Notes to the Editor

Orientation averages for drawn rubber networks

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INTRODUCTION

When a rubber network is drawn, the segments of the polymer chains which form the network become preferentially aligned with respect to the axis of stretching. Using Treloar's model[1] for a rubber consisting of freely jointed statistical segments, Roe and Krigbaum[2] derived expressions for some of the coefficients in an expansion of the distribution function of segmental orientations in terms of Legendre polynomials. Most methods of studying molecular orientation in polymers can determine only one or a few of these coefficients, rather than the complete distribution of orientations, so that their theoretical prediction and comparison with experimentally determined values is a useful way of checking the validity of any theory of rubber elasticity which may subsequently be used to predict the elastic, photoelastic or other properties of the rubber.

In their derivation of expressions for the coefficients of the second, fourth and sixth order polynomials Roe and Krigbaum, used an expansion of the inverse Langevin function given by Kuhn and Grün[3] which applies only to low orientation of the segments with respect to the end-to-end vector of a chain. They also derived an expression for the coefficient of the second order polynomial using an approximate expression for the inverse Langevin function given by Treloar[1]. This leads to a closed three term expression for the second order coefficient which is very similar to the first three terms in the expression calculated using Kuhn and Grün's expansion, which are, however, only the first terms of an infinite series.

This Note has three purposes. The first is to show that if the inverse Langevin function is evaluated using Treloar's expression the predicted coefficient of the second order Legendre polynomial has a value close to that given by the first three terms derived by Roe and Krigbaum with the use of Kuhn and Grün's expansion, whereas the coefficient of the fourth order Legendre polynomial has a value much greater than that given by the first two terms derived by Roe and Krigbaum, except for very low values of draw ratio or very high values of the number of random links, N, between adjacent crosslink points. The second purpose is to show directly that if the inverse Langevin function is evaluated numerically, values of both the second and fourth order coefficients are obtained which are essentially the same as those derived using Treloar's expression. The third purpose is to show that by a simple additional assumption the predictions of the model can be extended beyond the draw ratio $N^{1/2}$. This is the limit of the conventional rubber theory because at this draw ratio chains initially pointing in the draw direction become fully extended.

LOW DRAW RATIO REGION

Roe and Krigbaum's treatment† is equivalent to showing that if $N(\theta)$ is the probability per unit solid angle that a random link makes the angle θ with the draw direction, then:

$$\langle P_l(\cos\theta)\rangle = 2\pi \int_0^\pi N(\theta) P_l(\cos\theta)\sin\theta \, d\theta$$

$$= \int_{-1}^{1} \frac{\lambda^3 \langle P_l(\cos\theta')\rangle P_l(\cos\Theta)d(\cos\Theta)}{2[\lambda^3 - (\lambda^3 - 1)\cos^2\Theta]^{3/2}} \qquad (1)$$

where $P_l(x)$ is the lth order Legendre polynomial[4] in x, the angled brackets denote the value averaged over the distribution function and λ is the draw ratio. Θ is the angle between the draw direction and the end-to-end vector of a typical chain after drawing and θ' is the angle between a typical segment in the chain and the end-to-end vector. The values of $\langle P_l(\cos\theta')\rangle$ for $l = 0, 2$ and 4 which, apart from normalization factors, are the same as C_0, C_2 and C_4 given by Roe and Krigbaum, are:

$$C_0 = 1$$

$$C_2 = 1 - \frac{3t}{\beta} \qquad (2)$$

$$C_4 = 1 - \frac{10t}{\beta} + \frac{35}{\beta^2} - \frac{105t}{\beta^3}$$

where:

$$\beta = L^{-1}(t) \qquad (3)$$

$$t = \frac{r}{Nl_s} \qquad (4)$$

where L^{-1} is the inverse Langevin function, l_s is the length of a statistical segment and r is the stretched length of the chain. r and Θ are related by:

$$r^2 = \frac{Nl_s^2\lambda^2}{[\lambda^3 - (\lambda^3 - 1)\cos^2\Theta]} \qquad (5)$$

Any required value of $\langle P_l(\cos\theta)\rangle$ is obtained by substituting the appropriate value of C_l obtained from equation (2) into equation (1) after first expressing β, and hence C_l, explicitly in terms of t.

Using the expansion given by Kuhn and Grün, viz:

$$\beta = 3t + \frac{9t^3}{5} + \frac{297t^5}{175} + 0(t^7) \qquad (6)$$

Roe and Krigbaum obtain:

$$\langle P_2(\cos\theta)\rangle =$$

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† Roe and Krigbaum use normalized Legendre polynomials, whereas we do not. In this Note $P_0(x) = 1$, $P_2(x) = (3x^2 - 1)/2$ and $P_4(x) = (3 - 30x^2 + 35x^4)/8$.

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$$\frac{1}{5N}\left(\lambda^2-\frac{1}{\lambda}\right)+\frac{36}{875N^2}\times$$

$$\left(\lambda^4+\frac{\lambda}{3}-\frac{4}{3\lambda^2}\right)+\frac{108}{6125N^3}\times$$

$$\left(\lambda^6+\frac{3\lambda^3}{5}-\frac{8}{5\lambda^3}\right)+0\left(\frac{\lambda^8}{N^4}\right) \qquad \text{(7a)}$$

$$\langle P_4(\cos\theta)\rangle =$$

$$\frac{3}{175N^2}\left(\lambda^4-2\lambda+\frac{1}{\lambda^2}\right)+$$

$$\frac{216}{13475N^3}\left(\lambda^6-\frac{4\lambda^3}{5}-\frac{7}{5}+\frac{6}{5\lambda^3}\right)$$

$$+0\left(\frac{\lambda^8}{N^4}\right) \qquad \text{(7b)}$$

Using Treloar's closed expression

$$1-\frac{3t}{\beta}=\frac{3t^2}{5}+\frac{t^4}{5}+\frac{t^6}{5} \qquad \text{(8)}$$

to evaluate β they obtain an expression equivalent to:

$$\langle P_2(\cos\theta)\rangle=\frac{1}{5N}\left(\lambda^2-\frac{1}{\lambda}\right)+$$

$$\frac{1}{25N^2}\left(\lambda^4+\frac{\lambda}{3}-\frac{4}{3\lambda^2}\right)+$$

$$\frac{1}{35N^3}\left(\lambda^6+\frac{3\lambda^3}{5}-\frac{8}{5\lambda^3}\right) \qquad \text{(9)}$$

but they do not evaluate $\langle P_4(\cos\theta)\rangle$ using Treloar's expression, which we have done.

Using this expression we find:

$$C_4=\frac{1}{225}\left[-5t^2+94t^4-151t^6+7(16t^8+9t^{10}+12t^{12}+3t^{14}+t^{16})\right] \qquad \text{(10)}$$

Since from equations (4) and (5)

$$t^2=\frac{\lambda^2}{N}\Big/\left[\lambda^3-(\lambda^3-1)\cos^2\Theta\right] \qquad \text{(11)}$$

equation (1) shows that we need to evaluate integrals of the type:

$$I_m=\int_{-1}^{1}\frac{(3-30\xi^2+35\xi^4)\mathrm{d}\xi}{(a-b\xi^2)^{m/2}} \qquad \text{(12)}$$

where $\xi=\cos\Theta$, $a=\lambda^3$ and $b=\lambda^3-1$. It may readily be shown that:

$$I_m=\frac{1}{m-2}\left\{\frac{6}{a}+\frac{10}{b}+\frac{6}{m-4}\times\left[\frac{m-3}{a^2}+\frac{10}{ab}-\frac{35}{b^2}\right]+\frac{3}{m-4}\left[\frac{(m-5)(m-3)}{a^2}+\frac{10(m-5)}{ab}+\frac{35}{b^2}\right]I^0_{m-4}\right\} \qquad \text{(13)}$$

where

$$I^0_m=\int_{-1}^{1}\frac{\mathrm{d}\xi}{(a-b\xi^2)^{m/2}} \qquad \text{(14)}$$

It may also be shown that

$$I^0_m=\frac{1}{a(m-2)}\left[2+(m-3)I^0_{m-2}\right] \qquad \text{(15)}$$

so that

$$I^0_3=2/\lambda^3 \qquad \text{(16)}$$

Since

$$I^0_1=2[\sin^{-1}(1-1/\lambda^3)^{1/2}]/(\lambda^3-1)^{1/2}$$

$$=2[\tan^{-1}(\lambda^3-1)^{1/2}]/(\lambda^3-1)^{1/2} \qquad \text{(17)}$$

all the required values of I_m are readily obtained. $\langle P_4(\cos\theta)\rangle$ is then obtained explicitly as equation (18).

Tables 1a and *1b* show, for $N=10$ and $N=50$, respectively, values of $\langle P_2(\cos\theta)\rangle$ calculated from equation

Table 1a $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ for $N=10$

	$\langle P_2(\cos\theta)\rangle$			$\langle P_4(\cos\theta)\rangle$		
λ	Equation (7a)	Equation (9)	Numerical calculation	Equation (7b)	Equation (18)	Numerical calculation
1.50	0.034	0.034	0.034	0.001	0.001	0.001
2.00	0.078	0.078	0.078	0.003	0.005	0.004
2.50	0.138	0.140	0.140	0.010	0.016	0.015
3.00	0.220	0.228	0.228	0.024	0.060	0.060
3.16	0.253	0.263	0.263	0.032	0.096	0.096

Table 1b $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ for $N=50$

	$\langle P_2(\cos\theta)\rangle$			$\langle P_4(\cos\theta)\rangle$		
λ	Equation (7a)	Equation (9)	Numerical calculation	Equation (7b)	Equation (18)	Numerical calculation
2.00	0.014	0.014	0.014	0.000	0.000	0.000
4.00	0.068	0.068	0.068	0.002	0.004	0.002
6.00	0.172	0.175	0.175	0.015	0.027	0.025
7.07	0.258	0.268	0.269	0.033	0.098	0.098

Explicit expression – equation (18) – for $\langle P_4(\cos\theta)\rangle$:

$$\langle P_4(\cos\theta)\rangle = \frac{-\lambda^5}{360N}\left\{\frac{8\lambda^6+33\lambda^3-6}{3\lambda^6(\lambda^3-1)} - \frac{35}{(\lambda^3-1)^2}\left[1-\frac{\tan^{-1}(\lambda^3-1)^{1/2}}{(\lambda^3-1)^{1/2}}\right]\right\}$$
$$+\frac{94}{1125N^2}\left(\lambda^4-2\lambda+\frac{1}{\lambda^2}\right)-\frac{151}{1575N^3}\left(\lambda^6-\frac{4\lambda^3}{5}-\frac{7}{5}+\frac{6}{5\lambda^3}\right)$$
$$+\frac{112}{2025N^4}\left(\lambda^8-\frac{2\lambda^5}{7}-\frac{37}{35}\lambda^2-\frac{36}{35\lambda}+\frac{48}{35\lambda^4}\right)$$
$$+\frac{7}{275N^5}\left(\lambda^{10}-\frac{5\lambda^4}{7}-\frac{22\lambda}{21}-\frac{16}{21\lambda^2}+\frac{32}{21\lambda^5}\right)$$
$$+\frac{84}{2925N^6}\left(\lambda^{12}+\frac{2\lambda^9}{11}-\frac{5\lambda^6}{11}-\frac{200\lambda^3}{231}-\frac{32}{33}-\frac{128}{231\lambda^3}+\frac{128}{77\lambda^6}\right)$$
$$+\frac{7}{1125N^7}\left(\lambda^{14}+\frac{4\lambda^{11}}{13}-\frac{37\lambda^8}{143}-\frac{290\lambda^5}{429}-\frac{2720\lambda^2}{3003}-\frac{2624}{3003\lambda}-\frac{384}{1001\lambda^4}+\frac{256}{143\lambda^7}\right)$$
$$+\frac{7}{3825N^8}\left(\lambda^{16}+\frac{2\lambda^{13}}{5}-\frac{7\lambda^{10}}{65}-\frac{28\lambda^7}{55}-\frac{112\lambda^4}{143}-\frac{128\lambda}{143}-\frac{128}{165\lambda^2}-\frac{512}{2145\lambda^5}+\frac{4096}{2145\lambda^8}\right)$$

(9), which is based on Treloar's expression, and from the three-term expression in equation (7a) together with values of $\langle P_4(\cos\theta)\rangle$ calculated from equation (18) and from the two term expression in equation (7b). It is seen that expression (7a) slightly underestimates $\langle P_2(\cos\theta)\rangle$, whereas expression (7b) seriously underestimates $\langle P_4(\cos\theta)\rangle$ for all except the lowest values of λ.

It is useful to compare the values given by equations (9) and (18) with those obtained using a numerical evaluation of the inverse Langevin function, together with numerical integration of equation (1). For numerical integration it is preferable to rewrite equation (1) in terms of $\cos\Theta_0$ where Θ_0 is the angle which the end-to-end vector makes with the draw direction before drawing. Equal numbers of chains are then contained in equal intervals of $\cos\Theta_0$. The results of the numerical evaluation are compared with those obtained from equations (9) and (18) in *Tables 1a* and *1b*. It is seen that for all practical purposes equations (9) and (18) give satisfactory results. Since the use of these equations to evaluate $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ for a particular value of N and λ is much more straightforward than the method of numerical integration, this will generally be preferable.

HIGH DRAW RATIO REGION

It has already been pointed out that equation (1) applies only for values of $\lambda < N^{1/2}$; because at the critical draw ratio $\lambda_c = N^{1/2}$ chains whose end-to-end vectors are originally in the draw direction become fully extended. Above λ_c chains which were not originally parallel to the draw direction may also become fully extended. In order to obtain an approximation to the behaviour of the network above λ_c the following simple assumptions have been made.

(1) Any chain which becomes fully extended subsequently rotates as a rigid rod whose orientation changes like the join of two points in a body undergoing an affine deformation.

(2) The end-to-end vectors of chains which are not fully extended continue to rotate and extend affinely.

These two assumptions are clearly incompatible and their use is simply a mathematical device to allow the calculation to be performed for $\lambda > \lambda_c$. In reality, once any chains are fully extended either departure from affine deformation must take place (and it may in fact take place before this), chains must slip at the crosslink points or chains must break. All of these effects may take place and it does not seem possible to predict in any simple way whether the present assumptions will lead to higher or lower values of $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ than the 'true' values. For values of λ not much greater than λ_c they may lead to values not too far distant from the 'true' ones.

Mathematically, the assumptions are expressed by setting C_2 and C_4 equal to unity for chains which have become fully extended. These chains are those for which Θ in the stretched rubber is less than Θ_c, where Θ_c is given by $\lambda^2/N = \lambda^3 - (\lambda^3 - 1)\cos^2\Theta_c$‡. The results have been evaluated using Treloar's expression only for the limit $\lambda, N \to \infty$ with $x = \lambda^2/N$ finite, and have been quoted previously[5]. They are, for $x > 1$:

$$\langle P_2(\cos\theta)\rangle = 1 - \frac{128}{175x^{1/2}} \qquad (19)$$

$$\langle P_4(\cos\theta)\rangle = 1 - \frac{0.9022}{x^{1/2}}$$

These results have also been evaluated for $N = 10$ and $N = 50$, using the numerical method of calculating the inverse Langevin function and evaluating the modified integral in equation (1). Values calculated from equation (19) and by the numerical method are tabulated in *Tables 2a* and *2b* and it is seen that even for a value of N as low as 10 equation (19) gives results that are adequate for most purposes. These Tables also show the fraction of chains that are in the fully extended state (*FEF*).

‡ In ref 5 this equation is incorrectly stated to apply to the angle in the unstretched rubber.

Table 2a $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ for $N = 10$

	$\langle P_2(\cos\theta)\rangle$		$\langle P_4(\cos\theta)\rangle$		
λ	Equation (19)	Numerical calculation	Equation (19)	Numerical calculation	*FEF*
3.5	0.339	0.335	0.185	0.183	0.099
4.0	0.422	0.417	0.287	0.281	0.213
4.5	0.486	0.481	0.366	0.358	0.301
5.0	0.537	0.534	0.429	0.423	0.371
7.5	0.692	0.688	0.620	0.611	0.581
10.0	0.769	0.766	0.715	0.707	0.685
15.0	0.846	0.844	0.810	0.804	0.790
20.0	0.884	0.883	0.857	0.853	0.842

Table 2b $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ for $N = 50$

	$\langle P_2(\cos\theta)\rangle$		$\langle P_4(\cos\theta)\rangle$		
λ	Equation (19)	Numerical calculation	Equation (19)	Numerical calculation	*FEF*
8.0	0.354	0.355	0.203	0.206	0.116
10.0	0.483	0.483	0.362	0.363	0.293
15.0	0.655	0.655	0.575	0.575	0.529
20.0	0.741	0.742	0.681	0.681	0.647
25.0	0.793	0.793	0.745	0.744	0.717
30.0	0.828	0.827	0.787	0.787	0.764

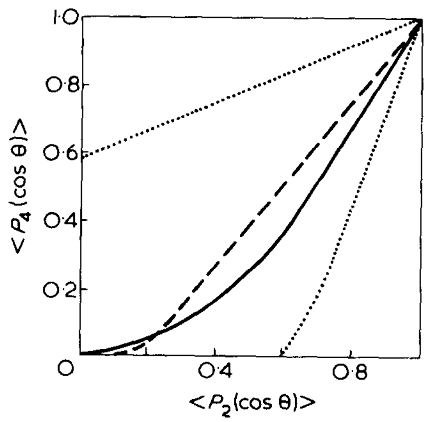

Figure 1 $\langle P_4(\cos\theta)\rangle$ as a function of $\langle P_2(\cos\theta)\rangle$. · · · · · · · , Upper and lower bounds on $\langle P_4(\cos\theta)\rangle$ for a given value of $\langle P_2(\cos\theta)\rangle$; ———, pseudo-affine rigid rod rotation theory; — — — —, modified rubber theory, present work

DISCUSSION

Despite the simplicity of the basic rubber model employed and the assumptions made to extend it to draw ratios $>\lambda_c$, the values predicted for both $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ have been shown to be in reasonably good agreement with experimental determinations of $\langle P_2(\cos\theta)\rangle$ and $\langle P_4(\cos\theta)\rangle$ for poly(ethylene terephthalate) drawn at 80°C, provided that the value of N is chosen appropriately, and a simple method of determining N has been given[6].

If samples drawn under similar conditions to a wide range of draw ratios are not available, it is possible to form some idea of whether the present model for the production of orientation is applicable by comparing the relationship between the values of $\langle P_4(\cos\theta)\rangle$ and $\langle P_2(\cos\theta)\rangle$ observed with that predicted by the present model and with that predicted by the other model frequently used in discussing the development of orientation, the pseudo-affine rigid rod rotation model[7]. *Figure 1* shows the mathematical limits on $\langle P_4(\cos\theta)\rangle$ for a given $\langle P_2(\cos\theta)\rangle$, together with the relationship between these quantities predicted on the basis of the pseudo-affine model and on the basis of equations (9), (18) and (19). Equations (9) and (18) have been used in the limit N, $\lambda \rightarrow \infty$ with $x = \lambda^2/N$ finite, but evaluation for finite N as low as 5 by the numerical method shows differences in the predicted $\langle P_4(\cos\theta)\rangle$ only of order 10^{-3}, and these occur only for $\langle P_2(\cos\theta)\rangle$ less than about 0.2.

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Cell cracking in open cell rigid polymeric foams

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INTRODUCTION

Water-soluble inorganic salts dispersed in polymers can be leached out by subjecting the polymer/salt particles to immersion in water. The leaching method was employed by Fossey and Smith[1] to produce polyethylene foams and by Gregorian[2] to prepare cross-linked microporous polyolefin films. Nielsen and Lee[3] studied the mechanical properties of polystyrene filled with ground rock salt and polystyrene foams produced by extracting the salt with water. A similar technique was used by Smith[4] to prepare polyurethane foams, and has also been applied to the manufacture of microcellular

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