affine deformation.

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